Reactions Of First-Row Transition Metal Complexes In Bis(alkoxide) Ligand Environments With Diazoalkanes: Formation Of Carbenes Versus Reductive Coupling To Form Bridging Tetrazenes

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REACTIONS OF FIRST-ROW TRANSITION METAL COMPLEXES IN BIS(ALKOXIDE) LIGAND ENVIRONMENTS WITH DIAZOALKANES: FORMATION OF CARBENES VERSUS REDUCTIVE COUPLING TO FORM BRIDGING TETRAZENES

by

AMANDA GRASS

DISSERTATION

Submitted to the Graduate School of Wayne State University, Detroit, Michigan in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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Approved By:

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CHAPTER ONE INTRODUCTION


1.1. Introduction

Group-transfer catalysis is one of the major research areas in contemporary organometallic chemistry, including carbene, nitrene, and oxo transfer. The focus of my dissertation is on newly emerging field of carbene transfer chemistry. Carbene complexes of base (3d) transition-metals are attractive functionalities in group transfer, enabling sustainable formation of new C-N, C-O, and C-C bonds.\(^1\) While carbene complexes have been synthesized by a variety of synthetic routes, diazoalkanes/diazoesters offer several synthetic advantages as carbene sources. First, diazoalkanes can be readily synthesized. Second, the only by-product of diazoalkane utilization is environmentally friendly dinitrogen. Third, the facile nature of carbene formation from diazoalkane precursors is beneficial to catalytic turnover (Figure 1). Some of the most attractive transformations mediated by carbene complexes\(^2\) include C-H bond activation,\(^3\) cyclopropanation of alkenes,\(^4\) and formation of heteroallenes (ketenes,\(^5\) ketenimines\(^6\)) via direct coupling with CO/CNR (Figure 1).

![Figure 1](image-url)

**Figure 1.** Formation of metallocarbenes from diazoalkanes and selected group transfer reactions.
1.2. Classes of carbenes present in the literature

The reactivity of transition metal carbone complexes is determined by their electronic nature, which is regulated, in part, by the ancillary ligand type and metal.\(^7\) While the field of carbone complexes is vastly growing, the two earliest examples which clearly define the vast ends of the spectrum are those of Fischer and Schrock carbenes. Fischer type carbenes consist of middle/late low-valent transition metals surrounded by soft, strong field ligands.\(^8\) The first published example, M(CO)\(_5\)(=CMe(OMe)) (M = Cr(0), Mo(0), W(0)), was synthesized by electrophilic attack on group 6 hexacarbonyl complexes.\(^8\) In contrast, Schrock type carbenes (alkylidenes) consist of early, high valent metals surrounded by hard, weak field ligands.\(^9\) The first examples of Schrock carbenes were synthesized by α-H abstraction from metal alkyl complexes, producing M(Np)\(_3\)(=CH\(_{tBu}\)) (M = Nb(V), Ta(V); Np = CH\(_{2tBu}\)).\(^10\) Fischer type carbenes possess long M=C bonds and usually exhibit electrophilic reactivity at the carbone carbon. In contrast, Schrock type carbenes possess short M=C bonds and undergo nucleophilic reactivity at the carbone carbon. A typical example of well-studied Schrock carbenes (Figure 2) includes hard alkoxide/imido ligation, W(VI) metal centers, and coordinative unsaturation, which allows substrate (olefin) coordination. The difference in reactivity of these two classes of carbenes is demonstrated in the products generated upon reaction with olefins. Fischer carbenes undergo cyclopropanation, whereas Schrock carbenes undergo olefin metathesis chemistry that is accomplished via the [2+2] transformations (Figure 2). More recently, metal carbone complexes featuring radical character on the carbone carbon received growing attention, particularly due to their pronounced ability to promote C-H bond activation and C-C bond formation.\(^11\)

![Figure 2. Reactivity of Fischer and Schrock carbenes with olefins.](image-url)
A significant number of studies during the last decade demonstrated formation of stable carbene complexes of late transition-metals with strong-field ligands that combine strong σ-donation and some degree of π-acceptance (e.g. N-heterocyclic carbenes\textsuperscript{12} or phosphines\textsuperscript{13}). Strong field ligands stabilize these complexes for two reasons: (1) these ligands are good π acceptor ligands and lead to low-spin complexes; (2) these ligands are also strong σ donors and therefore enable higher formal oxidation states at the mid and late transition metals. Several examples of such systems formed from diazoalkanes are shown in Figure 3. Group 10 carbene complexes reported by Hillhouse and Iluc possess chelating phosphine ligands which have short M-C bonds of 1.836(2) Å for Ni and 1.942(3) Å for Pt. Both systems undergo stochiometric carbene transfer reactivity, exhibiting nucleophilic character at the carbene carbon.\textsuperscript{14, 15} The cationic iron carbene containing a Cp* ring and phosphines also exhibits a short Fe-C bond of 1.787 Å. Yet this complex was remarkably stable and exhibited electrophilic character at the carbene carbon.\textsuperscript{16} However, the use of these strong-field ligand platforms to stabilize an isolable carbene complex can inhibit catalytic group transfer. In sharp contrast, the use of relatively weak-field nitrogen-based ligands (e.g. dipyrromethene) was found to facilitate catalytic nitrene transfer chemistry via reactive electrophilic radical-based nitrenes.\textsuperscript{17} The use of other weak-field ligands may also lead to similar radical-based catalytic carbene transfer chemistry.

![Figure 3](image)

\textbf{Figure 3.} Selected carbene complexes of late transition metals with strong-field ligands.

Alkoxides have a pronounced weak-field character that can potentially form reactive carbenes. Alkoxides were rarely used as supporting ligands for the middle and late transition metals, being more common in the chemistry of early metals. The combination of hard alkoxide ligands with late metals may
lead to intriguing complexes, as such systems would combine characteristics of both Fischer and Schrock carbenes. Furthermore, such systems may lead to new reactivities not yet observed in the literature.

1.3. Formation and design of discrete alkoxide complexes

Alkoxides are among the most common and easily synthesizable ligands for transition metals. Until relatively recently, however, alkoxides were mostly employed as ligands at oxophilic early transition metals, for which alkoxides were considered to be a natural fit due to the hard-hard match of ligand and metal. The recent interest in alkoxides as ancillary ligands at later transition metals, particularly 3d, was primarily due to the formation of strong metal-alkoxide bonds. The higher electronegativity of oxygen (compared with carbon or nitrogen), however, should result in alkoxide being a weaker σ-donor than amide and alkyl. The presence of the occupied π-symmetry orbitals on the oxygen leads to π-donor character of the alkoxide. Due to the combination of weak σ-donation and π-donation, alkoxides could be considered among the weakest-field ligands. The weak-field nature could subsequently lead to the reactive carbene functionality due to the anticipated high-spin configurations at the metal centers in these complexes. However, the sterics imposed by alkoxide ligands can be problematic. The cone angle of amido [NR₂] and alkyl [CR₃] ligands, featuring two and three R groups, respectively, is much larger than that of an alkoxide [OR], which features a single substituent.

The lack of steric protection and the presence of the lone pairs on the oxygen makes formation of well-defined mononuclear complexes difficult, instead resulting in cluster formation. This is particularly common for the π-basic later metals. The presence of filled d orbitals prevents π-donation from the alkoxide lone pairs, increases their basicity, and leads to bridging. For example, simple tert-butoxo [OCMe₃] (or smaller) alkoxides result in cluster formation. Two methods to synthesize discrete alkoxide complexes of low nuclearity include electron-withdrawing or extremely bulky substituents at the alkoxide carbon. The electron-withdrawing substituents are effective at reducing the basicity of reactive lone pairs on oxygen. Thus, even relatively non-bulky ligands (e.g. [OC(CF₃)₃]), comparable in size to [OC(CH₃)₃], form mononuclear complexes. In contrast, extremely bulky alkoxides simply prevent bridging by steric congestion, while maintaining π-basicity of the oxygen lone pairs. Furthermore, the steric bulk of the
alkoxide can be carefully modified to selectively form alkoxide complexes featuring different nuclearities and coordination numbers. Thus, it is hypothesized that steric bulk can lead to the low-coordinate mononuclear environments in which the electronic nature of the functionality of interest (carbene) can be affected via enhanced π-basicity of the alkoxide oxygen (Figure 4).

**Figure 4.** Steric and electronic aspects of alkoxide coordination in M(OR)₂(=CR₂) complexes.

A large variety of alkoxide ligands [OCR₃] featuring identical or different R groups can be easily synthesized by nucleophilic attack of an organometallic reagent on the corresponding ketone/ester (Figure 5), resulting in the lithiated form of the ligand. The acidic workup results in the protonated, stable, and generally more easily handled form of the ligand. Alkoxide complexes are most commonly synthesized via salt metathesis using an alkoxide salt (i.e. EOR₃, E = Li⁺, Na⁺, K⁺, Tl⁺) or via protonolysis of HOR₃ with metal amides.

**Figure 5.** Typical synthetic routes to the alkoxide ligands.
In past years, many different [OCR₃] featuring identical or different R groups were synthesized. [OC'Bu₃] (“tritox”) is a thoroughly studied bulky alkoxide ligand, whose transition metal chemistry was studied early by the groups of Wolczanski and Power. Tritox was proposed to be a steric (similar cone angle and symmetrical shape) and electronic (potentially one σ and two π orbitals donor) analogue of ubiquitous cyclopentadienyl (Cp). Tritox is more σ-withdrawing than cyclopentadienyl and is expected to form more electrophilic and reactive metal centers. The steric bulk of [OC'Bu₃] led to the selective formation of the bis(alkoxide) [M(OC'Bu₃)₂] complexes with transition metals. However, the utilization of tritox as an ancillary ligand in group-transfer chemistry was hampered by its several deficiencies. At early transition metal complexes, tritox underwent facile decomposition to a metal-oxo and organic products from heterolytic splitting of the O-CR₃ bond. This decomposition was particularly favored for heavier early transition metals (Zr, Ta), likely due to the strength of the ensuing metal-oxo bonds. Another decomposition pathway included C-C bond cleavage, as was observed for Cr to give Cr(II)(OC'Bu₃)₂(OC'Bu₂H) upon heating [Cr(II)(OC'Bu₃)₂Li(THF)₂] in hexanes. Furthermore, tritox complexes possessing three tert-butyl groups often exhibited poor crystallinity, thus inhibiting structural characterization by X-ray crystallography. As a result, Wolczanski and coworkers shifted their focus to the related [OSi'Bu₃] ligand (“silox”), which exhibited similar stereoelectronic properties with a more stable O-Si bond and higher crystallinity. It should be noted that 3d transition metals form less stable metal-oxo bonds, particularly at middle and late ones, thus generating highly stable [M(OC'Bu₃)₂] complexes. Similarly, other bulky symmetrical alkoxides, such as [OCPh₃] and [OCCy₃] (Cy = cyclohexyl, Figure 6) formed stable bis(alkoxide) complexes with later 3d transition metals.

![Figure 6. Commonly used bulky symmetric alkoxides (siloxides) forming mononuclear 3d complexes.](image-url)
The promise of bulky alkoxides as weak-field ancillary ligands prompted other groups to explore additional ligand candidates of non-symmetric alkoxides [OCR,R’] (Figure 7). The motivation behind breaking the perfect “conical symmetry” of [OCR] species by installing one significantly different R’ group was to improve their conformational adaptivity. This gives a means to achieve more robust and less labile structures locked in a preferred orientation to result in tighter packing, more stable complexes, and higher crystallinity.20a Furthermore, permutation of different R/R’ groups creates a larger number of new ligand candidates [OCR,R’] as opposed to a limited number of [OCR]. Most of the recent efforts focused on three kinds of non-symmetric bulky alkoxides, [OC’Bu₂H], [OC’Bu₂Me], and [OC’Bu₂Ph] (or its derivative [OC’Bu₂(3,5-Ph₂Ph)], (Figure 7). In all cases, two tert-butyl substituents were retained to keep the ligand sufficiently bulky and soluble in low-polarity solvents, while creating a steric gradient accessible through the third substituent.

![Figure 7. Recently designed bulky non-symmetric alkoxides forming mononuclear 3d complexes.](image)

Changing one of the R groups on the alkoxide ligand to the smallest possible group, a hydrogen, led to both tris- and tetrakis(alkoxide) complexes (Figures 8 and 9).27 While protonolysis was not achievable with chromium and vanadium amides, even in boiling toluene, tris- and tetrakis(alkoxide) complexes were synthesized via salt metathesis with chromium salts. One disadvantage of synthesizing alkoxide complexes via salt metathesis is that it often leads to systems where the alkali metal remains attached. This is a particularly common occurrence when coordinating solvents such as THF are present. Indeed, reaction of LiOCH’Bu₂ and CrCl₃(THF)₃ in ether gave [Cr[OC’BuH₂]₂(μ²-OC’Bu₂Me)₂Li(THF)]. The bridging alkoxide features an elongated Cr-O bond for the bridging alkoxides and shorted Cr-O bonds
for the terminal alkoxides. This complex reacts with O$_2$ to form monomeric Cr$^{IV}$(OC'Bu$_2$H)$_4$, which is also achieved by treating CrCl$_3$ with LiOCH'Bu$_2$ in ether. Treating FeCl$_3$ with LiOCH'Bu$_2$ in ether gave [Fe$^{III}$(OC'Bu$_2$H)$_2$(μ$_2$-OC'Bu$_2$Me)$_2$Li(OC'Bu$_2$H)], similar to the analogous reaction with CrCl$_3$. In the case of iron, [OC'Bu$_2$H] is coordinated to lithium in contrast to THF observed with chromium (Figure 8). The coordination of alkoxide versus ether showcases its strength as a ligand. The lack of formation of Fe$^{IV}$(OC'Bu$_2$H)$_4$ is primarily due to chromium being more readily oxidized than iron and that iron is much more commonly found in the trivalent form than the tetravalent form. In contrast with chromium and iron, manganese and cobalt complexes of [OC'Bu$_2$H] can be synthesized from the corresponding manganese and cobalt amides, presumably due to the smaller size of Mn and Co as compared with Cr and Fe (Figure 9). Treatment of Mn(N(SiMe$_3$)$_2$)$_2$ with HOC'Bu$_2$H gave the trimeric species [Mn$^{II}$(OC'Bu$_2$H)(μ$_2$-OC'Bu$_2$Me)$_2$]$_2$Mn$^{II}$, where two manganese centers contain one terminal and two bridging alkoxide ligands, with the third manganese is bound to four bridging alkoxide ligands. In contrast, the reaction of Co(N(SiMe$_3$)$_2$)$_2$ with HOC'Bu$_2$H in ether produced the dimeric tris(alkoxide) species Co$^{II}$(OC'Bu$_2$H)(μ$_2$-OC'Bu$_2$Me)$_2$ featuring one terminal and two bridging alkoxide ligands.

Figure 8. Synthesis of Cr and Fe tetra(alkoxides) of [OC'Bu$_2$H].
Figure 9. Synthesis of Mn and Co tetra and tris(alkoxides) of [OC'Bu₂H].

To prevent the formation of tetra(alkoxide) complexes M(OC'Bu₂H)₄ inherent with [OC'Bu₂H], the Nocera group investigated the slightly bulkier ligand [OC'Bu₂Me]. Nocera and coworkers postulated that the R group of steric impact between H and 'Bu would lead to selective formation of tris(alkoxide) species. [OC'Bu₂Me] (ditox) led to several tris(alkoxide) complexes across the first-row transition series, featuring either trigonal planar, trigonal monopyramidal, or tetrahedral structures, depending on whether the solvent coordinated to the metal. Ditox complexes exhibited high crystallinity due, in part, to the preferred “head-to-tail” circular arrangement of [OC'Bu₂Me] that positioned the smaller methyl group next to the tert-butyl group of the adjacent ligand.

Tris(alkoxide) complexes [M''(OC'Bu₂Me)₃]⁺ (M = Mn-Co) and [M''(OC'Bu₂Me)₃] (M = V, Cr, Fe) were synthesized via salt metathesis with three equivalents of LiOC'Bu₂Me (or KOC'Bu₂Me) and the MX₂/MX₃ precursors. The M(II) tris(ditox) complexes were initially isolated as distorted trigonal planar “ate” species [M''(OC'Bu₂Me)(μ²-OC'Bu₂Me)₂M'(THF)ₙ] (M = Mn, Fe; M' = Li, K; n = 2, 1) (Figure 10). Intercalation of alkali metal in these complexes results in one terminal and two bridging alkoxide ligands with two wide and one contracted RO-M-OR angles. However, abstraction of the alkali metal with a suitable crown ether leads to the isolation of well-defined mononuclear anions [M''(OC'Bu₂Me)₃]⁻ (M = Mn, Fe), both exhibiting trigonal planar geometries with nearly identical RO-M-OR angles. Magnetic susceptibility measurements indicate high-spin states in all cases, which are close to spin-only values. In contrast, reactions of MCl₃ (M = V, Cr, Fe) with three equivalents of ditox resulted in [M''(OC'Bu₂Me)₃L]
(L = THF, absent; Figure 11). The vanadium and iron complexes contain bound THF ligand occupying the axial position of the distorted trigonal monopyramidal structures. In contrast, chromium resulted in trigonal planar geometry, lacking bound solvent molecule. All of the tris(alkoxide) complexes exhibit high-spin configurations, consistent with the weak-field nature of the alkoxide ligand.

\[
\text{MCl}_2 + 3 \text{LiOR} \xrightarrow{\text{THF}} \text{RO-} \text{M-} \text{Li-} \text{THF}
\]

\[
\text{MCl}_2 + 3 \text{KOR} \xrightarrow{\text{THF}} \text{RO-} \text{M-} \text{K} \text{THF}
\]

\[\text{M = Mn, Fe} \quad \text{OR = O} \quad \text{Me}
\]

\[\text{OR = O} \quad \text{Me} \quad \text{Bu}
\]

\[
\text{MCl}_3 \text{L}_3 + 3 \text{LiOR} \xrightarrow{\text{THF}} \text{RO-} \text{M-} \text{OR}
\]

\[\text{M = V, Cr, L = THF} \quad \text{M = V, Fe, L = THF} \quad \text{M = Cr, L absent}
\]

**Figure 10.** Synthesis of \([\text{M}^{\text{II}}(\text{OC}^\text{tBu}_2\text{Me})_3]\)^{\text{+}} species.

**Figure 11.** Synthesis of \([\text{M}^{\text{III}}(\text{OC}^\text{tBu}_2\text{Me})_3]\)L species.

The third non-symmetric alkoxide ligand system investigated in the context of group-transfer chemistry is [OC^tBu_2Ph]. The design of [OC^tBu_2Ph] resulted from the desire to form bis(alkoxide) species selectively, by replacing one of the R groups of [OC^tBu_3] to something of steric impact between Me and tBu. The steric impact of a phenyl ring is significantly larger than methyl and is expected to prevent
formation of tris(alkoxide) ligation observed for [OC'Bu₂Me]. Furthermore, the phenyl group increases crystallinity, and the steric properties of the complex can be easily modified via ortho, meta, or para substitution. Substitution in the meta positions produced a slightly bulkier variant of [OC'Bu₂Ph], [OC'Bu₂(3,5-Ph₂Ph)].

Substitution at the meta position, in contrast with the ortho position, prevents unwanted intramolecular C-H activation. Studies conducted so far demonstrated selectivity of [OC'Bu₂Ph] towards formation of bis(alkoxide) platforms, albeit tris(alkoxide) ligation for [OC'Bu₂Ph] was also shown to be possible for Fe and Cr. In contrast, [OC'Bu₂(3,5-Ph₂Ph)] was shown to exclusively form M(OC'Bu₂(3,5-Ph₂Ph))₂ complexes, even in the presence of 3:1 ratio of [OC'Bu₂Ph]:[M].

Two synthetic routes were found to lead reliably to M(OR)₂(THF)₂ complexes (M = Cr-Co; OR = OC'Bu₂Ph, OC'Bu₂(3,5-Me₂Ph)). Salt metathesis of MCl₂ (M = Cr-Co) with LiOC'Bu₂Ph initially formed interesting small clusters [M₂Li₂Cl₂(OC'Bu₂Ph)₄] featuring seesaw geometry at the transition metals. The reaction likely proceeded via [MLiCl(OC'Bu₂Ph)₂(THF)₂] intermediates (observed directly only for iron) (Figure 12). For nickel, the reaction stopped at the [NiLiCl(OC'Bu₂Ph)₂(THF)₂] (or [NiLiBr(OC'Bu₂Ph)₂(THF)₂]) intermediate, and did not proceed further. Abstraction of the intercalated Li and Cl was achievable for M = Mn - Co by subsequent treatment of the clusters [M₂Li₂Cl₂(OC'Bu₂Ph)₄] with TlPF₆. Precipitation of TlCl and LiPF₆ forms the desired monometallic species M(OR)₂(THF)₂. However, [Cr₂Li₂Cl₂(OC'Bu₂Ph)₄] failed to produce an isolable product and thus was synthesized via protonolysis of Cr(N(SiMe₃)₂)₂(THF)ₙ with HOC'Bu₂Ph. The protonolysis route was also used to synthesize Cr and Fe bis(alkoxide) complexes with the bulkier alkoxide [OC'Bu₂(3,5-Ph₂Ph)] (Figure 13). Treatment of M(N(SiMe₃)₂)₂(THF)ₙ with HOC'Bu₂(3,5-Ph₂Ph) yielded Fe(OC'Bu₂(3,5-Ph₂Ph))₂(THF)₂ (M = Cr, Fe). Notably, the bulkier second generation alkoxide produced the monomeric chromium species, in contrast to the dimer observed for [OC'Bu₂Ph].
Figure 12. Reactions of MCl₂ (M = Cr - Ni) with two equivalents of LiOC\textsubscript{t}Bu\textsubscript{2}Ph leading to the formation of M(OC\textsubscript{t}Bu\textsubscript{2}Ph\textsubscript{2})(THF)\textsubscript{2} for M = Mn-Co.

Figure 13. Reactions of metal-amide precursors with HOC\textsubscript{t}Bu\textsubscript{2}Ph and HOC\textsubscript{t}Bu\textsubscript{2}(3,5-Ph\textsubscript{2}Ph).

M(OC\textsubscript{t}Bu\textsubscript{2}Ph\textsubscript{2})(THF)\textsubscript{2} and M(OC\textsubscript{t}Bu\textsubscript{2}(3,5-Ph\textsubscript{2}Ph\textsubscript{2}))(THF)\textsubscript{2} species exhibit coordination geometries intermediate between seesaw and tetrahedral. The RO-M-OR angles were in the range between 130-139 ° for [OC\textsubscript{t}Bu\textsubscript{2}Ph]; slightly wider angles of 142° (Fe) and 147° (Cr) were observed for complexes of bulkier [OC\textsubscript{t}Bu\textsubscript{2}(3,5-Ph\textsubscript{2}Ph)]. THF-M-THF angles were in the 85-95 ° range.

1.4. Alkoxides as Supporting Ligands for Schrock carbenes Mo(OR)\textsubscript{2}(=NAr)(=CHR)

Interest in pursuing carbene complexes with alkoxide ligation was sparked by the success of their use as ancillary ligands in Schrock-type carbenes, commonly used as olefin and alkyne metathesis catalysts.
The generalized structure of Schrock olefin metathesis pre-catalyst is $\text{Mo}(\text{X})_2(=\text{CHR})(=\text{NR'})$ where at least one or both X ligands are hard alkoxides.\textsuperscript{9} Alkoxides are an excellent match in these structures to support high-oxidation-state, hard Mo(VI) centers. Exposing Mo(OCMe(CF$_3$)$_2$(CHR)(NAr) to LiO'Bu in pentane gave [Mo(O'Bu)$_2$(CHR)(NAr)], which was shown to serve as initiators for living cyclopolymerization of diethylidipropargylmalonate.\textsuperscript{33} X-ray structural studies revealed monomeric tetrahedral structures and syn geometry of the alkylidene functionality. Other, fluorinated, alkoxide complexes of molybdenum active in polymerization reactivity include Mo(OC(C$_6$F$_5$)$_3$)$_2$(NC$_6$F$_5$)(CHCM$_2$Ph) and Mo(NC$_6$F$_5$)(CHCM$_2$Ph)(OC(CF$_3$)$_2$)$_2$. These complexes were obtained from an octahedral Mo(VI) bis(triflate) precursor in good yields; related W(VI) complexes were synthesized and investigated as well.\textsuperscript{34} The combination of alkoxide and pyrrolide ligands (in addition to imido and alkylidene) allowed formation of stereogenic metal center to improve selectivity in enyne ring-closing metathesis to give endo products exclusively.\textsuperscript{35} Related bimetallic Mo complexes linked through the di(alkylidene) functionality were synthesized and structurally characterized, and their ring-opening metathesis polymerization (ROMP) reactivity was investigated.\textsuperscript{36}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{schrock_alkyldene_catalysts.png}
\caption{Synthesis of Schrock-alkylidene catalysts active in various polymerization chemistries.}
\end{figure}
1.6. Previously Reported Carbene Complexes of Cobalt

The scope of isolable non-NHC cobalt carbene complexes is relatively few in number. The majority of these cases is limited to complexes featuring low-oxidation state Co(0)/Co(I) and are characterized as Fischer type carbenes possessing elongated Co-C bonds ([Figure 15]).\textsuperscript{37} The two earliest reported structurally characterized examples are the cobalt triphenyl germanyl\textsuperscript{37a} and triphenyl stannyl\textsuperscript{37c} complexes possessing long Co-C bonds of 1.91 Å and 1.999(4) Å, respectively. Both of these complexes feature strong-field carbonyl and/or phosphine ancillary ligands with heteroatom substituents on the carbene carbon, typical of Fischer carbenes. The Zr-Co carbene complex containing the amido-phosphine ligand bridging the Zr-Co metals features a long Co-C bond of 1.906(2) Å.\textsuperscript{37d} The fluorinated cobalt carbene contains the shortest Co-C bond of 1.740(1) Å due to the electron-withdrawing substituents, but was nonetheless characterized as a Co(I) Fisher carbene.\textsuperscript{37e} In all these cases the carbene was characterized as a neutral dative ligand, in contrast to the dianionic nature of Schrock carbenes.

\textbf{Figure 15.} Selected examples of structurally characterized Co(I) carbenes.

In contrast, the Co(III) porphyrin carbene radicals have recently been reported to catalyze various C-C bond formation reactions.\textsuperscript{38} However, the high reactivity of these species has precluded their isolation and their electronic structures have been probed through DFT and radical trapping experiments, as well as by cryogenic EPR studies. Furthermore, several of these carbene transfer systems were shown to be highly enantioselective in asymmetric C-C bond formation reactions ([Figure 16]). By substituting the meso-phenyl groups on the porphyrin ring with a chiral cyclopropanecarboxamide containing two contiguous stereocenters, several $D_2$-symmetric chiral amidoporphyrins cobalt complexes were reported. The use of the harder porphyrin ligand, in contrast to softer phosphine/carbonyl groups facilitated a more reactive
carbene. The use of the even harder alkoxide ligation is expected to lead to a reactive carbene to undergo novel chemical transformations.

**Figure 16.** D$_2$-symmetric chiral amidoporphyrins cobalt complexes active in C-C bond formation.

### 1.7. Synthesis and Characterization of the First High-Valent Cobalt Carbene in a Bis(alkoxide) Ligand Environment

As mentioned above, heretofore the alkoxides were mostly used as ancillary ligands for the hard, high-oxidation state early transition metal-alkylidene complexes. Exploration into the alkoxide-supported carbene complexes, particularly of later transition metals, is lacking. The alkoxide ligation is expected to lead to a high-oxidation state novel carbene, whose electronic structure and reactivity are of interest. Recently, our group has reported the first example of the bis(alkoxide)-supported cobalt carbene complex, Co(OR)$_2$(=CPh$_2$) (OR = [OC$_t$Bu$_2$Ph]).$^{39}$ Treating Co(OC$_t$Bu$_2$Ph)$_2$(THF)$_2$ with diphenyldiazomethane N$_2$CPh$_2$ led to the isolation of Co(OC$_t$Bu$_2$Ph)$_2$(=CPh$_2$). Co(OC$_t$Bu$_2$Ph)$_2$(=CPh$_2$) exhibited a surprisingly short Co-$\text{C}_{\text{carbene}}$ bond (1.773 Å), suggesting formation of a Schrock-type alkylidene (Figure 17). This is the second shortest Co-C bond exhibited by a cobalt carbene; the shortest Co-C bond being 1.740(1) Å in the Co(PPh$_3$)Cp(=CFR$_1$) (R$_1$ = F, CF$_3$) discussed above.$^{37}$ Interestingly, solution magnetic measurements showed Co(OC$_t$Bu$_2$Ph)$_2$(=CPh$_2$) to be low-spin (S = $\frac{1}{2}$), in contrast to the high-spin nature expected of an alkoxide species. The electronic structure of the complex was further investigated to understand the nature of the carbene functionality. EPR analysis supports the ground state S = $\frac{1}{2}$ species ($g_x = 3.04(1)$, $g_y =
2.17(1), and $g_z = 1.91(1)$, where the unpaired electron is localized on the cobalt center, as seen from the eight-line hyperfine splitting.\textsuperscript{39} Cyclic voltammetry shows three reduction events at $-1.17 \, \text{V}$, $-2.46 \, \text{V}$, and $-3.16 \, \text{V}$, with the first two being quasi-reversible, supporting formation of a high-valent species. DFT calculations at the B3LYP/6-31G(d) level of theory gave Mulliken spin densities of 1.77 and -0.68 on cobalt and carbene carbon atoms, respectively, suggesting two $\alpha$ spins on cobalt and one $\beta$ spin on the carbene. This supported this species as an intermediate-spin Co(III) antiferromagnetically coupled to a carbene radical. However, the large $S_{\alpha\beta}$ value of 0.64 for the magnetically coupled orbitals suggested Co-C $\pi$ bonding, characteristic of a Co$^{IV}$ alkylidene. The interpretation of this species as lying in between the two electronic configurations lends further support in comparing the spin density on the carbene for the cobalt carbene to the analogous rhodium bis(alkoxide) alkylidene. The Mulliken spins are sensitive to functional,\textsuperscript{40} with a larger range of $-0.44$ (closer to Co$^{IV}$ alkylidene) to $-0.82$ (near the ideal values for Co$^{III}$ carbene radical) was found compared with a range of -0.1 to -0.2 for the Rh$^{IV}$ carbene. Thus, and “ideal” Rh alkylidene still possesses non-negligible spin density on the carbene moiety.

![Figure 17](image-url) Synthesis of the first high-valent cobalt carbene with diazoalkane.

1.8. Research Goals and Objectives

The overall goal of this research is to study novel late transition-transition metal carbene complexes in hard bis(alkoxide) ligand environments and their subsequent reactivity in group transfer chemistry. The use of late 3d transition metals offer the advantage over precious metals (e.g. Pd, Rh) of being more environmentally friendly, highly abundant, as well as cost-effective. The late transition metal in combination with hard alkoxide ligands is expected to make the carbene group more reactive and allow carbene transfer to a substrate. In contrast, strong-field ligands tend to stabilize the carbene functionality towards further transformations.
The alkoxide ligand presented in this body of work is the aforementioned [OC\textsuperscript{t}Bu\textsubscript{2}Ph], abbreviated [OR] henceforth (Figure 18). This bulky alkoxide ligand has previously been shown to form quasi low-coordinate bis(alkoxide) complexes for \(M = \text{Cr-Co}\), whose coordination chemistry is discussed above (1.3).

These complexes are most often isolated as THF bound adducts, which allow for isolation of systems with an open coordination site via readily dissociation of THF in presence of a suitable carbene precursor, a diazoalkane. The overall features of our system (Figure 18) allow us to obtain well-behaved mononuclear carbene complexes and to study their electronic structure and reactivity.

Figure 18. Quasi low-coordinate bis(alkoxide) system utilized in this work.

The overall goal of this work is to investigate the formation of the novel late-transition-metal carbene complexes in the bulky bis(alkoxide) ligand environment (by reactions with diazoalkanes) and explore their subsequent reactivity. This will be achieved in the following objectives:

- **Reactivity of Cobalt Bis(alkoxide) Complexes in Carbene Transfer Towards Isocyanides to form Ketenimines.** Reactivity of Co(OR)\textsubscript{2}(\equiv\text{CPh})\textsubscript{2} and related cobalt-carbene complexes resulting from diazoesters towards group transfer to isocyanides to form ketenimines will be presented in Chapter 2.

- **One Electron Reduction Transforms High-Valent Low-Spin Cobalt Alkylidene into High-Spin Cobalt(II) Carbene Radical.**
Synthesis and characterization of the reduced cobalt carbene complex \([\text{Co(OR)}_2(=-\text{CPh}_2)]^-\) and its reactivity in C-C bond formation will be presented in **Chapter 3**.

*Transition Metal-mediated Reductive Coupling of Diazoesters*. Reactivity of related iron bis(alkoxides) \(\text{Fe(OR)}_2(\text{THF})_2\) towards diazoalkane/diazoesters to undergo reductive coupling, in contrast to carbene formation, will be presented in **Chapter 4**.
CHAPTER TWO REACTIVITY OF COBALT BIS(ALKOXIDE) COMPLEXES IN CARBENE TRANSFER TOWARDS ISOCYANIDES TO FORM KETENIMINES

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2.1. Introduction: Syntheses and Reactions of Ketenimines

Ketenimines $R^1(R^2)C=C=NR^3$ are reactive organic species that are similar in their properties, stability, and chemical reactivity to ketenes $R^1(R^2)C=C=O$ and allenes $R^1(R^2)C=C=CR^3(R^4)$. Similar to ketenes, ketenimines undergo nucleophilic reactivity at the terminal carbon and electrophilic reactivity at the central carbon and are commonly used as reactive precursors in organic synthesis. Due to their reactive nature, ketenimines can serve as highly useful synthons in the production of nitrogen-containing molecules. However, ketenimines are generally synthesized stoichiometrically, leading to significant amount of by-products and unwanted side reactions. Ketenimine formation has been reported with diazoalkane and isocyanide (Figure 19). However, it usually requires thermolysis or photolysis in the absence of a transition metal. The use of transition metal catalysis enables formation of ketenimines from diazoalkanes and isocyanides under milder conditions and leads to smaller amounts of by-products. However, catalytic ketenimine formation from isocyanides and transition metal carbene species is relatively rare. The reaction of transition metal catalysts with diazoalkanes and isocyanides generally proceeds via the initial formation of carbene intermediates and dinitrogen (Figure 20). At the next step, isocyanide attacks the carbene to form a metal-bound ketenimine that needs to dissociate from the metal to enable the full catalytic turnover. Catalytic turnover often fails as in most cases the ketenimine group remains bound to the transition metal. Successful elimination of free ketenimine has been achieved with Fischer type carbenes, but the need to restore the carbene group in such complexes generally prevented catalysis. Rare examples of the catalytic formation of ketenimines from isocyanides and diazoalkanes are presented in Figure 21. In both cases, the catalytic formation of ketenimine required heating and had limited reaction scope; only $Ph_2C=C=NTBu$ was observed for the nickel complex and $PhHC=C=NTBu$ for the rhodium
Notably for the nickel species, it was shown that ketenimine formation occurred via coordination of isocyanide to the one metal center of the bridged-carbene species.

\[
\text{N}_2 \quad + \quad \text{CNR}^3 \quad \xrightarrow{\Delta \text{ or } h\nu} \quad \text{C} = \text{C} = \text{N}^1 \quad \text{R}^1 \quad \text{R}^3
\]

Figure 19. Stoichiometric formation of ketenimines from diazoalkane and isocyanide.

As noted above, the first high-valent cobalt carbene Co(OR)\(_2\)(=CPh\(_2\)) was isolated upon reaction of Co(OR)\(_2\)(THF)\(_2\) with N\(_2\)CPh\(_2\) (OR = OC\(_{\text{tBu}}\)Ph). Initial reactivity studies on this complex focused on cyclopropanation between Co(OR)\(_2\)(=CPh\(_2\)) or Co(OR)\(_2\)(THF)\(_2\) and styrene. However, the reaction produced only small amount (10% yield or less) of the cyclopropane product, even at elevated temperatures. As this lack of reactivity could be due to overall steric effects associated with the coordination of the \(\eta^2\) substrate (an olefin), we decided to pursue reactivity studies with an intrinsically smaller, \(\eta^1\), substrate, isocyanide. Whereas the reaction of carbene with olefins produces cyclopropane, a successful reaction
between carbene and isocyanides is expected to produce ketenimines. This chapter demonstrates successful high-yield formation of ketenimines from the reaction of complex 2 and isocyanides. A catalytic extension of this reaction for select substrates and mechanistic investigations are also described.

2.2. Stoichiometric Reactivity of Co(OR)\(_2\)(=CPh\(_2\)) with Isocyanides

Exposure of 2 to 1 equivalent of 2,6-dimethylphenyl isocyanide CN(2,6-Me\(_2\)C\(_6\)H\(_3\)) at room temperature in C\(_6\)D\(_6\) resulted in a color change to dark red-brown. Monitoring the reaction by NMR showed clean formation of the respective ketenimine 3, along with total consumption of free isocyanide (Figure 22 and 23). Formation of 3 was also confirmed by GC-MS of the purified reaction mixture. Quantitative inspection of the NMR spectrum of the reaction mixture (with internal standard) showed ~30% conversion to 3, despite all of the free isocyanide being consumed. Isocyanide is an excellent ligand for transition metals and thus it was hypothesized that the remaining isocyanide is used to form a cobalt mono- or bis(isocyanide) complex. In partial support of this hypothesis, the NMR spectrum demonstrated signals which could be consistent with the presence of a new paramagnetic metal products. To further test this hypothesis, we pursued independent synthesis of such complexes. Exposing 1 to excess CN(2,6-Me\(_2\)C\(_6\)H\(_3\)) at room temperature in THF resulted in a color change to dark red. Recrystallization of the crude reaction mixture in ether at -35 °C overnight resulted in the isolation of red crystals of the cobalt bis(isocyanide) complex 4 (see below and Appendix B for the characterization of 4). Comparison of the \(^1\)H NMR spectrum of pure 4 to the spectrum of the crude reaction mixture between 2 and CN(2,6-Me\(_2\)C\(_6\)H\(_3\)) displayed peaks attributable to 4 in the spectrum. This experiment confirmed our hypothesis that bis(isocyanide) complex is a byproduct in the reaction, and therefore excess isocyanide is needed to obtain higher yields of the ketenimine product.

Exposure of 2 to excess CN(2,6-Me\(_2\)C\(_6\)H\(_3\)) resulted in significantly higher yield of 3 (85%). Stoichiometric ketenimine formation was also probed by exposing 2 to three additional isocyanides under the same reaction conditions (excess isocyanide). Reactions with adamantyl isocyanide, 4-methoxyphenyl isocyanide, and 3-chloro-6-methyl isocyanide resulted in clean formation of the respective ketenimines 5–7 in 86%, 97%, and 66% yield by \(^1\)H NMR, respectively. The nature of the products was confirmed by GC-
MS. Furthermore, isolation of cobalt bis(isocyanide) complexes \(8\) and \(9\) were achieved under conditions similar to that of \(4\) with adamantyl and 4-methoxyphenylisocyanide, respectively. While a similar color change was noted in the reaction of \(1\) with 2-chloro-6-methylphenyl isocyanide, attempted workup and recrystallization did not lead to an isolable species.

**Figure 22.** Formation of ketenimines and cobalt bis(isocyanide) complexes.

**Figure 23.** \(^1\)H NMR spectrum of the reaction between \(2\) and CN(2,6-Me\(_2\)C\(_6\)H\(_3\)) giving \(3\).
2.3. Characterization of Cobalt Bis(isocyanide) Complexes

Cobalt bis(isocyanide) complexes 4, 8, and 9 were obtained in 88, 80, and 78 % yields, respectively, and characterized by NMR, IR, and UV-vis spectroscopies, magnetic measurements, X-ray crystallography (4 and 9), and elemental analyses. Spin states of complexes 4, 8, and 9 are of interest as they contain a combination of strong-field (isocyanide) and weak-field (alkoxide) ligands. \(^{29-32}\) H NMR of all complexes displayed well-resolved paramagnetically shifted NMR spectra spread over approximately 30 ppm. We were able to fully assign all the resonances in the NMR spectra. The tert-butyl resonances of the alkoxide ligand (OC\(^{t}\)Bu\(_2\)Ph) resonate at 19.02, 19.26, and 18.95, for 4, 8, and 9, respectively. The phenyl groups of the alkoxide ligands appear as three distinct resonances at 20.88/20.90/19.96 ppm, 17.80/16.78/16.93 ppm, and 10.34/10.02/9.84 ppm for 4, 8, and 9, respectively. Resonances attributable to the isocyanide substituent are all shifted upfield. Solution magnetic properties, as obtained by the Evans method, confirm the high-spin nature of the complexes, all exhibiting a solution magnetic moment of 3.9 ± 0.4 \(\mu_B\) (C\(_6\)D\(_6\), room temperature), consistent with high-spin \(d^7\) Co(II) complexes (\(S = 3/2,\) spin-only). IR spectroscopy of the C≡N stretch for aryl isocyanides 4 and 9 appears at 2160 and 2168 cm\(^{-1}\), respectively, consistent with previously reported cobalt(II) aryl isocyanide complexes.\(^{50}\) The C≡N stretch for the alkyl (adamantyl) isocyanide complex 8 is at a lower energy of 2122 cm\(^{-1}\). While complexes of \(C\_2v\) symmetry should display two signals for the C≡N stretch, the appearance of only one may be due to peaks overlapping, as they appear somewhat broadened. This finding is consistent with the IR spectrum of the iron analogue of 4.\(^{49b}\)

X-ray quality crystals were obtained for complexes 4 and 9. The structures display crystallographic \(C_2\) symmetry and are shown in Figure 24 and 25, respectfully. Experimental crystallographic parameters are given in Table 1. Both complexes are distorted tetrahedral with a similarly wide angle between the alkoxide ligands of O-Co-O angle of 118.4(1)°/118.8(1)° and Co-O bonds lengths 2.039(2) Å/2.023(2) Å for 4/9, respectfully. In contrast, the metrical parameters of the isocyanide ligands display notable differences, presumably due to the different steric impacts of aryl groups. The Co–C bonds 2.039(2) Å/2.023(2) Å and C–Co–C angles 103.4(1)°/97.5(1)° for 4/9, respectfully displays the less congested environment around cobalt for smaller CN(4-OMe-C\(_6\)H\(_4\)). While crystals of 8 did not diffract, its molecular
composition was supported by elemental analysis, along with the similarities to the $^1$H NMR, IR, and UV-Vis spectra of 4 and 9.

Figure 24. X-ray structures of complex 4, 50% probability ellipsoids. H atoms were omitted for clarity. Selected bond distances (Å) and angles (°) for 4: Co–O1, 1.850(1); Co–C1, 2.039(2); C1–N1, 1.151(2); O1–Co–O1’, 118.4(1); C1–Co–C1’, 103.4(1).
Figure 25. X-ray structures of complex 9. 50% probability ellipsoids. H atoms were omitted for clarity. Selected bond distances (Å) and angles (°) for 9: Co–O1, 1.848(1); Co–C1, 2.023(2); C1–N1, 1.157(2); O1–Co–O1’, 118.8(1); C1–Co–C1’, 97.5(1).
Table 1. Experimental crystallographic parameters for 4 and 9.

<table>
<thead>
<tr>
<th>Complex</th>
<th>4</th>
<th>9</th>
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<tbody>
<tr>
<td>formula</td>
<td>$C_{24}H_{32}Co_{0.50}NO$</td>
<td>$C_{23}H_{30}Co_{0.50}NO_2$</td>
</tr>
<tr>
<td>Fw</td>
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<td>381.95</td>
</tr>
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<td>Monoclinic</td>
</tr>
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<td>$C2/c$</td>
</tr>
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<tr>
<td>$b$ (Å)</td>
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<td>9.3732(6)</td>
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<tr>
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<td>114.872(6)</td>
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<tr>
<td>$\gamma$ (deg)</td>
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<td>90.00</td>
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<td>4052.4(5)</td>
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<td>8</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
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<td>0.468</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
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<td>0.0351</td>
</tr>
<tr>
<td>GOF</td>
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<td>1.027</td>
</tr>
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</table>

DFT calculations were conducted to probe the energy difference between the doublet and quartet spin states. The calculations were done using the OPBE functional, which is known for its exceptional ability at predicting spin states,$^{51}$ as spin state splitting is a well-known obstacle for DFT.$^{52}$ As both 4 and 9 exhibited high-spin configurations, the calculations were conducted on their simplified model featuring phenyl isocyanide. Both mono- (10) and bis(isocyanide) (11) complexes are feasible products, and therefore the electronic structure of both complexes were calculated at the OPBE-APFD-SMD(benzene)/def2-
TZVP//OPBE/6-31G(d) level of theory.\textsuperscript{51,53} Formation of the mono(isocyanide) complex 10 is predicted to be energetically favorable as a low-spin doublet by 3.9 kcal/mol, whereas the bis(isocyanide) complex 11 favors the high-spin quartet by 3.0 kcal/mol. This finding is in agreement with a low- to high-spin crossover, despite the presence of strong-field isocyanide ligands. To understand this, we compared the frontier molecular orbitals of the low-spin doublet mono- and bis(isocyanide) species (\textbf{Figure 26}). There is a 0.8 eV increase in the HOMO upon coordination of a second isocyanide ligand due to the bonding interaction in this orbital switching from nonbonding to antibonding character, which becomes the SOMO in the doublet bis(isocyanide) species. Importantly, this compresses the energy gap of these three d orbitals from 1.7 eV to 1.1 eV upon coordination of the second isocyanide ligand, thus enabling the high-spin configuration observed for 4, 8, and 9.

\textbf{Figure 26.} Frontier orbital diagram for doublet species of mono-(left) (10) and bis(isocyanide) (right) (11) species. Orbital energies are based on alpha orbital energies only, and isosurface plots use isocontour value of 0.05 au.
2.4. Computational Investigation of the Mechanism of Carbene Transfer

We interrogated the mechanism of ketenimine formation by DFT calculations. The computational work was done in collaboration with the group of Prof. Lord at Grand Valley State University. Fundamentally, two diverging mechanistic possibilities exist for the C-C bond formation step. For the coordinatively saturated Fischer carbenes, the C-C bond formation was shown to occur through a direct nucleophilic attack at the carbene carbon.\(^{46}\) Alternatively, C-C bond formation can be preceded by the initial coordination of isocyanide to the metal center prior to C=C bond formation.\(^{6b,6c}\) Both C-C bond formation mechanisms were considered in our analysis. After bond formation between the carbene and isocyanide groups, the ketenimine can bind through the C=C bond (12), the C=N bond (14), or the N lone pair (15). Formation of all these species was calculated on the doublet and quartet energy level surfaces, denoted D and Q, respectively. Inspection of Figure 27 shows the major differences between these two energy level surfaces is in the mechanism of ketenimine formation. In the doublet energy level pathway, ketenimine is formed via coordination to the cobalt center, whereas the quartet energy level surface has isocyanide directly attacking the carbene carbon. Carbene complex 2\(_D\) was shown to be 3.9 kcal/mol lower in energy than 2\(_Q\), consistent with the previously reported electronic structure (S=1/2).\(^{39}\) From there, isocyanide binds to the cobalt center to afford 13. The formation of 13 is exergonic by 0.3 kcal/mol, with a barrier (2−13−TSD) of 17.9 kcal/mol relative to 2\(_D\) and isocyanide. The quartet energy level surface demonstrates that direct isocyanide attack at the carbene is much higher in energy with a barrier (2−13−TSQ) of 32.4 kcal/mol, inconsistent with the reaction mild experimental conditions. From intermediate 13\(_D\), formation of the C=C bond by insertion of the isocyanide into the carbene carbon is favorable with a barrier of (13−12−TSD) 7.2 kcal/mol. However, a spin-state crossover to the quartet energy level surface occurs during this transition, as 12\(_Q\) is favored over 12\(_D\) by 6.9 kcal/mol. After formation of the C=C bond, the ketenimine bound species can isomerize to C=N and N-bound isomers, being exergonic by 8.6 kcal/mol and 13.6 kcal/mol for 14 and 15, respectfully. However, ketenimine dissociation from 12\(_Q\) to give [Co(OR)\(_2\)] (16) is more favorable then various isomerizations, being exergonic by 12.6 kcal/mol with a barrier of 12−16−TSQ of 5.8 kcal/mol.
The Mulliken spin density of $2_D$ is 1.3 on the Co and $-0.4$ on the carbene C, consistent with a formulation between low-spin Co(IV) and intermediate-spin Co(III). The Mulliken spins upon coordination of isocyanide to the cobalt center in $13_D$ are similar at 1.1 and $-0.3$, suggesting no qualitative change in the electronic structure upon isocyanide binding. Following the C–C bond formation in $12_Q$, the spin on Co is 2.3 (2.9 including spins on the alkoxide ligands) and negligible on ketenimine. This agrees with a high-spin, $S = 3/2$ Co(II) ion, suggestive of reductive elimination occurring simultaneously with insertion.

Upon ketenimine dissociation, diazoalkane or isocyanide can bind to 16, giving the diazoalkane complex 17 or the mono(isocyanide) complex 10, respectively (Figure 28). Diazoalkane binding would be the productive pathway, as its formation leads to the carbene complex. However, binding of isocyanide is more favorable by 19.9 kcal/mol with a barrier of $16–10–TSQ$, being 6.5 kcal/mol. Binding of a second isocyanide to form 11 is slightly exergonic relative to 10 by 0.3 kcal/mol, providing evidence for formation of the bis(isocyanide) complexes in this reaction. Diazoalkane binding to give complex $17_Q$ is favored over
by 2.1 kcal/mol. Formation of $17_Q$ from $16_Q$ is only exergonic by 4.9 kcal/mol with a small barrier of 3.9 kcal/mol. These data point at the bis(isocyanide) complex $11_Q$ potentially being a thermodynamic sink in this transformation (15 kcal/mol more stable than $17_Q$). This finding provides rationale for the lack of catalytic turnover for N$_2$CPh$_2$ (vide infra).

Figure 28. Potential energy surface for the formation of isocyanide (right) and diazoalkane (left) adducts from $16_Q$. Gibbs free energies in kcal/mol.

2.5. Catalytic Carbene Transfer to Isocyanides to Form Ketenimines

Based on the high-yielding stoichiometric formation of ketenimines, we probed the catalytic potential of this reaction. Catalytic turnover using 10 mol% of I in C$_6$D$_6$ at room temperature over 24 hours was investigated (Table 2). Increased catalyst loading at 20 mol% was also tested in selected cases. In addition to the carbene precursor Ph$_2$CN$_2$, two commonly utilized diazoesters, methyl phenyldiazoacetate and ethyl diazoacetate were investigated. Two aryl isocyanides differing in their steric and electronic properties were used: 2,6-dimethylphenyl and 4-methoxyphenyl isocyanide. Additionally, three alkyl isocyanides differing in steric bulk were evaluated: tertiary adamantyl isocyanide, secondary cyclohexyl isocyanide, and primary benzyl isocyanide. Furthermore, formation of the respective azine and olefin by-
products were monitored, as these species are commonly observed in carbene chemistry.\textsuperscript{55} Utilizing diphenyldiazomethane with 2,6-dimethylphenyl isocyanide, 4-methoxyphenyl isocyanide, or cyclohexyl isocyanide (Table 2, entries 1-3) shows only stoichiometric or substoichiometric formation of the corresponding ketenimines. However, changing the carbene precursor to diazoesters enabled catalytic turnover. While no reaction was observed with the bulkier methyl phenyldiazoacetate and 2,6-dimethylphenyl isocyanide (Table 2, entry 4), 4-methoxyphenyl isocyanide demonstrated approximately three turnovers (Table 2, entry 5). Switching to alkyl isocyanides (Table 2, entries 6-8) show slightly differing reactivity based on the steric bulk of the isocyanide utilized. For adamantyl and cyclohexyl isocyanide, approximately 3-4 turnovers were observed (yields of 35% and 42%, respectively). Two turnovers are observed for the less bulky benzyl isocyanide. The improved reactivity of alkyl versus aryl isocyanides may be due to the formation of the less stable bis(isocyanide) complex 11 with alkyl isocyanides, which allows regeneration of the carbene complex.
Table 2. Catalytic formation of ketenimines from diazoalkane/diazoester and isocyanide with 1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Diazoalkane</th>
<th>Isocyanide</th>
<th>Mol % cat</th>
<th>Ketenimine</th>
<th>Yield (%)</th>
<th>Conversion (%)</th>
<th>By-products (I/II/III) (%)</th>
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<tr>
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<td>CN</td>
<td>10</td>
<td>Ph</td>
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<tr>
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*% conversion of diazoalkane.*
Next, the reactivity of commercially available ethyl diazoacetate was studied. Adamantyl isocyanide forms the corresponding ketenimine in quantitative yield (10 turnovers, Table 2, entry 11). Switching to the less bulky cyclohexyl isocyanide led to lower yield of the corresponding ketenimine in 48% yield (Table 2, entry 12a), which further decreased upon using primary benzyl isocyanide (28% yield of the product). Similar to methyl phenyldiazoacetate, no ketenimine product formation was observed for the mixture of ethyl diazoacetate and 2,6-dimethylphenyl isocyanide (Table 2, entry 9).

In order to see if increasing the catalyst loading would improve reactivity, 20 mol% of 1 was investigated with selected isocyanide (cyclohexyl). The yield of ketenimine doubled (84%) with methyl phenyldiazoacetate (Table 2, entry 7b). A smaller but improved yield of 71% was observed with ethyl diazoacetate (Table 2, entry 12b). The larger number of by-products produced with methyl phenyldiazoacetate compared with ethyl diazoacetate at 10 mol% catalyst loading may explain the differences in the improved yield at 20 mol% catalyst loading. Notably, control experiments combining methyl phenyldiazoacetate/ethyl diazoacetate and adamantyl/cyclohexyl isocyanide in the absence of complex 1 demonstrated no formation of ketenimine and/or conversion of the diazoalkane under the identical reaction conditions (RT, C_6D_6, 24 h).

As noted above, by-products formation, including azine, cis-olefin, and trans-olefin, were monitored in all cases. While diphenyldiazoalkane led primarily to the formation of benzophenone azine as the sole by-product, little to no by-products were observed for ethyl diazoacetate. In contrast, significant amounts of all three by-products were observed for methyl phenyldiazoacetate: trans-olefin (dimethyl 2,3-diphenylfumarate), cis-olefin (dimethyl 2,3-diphenylnmaleate), and the corresponding azine (dimethyl 2,2'- (hydrazine-1,2-diylidene)bis(2-phenylacetate)). The reactions involving cyclohexyl and 4-methoxyphenyl isocyanide resulted in the most significant yields of these by-products. As noted above, increasing the catalyst loading of cyclohexyl isocyanide decreased formation of these species. The cis-olefin and azine were formed in 16% and 17% yield, respectively at 10 mol% yield versus a ~5% yield each for all three by-products at 20 mol% yield. With 4-methoxyphenyl isocyanide, 50% of the diazoester is converted with formation of the trans-olefin, cis-olefin, and azine in 5%, 15%, and 5%, respectively. Notably, adamantyl
isocyanide formed trace amounts of the trans-olefin (<2%) and no by-products are observed in the NMR with benzyl isocyanide. The lack of observed olefin/azine by-products for benzyl isocyanide/methyl phenyldiazoacetate reaction may be due to formation of additional unidentified by-products (for example, resulting from further reactions of unstable ketenimine). In most of the cases, formation of ROH was also observed by NMR and GC-MS.

2.6. Differences in the Reactivity between Diazoalkane N₂CPh₂ and Diazoesters

In order to understand the differences in catalytic turnover between diazoalkane and diazoester, stoichiometric mechanistic experiments were conducted (Figure 29). As noted above, the bis(isocyanide) complexes Co(OR)₂(CNR')₂ was previously hypothesized to be a thermodynamic sink in the mechanism by DFT calculations. Treatment of carbene complex 2 with 2,6-dimethylphenyl isocyanide showed formation of the bis(isocyanide) complex 3. However, the reaction is not reversible as the addition of diphenyldiazomethane to 3 in THF or C₆D₆ retained the red color of 3 and failed to produce black-brown color indicative of 2. NMR spectra confirmed the lack of reactivity, as peaks of unreacted 3 and diphenyldiazomethane remained present. In contrast, treatment of Co(OR)₂(CNAd)₂ (8) with ethyl diazoacetate enabled turnover. NMR monitoring of the reaction indicated formation of the ketenimine product and disappearance of 8. This different reactivity is attributed to the presence of the coordinating α-carbonyl group in diazoester, which enables substitution of the isocyanide ligands from the bis(isocyanide) complex.

![Figure 29](image-url)  
*Figure 29.* Different reactivity of Co(OR)₂(CNR')₂ with diphenyldiazomethane and ethyl diazoacetate.
2.7. Investigation of a Cobalt Carbene Featuring Diazoester Substituent, [Co(OR)$_2$(=C(CO$_2$Me)Ph)]

It is likely that the formation of ketenimines proceeds via the same cobalt-carbene intermediate for the diazoesters as for the diazoalkane (2). Thus, we attempted to synthesize and characterize carbene complexes with ester substituents. As the bulkier “push-pull” methyl phenyldiazoacetate is likely to result in a more stable carbene complex, our efforts focused on this carbene. Adding methyl phenyldiazoacetate to a stirring solution of 1 in C$_6$D$_6$ led to an immediate color change to dark brown, similar to the observed in the formation of 2. NMR characterization of the crude reaction mixture suggested formation of the major paramagnetic product, postulated [Co(OR)$_2$(=C(CO$_2$Me)Ph)] (18), along with unreacted diazoalkane. As the paramagnetic nature of the cobalt carbene precluded reliable identification by NMR, the reaction was also monitored by UV-Vis spectroscopy. The UV-Vis spectrum of an aliquot of the reaction mixture upon immediate addition of methyl phenyldiazoacetate displayed a single peak around 560 nm. The spectrum of 18 was similar to that of 2, which displays a single peak in at 483 nm. Both spectra were very different from the cobalt precursor 1 (Figure 30). Despite the bathochromic shift of the peak in 18 compared to 2, its appearance provides evidence for its initial formation. Monitoring this reaction over 50 minutes showed gradual disappearance of the peak at 560 nm and growth of a peak at 648 nm (see Appendix B). Attempted crystallization of “Co(OR)$_2$(=C(CO$_2$Me))Ph” yielded instead crystals of trans-olefin 19 (see Appendix B), whose characterization was previously reported (Figure 31). While the structure of 19 is different from previous reported structures of the trans-olefin (C=C bond is 1.336(2) Å in 19 versus 1.402 and 1.342 Å in earlier reported structures), it is identical to the C=C bond distance in the structure of cis-olefin. Formation of olefin supports the existence of the transient carbene in our system, which undergoes dimerization in the absence of additional substrate.
Figure 30. UV-Vis spectrum of 1, 2, and 18 supporting formation of the transient “Co(OR)₂(=C(C₂O₂Me)Ph)”.

Figure 31. Proposed formation and decomposition of 18 to give 19.

Based on DFT calculations in combination with stoichiometric and catalytic reactions presented above, a possible catalytic mechanism is presented in Figure 32. Initial coordination of isocyanide to the cobalt-carbene complex occurs to form the mono(carbene) mono(isocyanide) complex 13. Next, C-C bond formation occurs to form the ketenimine complex 12. Further addition of isocyanide leads to the
dissociation of free ketenimine and forms the bis(isocyanide) complex 11. For the more reactive diazoester substrate, cobalt carbene is regenerated, enabling overall catalytic turnover.

**Figure 32.** Proposed catalytic mechanism for the formation of ketenimines with [Co(OR)$_2$] system.

2.7. Summary and Conclusions

This chapter focused on the reactivity studies of the first high-valent cobalt carbene complex 2. The combination of Fischer and Schrock characteristics in one carbene complex allows for unique reactivity of the system. Although 2 fails to undergo efficient cyclopropanation reactivity, the use of an intrinsically less bulky $\eta^1$ isocyanide substrate leads to facile high-yielding formation of ketenimines. Stoichiometric experiments demonstrate the formation of cobalt bis(isocyanide) complexes Co(OR)$_2$(CNR')$_2$ as by-products in ketenimine formation. Co(OR)$_2$(CNR')$_2$ complexes were independently synthesized from Co(OR)$_2$(THF)$_2$ (1) and were characterized by X-ray diffraction, NMR spectroscopy, elemental analysis, UV-Vis spectroscopy, and IR spectroscopy. All the resonances of Co(OR)$_2$(CNR')$_2$ can be identified in their paramagnetically shifted NMR spectra, allowing for their identification of their formation in the stoichiometric reactions to form ketenimine from 2. DFT calculations suggest ketenimine formation occurs by initial coordination of the isocyanide to the cobalt center, in contrast to direct attack on the carbene carbon. Intramolecular insertion from this intermediate is followed by the reductive elimination. The resulting ketenimine complex readily dissociates free ketenimine to form the bis(isocyanide) product.
Catalysis was investigated with both diazoalkane/diazoester and aryl/alkyl isocyanides at room temperature. While only stoichiometric reactivity was obtained with diazoalkane, the use of diazoester enables turnover. The possibility of turnover with diazoesters is likely due to the more facile substitution/dissociation of isocyanide by a diazoester (as opposed to diazoalkane) which enables regeneration of the cobalt carbene intermediate. Formation of ketenimines was more favored for bulky alkyl isocyanides (adamantyl and cyclohexyl) than non-bulky alkyl (benzyl) or aryl isocyanides. Significant amount of azine and olefin by-products were observed in the reaction with methyl phenyl diazoacetate and cyclohexyl or 4-methoxyphenyl isocyanide. Increasing catalyst loading improves the yield by decreasing byproduct formation and utilizing the less sterically bulky ethyl diazoacetate results in no byproduct formation.

2.8. Experimental Details

**General Methods and Procedures.** All reactions involving air-sensitive materials were executed in a nitrogen-filled glovebox or by standard Schlenk line procedures. Cobalt chloride, ethyl diazoacetate (15% solution in toluene), 2,6-dimethylphenyl isocyanide, 4-methoxyphenyl isocyanide, 2-chloro-6-methylphenyl isocyanide, benzyl isocyanide, cyclohexyl isocyanide, trimethoxybenzene, and hexamethylbenzene were purchased from Sigma-Aldrich. Adamantyl isocyanide was purchased from Alfa Aesar. The syntheses of complexes 129b and 239 were reported previously. Diphenyl diazomethane58 and methyl phenyl diazoacetate59 were synthesized according to reported literature procedures. All solvents were purchased from Fisher Scientific and were of HPLC grade. The solvents were purified using an MBRAUN solvent purification system and stored over 3 Å molecular sieves. Deuterated benzene was purchased from Cambridge Laboratories, degassed under argon, and stored over 3 Å molecular sieves. Ethyl diazoacetate was degassed under argon before use. The complexes were characterized using NMR, IR, UV/vis spectroscopies, X-ray crystallography, elemental analysis, and solution magnetometry by the Evans method. NMR and GC-MS spectra were recorded at the Lumigen Instrument Center (Wayne State University). NMR was performed on a Varian Mercury or Agilent 400 MHz Spectrometer in C6D6 at room temperature. Chemical shifts and coupling constants (J) were reported in parts per million (δ) and hertz
(Hz), respectively. IR spectra of powdered samples were recorded on a Shimadzu IR Affinity-1 FT-IR Spectrometer outfitted with a MIRacle10 attenuated total reflectance accessory with a monolithic diamond crystal stage and pressure clamp. UV−visible spectra were obtained on a Shimadzu UV-1800 spectrometer. Elemental analyses were performed by Midwest Microlab LLC. Formation of the ketenimines and organic by-products was confirmed by GC-MS using Agilent 6890N spectrometer, Thermo TG5MS 30 m × 0.32 mm × 0.25 μm column, 7683 series injector, and Agilent 5973 detector.

**X-ray Crystallographic Details.** The structures of Co(OR)$_2$(CNR)$'$_2 complex 4, 9, and 19 were confirmed by X-ray diffraction analysis. The crystals were mounted on a Bruker APEXII/Kappa three circle goniometer platform diffractometer equipped with an APEX 2 detector. A graphic monochromator was employed for wavelength selection of the Mo Kα radiation (λ = 0.71073 Å). The data were processed and the structure was solved using the APEX 2 software supplied by Bruker AXS. The structure was refined by standard difference Fourier techniques with SHELXL (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms were placed in calculated positions using a standard riding model and refined isotropically; all other atoms were refined anisotropically.

**Computational Details.** Density functional theory calculations were performed using Gaussian 09 with default grids and density fitting. Geometry optimizations at the OPBE/6-31G(d) level of theory were followed by stability calculations to ensure the reliability of the wave function. Frequency calculations at the same level of theory were used to verify stationary points as minima or first-order saddle points based on the harmonic frequencies and to derive thermodynamic corrections using standard approximations to estimate enthalpies, entropies, and Gibbs free energies. Follow-up single point calculations using the much more flexible def2-TZVP basis set included dispersion corrections based on the APFD functional and implicit solvation effects (benzene) based on the SMD model. Triple-zeta free energies were estimated as $G_{TZ} = G_{DZ} − E_{DZ} + E_{TZ}$. See Appendix B for a summary of all thermodynamic values.

**Synthesis of Co(OR)$_2$(CN(2,6-Me$_2$C$_6$H$_3$))$_2$ (4).** A THF solution of 2,6-dimethylphenyl isocyanide (66 mg, 0.50 mmol) was added to a stirred blue THF solution of cobalt bis(alkoxide) 1 (80 mg, 0.13 mmol).
There was an immediate color change of the solution to dark red. The reaction was stirred for 2 h, after which the volatiles were removed in vacuo. The resulting red residue was dissolved in diethyl ether (henceforth, ether), filtered, and placed in the freezer overnight at −35°C to afford X-ray quality crystals of 3 (84 mg, 88% yield). ¹H NMR (400 MHz, C₆D₆) δ 20.88 (2H, Δν1/2 38 Hz, OR-Ph), 19.02 (36H, Δν1/2 229 Hz, tBu), 17.80 (4H, Δν1/2 22 Hz, OR-Ph), 10.34 (4H, Δν1/2 20 Hz, OR-Ph), 2.92 (6H, Δν1/2 20 Hz, CNR-Ph), −6.81 (12H, Δν1/2 40 Hz, Me). IR (cm⁻¹): 2955 (w), 2878 (w), 2816 (s), 2160 (s), 1489 (w), 1381 (m), 1280 (w), 1088 (m), 1018 (m), 734 (w), 903 (w), 841 (w). 772 (s), 741 (s), 702 (s), 478 (m). λmax (εM_1) 747 (661), 550 (612), 469 (417). μeff = 3.9 ± 0.4 μB (calcd 3.9). Anal. Calcd for C₄₈H₆₄N₂O₂Co: C, 75.9; H, 8.5; N, 3.7. Found: C, 75.5; H, 8.4; N, 3.8.

**Synthesis of Co(OR)₂(CNAd)₂ (8).** A THF solution of adamantyl isocyanide (74 mg, 0.46 mmol) was added to a stirred blue THF solution of cobalt bis(alkoxide) 1 (74 mg, 0.12 mmol). There was an immediate color change of the solution to dark red. The reaction was stirred for 2 h, upon which the volatiles were removed in vacuo. The resulting red residue was dissolved in ether, filtered, and placed in the freezer overnight at −35°C to give a red powder (75 mg, 80% yield). ¹H NMR (400 MHz, C₆D₆) δ 20.90 (2H, Δν1/2 39 Hz, OR-Ph), 19.26 (36H, Δν1/2 204 Hz, tBu), 16.78 (4H, Δν1/2 16 Hz, OR-Ph), 10.02 (4H, Δν1/2 14 Hz, OR-Ph), 0.63 (2H, Δν1/2 33 Hz, Ad), −0.63 (6H, Δν1/2 23 Hz, Ad), −1.25 (6H, Δν1/2 20 Hz, Ad), −2.11 (6H, Δν1/2 3 Hz, Ad), −4.50 (10H, Δν1/2 83 Hz, Ad). IR (cm⁻¹): 2956 (w), 2902 (w), 2855 (w), 2122 (s), 1450 (m), 1350 (w), 1312 (w), 1072 (m), 987 (w), 710 (w). λmax (εM₁) 751 (240), 550 (340), 464 (160). μeff = 3.9 ± 0.4 μB (calcd 3.9). Anal. Calcd for C₅₂H₇₆N₂O₂Co: C, 76.2; H, 9.3; N, 3.4. Found: C, 75.9; H, 9.2; N, 3.4.
78% yield). $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 19.96 (2H, $\Delta\nu_{1/2}$ 128 Hz, OR–Ph), 18.95 (36H, $\Delta\nu_{1/2}$ 288 Hz, $^3$Bu), 16.93 (4H, $\Delta\nu_{1/2}$ 22 Hz, OR–Ph), 9.84 (4H, $\Delta\nu_{1/2}$ 19 Hz, OR–Ph), 2.72 (6H, $\Delta\nu_{1/2}$ 58 Hz, OMe), 1.58 (8H, $\Delta\nu_{1/2}$ 23 Hz, CNR–Ph). IR (cm$^{-1}$): 2955 (w), 2901 (w), 2168 (s), 1605 (w), 1505 (s), 1381 (w), 1303 (w), 1258 (s), 1065 (s), 1018 (m), 857 (s), 748 (m), 718 (m), 687 (w). $\lambda_{\text{max}}$ (ε M$^{-1}$) 731 (990), 550 (555).

$\mu_{\text{eff}} = 3.6 \pm 0.4 \mu_B$ (calcd 3.9). Anal. Calcd for C$_{46}$H$_{60}$N$_2$O$_4$Co: C, 72.3; H, 7.9; N, 3.7. Found: C, 71.1; H, 7.5; N, 4.6.

**Reaction of 4 and Diphenyldiazomethane.** A C$_6$D$_6$ solution of diphenyldiazomethane (0.74 mL, 0.173 M) was added to a stirring dark red C$_6$D$_6$ solution of 4 (49 mg, 0.064 mmol). The reaction was stirred at room temperature for 5 h; no color change was observed. $^1$H NMR showed unreacted diphenyldiazomethane and peaks characteristic of 4.

**Reaction of 8 and Ethyl Diazoacetate.** A toluene solution of ethyl diazoacetate (0.2 mL, 1.1 M) was added to a stirring dark red C$_6$D$_6$ solution of 8 (90 mg, 0.11 mmol). A color change to dark brown with vigorous gas formation was observed. Reaction was stirred for 1 h at room temperature. NMR of the crude reaction mixture shows formation of ketenimine, although peaks were broadened. The reaction was filtered through a plug of silica. $^1$H NMR of the filtered reaction mixture showed formation of ketenimine.

**Reaction of 1 and Methyl Phenyldiazoacetate.** A hexane solution of methyl phenyldiazoacetate (0.13 mL, 0.6 M) was added to a stirring blue hexane solution of 1 (50 mg, 0.078 mmol). The reaction turns teal immediately and dark brown within a minute. The reaction was stirred at room temperature for 1 h. Volatiles were removed in vacuo. NMR of the crude reaction mixture was taken in C$_6$D$_6$ showing a hypothesized carbene (peaks assigned below) along with unreacted diazoester. Volatiles were removed in vacuo and the dark residue was dissolved in ether. Recrystallization at $-35$ °C gave colorless crystals of the respective olefin (13% yield). $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 37.73 (3 H, $\Delta\nu_{1/2}$ 384 Hz, PhCCO$_2$Me), 21.95 (6H, $\Delta\nu_{1/2}$ 180 Hz, PhCCO$_2$Me), 16.67 (2H, $\Delta\nu_{1/2}$ 28 Hz, Ph–OR), 12.77 (2H, $\Delta\nu_{1/2}$ 36 Hz, Ph–OR), 9.49 (36H, $\Delta\nu_{1/2}$ 220 Hz, $^3$Bu–OR), 9.30 (4H, Ph–OR), 5.26 (2H, $\Delta\nu_{1/2}$ 36 Hz, Ph–OR).

**General Procedure for Stoichiometric Formation of Ketenimines 3, 5-7.** A C$_6$D$_6$ solution of the isocyanide (3 equiv) and TMB (1 equiv) was added to a stirring C$_6$D$_6$ solution of 2 (1 equiv). A notable
color change occurred to either dark red (2,6-dimethylphenyl isocyanide and adamantyl isocyanide) or dark brown (4-methoxyphenyl isocyanide and 2-chloro-6-methylphenyl isocyanide). NMR of the reaction mixture was taken after 1 h and yield was calculated with reference to 1,3,5-trimethoxybenzene (TMB). Products 3 and 6 have been previously reported. The formation of ketenimines was also confirmed by GC-MS in all cases.

Characterization of Ph$_2$C=C=N(2,6-Me$_2$-C$_6$H$_3$) (3). $^1$H NMR (400 MHz, C$_6$D$_6$) δ 7.36 (d, J = 4 Hz, 4H, o-Ph), 7.13 (t, J = 4 Hz, 4H, m-Ph), 7.01 (t, J = 4 Hz, 2H, p-Ph), 6.83 (bs, 3H, NC$_6$H$_3$), 2.22 (s, 6H, Me).

Characterization of Ph$_2$C=C=NaN (5). $^1$H NMR (400 MHz, C$_6$D$_6$) δ 7.50 (d, J = 4 Hz, 4H, o-Ph), 7.19 (t, J = 4 Hz, 4H, m-C$_6$H$_3$), 7.03 (t, J = 4 Hz, 2H, p-Ph), 1.89 (s, 6H), 1.83 (s, 3H), 1.41 (t, J = 12 Hz, 6H).

Characterization of Ph$_2$C=C=N(4-OMe-C$_6$H$_4$) (6). $^1$H NMR (400 MHz, C$_6$D$_6$) δ 7.44 (d, J = 8 Hz, 4H, o-Ph), 7.28 (d, J = 8 Hz, 2H, o-NC$_6$H$_4$), 7.12 (t, J = 8 Hz, 4H, p-Ph), 7.02 (t, J = 8 Hz, 1H, m-NC$_6$H$_3$), 3.19 (s, 3H, Me).

Characterization of Ph$_2$C=C=N(2-Cl-6-Me-C$_6$H$_3$) (7). $^1$H NMR (400 MHz, C$_6$D$_6$) δ 7.40 (d, J = 8 Hz, 4H, o-Ph), 7.13 (t, J = 8 Hz, 4H, m-C$_6$H$_3$), 7.01 (t, J = 8 Hz, 2H, p-Ph), 6.99 (d, J = 8 Hz, 1H, m-NC$_6$H$_3$Cl), 6.63 (d, 1H, m-NC$_6$H$_3$Me), 2.06 (s, 3H, Me).

General Procedure for Catalytic Formation of Ketenimines in Table 2. A C$_6$D$_6$ solution of the isocyanide (12 equiv), diazoalkane/diazoester (10 equiv), and TMB or hexamethylbenzene (HMB) (1 equiv) was added to a stirred C$_6$D$_6$ solution of 1. A notable color change occurred to either dark red (2,6-dimethylphenyl isocyanide and adamantyl isocyanide) or dark brown (4-methoxyphenyl isocyanide, cyclohexyl isocyanide, and benzyl isocyanide) for methyl phenyldiazoacetate. A color change to orange occurred with ethyl diazoacetate and all isocyanides except 4-methoxyphenyl isocyanide and 2,6-dimethylphenyl isocyanide. Evolution of N$_2$ was observed in most cases. NMR of the reaction mixture was taken after 24 h, and yield was calculated with reference to internal standard. Major by-products were identified by NMR and GC-MS. All products were confirmed by GC-MS analysis of silica plugs of each
reaction. Isolation of the ketenimines was done by removing all volatiles, dissolving in a minimal amount of hexane, and passing through a Pasteur pipet full of silica. HOR and standard were eluted via addition of 50 mL of hexane to solvent. Product was obtained by passing a 40 mL solution 5−10% ether/hexane solution through the pipet. Low isolated yields were obtained due to the high co-elution with HOR, standard, and by-products.

Synthesis and characterization of ketenimines Ph₂C=C=N(2,6-Me₂C₆H₃), Ph₂C=C=N(4-OMeC₆H₄), and Ph₂C=C=NCy have been previously described. Other ketenimines Ph₂C=C=N(2-Cl-6-Me-C₆H₃), Ph₂C=C=NAd, (Ph)(COOMe)C=C=NAd, (Ph)(COOMe)C=C=NCy, (Ph)(COOMe)C=C=NBn, (H)(COOEt)C=C=NAd, (H)(COOEt)C=C=NCy, and (H)(COOEt)C=C=NBn have not been previously reported. All ketenimines reported in this work were identified by ¹H NMR and GC-MS. The ketenimines which were obtained in high yields in catalytic reactions with (Ph)(COOMe)C=C=NAd and (H)(COOEt)C=C=NAd were further purified, isolated as yellow oils, and characterized by ¹H NMR and ¹³C NMR. NMR signals for the observed ketenimines in Table 2, entries 1 and 2 are reported above (for the stoichiometric reactions); they were also observed in the catalytic NMR reactions. However, some of the peaks were found to be hidden under starting material, due to the poor catalytic performance with 2,6-dimethylphenyl isocyanide. For Table 2, entry 3, Ph₂C=C=NAd, the shifts were confirmed by comparing to literature reports:⁶⁶ ¹H NMR (400 MHz, C₆D₆) δ 7.46 (d, 4H, o-Ph), 7.18 (t, 4H, m-Ph), 7.08 (t, 2H, p-Ph), 3.29 (m, 1H, CNH), 1.87 (m, 2H, equatorial NCy), 1.51 (m, 2H, NCy), 1.3 (m, 3H, NCy), 0.96 (m, 3H, NCy).

Characterization of (Ph)(COOMe)C=C=N(4-OMeC₆H₄) (entry 5). ¹H NMR (400 MHz, C₆D₆) δ 7.91 (d, J = 8 Hz, 2H, o-Ph), 7.19 (t, J = 8 Hz, 2H, m-Ph), 7.07 (d, J = 8 Hz, 2H, p-Ph−CNR), 7.03 (t, J = 8 Hz, 1H, p-Ph), 6.51 (d, J = 8 Hz, 2H, m-Ph−CNR), 3.44 (3H, s, CO₂Me), 3.13 (s, 3H, Ar−OMe).

Characterization of (Ph)(COOMe)C=C=NBn (entry 6). ¹H NMR (400 MHz, C₆D₆) δ 7.95 (d, J = 8 Hz, 2H, o-Ph), 7.27 (t, J = 8 Hz, 2H, m-Ph), 7.02 (t, J = 8 Hz, 1H, p-Ph), 3.52 (s, 3H, Me), 1.84 (s, 6H, Ad), 1.77 (s, 3H, Ad), 1.35 (s, 6H, Ad).
Characterization of \((\text{Ph})(\text{COOMe})\text{C=C=NCy}\) (entry 7). $^1$H NMR (400 MHz, C$_6$D$_6$) δ 7.91 (d, J = 8 Hz, 2H, o-Ph), 7.24 (t, J = 8 Hz, 2H, m-Ph), 7.02 (t, J = 8 Hz, 1H, p-Ph), 3.33 (sept, J = 4 Hz, 1H, CNH), 1.69 (m, 2H, Cy), 1.43 (m, 2H, Cy), 1.32 (m, 3H), 1.19 (m, 1H), 0.92 (m, 3H). $^{13}$C NMR (100 MHz, C$_6$D$_6$) δ 172.13 (−C=C=N−), 168.92 (COOMe), 132.65 (ipso-Ph), 129.20 (o-Ph), 127.5 (m-Ph), 126.2 (p-Ph), 61.40 (COOMe), 51.36 (Cy), 34.05 (Cy), 25.58 (Cy), 24.55 (Cy).

Characterization of \((\text{Ph})(\text{COOMe})\text{C=C=NBn}\) (entry 8). $^1$H NMR (400 MHz, C$_6$D$_6$) δ 7.68 (d, J = 8 Hz, 2H, o-Ph), 7.16 (t, J = 8 Hz, 2H, m-Ph), 7.02 (m, 5H, Ph−Bn), 6.98 (t, J = 8 Hz, 1H, p-Ph), 3.44 (s, 3H, OMe).

Characterization of \((\text{H})(\text{COOEt})\text{C=C=NAc}\) (entry 11). $^1$H NMR (400 MHz, C$_6$D$_6$) δ 4.28 (s, 1H, HCO$_2$CH$_2$CH$_3$), 4.07 (q, J = 8 Hz, 2H, HCO$_2$CH$_2$CH$_3$), 1.78 (s, 3H, Ad), 1.76 (s, 6H, Ad), 1.36 (s, 6H, Ad), 1.01 (q, J = 8 Hz, 3H, HCO$_2$CH$_2$CH$_3$). $^{13}$C NMR (100 MHz, C$_6$D$_6$) δ 171.87 (−C=C=N−), 169.11 (COOEt), 61.64 (Ad), 60.21 (OCH$_2$CH$_3$), 51.82 (−C=C=N−), 44.06 (Ad), 36.24 (Ad), 30.32 (Ad), 14.93 (OCH$_2$CH$_3$).

Characterization of \((\text{H})(\text{COOEt})\text{C=C=NCy}\) (entry 12). $^1$H NMR (400 MHz, C$_6$D$_6$) δ 4.22 (s, 1H, HCO$_2$CH$_2$CH$_3$), 4.06 (q, J = 8 Hz, 2H, HCO$_2$CH$_2$CH$_3$), 3.17 (sept, J = 4 Hz, 1H, CNH), 1.58 (m, 2H, Cy), 1.41 (m, 2H, Cy), 1.25 (m, 3H), 1.16 (m, 1H), 0.98 (q, J = 8 Hz, 3H, HCO$_2$CH$_2$CH$_3$), 0.91 (t, J = 8 Hz, 3H).

Characterization of \((\text{H})(\text{COOEt})\text{C=C=NBn}\) (entry 13). $^1$H NMR (400 MHz, C$_6$D$_6$) δ 4.14 (s, 2H, Bn), 4.10(s, 1H, HCO$_2$CH$_2$CH$_3$), 4.00 (q, J = 8 Hz, 2H, HCO$_2$CH$_2$CH$_3$), 0.94 (q, J = 8 Hz, 3H, HCO$_2$CH$_2$CH$_3$).
CHAPTER THREE ONE ELECTRON REDUCTION TRANSFORMS HIGH-VALENT LOW-SPIN COBALT ALKYLIDENE INTO HIGH-SPIN COBALT(II) CARBENE RADICAL

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3.1. Introduction

As noted in the introduction, transition-metal carbene complexes are important organometallic functionalities in formation of new C-C, C-N, and C-O bonds. The reactivity exhibited by a carbene complex is dictated by its electronic structure. Thus, a multitude of carbene types are known, depending on the transition metal and its oxidation state, the choice of ancillary ligands, and the substituents on the carbene. The two earliest classes of carbenes which define the electrophilic and nucleophilic ends of the spectrum are those of Fischer and Schrock. More recently, there has been an increase in various types of transition-metal carbene radical complexes which exhibit prominent C-H bond activation and C-C bond formation chemistry.

As was discussed in the Introduction and Chapter Two, we have synthesized and studied the reactivity of the first high-oxidation state cobalt-carbene complex Co(OR)$_2$(=CPh)$_2$ (2) and related species, that featured hard bis(alkoxide) ligand environment combined with low coordination number. Spectroscopic, structural, and computational studies suggested that Co(OR)$_2$(=CPh)$_2$ (2) possessed a combination of carbene-radical and alkylidene-like (Schrock carbene-like) character. This complex exhibited reactivity with isocyanides to produce ketenimines via initial coordination of isocyanide to the electrophilic cobalt center. This reactivity, exhibited by 2, was consistent with its electrophilic alkylidene-like character. Herein we demonstrate that one-electron reduction of 2 retains the overall structure while transforming the electronic nature from low to high spin with pronounced carbene radical character. Additionally, its reactivity towards isocyanides is compared with that of neutral carbene.
3.2. Synthesis and Characterization of \([\text{Co(OR)}_2(=\text{CPh}_2)][\text{CoCp}^*]_2\]

Inspection of the CV spectrum of 2 revealed three reduction events with the first two being quasi-reversible (-1.2 V and -2.5 V). Thus, we became interested in the chemical reduction of 2. Treating a cold, dark-brown solution of 2 in ether with a suspension of decamethylcobaltacene in ether resulted in an immediate color change to muddy brown. The reaction was allowed to warm to room temperature and stirred for 45 minutes. The suspension was filtered and the solid was washed with copious amounts of ether. The remaining solid was dissolved in a minimal amount of THF and layered with ether. Recrystallization at -35 °C for 5 days resulted in brown crystals. X-ray characterization and elemental analysis supported formation of \([\text{Co(OR)}_2(=\text{CPh}_2)][\text{CoCp}^*]_2\) (20, Figure 33). 20 recrystallizes in the triclinic space group with \([\text{Co(OR)}_2(=\text{CPh}_2)]\) anion and \([\text{CoCp}^*]_2\) cation in the asymmetric unit. The crystal structure is shown in Figure 34 with experimental crystallographic parameters in Table 3. The structure of the \([\text{Co(OR)}_2(=\text{CPh}_2)]\) anion demonstrates trigonal planar geometry similar to 2. Inspection of the Co-C bond demonstrates an elongation to 1.923(2) Å, significantly longer than the Co-C bond in 2 (1.773(3) Å). The elongation of the cobalt-carbene bond suggests formation of a carbene possessing Fischer-like character, in contrast to the Schrock-like nature for 2. Furthermore, the Co-O bonds of 1.852(3) Å in 20 are also considerably longer compared with 2 (1.765(2)) and are close to Co-O bonds in 1 (1.849(1) Å). These similarities in the cobalt alkoxide bond lengths between 1 and 20 suggests that a metal-centered reduction occurs, which forms Co(II) center in 20. Close inspection of the carbene aryl C-C bonds reveals slight bond distance alternation for both 3 and 2, consistent with the radical nature of the carbene (see Appendix C).

![Figure 33](image-url). Reduction of 2 to give 20.
Figure 34. X-ray crystal structure of 20, 50% probability ellipsoids. H atoms were omitted for clarity. Selected bond distances (Å) for 20: Co–O1, 1.852(1); Co–O2, 1.849(1); Co–C, 1.923(2).
In addition to X-ray crystallography and elemental analysis, 20 was characterized by $^1$H NMR, IR, and UV-Vis spectroscopy, and magnetic measurements (see Appendix C). The $^1$H NMR spectrum of 20 in THF-$d_8$ spans a wide range of 152 ppm (108 ppm to -44 ppm), consistent with its paramagnetic nature. The UV-vis spectrum of 20 exhibits peaks at 500, 648, and 712 nm. Magnetic measurements on 20 were conducted both in solution (Evans method) and in solid state (magnetic susceptibility measurements, SQUID). Notably, the solution magnetic moment of 4.2(3) μB suggests a high-spin cobalt carbene, in
contrast to the low-spin nature of 2 (2.0 μB ± 0.2 μB). The solution magnetic moments are similar to those obtained by magnetic susceptibility measurements. Measurements were performed in the temperature range of 2 K to 300 K at 0.1 T. Both 2 and 20 follow Curie-Weiss behavior, as evidenced by the linear relationship between $\chi^{-1}$ vs. T (Figure 35 and 36). Fitting the susceptibility data gave effective magnetic moments of 2.19 μB for 2 and 4.03 μB for 20, again consistent with their low-spin and high-spin natures, respectively.

**Figure 35.** Variable-temperature magnetic susceptibility data for 20 measured at 1000 Oe.
Due to the presence of an additional quasi-reversible reduction wave in the CV of 2, further reduction of 20 was attempted. Treating a THF solution of 20 with decamethylcobaltacene resulted in no color change. The reaction was allowed to stir for 5 hours at room temperature. The solution was concentrated, layered with ether, and set up for recrystallization at -35 ºC for 5 days. Characterization of the reaction products by spectroscopic, crystallographic, and analytical methods demonstrated that no reduction of 20 to the dianionic species took place. Attempted crystallization of 20 led to the isolation of the isomer of 20, denoted 20a. In contrast to 20, 20a crystallizes in the C2/c space group. The Co-C bond of 1.919(5) Å and Co-O bond of 1.861(5) Å are virtually identical to 20, supporting the notion that 20a is simply a conformational isomer of 20. The only notable difference in the structure is a different conformation of the alkoxide ligand so that both phenyl rings are pointed away from the carbene moiety. The structure occupies a special position (C2) axis so only half of the cation/anion constitutes an asymmetric unit. The structure of 20a is shown in Figure 37 with crystallographic parameters in Table 4.

Figure 36. Magnetic susceptibility and inverse susceptibility for 2.
Figure 37. X-ray crystal structure of 20a, 50% probability ellipsoids. H atoms were omitted for clarity. Selected bond distances (Å) for 20a: Co–O1, 1.858(5); Co–O1’, 1.858(5); Co–C, 1.919(5).
Table 4. Experimental crystallographic parameters for 20a.

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<tr>
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3.3. DFT Calculations of [Co(OR)₂(=CPh₂)]⁺

DFT calculations were performed at the B3LYP/6-31G(d) level of theory,⁶⁹ based on the earlier calculations performed on 2,³⁹ to understand the electronic structure of 20. Calculations were performed on the anionic fragment of 20 for simplicity, denoted 20’. Singlet and triplet states corresponding to anti- and ferromagnetically coupled low-spin Co(II) and carbene radical were found to be higher (+15-16 kcal/mol) in free energy than the triplet and quintet states corresponding to anti- and ferromagnetically coupled high-
spin Co(II) and carbene radical, respectively. Both the triplet antiferromagnetically coupled and quintet ferromagnetically coupled high-spin Co(II) states were found to be within 1 kcal/mol difference in energy, consistent with the experimental magnetic moment that is intermediate between the spin-only values expected for a triplet or quintet state. DFT predicts the triplet state to be lowest in energy. Mulliken spin analysis of the [Co(OR)₂] and [CPh₂] fragments shows spins of 2.87 and −0.87 in 20’, in contrast to 1.89 and −0.89 for 2.³⁹ This supports a metal centered reduction in 20’ to a high-spin cobalt(II) ion antiferromagnetically coupled to a carbene radical anion with thermal population of the corresponding ferromagnetic state. This is in contrast to the low-spin nature of 2 which possesses antiferromagnetic coupling between the cobalt and carbene radical.³⁹ The singly occupied molecular orbitals (SOMOs) for 20’, as determined by a corresponding orbital analysis, are shown in for the S = 1 state in Figure 38. The corresponding orbital analysis for the S = 2 state can be found in Appendix C.

Figure 38. Corresponding orbital diagram (iso = 0.05 au) of 20’, S = 1.
3.4. Reactivity of [Co(OR)₂(=CPh₂)][CoCp*₂] with Isocyanides

As discussed in Chapter 2, Co(OR)₂(=CPh₂) (2) exhibited facile reactivity with isocyanides to form ketenimines. Furthermore, catalytic formation of ketenimines was observed with diazoesters and both aryl and alkyl isocyanides.⁴⁷ To compare the reactivities of neutral and anionic carbenes of 2 and 20, respectively, 20 was exposed to 2,6-dimethylphenyl isocyanide (CN-Me₂C₆H₃). Benzene solution of 2,6-dimethylphenyl isocyanide was added to a suspension of 20 in benzene. A color change to dark purple was observed after 20 minutes and the solution was stirred at room temperature for additional two hours. Solvent was removed in vacuo, and the product was dissolved in ether and filtered. The solution was concentrated and allowed to recrystallize at -35 °C for one week to afford a mixture of orange and dark purple crystals. The similar solubilities of the two crystals hampered fractional crystallization of the species, which were hence mechanically separated. X-ray diffraction studies on the two complexes revealed formation of the cobalt(0) isocyanide complex Co₂(CN-Me₂C₆H₃)₈ (21) as orange crystals and Ph₂C(H)C(NXyl)C(H)[Cp(Me)₄CoCp*] (22) as purple crystals (Figure 39). The cobalt isocyanide compound 21 has been previously reported.⁷⁰ Its structure and ¹H NMR spectrum were consistent with those previously reported. The crystal structure of 21 can be found in Appendix C. The crystal structure of 22 is presented in Figure 40 with pertinent experimental crystallographic parameters in Table 5. Compound 22 is intriguing and appears to have formed via reaction of an in situ formed ketenimine with the decamethylcobaltacenium counter ion in 20. 20 can be approximated as two resonance structures: zwitterionic compound form 22’ Ph₂C(H)C(NXyl)C(H)[Cp(Me)₄Co²⁺Cp*] that contains decamethylcobaltocenium covalently linked to enamide with delocalized negative charge, and form 22’’, that contains Cp*-Co(I)-tetramethylfulvene further conjugated to the (C1=N) imine (Figure 41). The X-ray structure of 22 is in agreement with 22’’. Inspection of the crystal structure reveals bond distances within the [NC1C2C3] fragment and relatively narrow dihedral angle between the [NC1C2] plane and tetramethylfulvene (~18 °) to be consistent with the delocalized conjugated system. 22 consists of anion delocalized over the enamine [NCC] system which is further conjugated to the cobaltocene cation. The formulation of the metal fragment as tetramethylfulvene-Co(I) is further supported by a significantly longer
Co-C3 bond (2.216(3)) compared with bonds to other carbons (Co-C5/C6/C7/C8, 2.011-2.064 Å). \(^1\)H NMR spectrum of isolated 22 (C\(_6\)D\(_6\)) is consistent with the solid-state structure, containing a singlet for the allylic Ph\(_2\)C(H)C proton at 3.82 ppm and a singlet for the vinylic proton at 5.34 ppm (see Appendix C). 22 likely originates from the activation of decamethylcobaltocene by transient ketenimine Ph\(_2\)C=C=N(2,6-Me\(_2\)C\(_6\)H\(_3\)). We also note that the reaction was accompanied by the formation of ROH, which was observed by NMR spectroscopy.

![Figure 39](image)

**Figure 39.** Reaction of 20 with 2,6-dimethylisocyanide to give 21 and 22.

![Figure 40](image)

**Figure 40.** X-ray crystal structure of 22, 50% probability ellipsoids. H atoms were omitted for clarity. Selected bond distances (Å) for 22: N–C1, 1.302(2); C1–C2, 1.412(4); C2–C3, 1.414(4); Co–C3, 2.216(3); Co–C5, 2.010(3); Co–C6, 2.055(3); Co–C7, 2.063(3), Co–C8, 2.015(3).
Table 5. Experimental crystallographic parameters for 22.

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Figure 41. Resonance structures of 22.
It is likely that the first step of 22 formation involves carbone transfer to form ketenimine. To provide further evidence for the initial formation of ketenimine in the reaction of 22 with isocyanides, 22 was treated with adamantyl isocyanide, that is expected to lead to the less electron deficient and therefore more stable ketenimine product. Addition of adamantyl isocyanide to an ether solution of 20 showed a color change to dark-brown (Figure 42). The reaction was stirred for 3 hours at room temperature. The formation of the respective ketenimine was observed in 55% yield by NMR. Its formation was also confirmed by GC-MS (see Appendix C).

![Figure 42. Synthesis of ketenimine Ph₂C=C=NAd from 20 and adamantyl isocyanide.](image)

3.5. Synthesis and Characterization of \([\text{Co(OR)}_2(=\text{CPh}_2)][\text{K}(18\text{-crown-6})]\)

To obtain further evidence for the formation of the \(\text{Ph}_2\text{C}=\text{C}=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\) intermediate, we have attempted preparation of the cobalt precursor with a less reactive counterion. \(\text{KC}_8\) was utilized as the reducing agent towards such species. Addition of \(\text{KC}_8\) to a stirring THF solution of 2 in the presence of 18-crown-6 resulted in a color change to russet brown. The reaction was stirred at room temperature for one hour. Removal of volatiles \textit{in vacuo} resulted in a brown residue. The residue was dissolved in a 15:1 ether:THF mixture, filtered, and concentrated \textit{in vacuo}. Recrystallization at -35°C yielded dark-brown crystals of \([\text{Co(OR)}_2(=\text{CPh}_2)][\text{K}(18\text{-crown-6})]\) (23, Figure 43). However, the crystals were not suitable for X-ray crystallography and its structure was confirmed by elemental analysis. 23 was also characterized by IR, UV-Vis, and NMR spectroscopy (see Appendix C). Similarities in the UV-Vis and IR spectra to 20 further supported its formation.
3.6. Reactivity of [Co(OR)$_2$(=CPh)$_2$][K(18-crown-6)] with Isocyanides

Having synthesized a reduced carbene possessing a less reactive counterion, reactivity of 23 towards isocyanides was explored. Exposure of 2,6-dimethylphenyl isocyanide to a stirring benzene/ether solution at 23 at -35°C resulted in an immediate color change to green before darkening to green-brown. The reaction was allowed to stir at room temperature for 45 minutes. The volatiles were removed *in vacuo* to afford a green-brown residue. The residue was washed repeatedly with hexanes and the washings indicated formation of the ketenimine product Ph$_2$C=C=N(2,6-Me$_2$C$_6$H$_3$) and Co$_2$(CN(2,6-Me$_2$C$_6$H$_3$))$_8$ (Figure 44). $^1$H NMR of the reaction can be found in Appendix C. This result shows that in the absence of the relatively acidic CoCp$^*_2$, ketenimine formation is feasible with 2,6-dimethylisocyanide.

![Figure 43](image-url)  
**Figure 43.** Synthesis of [Co(OR)$_2$(=CPh)$_2$][K(18-crown-6)] (23).

![Figure 44](image-url)  
**Figure 44.** Formation of ketenimine Ph$_2$C=C=N(2,6-Me$_2$C$_6$H$_3$) and 21 from 23.

3.7. Mechanism of the formation of 22

The proposed mechanism for the formation of 22 is shown in Figure 45. Based on the evidence presented in 3.5 and 3.6, it is likely that the reaction is initiated by the formation of ketenimine Ph$_2$C=C=N(2,6-Me$_2$C$_6$H$_3$). This reactive ketenimine forms in the vicinity (can be directly coordinated to Co(OR)$_2$) of the potentially reactive decamethylcobaltocenium counterion. Decamethylcobaltacenium
counterions in the coordination sphere of transition metal complexes have been reported to undergo deprotonation \textit{in situ}, which was facilitated by the reduction of cobalt. In these reports, the \([\text{CoCp}^*\text{Cp}^*']\) fragment has been described as a Co(I) tetramethylfulvene complex.\textsuperscript{71} In the present case, deprotonation of decamethylcobaltocenium is supported by the \textit{in situ} observation of ROH. A feasible pathway for formation of 22 involved deprotonation of one of the methyl groups of “decamethylcobaltacenium” (or \(\text{Cp}^*\text{Co}(I)\) tetramethylfulvene complex) which undergoes nucleophilic attack on the in situ formed ketenimine.\textsuperscript{68} This is followed by proton transfer to the former carbene carbon, resulting in a single C-C bond between the terminal and central carbons of the former ketenimine. This proton transfer is facilitated by the formation of conjugated \(\text{Cp}^*\text{Co}(I)\) tetramethylfulvene-imine system (\textbf{Figure 45}). However, it is also possible that the reaction proceeds via radical H-atom abstraction from the decamethylcobaltacenium methyl group.\textsuperscript{72} Previous reports support this H-atom abstraction reactivity for the decamethylcobalaceium counterion and ketenimines have been reported to exhibit radical reactivity in the presence of radical initiators.\textsuperscript{73}

\textbf{Figure 45.} Possible mechanism for the formation of 22.
3.7. Summary and Conclusions

In summary, one-electron reduction of the high-valent cobalt carbene 2 with decamethylcobaltacene resulted in a metal-centered reduction to give 20. The reduction is also feasible using potassium graphite to give 23. Both reduced compounds react with isocyanides to form ketenimines and the Co(0) isocyanide complex 21. In the case of the reaction of 2,6-dimethylphenyl isocyanide with 20, the counter-ion is deprotonated and undergoes nucleophilic attach at the in situ formed ketenimine to form 22. By performing the same reaction with 23 possessing a less reactive counterion (K\(^+\)), free ketenimine is observed.

3.8. Experimental Details

**General Methods and Procedures.** All reactions involving air-sensitive materials were executed in a nitrogen-filled glovebox or by standard Schlenk line procedures. Cobalt chloride, bis(pentamethylcyclopentadienyl)cobalt(II), 2,6-dimethylphenyl isocyanide, and trimethoxybenzene were purchased from Sigma-Aldrich. Adamantyl isocyanide was purchased from Alfa Aesar. Potassium graphite and thallium hexafluorophosphate were purchased from Strem. The syntheses of complexes 1\(^{29}\) and 2\(^{19}\) were reported previously. Diphenyldiazomethane were synthesized according to a reported literature procedure.\(^{38}\) All solvents were purchased from Fisher Scientific and were of HPLC grade. The solvents were purified using an MBRAUN solvent purification system and stored over 3 Å molecular sieves. Deuterated benzene (C\(_6\)D\(_6\)) was purchased from Cambridge Laboratories and deuterated tetrahydrofuran (THF-d\(_8\)) was obtained from Sigma Aldrich. Both were degassed under argon, and stored over 3 Å molecular sieves. The complexes were characterized using NMR, IR, and UV/vis spectroscopy, X-ray crystallography, SQUID magnetometry, elemental analysis, and solution magnetometry by the Evans method. NMR and GC-MS spectra were recorded at the Lumigen Instrument Center (Wayne State University). NMR was performed on a Varian Mercury or Agilent 400 MHz Spectrometer in C\(_6\)D\(_6\) or THF-d\(_8\) at room temperature. Chemical shifts and coupling constants (J) were reported in parts per million (\(\delta\)) and hertz (Hz), respectively. IR spectra of powdered samples were recorded on a Shimadzu IR Affinity-1 FT-IR Spectrometer outfitted with a MIRacle10 attenuated total reflectance accessory with a monolithic
diamond crystal stage and pressure clamp. UV–visible spectra were obtained on a Shimadzu UV-1800 spectrometer. SQUID magnetometry was performed at the Magnetic Properties Measurement System Facility at University of South Carolina. Elemental analyses were performed by Midwest Microlab LLC. Formation of the ketenimine and organic by-products was confirmed by GC-MS using Agilent 6890N spectrometer, Thermo TG5MS 30 m × 0.32 mm × 0.25 μm column, 7683 series injector, and Agilent 5973 detector.

**X-ray Crystallographic Details.** The structures of 20, 20a, 21, and 22 were confirmed by X-ray analysis. The structures of 239 and 2174 was previously reported. Whereas the crystal data parameters for 21 matched those previously reported,74 its refinement parameters are slightly different and therefore are reported in Appendix C. The crystals were mounted on a Bruker APEXII/Kappa three circle goniometer platform diffractometer equipped with an APEX-2 detector. A graphic monochromator was employed for wavelength selection of the Mo Kα radiation (λ = 0.71073 Å). The data were processed and the structure was solved using the APEX-2 software supplied by Bruker-AXS. The structure was refined by standard difference Fourier techniques with SHELXL (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms were placed in calculated positions using a standard riding model and refined isotropically; all other atoms were refined anisotropically. The structure of 20a was of relatively low quality, due to weak diffraction and the disordered solvent. As we were not able to model the solvent satisfactorily, SQUEEZE was used.

**Computational Details.** Density functional theory calculations were carried out using Revision D01 of Gaussian 09.60 Geometry optimizations were performed at the B3LYP/6-31G(d) level of theory.69 All optimized structures were confirmed to have stable wavefunctions75 and to be minima on the potential energy surface.61

**SQUID Measurements.** Solid state magnetic measurements were conducted on a Quantum Design Magnetic Properties Measurement System (QD-MPMS3). Data were collected under zero-field cooled (zfc) conditions from 2-300 K in an applied field of 1000 Oe. Observed magnetic moments were determined from Curie-Wiess fits. For the susceptibility of 2, an appreciable temperature independent
contribution was observed. For this reason, a modified Curie-Weiss law, \( \chi = \chi_0 + C/(T - \theta) \) where \( \chi_0 \) is the temperature independent term, was used. The raw data were corrected for sample shape and radial offset effects using the method reported by Morrison and zur Loye.\(^7\)

**Synthesis of \([\text{Co(OR}_2]\text{(CPh}_2\text{)}][\text{CoCp}^*\text{]}\) (20).** A suspension of CoCp\(^*\) (46 mg, 0.138 mmol) in diethyl ether was added to a stirring dark-brown ether solution of Co(OR\(_2\))(CPh\(_2\)) (2, 85 mg, 0.128 mmol) at -35°C. There was an immediate color change to lighter brown. The reaction was allowed to warm to room temperature and stirred for 1 hour. The solution was filtered, washed with diether ether, dissolved in THF, filtered, and dried in vacuo. Subsequent recrystallization of a THF solution layered with diethyl ether at -35°C yields X-ray quality crystals of 20 (76 mg, 60% yield). \(^1\)H NMR (400 MHz, THF-d\(_8\)) \( \delta \) 108.4 (5H, Ph), \( \delta \) 45.4 (1H, OR-Ph), \( \delta \) 11.4 (2H, OR-Ph), \( \delta \) 8.10 (5H, OR-Ph), \( \delta \) 7.74 (4H, OR-Ph), \( \delta \) 6.19 (18H, OR-'Bu), -4.46 (30H, Cp\(^*\)), -44.22 (5H, Ph). IR (cm\(^{-1}\)): 2974 (w), 2947 (w), 2885 (w), 1558 (m), 1474 (m), 1377 (m), 1280 (w), 1142 (w), 1061 (s), 1022 (w), 945 (m), 891 (m), 844 (w), 799 (w), 741 (m), 702 (s). \( \lambda_{\text{max}} \) (\( \varepsilon \text{M} \cdot \text{L}^{-1} \cdot \text{cm}^{-1} \cdot \text{mol}^{-1} \)) 500 nm (2040), 648 nm (760), 712 nm (590). \( \mu_{\text{eff}} \) (Evans method) = 4.2 ± 0.2 \( \mu_B \) (calcd 4.9). Anal. Calcd for C\(_{63}\)H\(_{92}\)O\(_2\)Co: C, 75.72; H, 9.28, Found: C, 76.08; H, 8.92.

**Synthesis of \([\text{Co(OR}_2]\text{(CPh}_2\text{)}][\text{K(18-crown-6)}\] (23).** A THF solution of 18-crown-6 (41 mg, 0.154 mmol) in was added to a stirring dark-brown THF solution of Co(OR\(_2\))(CPh\(_2\)) (88 mg, 0.132 mmol), followed by a suspension of KC\(_8\) (24 mg, 0.175 mmol) in THF. There was a color change to russet brown after 5 minutes and the reaction was stirred for 1 hour at room temperature. Solvent was removed in vacuo to afford a brown residue. The residue was dissolved in a solution of 15:1 diethyl ether:THF, filtered, and washed with additional diethyl ether. The filtrate was concentrated in vacuo. Subsequent recrystallization at -35 °C yields crystals of 23 (50 mg, 39% yield). IR (cm\(^{-1}\)): 2970 (w), 2947 (w), 2885 (w), 1473 (w), 1350 (w), 1103 (s), 1065 (s), 964 (m), 748 (m), 702 (s). \( \lambda_{\text{max}} \) (\( \varepsilon \text{M} \cdot \text{L}^{-1} \cdot \text{cm}^{-1} \cdot \text{mol}^{-1} \)) 503 nm (620), 651 nm (200), 712 nm (160). Anal. Calcd for C\(_{55}\)H\(_{80}\)O\(_8\)Co: C, 68.30; H, 8.34 Found: C, 67.97; H, 8.37.

**Reaction of \([\text{Co(OR}_2]\text{(CPh}_2\text{)}][\text{CoCp}^*\text{]}\) with 2,6-dimethylphenyl isocyanide.** A benzene solution of CN(2,6-Me\(_2\)C\(_6\)H\(_3\)) (40 mg, 0.303 mmol) in benzene was added to a stirring solution of [Co(OR\(_2\))(CPh\(_2\))][CoCp\(^*\)] (93 mg, 0.0962 mmol) in benzene at room temperature. There was a color
change to dark purple-black after 20 minutes and solution was stirred for an additional 2 hours. Solvent was removed in vacuo to afford a dark purple residue. The residue was dissolved in diethyl ether, filtered, and washed with additional diethyl ether. The filtrate was concentrated in vacuo and subsequent recrystallization at -35°C yielded mixture of X-ray quality crystals of orange Co₂(CN(2,6-Me₂C₆H₃))₈ (21) and purple CoCp₂*(Me₂C₅Me₂C(H)(η₂C(CN(2,6-Me₂C₆H₃))(C(H)Ph₂)) (22). The products display similar solubility in organic solvents and crystallize together. Orange and purple crystals were mechanically separated to give 22 mg (20% yield) of 21 and 22 mg (49%) of 22, and further characterized. Synthesis, spectroscopic, and structural characterization of orange Co₂(CN(2,6-Me₂C₆H₃))₈ was previously reported. ¹H NMR spectrum of 21 matched literature spectrum and is reported below. ¹H NMR (400 MHz, C₆D₆) of 21: δ 6.78 (br, 24H), 2.39 (s, 48H).

Reaction of [Co(OR)₂(CPh₂)][K(18-crown-6)] with 2,6-dimethyl phenyl isocyanide. A solution of CN(2,6-Me₂C₆H₃) (8.7 mg, 0.0663 mmol) in benzene/ether was added to a stirring solution of [Co(OR)₂(CPh₂)][K(18-crown-6)] (50 mg, 0.0519 mmol) in benzene/ether at -35°C. There was a color change to dark green immediately and solution was stirred for 45 minutes, after which the solution transitions to a greenish brown. Solvent was removed in vacuo to afford a dark brown-green residue. The residue was washed repeatedly with hexanes. ¹H NMR of the residue shows formation of the previously reported ketenimine and Co₂(CN(2,6-Me₂C₆H₃))₈ (21). The hexane washings were concentrated at -35 °C to afford 21 in 18% yield.

Reaction of [Co(OR)₂(CPh₂)][CoCp*₂] with adamantyl isocyanide. A ether solution of CNAd (21 mg, 0.130 mmol) was added to a stirring brown-green suspension of [Co(OR)₂(CPh₂)][CoCp*₂] (29 mg, 0.029 mmol) in ether at room temperature. After 20 minutes, the reaction turned russet brown. The
solution gradually darkened and was stirred for 3 hours total at room temperature. The solvent was removed in vacuo to afford a dark brown residue. The residue was dissolved in a 1:1 hexane:ether solution and filtered through a silica plug. The solvent was removed in vacuo and the faint yellow oil was shown by $^1$H NMR to be the previously reported ketenimine (approximately 55% yield), in addition to free isocyanide and hydrolyzed ligand. GC-MS confirmed the presence of the ketenimine as the major product.
CHAPTER FOUR TRANSITION METAL-MEDIATED REDUCTIVE COUPLING OF DIAZOESTERS

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4.1. Introduction

Diazoalkanes are commonly used reagents in organic synthesis. Their most common reactivity mode involves dinitrogen extrusion to form a reactive carbene. Accordingly, diazoalkanes are frequently used as a carbene source to participate in cyclopropanation, C-H bond activation, and other C-C coupling reactions. The activation of diazoalkanes toward N₂ elimination/carbene formation typically requires transition metal catalysis. In some cases, forcing conditions such as heat or photolysis are required to achieve this transformation. Formation of a carbene complex upon dinitrogen elimination depends on the stereoelectronic environment of the complex. However, carbene formation is not the only reactivity mode exhibited by diazoalkanes at transition metal centers. Formation of diazoalkane complexes can occur via coordination to the metal center via the terminal nitrogen in a κ¹ fashion or through the π system of the diazoalkane via the N-N bonds. In some cases, formation of cycloadducts is observed. Formation of a metal-nitrogen multiple bond is common with diazoalkane complexes possessing early metals. Examples of diazoalkane coordination modes to transition metals is presented in Figure 46.

Figure 46. Coordination modes of diazoalkanes to transition metals.

In addition to the formally two-electron reaction modes described above, diazoalkanes can also exhibit one-electron radical reactivity, which can lead to the reductive coupling. Reductive coupling of diazoalkanes through the carbons has been previously reported. Examples of reductive coupled products
of tungsten phosphine and molybdenum amide complexes are shown in Figure 47.

Figure 47. Reductive coupling of diazoalkane complexes through the carbon atoms.

There are significant parallels between the reactivity of diazoalkanes and related organoazides reagents. Similar to diazoalkanes, organoazides typically undergo two-electron reductive splitting to afford nitrenes. However, organoazides can also undergo one-electron reductive coupling through the terminal nitrogens to afford hexazene moieties. In contrast to organoazides, reductive coupling of diazoalkanes through the terminal nitrogens is rare, and has been demonstrated only in one example involving the highly reducing main-group metal, Mg\(^{ll}\)(nacnac). Herein is described the first transition-metal example of the reductive coupling of diazoesters through the terminal nitrogens to give a tetrazene-linked, dinucleating ligand.

4.2. Reactivity of Fe(OR)\(_2\)(THF)\(_2\) with Diazoalkane and Formation of Tetraphenylazine

In the previous chapter, the reactivity of Co(OR)\(_2\)(THF)\(_2\) with diazoalkanes was described. Co(OR)\(_2\)(THF)\(_2\) facilitates reductive splitting of diazoalkanes to form Co-carbene complex 2 and dinitrogen. In the previous report on the synthesis and characterization of 2, the reactivity of Fe(OR)\(_2\)(THF)\(_2\) (24) towards diphenyldiazoalkane was also studied. In contrast to 1, treatment of the iron analogue 24 with diphenyldiazomethane resulted in formation of tetraphenylazine and an unidentified iron species. Formation of the azine product was presumed to occur through a carbene decomposition pathway
where a reactive carbene species couples with free diazoalkane (Figure 49, top). Such decomposition pathways are common in carbene transfer chemistry and were shown to occur with our cobalt system. However, an alternate pathway for formation of azine is possible. This pathway involves reductive coupling and subsequent N$_2$ extrusion from the tetrazene-bridged intermediate. Such a transformation was reported to occur with highly reducing Mg(nacnac) system, where N$_2$ loss from the bridging-tetrazene species resulted in a bridging imido complex. Ensuing oxidation of this species eliminates the corresponding azine (Figure 48).

Figure 48. Reductive coupling of organic azides and diazoalkanes at the terminal nitrogens to give hexazene and tetrazene species with [Mg(nacnac)].

The iron bis(alkoxide) complex 24 was previously reported to undergo reductive coupling with adamantyl azide to give the hexazene complex ($\mu$-κ$^2$κ$^2$-AdN$_6$Ad)[Fe(OR)$_2$](25, Figure 49),$^{49a}$ similar to the reactivity observed with Mg(nacnac) (Figure 48). Thus, it is conceivable that 24 forms azine via reductive coupling of diphenyldiazoalkane in a similar fashion to the magnesium system (Figure 48). In contrast to magnesium, iron is a redox-active metal and can undergo facile reduction to Fe(II) and eliminate azine, thus precluding the need for the external oxidant, oxygen. Due to the facile Fe(II)/Fe(III) redox chemistry, azine formation has the potential to be catalytic from an alternative pathway involving an iron carbene complex (Figure 50). Utilizing 10 mol % 24 and diphenyldiazoalkane in C$_6$D$_6$ resulted in complete
conversion to tetraphenylazine. This result highlights the potential of 24 to participate in reductive coupling chemistry.

**Figure 49.** Carbene formation versus diazoalkane reductive coupling to give azine.

**Figure 50.** Catalytic formation of azine proceeding via an Fe(II)/Fe(III) redox cycle.

### 4.3. Reactivity of Fe(OR)₂(THF)₂ with Diazoesters Resulting in Tetrazene-Bridged Complexes

With the intent of isolating the reductively coupled iron intermediate postulated for the diphenyldiazomethane (Figure 49), 24 was reacted with a diazoester. In contrast to diphenyldiazomethane, diazoesters possess an α-carbonyl group, which can also coordinate to the metal and thus is potentially useful for stabilizing the reductively coupled species. The reductively coupled product in this case would
feature the more stable metallacyclohexane ring in contrast to a metallacyclobutane ring formed with diazoalkane. Furthermore, diazoesters proved to be superior substrates to diazoalkanes in the cobalt bis(alkoxide) chemistry of 1 and could lead to similarly superior reactivity with iron. Exposing a faint yellow hexane solution of iron bis(alkoxide) 24 to a bright yellow hexane solution of methyl phenyldiazoacetate at room temperature resulted in an immediate color change to dark brown. A further color change to burgundy was noted after the first 10 minutes with no observable gas evolution and the reaction was stirred for an hour. Subsequent work-up and recrystallization from ether at -35 °C resulted in dark purple X-ray quality crystals of 26 (Figure 51 and 52). Similarly, the use of two other diazoesters (ethyl phenyldiazoacetate and ethyl (4-bromophenyl)diazoacetate) under identical reaction conditions resulted in a similar color change from yellow to brown to burgundy to give purple crystals of 27 and 28, respectively (Figure 51). Despite the crystals not being of X-ray quality, their structures were supported by elemental analysis. Their similar spectroscopic (IR, UV-vis, and Mössbauer) signatures to that of 26 also provided strong support for their analogous structures.

![Figure 51](image-url)

**Figure 51.** Formation of tetrazene-bridged iron complexes 26-28 via reductive coupling of diazoester.

The X-ray structure of 26 revealed formation of the tetrazene-bridged species $[\mu-\kappa^2:\kappa^2-$MeO$_2$CC(Ph)NNNCC(Ph)CO$_2$Me]$[\text{Fe(OR)}_2]_2$ formed via reductive coupling of diazoesters at the terminal nitrogens (Figure 52), with pertinent crystallographic parameters presented in Table 6. Each iron center is coordinated to two alkoxide ligands, in addition to nitrogen and the carbonyl oxygen of the diazoester. Comparison of the crystal structure of 26 to the previously reported hexazene-bridged iron(III) bis(alkoxide) 25 demonstrates similar Fe-OR bond lengths (avg. 1.784 Å in both species). The hexazene complex 25 was established to consist of two high-spin Fe(III) and a dianionic hexazene ligand by DFT
calculations. These results suggest formation of two Fe(III) and a dianionic tetrazene
[MeO₂CC(Ph)NNNCC(Ph)CO₂Me] ligand in 26. Furthermore, the central N-N bond of the chelate is close
to that of a single bond, similar to 25 (1.394(2) Å and 1.418(2) Å in 26 and 25, respectively). Comparison
of the intraligand [ONNNNO] bond distances in 26 with that of free diazoester and the planarity in each
ring suggests significant electron delocalization within the O,N-chelate rings.86

Figure 52. Crystal structure of complex 26. [Fe₂(κ²:κ²-MeO₂CC(Ph)NNNCC(Ph)CO₂Me)(OR)₄], 50% probability ellipsoids. 19 H atoms and co-crystallized ether molecule are omitted for clarity. Selected bond
distances (Å) and angles (º): Fe – O1, 1.785(1); Fe – O2, 1.783(1), Fe – O3, 2.002(1), Fe – O3’, 2.034(1);
O3 – C1, 1.249(2); C1 – C2, 1.436(2); C2 – N1, 1.333(2); N1 – N2, 1.308(2); N2 – N2’, 1.394(2); O2 –
Fe – O1, 119.29(5); O2 – Fe – N1, 114.71(5); O1 – Fe1 – N1, 123.36(5); O3 – Fe – N2, 82.01; O3 – Fe –
O2, 102.90(5); O3 – Fe – O1, 100.89(5).
Table 6. Experimental crystallographic parameters for 26.

<table>
<thead>
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<tr>
<td>Formula</td>
<td>C$<em>{78}$H$</em>{108}$Fe$_2$N$_4$O$_8$×2C$<em>4$H$</em>{10}$O</td>
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<tr>
<td>Fw</td>
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<tr>
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<tr>
<td>space group</td>
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<tr>
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</tr>
<tr>
<td>$b$ (Å)</td>
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</tr>
<tr>
<td>$c$ (Å)</td>
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<tr>
<td>$a$ (deg)</td>
<td>90.00</td>
</tr>
<tr>
<td>$\beta$ (deg)</td>
<td>110.103(3)</td>
</tr>
<tr>
<td>$\gamma$ (deg)</td>
<td>90.00</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
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</tr>
<tr>
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</tr>
<tr>
<td>$Z$</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>100(2)</td>
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<tr>
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</tr>
<tr>
<td>$wR_2$ (all data)</td>
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<tr>
<td>$R_1$ [(I&gt;2$\sigma$)]</td>
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<td>$wR_2$ [(I&gt;2$\sigma$)]</td>
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</tr>
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An overlay of the IR spectra of 26-28 shows similarities in the prominent signals, supporting formation of the tetrazene-bridged species (Figure 53). A comparison of previously reported IR of tetrazene and hexazene complexes allows for assignment of the peaks at 1555, 1260, 1150, and 1005 cm⁻¹ to be the C=O ester, tetrazene N–C/N–N, and alkoxide C–O stretching vibrations, respectively. DFT calculated stretches at 1570, 1335, 1224, and 1060 cm⁻¹ for the motions that have significant intensity compare with the experimental results. The UV-Vis spectra display a peak at 516 nm for 26-28.

**Figure 53.** IR spectrum overlay of 26-28 displaying similarities in the major peaks at 1555, 1260, 1150, and 1005 cm⁻¹.

A zero-field $^{57}$Fe Mössbauer experiment was conducted to elucidate the oxidation state of the iron centers and tetrazene ligand (in collaboration with Prof. Stoian at the University of Idaho). The spectrum recorded at 80 K of a neat powder sample of 26 reveals a well-defined quadrupole doublet. This doublet accounts for ~97% of the iron present in the sample with parameters of $\delta = 0.55(1)$ mm s⁻¹ and $\Delta E_Q = 2.52(3)$ mm s⁻¹ (Figure 54). Comparison of these parameters to the previously reported Fe(OR')₃(ArNNNNAr) (where R' = C'Bu₃(3,5-Ph₂Ph) and Ar = 4-MeOPh, 3,5-Me₂Ph) of $\delta = 0.49$ mm s⁻¹ and $\Delta E_Q = 2.20$ mm s⁻¹ revealed similarities, supporting comparable electronic structures of these systems.³¹
The latter species was shown to originate from a high-spin iron(III) ion with the S = 5/2 iron spin antiferromagnetically coupled to the S = 1/2 of an anionic tetrazene ligand. Based on the above, 26 will consist of two high-spin S = 5/2 Fe(III) ions antiferromagnetically coupled to an anionic S = 1 tetrazene ligand. The resonances observed for 26 are considerably broader than those of Fe(OR')_2(ArNNNNAr) (Γ_{LR} = 0.68/0.75 mm s\(^{-1}\) vs. Γ = 0.33 mm s\(^{-1}\)). While the increased linewidth might be indicative of structural heterogeneities, it might also originate from unresolved magnetic hyperfine splitting. The spectra of 27 and 28 exhibit very similar spectral parameters to the spectrum of 26 suggesting formation of analogous tetrazene-bridged species (see Appendix D).

**Figure 54.** \(^{57}\)Fe Mössbauer spectrum recorded in zero field at 80 K for 26 and simulation (red trace).

The stability of 26 in solution was investigated, in order to compare to the proposed tetrazene analogue derived from diphenyldiazoalkane. Monitoring the solution of 26 (0.178 mM) at room temperature exhibited a slow color change from purple to dark brown over 5 days. UV-Vis of the solution showed decay of the peak at 516 nm (26), and growth of a peak at 378 nm. The spectrum showing the decomposition sampled once a day is presented in **Figure 55**. Approximately 20% of 26 remains after 5 days. A kinetics study of the decomposition of 26 was found to follow first-order with k = 4 x 10^{-6} s\(^{-1}\) by analyzing samples of 26 over time (see Appendix D for decomposition rate data). Thermolysis of 26 at 50°C overnight led to full decomposition with a color change to yellow-brown. While \(^1\)H NMR of the resulting solution consists
of only broad resonances, the GC-MS spectrum contains the corresponding azine, free diazoalkane, and the alkoxide ligand. No olefin was observed in GC, suggesting, albeit indirectly, that carbene formation does not occur. These results support decomposition of the tetrazene-bridged ligand to eliminate azine, as hypothesized for the catalytic formation of azine by 24 with diphenyldiazoalkane. This decomposition is significantly slower for the tetrazene-bridged bis(diazenylacetate) species 26 due to the chelating nature of the tetrazene-bridged ligand in 26.

Figure 55. UV-Vis spectrum of 26 showing decomposition over 5 days.
4.4. DFT Calculations on Carbene Formation versus Reductive Coupling with Cobalt and Iron Bis(alkoxides)

Differing reaction pathways were found for the cobalt and iron bis(alkoxide) complexes 1 and 24, respectively. Thus, DFT calculations were conducted on the cobalt and iron diazoester complexes to elucidate why carbene transfer occurs with cobalt and reductive coupling with iron (Figure 56). DFT calculations on the methyl phenyldiazoacetate intermediate suggest that iron is most stable in the quintet state with a high-spin Fe(III) antiferromagnetically coupled to the diazoester ion. The κ² isomer is slightly more stable than the κ¹ isomer. Reduction of the diazoester involves an N–N π* orbital and formation of the stable six-membered metallacycle prevents N₂ expulsion. The high barrier towards N₂ expulsion from the κ¹ iron diazoester adduct of 29.3 kcal/mol suggests why the carbene does not form. In contrast, the coupling of two κ² iron diazoester adducts is predicted to have no enthalpic barrier, thus being the preferred pathway. An upper limit of the entropic barrier of ~17 kcal/mol can be approximated using the entropy loss for formation of 26 from two κ² iron diazoester adducts. The much lower barrier for reductive coupling versus N₂ expulsion for iron showcases the observed experimental results. The reaction to form the quintet iron carbene is exergonic by -11.4 kcal mol⁻¹. In contrast, reductive coupling to form 26 from two κ² iron diazoester adducts is exergonic by -25.9 kcal mol⁻¹. A similar comparison to cobalt illustrates why reductive coupling was not observed.\(^{47}\) Reduction of diazoester to form the κ² high-spin cobalt(III) diazoester adduct is disfavored as compared with iron due to the lower reducing potential of Co(OR)₂.\(^{29a, b}\) Carbene formation with cobalt is competitive as compared with iron due to the unfavorable equilibrium which must be overcome to form two κ² cobalt diazoester adducts before reductive coupling occurs. N₂ elimination from the κ¹ cobalt diazoester adduct to form the carbene is exergonic by -3.5 kcal mol⁻¹, explaining the preference for carbene formation over reductive coupling.
Figure 56. DFT calculations on the diazoester adducts to rationalize the differing reactivities observed between iron and cobalt.

4.5. Summary and Conclusions

In conclusion, Fe(OR)$_2$(THF)$_2$ undergoes reductive coupling chemistry in contrast to the carbene reactivity observed for Co(OR)$_2$(THF)$_2$. The reactivity described above marks the unprecedented reductive coupling at a transition metal through the terminal nitrogens of methyl phenyldiazoacetate to form a dinuclear complex featuring a dinucleating tetrazene-bridged bis(diazenyl)acetate ligand. The electronic structure was probed by spectroscopic, structural, and computational means to consist of two high-spin iron (III) centers each antiferromagnetically coupled to the monoanionic 2-diazenylacetate chelate. DFT calculations helped elucidate the different reactivity observed between cobalt and iron, which proceeds via the diazoester adducts. In the case of iron, this adduct is κ$^2$ bound which develops significant radical character at the terminal nitrogen. The κ$^2$ adduct is disfavored in the case of cobalt and carbene formation occurs via dinitrogen expulsion from the κ$^1$ diazoester adduct. The isolation of the reductively coupled product provides insight into the reactivity of Fe(OR)$_2$(THF)$_2$ with diphenyldiazoalkane which resulted in
azine formation, and provides further insight into the uniquely mild metalloradical chemistry observed with Fe(OR)$_2$(THF)$_2$.

4.6. Experimental Details

**General Methods and Procedures.** All reactions involving air-sensitive materials were executed in a nitrogen-filled glovebox or by standard Schlenk line procedures. Iron chloride and thallium hexafluorophosphate was purchased from Strem; other reagents were purchased from Sigma Aldrich. The synthesis of complex 24 was reported previously.$^{49a}$ The diazoesters were synthesized according to a reported literature procedure.$^{59}$ All solvents were purchased from Fisher Scientific and were of HPLC grade. The solvents were purified using an MBRAUN solvent purification system and stored over 3-Å molecular sieves. Deuterated benzene was purchased from Cambridge Laboratories, degassed under argon, and stored over 3-Å molecular sieves. The complexes were characterized using IR, UV/Vis spectroscopies, X-ray crystallography, elemental analysis, and solution magnetometry by the Evans method. NMR and GC-MS spectra were recorded at the Lumigen Instrument Center (Wayne State University). NMR was performed on a Varian Mercury or Agilent 400 MHz Spectrometer in C$_6$D$_6$ at room temperature. Chemical shifts and coupling constants (J) were reported in parts per million (δ) and hertz (Hz), respectively. IR spectra of powdered samples were recorded on a Shimadzu IR Affinity-1 FT-IR Spectrometer outfitted with a MIracle10 attenuated total reflectance accessory with a monolithic diamond crystal stage and pressure clamp. UV-visible spectra were obtained on a Shimadzu UV-1800 spectrometer. Elemental analyses were performed by Midwest Microlab LLC. Formation of the organic by-products was confirmed by GC-MS using Agilent 6890N spectrometer, Thermo TG5MS 30m × 0.32mm × 0.25μm column, 7683 series injector and Agilent 5973 detector. The $^{57}$Fe Mössbauer spectrum was recorded using a spectrometer equipped with a LN$_2$-cooled cryostat. The spectrometer was operated in constant acceleration mode. The isomer shift is quoted against the center of a zero-field spectrum recorded at room temperature for an iron metal-foil.

**X-ray Crystallographic Details.** Crystals of compounds 26-28 were grown at -33 °C from concentrated ether solutions; in all cases, very dark purple-brown crystals were obtained. The structure of complex 26 was confirmed by X-ray diffraction analysis. The crystals of 27 and 28 were found to be highly
unstable outside of their respective solutions. The decomposition of the crystals was indicated by the progressive transformation (within 1-2 minutes of exposure) of the single-crystal diffraction pattern into a powder-like diffraction pattern. The crystal of 26 was mounted on a Bruker APEXII/Kappa three circle goniometer platform diffractometer equipped with an APEX-2 detector. A graphic monochromator was employed for wavelength selection of the Mo Kα radiation (λ = 0.71073 Å). The data were processed and the structure was solved using the APEX-3 software supplied by Bruker-AXS. The structure was refined by standard difference Fourier techniques with SHELXL (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms were placed in calculated positions using a standard riding model and refined isotropically; all other atoms were refined anisotropically. Only half of a molecule of 22 (and one molecule of ether solvent) occupies an asymmetric unit, hence Z = 2.

**Computational Details.** DFT calculations were performed using Gaussian 09 with default grids and density fitting (when possible). Geometry optimizations at the BP86-D3/def2-SVP level of theory were followed by stability calculations to ensure Aufbau electron configurations and harmonic frequency calculations to establish optimized structures as minima. Thermodynamic corrections used standard approximations to estimate enthalpies, entropies, and Gibbs free energies based on the unscaled harmonic frequencies at 298.15 K. Follow-up single point calculations at the B3LYP-D3/def2-TZVP level of theory simulated the effects of solvent (n-hexane) using the SMD implicit solvation model. Triple-zeta free energies were estimated as $G_{TZ} = G_{DZ} - E_{DZ} + E_{TZ}$.

**Synthesis of (Fe(OR)$_2$)$_2$[μ-κ$^2$:κ$^2$-(OC(OMe)C(Ph)NN)$_2$] (26).** A yellow solution of diazoester in hexane (0.11 mL, 0.066 mmol) was added to the pale-yellow hexane solution of Fe(OR)$_2$(THF)$_2$ (43 mg, 0.067 mmol). There was an immediate color change to dark brown, which transitions to burgundy within 10 minutes. The reaction was stirred for 1 h at room temperature, during which solid crashed out. The volatiles were removed in vacuo, the resulting brown residue was washed with ether, dissolved in THF, filtered, and dried in vacuo. Subsequent recrystallization from diethyl ether at 35°C yields X-ray quality crystals of 26 (37 mg, 81% yield). IR (cm$^{-1}$): 2970 (w), 2878 (w), 1559 (m), 1489 (w), 1443 (w), 1265 (s),
Synthesis of (Fe(OR)$_2$)$_2$[μ-κ$^2$-κ$^2$-(OC(OEt)C(Ph)NN)] (27). A yellow solution of diazoester in hexane (0.50 mL, 0.086 mmol) was added to a pale-yellow hexane solution of Fe(OR)$_2$(THF)$_2$ (53 mg, 0.083 mmol). There was an immediate color change to dark brown, which transitions to burgundy within 10 minutes. The reaction was stirred for 1 h at room temperature, during which solid crashed out. The volatiles were removed in vacuo, the resulting brown residue was washed with ether, dissolved in THF, filtered, and dried in vacuo. Subsequent recrystallization from ether at 35°C yields 27 as a purple solid after 4 days (46 mg, 81% yield). IR (cm$^{-1}$): 2970 (w), 2878 (w), 2338 (w), 1558 (m), 1258 (m), 1142 (s), 1042 (m), 1003 (s), 702 (s), 648 (s). $\lambda_{\max}$ (εM (L$^{-1}$ cm$^{-1}$ mol$^{-1}$)) 516 (22727). $\mu$ = 7.3 ± 0.7 μB (calcd 8.4). Anal. Calcd for C$_{80}$H$_{112}$N$_4$O$_8$Fe$_2$: C, 70.16; H, 7.26; N, 3.67. Found: C, 70.25; H, 7.32; N, 3.49.

Reaction of 10 mol% of 24 and Ph$_2$CN$_2$. A C$_6$D$_6$ solution of the Ph$_2$CN$_2$ (0.2051mL, 0.5M) and TMB (1 equiv) was added to a stirred solution of 24 (0.0205 mmol, 0.0410 M). A notable color change occurred to dark brown. NMR of the reaction mixture was taken after 24 hours and 100% yield to Ph$_2$CNNCPPh$_2$ was calculated with reference to internal standard (TMB).
Monitoring decomposition of 26 by UV-Vis. A THF solution of 26 (0.0036 M) was stirred at RT for 5 days. Every 24 hours, a 0.1 mL aliquot of the solution was diluted to 6 mL and the UV-Vis spectrum was recorded. The concentrations of the solutions were determined from a calibration curve of known concentrations of 26. The color transitions from dark purple to brown over time and the characteristic peak at 518 nm decreases and a shoulder at 378 nm grows in on the third day.
CHAPTER 5 CONCLUSIONS AND FUTURE DIRECTIONS

The work described in this dissertation focused on the investigation of carbene/diazoalkane chemistry at late 3d metals in weak-field bis(alkoxide) ligand environment. This research was motivated by the need to develop reactive and cost-effective carbene transfer catalysts. Furthermore, late transition-metal chemistry featuring hard alkoxide ligand environments is understudied. It was anticipated that while the strong-field (π-accepting/σ-donating) ligand environments (phosphines, carbonyls, isocyanides, N-heterocyclic carbenes) form stable Fischer-type carbene complexes at late metals, weak-field (π-donating) alkoxide ligation may result in reactive Schrock carbenes, or carbene radicals prone to new C-C bond formation. The work described here confirmed our initial hypothesis. The key findings (detailed below) include facile and catalytic C-C bond formation mediated by the high-valent Co(OR)$_2$(=CR'R'') species, synthesis of a new Co(II)-carbene with the pronounced radical character at the carbene and its ability to form new C-C bonds, and unprecedented radical coupling reactivity mediated by an iron complex.

The weak-field alkoxide ligation was shown to lead to a novel carbene complex Co(OR)$_2$(=CR'R''), in contrast to systems featuring strong-field ligand environments. Chapter 2 demonstrates that Co(OR)$_2$(=CR'R'') species form ketenimines upon reaction with isocyanides under mild reaction conditions. This transformation is novel, as ketenimine formation from carbene complexes and isocyanides is rare. The formation of ketenimines was accompanied by the formation of cobalt bis(alkoxide) bis(isocyanide) by-products. Computational studies revealed that formation of ketenimines proceeded through nucleophilic attack of the isocyanide at the cobalt center prior to C-C bond formation, confirming the “alkylidene-like” nature of the high-valent metal species. This is in stark contrast to isocyanide attack at the (electrophilic) carbene carbon observed with Fischer carbenes. Elimination of free ketenimine formed the bis(isocyanide) complex. For selected carbene precursors (diazoesters), catalytic ketenimine formation was observed. Thus, ethyl diazoacetate enabled up to 10 turnovers with bulky alkyl isocyanides. Mechanistic experiments revealed that bis(isocyanide) complex acts as a thermodynamic sink, and that its relative stability towards substitution with carbene precursors dictates the feasibility of the catalytic cycle. Spectroscopic evidence for the additional carbene intermediates was obtained. Overall, these studies
demonstrate the feasibility and the catalytic potential of the late-metal “alkylidenes” enabled by the bis(alkoxide) ligation.

Electrochemical characterization of the cobalt carbene showed three redox events, of which the first was quasi-reversible and easily accessible by a variety of chemical reductants. One-electron chemical reduction of the parent carbene Co(OR)$_2$(CPh$_2$) was explored as a means to alter its electronic structure and reactivity. The reduction was accomplished using decamethylcobaltocene or potassium graphite. The resulting products [Co(OR)$_2$(CPh$_2$)](CoCp*) and [Co(OR)$_2$(CPh$_2$)](K(18-crown-6)) were isolated and characterized. Elucidation into the electronic structure of the reduced carbene by DFT calculation revealed the high-spin Co(II) triplet S = 1 state to be only 1 kcal/mol lower in energy than the quintet S = 2 state, differing in whether the carbene radical is anti-ferromagnetically or ferromagnetically coupled to cobalt, respectively. Mulliken spin analysis of the [Co(OR)$_2$] and [CPh$_2$] fragments shows spins of 2.87 and −0.87 for the slightly more stable triplet state. The reactivity of the reduced carbenes [Co(OR)$_2$(CPh$_2$)](CoCp*) and [Co(OR)$_2$(CPh$_2$)](K(18-crown-6)) with isocyanides was also investigated. While the reaction of [Co(OR)$_2$(CPh$_2$)](K(18-crown-6)) led to the formation of the respective ketenimine, the presence of the reactive [CoCp*]’ cation in [Co(OR)$_2$(CPh$_2$)](CoCp*) led to a different outcome. In this case, the initially formed ketenimine underwent a nucleophilic attack by deprotonated [CoCp*]’, eventually leading to the formation of imino-functionalized tetramethylfulvene complex of Co(I).

Having investigated the reactivity of cobalt bis(alkoxide) toward various diazoalkanes, the respective chemistry of iron bis(alkoxide) was explored. Exposure of the iron bis(alkoxide) complex with diphenyldiazoalkane resulted in azine formation. In contrast, exposure of the iron bis(alkoxide) to diazoesters resulted in the unprecedented reductive coupling at the terminal nitrogens to give the dinuclear tetrazene complex. Elucidation of the electronic structure of this complex by DFT calculations and Mössbauer experiments showed it to consist of two high-spin Fe(III) centers antiferromagnetically coupled to an anionic 2-diazenylacetate chelate. The isolation of this reductive coupled product, in conjunction with previously demonstrated reductive coupling of azides allowed to shed light on the reactivity of diphenyldiazoalkane, which likely forms the corresponding azine via a similar bimetallic tetrazene. DFT
calculations were performed to elucidate why carbene formation occurred with cobalt, whereas reductive coupling is observed with iron. It was found that reductive coupling occurs through the $\kappa^2$ diazoester adduct which is slightly more favored for iron over the $\kappa^1$ adduct. The $\kappa^2$ isomer stabilizes a radical in the chelate which coordinates to a high-spin M(III) species. Coupling of two diazoester radicals is essentially barrierless for iron. In contrast, cobalt disfavors the reduced $\kappa^2$ isomer due to formation of this reduced diazoester with a high-spin Co(III). Therefore, carbene formation occurs with cobalt upon dinitrogen extrusion from the $\kappa^1$ adduct.

In conclusion, utilization of weak-field bis(alkoxide) ligation lead to unique reactivity towards diazoalkane/diazoester. Carbene formation takes place with cobalt, whereas reductive coupling is observed for iron. The “alkylidene-like” carbene functionality in the coordination sphere of cobalt was novel, and likely enabled by the weak-field bis(alkoxide) ligation. This work increases our understanding of the nature of carbene complexes as function of different metals and/or ancillary ligand environments. Future studies in this project will focus on the design of the additional carbene complexes. One prominent drawback of this system was the lability of monodentate alkoxides, which possibly prevented catalytic reactivity with additional substrates, such as olefins. Our future studies are aimed at utilizing other alkoxide ligands. As mentioned in the Chapter 1, the synthesis of M(OC'Bu$_2$(3,5-Ph$_2$Ph))(THF)$_2$ complexes lead to superior reactivity due to selective formation of bis(alkoxide) complexes. While the tris(alkoxide) complex was not observed with iron or cobalt in this work, attempts to synthesize a chromium carbene lead to isolation of the tris(alkoxide) complex. Utilizing the bulkier ligand may lead to the desired chromium carbene chemistry. Formally chromium(IV) ($d^2$) carbenes are nearly unprecedented; it would be interesting to explore the electronic structures of such species. Will this be a typical Schrock carbene featuring electrophilic metal, nucleophilic carbon, and short metal-carbon bond? The additional steric bulk imposed by the phenyl substituent may also lead to the isolation and structural characterization of cobalt and chromium carbene complexes derived from diazoesters. Isolable carbenes featuring alkyl/ester groups (push/pull carbenes) are rare; it would be intriguing to compare their structural properties with analogous dialkyl (aryl) carbenes. In the context of catalytic ketenimine formation, the major roadblock on the route
to catalysis was the stability of the bis(isocyanide) complex and formation of by-products. Utilizing \( \text{Co(OC}^\text{Bu}_2(3,5-\text{Ph}_2\text{Ph})_2(\text{THF})_2 \) may lead to a bis(isocyanide) complex with increased lability of isocyanide ligands to improve turnover. Furthermore, the added steric bulk may diminish formation of azine and olefin by-products. In the context of reductive coupling, several key proposed intermediates may be observed utilizing the bulkier alkoxide ligand. Finally, employing chelating alkoxide\(^{90}\) prevents lability of the monodentate alkoxide ligand towards dissociation from the metal center and should improve catalysis and broaden its scope. In addition to catalytic formation of ketenimines, cyclopropanation chemistry is desirable, which was limited with our cobalt system likely due to the lability of our monodentate alkoxide. It is possible that chelating bis(alkoxide) or bulkier monodentate alkoxide will enable cyclopropanation reactivity in our systems.

In addition to modifying the structure of the complex, increasing carbene (precursor) scope is also worthwhile. In the context of diazoalkane, only \( \text{Ph}_2\text{CN}_2 \) was investigated. In addition to the “basic” \( \text{Ph}_2\text{CN}_2 \), the phenyl rings can also be modified with electron-donating/withdrawing substituents. Furthermore, replacing the phenyl ring with an alkyl group (or hydrogen) is expected to form a more reactive precursor. Typically, such diazoalkanes are unstable so \textit{in situ} generation via deprotonation of tosylhydrazones could be explored.\(^{91}\) In the context of diazoesters, most of the diazoesters we explored contained an aryl ring in addition to the ester group ([C(Ar)(CO\(_2\)R)]. The chemistry of other stabilizing groups such as vinyl has been investigated in carbene chemistry, and thus could be potentially explored in our system. The vinyl group generally provides a stabilizing effect, in similar to the phenyl group), but the smaller steric demand of the vinyl group may improve reactivity.

Our studies reveal a uniquely mild yet potent one-electron reagent, \( \text{Fe(OR)}_2(\text{THF})_2 \), which led to reductive coupling chemistry in contrast to carbene chemistry more commonly observed with diazoalkanes/diazoesters. Our future studies will focus on the exploration of reductive coupling chemistry of diazoalkane/diazoester with the related iron bis(alkoxide) featuring [OC^Bu_2(3,5-Ph_2Ph)] or a chelating alkoxide, as described above. The use of such ligands may potentially enable dissociation of tetrazene
(hexazene) from the metal centers, leading to nitrogen-rich organic molecules. Reductive coupling of small molecules will be also explored including N₂O and CO₂.
APPENDIX A

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Title: 10012. Alkoxide Ligands

Author: Stanislav Groysman and Amanda Grass

Publication: Comprehensive Coordination Chemistry III

Publisher: Elsevier

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Title: Group-transfer chemistry at transition metal centers in bulky alkoxide ligand environments
Author: Amanda Grass, Duleeka Wannipurage, Richard L. Lord, and Stanislav Groysman
Publication: Coordination Chemistry Reviews
Publisher: Elsevier
Date: 1 December 2019
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**Title:** Ketenimine Formation Catalyzed by a High-Valent Cobalt Carbene in Bulky Alkoxide Ligand Environment  
**Author:** Amanda Grass, Nicholas S. Dewey, Richard L. Lord, and Stanislav Groysman  
**Publication:** Organometallics  
**Publisher:** American Chemical Society  
**Date:** Feb 1, 2019  
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**Title:** One Electron Reduction Transforms High-Valent Low-Spin Cobalt Alkylidene into High-Spin Cobalt(II) Carbene Radical

**Author:** Amanda Grass, James Bellow, Gregory Morrison, Hans-Conrad zur Loye, Richard L. Lord, and Stanislav Groysman

**Publication:** Chemistry Communications

**Publisher:** Royal Society of Chemistry

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**Title:** Transition metal-mediated reductive coupling of diazoesters  
**Author:** Amanda Grass, Sebastian Stoian, Richard L. Lord, and Stanislav Groysman  
**Publication:** Chemistry Communications  
**Publisher:** Royal Society of Chemistry  
**Date:** 26 June 2019

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APPENDIX B

SUPPLEMENTARY MATERIAL FOR CHAPTER 2

1. Crystal Structures Not Shown in Chapter 2

Figure B.1. X-ray structures of complex 19, 50% probability ellipsoids. H atoms were omitted for clarity. Selected bond distances (Å) 19: C1–C1’, 1.336(2).
Table B.1. Experimental crystallographic parameters for 19.

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<tr>
<td>Fw</td>
<td>148.15</td>
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<tr>
<td>Crystal system</td>
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<tr>
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<td>P2₁/c</td>
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<tr>
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<tr>
<td>b (Å)</td>
<td>8.2376(10)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>11.9433(14)</td>
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<tr>
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</table>
2. Evans Method Formula and Procedures

The Evans method was performed on all complexes using a Wilmad coaxial insert (purchased from Aldrich) and a standard NMR tube. The sample was carefully weighed (10 – 20 mg) and dissolved in 1 mL C₆D₆ to afford solutions with known concentrations to perform the calculations. The solutions were added to the insert, and the insert was placed inside the outer NMR tube, which contained C₆D₆. NMR spectra were taken. The molar susceptibility $\chi_m$ of the compound was first calculated using Equation 1:\(^9\)

$$
\chi_m = \left( \frac{3\Delta\nu}{4\pi nm_0} + \chi_0 \right) M
$$

where $\Delta\nu$ is the peak separation (Hz), $m$ is the concentration of the solution (g/mL), $\nu_0$ is the spectrometer operating frequency in Hertz, $\chi_0$ is the molar susceptibility of the solvent (in cm$^3$/g), and $M$ is the molar mass of the compound (g/mol). Diamagnetic corrections were calculated using Pascals constants. The solution state effective magnetic moment ($\mu_{eff}$) was calculated using Equation 2:

$$
\mu_{eff} = \sqrt{(2.383 \times 10^3)(\chi_m)}
$$

Three measurements were taken, the average of the three and the corresponding standard deviation were calculated. The uncertainty was estimated to be at least 10%, based on weight measurement uncertainty.
Table B.2. Magnetic moments for complexes 4, 8, and 9 using the Evans method ($\mu_{\text{obs}}$ ($\mu_B$)).

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<td>Average</td>
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<td>3.99</td>
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<tr>
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<td>0.40</td>
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<tr>
<td>$\mu_{\text{calc}}$ ($\mu_B$)</td>
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</tbody>
</table>
3. NMR and GC-MS Spectra

Figure B.2. $^1$H NMR of Co(OR)$_2$(CN(2,6-Me$_2$C$_6$H$_3$))$_2$ (4).
Figure B.3. $^1$H NMR of Co(OR)$_2$(CNAd)$_2$(8).
Figure B.4. $^1$H NMR of Co(OR)$_2$(CN(4-MeOC$_6$H$_4$)$_2$ (9).
Figure B.5. $^1$H NMR of the reaction between 4 and diphenyldiazoalkane after 5 hours. Blue asterisks refer to peaks indicative of 4 and red asterisks refer to free diphenyldiazoalkane.
Figure B.6. $^1$H NMR of the reaction between 8 and ethyl diazoacetate after 1 hour shows broadened peaks. NMR of reaction mixture put through a silica plug is shown below. Purple asterisks denote ketenimine and red asterisks denoted ethyl diazoacetate.
Figure B.7. $^1$H NMR of a silica plug of reaction above (Figure B.6) showing HOR and ketenimine.
Figure B.8. $^1$H NMR of reaction of 1 and phenyl methyl phenyldiazoacetate in C$_6$D$_6$ after 1 hour showing unreacted diazoester and hypothesized carbene product formed in situ.
Figure B.9. $^1$H NMR of crystallized olefin obtained from reaction of 1 and methyl phenyldiazoacetate.
Inset: Zoom in of aromatic region showing a dd which appears at 7.92 ppm.
Figure B.10. $^1$H NMR of stoichiometric formation of N-(2,6-dimethylphenyl)-2,2-diphenylethen-1-imine ($\text{Ph}_2\text{CCN(C}_6\text{H}_4\text{-2,6-Me}_2\text{)}$) 3. Peaks at 10.42 correspond to Co(OR)$_2$(CN-2,6-Me$_2$C$_6$H$_4$)$_2$.

Figure B.11. MS of 3 (m/z of 297 corresponds to molecular ion).
Figure B.12. $^1$H NMR of stoichiometric formation of N-adamantanyl-2,2-diphenylethen-1-imine ($\text{Ph}_2\text{C}=\text{C}=\text{N-Ad}$) 5. Peak at 10.01 correspond to Co(OR)$_2$(CNAd)$_2$.

Figure B.13. MS of 5.
Figure B.14. $^1$H NMR of stoichiometric formation of N-(4-methoxyphenyl)-2,2-diphenylethen-1-imine (Ph$_2$C=C=N-C$_6$H$_4$-4-OMe) 6. Peaks at 9.94 and 2.35 correspond to Co(OR)$_2$(CN(4-MeOC$_6$H$_4$)$_2$).

Figure B.15. MS of 6 (m/z of 299 corresponds to the molecular ion).
Figure B.16. $^1$H NMR of stoichiometric formation of $\text{N-}(2\text{-chloro-6-methylphenyl})\text{-}2,2\text{-diphenylethen-1-imine Ph}_2\text{C=C=N-(2-Cl-4-Me-C}_6\text{H}_4)$ 7. Peaks at 10.43 correspond to $\text{Co(OR)}_2\text{(CN}(2\text{-Cl-6-MeC}_6\text{H}_4))_2$.

Figure B.17. MS of 7 (m/z of 317 corresponds to the molecular ion).
Figure B.18. $^1$H NMR of the isolated Ph$_2$C=C=N-(2-Cl-4-Me-C$_6$H$_3$) 7 obtained by extraction with 10:1 hexane:ether. Low amount of the isolated product (58%, 4 mg) prevented $^{13}$C NMR analysis.
Figure B.19. $^1$H COSY NMR (aromatic region) of isolated Ph$_2$C=C=N(2-Cl-4-Me-C$_6$H$_3$)$_7$ showing overlap of protons d and g in spectrum above.
Figure B.20. $^1$H NMR of catalytic reaction between diphenyldiazoalkane and 2,6-dimethyl phenyl isocyanide (entry 1, Table 2). Blue asterisks denote isocyanide starting material, red asterisks denote diazoalkane starting material, and orange asterisks denote azine byproduct. Peaks for b, c, e, and f are underneath diazoalkane starting material.
Figure II.B. $^1$H NMR of catalytic reaction between diphenyldiazoalkane and adamantyl isocyanide (entry 2, Table 2). Blue asterisks denote isocyanide starting material, red asterisks denote diazoalkane starting material, and orange asterisks denote azine byproduct. Peaks for e and f are underneath diazoalkane starting material.
Figure B.22. $^1$H NMR of catalytic reaction between diphenyl diazoalkane and cyclohexyl isocyanide (Table 2, entry 3). Blue asterisks denote isocyanide starting material, red asterisks denote diazoalkane starting material, orange asterisks denote azine byproduct, and purple asterisks denote HOR. Peaks for e, f, h, i, j, and k are underneath diazoalkane starting material.
Figure B.23. $^1$H NMR of catalytic reaction between methyl phenyl diazoacetate and 2,6-dimethylphenyl isocyanide (Table 2, entry 4). Blue asterisks denote isocyanide starting material and red asterisks denote diazoalkane starting material. Broadened peaks for isocyanide are likely due to its coordination to cobalt.
Figure B.24. $^1$H NMR of catalytic reaction between methyl phenyldiazoacetate and 4-methoxyphenyl isocyanide (Table 2, entry 5). Blue asterisks denote isocyanide starting material and red asterisks denote diazoalkane starting material. Approximately 50% of the diazoester is converted. In addition to the desired ketenimine, three major by-products appear as the trans olefin (7.91, 7.03, and 3.51 ppm, approximately 5%), cis olefin (7.62, 7.08, 6.85, 3.10 ppm, approximately 15%), and the corresponding azine (7.15, 6.85, 3.45 ppm, approximately 15%).
Figure B.25. $^1$H COSY spectrum of aryl region of the catalytic reaction between methyl phenyldiazoacetate and 4-methoxyphenyl isocyanide (Table 2, entry 5) after removal of HOR (silica plug).
Figure B.26. GC-MS of reaction mixture of Table 2, entry 5 (NMR is given in Figure B.24). See Figures B.27-B.32 for the assignment of the peaks based on their mass spectra.
Figure B.27. Retention time of 7.984: m/z of 162 indicating HMB-H⁺.

Figure B.28. Retention time of 8.456: m/z of 163 indicating ROH – 'Bu.
Figure B.29. Retention time of 10.130: m/z of 296 indicating cis olefin (also verified by NMR).

Figure B.30. Retention time of 10.249: m/z of 296 indicating trans olefin (verified by NMR).
Figure B.31. Retention time of 11.291: m/z = 265 indicates decomposition of azine (azine – COOMe).
Figure B.32. Retention time of 11.389: m/z of 281, indicating ketenimine (Ph(COOMe)C=C=NC6H4OMe) product.
Figure B.33. $^1$H NMR of catalytic reaction between methyl phenyldiazoacetate and adamantyl isocyanide (Table 2, entry 6). Blue asterisks denote isocyanide starting material and red asterisks denote diazoalkane starting material. Approximately 40% of the diazoester is consumed. In addition to the ketenimine, approximately 2% of the trans olefin (7.91, 7.03, and 3.51 ppm) is present.

Figure B.34. GC-MS of reaction mixture of Table 2, entry 6 forming Ph(COOMe)C=C=NAd. Major peaks are AdNC at 7.576, HMB at 7.952, HOR decomposition product at 8.427, and ketenimine products at 11.768 (see Figures B.35 – B.38 for details).
Figure B.35. Retention time of 7.576: m/z of 161, indicating adamantyl isocyanide.

Figure B.36. Retention time of 7.985: m/z of 162, indicating HMB-H⁺.
Figure B.37. Retention time of 8.495: m/z of 163, indicating ROH – tBu.

Figure B.38. Retention time of 11.768: m/z of 309, indicating ketenimine (Ph(COOMe)C=C=NA) product.
Figure B.39. $^1$H NMR of catalytic reaction between methyl diazophenylacetate and cyclohexyl isocyanide (Table 2, entry 7a) at 10 mol%. Blue asterisks denote isocyanide starting material, red asterisks denote diazoalkane starting material. Approximately 90% of the diazoester is converted. In addition to the desired ketenimine product, two major by-products are cis olefin (7.62, 7.08, 6.85, and 3.10 ppm, 17% yield), and the corresponding azine (7.15, 6.85, 3.45 ppm, 16% yield).
Figure B.40. GC-MS of reaction mixture of Table 2, entry 7a. Major peaks are ROH decomposition products at 7.124 and 8.451, HMB at 7.979, and ketenimine Ph(COOMe)C=NCy product at 10.498. (see Figures B.41 – Figure B.43 for details).

Figure B.41. Retention time of 7.979: m/z of 162, indicating HMB-H⁺.
Figure B.42. Retention time of 8.451: m/z of 163, indicating ROH –‘Bu.
Figure B.43. Retention time of 10.498: m/z of 257 MS indicates ketenimine product.
Figure B.44. Crude $^1$H NMR of catalytic reaction between methyl phenyldiazoacetate and cyclohexyl isocyanide (Table 2, entry 7b) at 20 mol%. No starting material is present with small amounts of by-products (approximately 5% of each byproduct) and ketenimine being the major byproduct.
Figure B.45. $^1$H NMR of the isolated Ph(COOMe)C≡C=NCy obtained using 1:10 ether:hexane fraction from reaction in Table 2, entry 7b.
Figure B.46. $^{13}$C NMR of isolated Ph(COOMe)C=C=NCy. Asterisks correspond to solvents.
Figure B.47. $^1$H COSY NMR of the alkyl region of isolated Ph(COOMe)C=NCy.
**Figure B.48.** GC-MS of the crude product obtained in Table 2, entry 7b. The major product (ketenimine) is at 10.507. Products at 7.761 and 10.124 correspond to small amount of methyl phenyldiazoacetate precursor and olefin (see Figures B.49 – Figure B.51 for details).

**Figure B.49.** Retention time of 10.507: m/z = 257 indicates Ph(COOMe)C=C=NCy product.
Figure B.50. Retention time of 7.761: m/z of 175 indicates methyl phenyldiazoacetate.

Figure B.51. Retention time of 10.124: m/z = 296 indicates olefin.
Figure B.52. $^1$H NMR showing trans olefin byproduct and third byproduct (7.15, 6.85, and 3.45 ppm), likely azine. Inset: Aromatic region shows doublet of doublets peak at 7.91 indicative of olefin. Peaks at 6.84 and 7.15 (hidden under solvent peak) correspond to peak at 3.45 shown by $^1$H COSY.
**Figure B.53.** $^1$H COSY NMR spectrum showing trans olefin byproduct (confirmed by NMR of pure crystals) and other byproduct (7.15, 6.85, and 3.45 ppm), likely azine, as described above.

**Figure B.54.** GC-MS of the mixture of trans olefin by-product and third by-product, likely azine (see Figures B.55 – B.56 for details).
Figure B.55. Retention time of 10.244: m/z = 296 indicates olefin.

Figure B.56. Retention time of 11.291: m/z = 265 indicates decomposition of azine (azine – COOMe).
Figure B.57. $^1$H NMR of ether phase showing the mixture of cis olefin by-product and ROH.

Figure B.58. GC-MS of another ether fraction shown above. Peak at 8.450 corresponds to ROH decomposition product and peak at 10.124 corresponds to the cis olefin by-product (see Figures B.59 – B.60 for details).
Figure B.59. MS of ROH - 'Bu (m/z of 162) eluting at 8.450.

Figure B.60. MS of the peak eluting at 10.130 corresponding to cis olefin byproduct.
Approximately 78% of the diazoester is consumed. No by-products are observed by NMR, but 58% of the diazoester cannot be accounted for in the NMR as product or by-products.
Figure B.62. $^1$H NMR of zoom on the aromatic region of the reaction mixture shown in Table 2, entry 8 above filtered through a silica plug to show the presence of peak c hidden under solvent signal.

Figure B.63. GC-MS of reaction mixture of Table 2, entry 8. Major peaks are HMB at 7.982, HOR decomposition product at 8.458, and ketenimine products at 10.029, 10.330, and 10.778 (see Figures B.64-B.68 for details).
Figure B.64. MS of HMB-H⁺ (eluting at 7.982) corresponding to m/z of 162.

Figure B.65. MS of ROH – ‘Bu (eluting at 8.458) with m/z of 163.
Figure B.66. MS of Ph(COOMe)C=C=NBn (eluting at 10.029) corresponds with m/z of 265.
Figure B.67. MS of Ph(COOMe)=C=NBn (eluting at 10.334) with m/z of 265.
Figure B.68. MS of Ph(COOMe)C=C=NBn (eluting at 10.778) with m/z = 265.
Figure B.69. $^1$H NMR of catalytic reaction between ethyl diazoacetate and 2,6-dimethyl isocyanide (Table 2, entry 9). Blue asterisks denote isocyanide starting material and red asterisk denote diazoalkane starting material.
Figure B.70. $^1$H NMR of catalytic reaction between ethyl diazoacetate and 4-methoxyphenyl isocyanide (Table 2, entry 10). No conversion of ethyldiazoacetate (red asterisks) and a broadened peak over isocyanide starting material is observed (blue asterisks).
Figure B.71. $^1$H NMR of catalytic reaction between ethyl diazoacetate and adamantyl isocyanide (Table 2, entry 11).
Figure B.72. GC-MS of reaction mixture of Table 2, entry 11 (formation of H(COOEt)C≡C=NAd). Major peaks are HMB eluting at 7.757, HOR decomposition product at 8.464, ketenimine decomposition product at 9.687, and ketenimine product at 10.054 (see Figures B.73 – B.74 for details).

Figure B.73. MS of HMB (m/z of 163) eluting at 7.757.
Figure B.74. MS of ROH – iBu (m/z of 163) eluting at 8.464.
Figure B.75. MS of ketenimine $+$ H$_2$O (m/z of 265) eluting at 9.867.
Figure B.76. MS of ketenimine (m/z of 247) eluting at 10.502.
Figure B.77. $^1$H NMR of 10 mol% catalytic reaction between ethyl diazoacetate and cyclohexyl isocyanide (Table 2, entry 12a). Red asterisks denote diazoester starting material.
Figure B.78. GC-MS of the reaction mixture of Table 2, entry 12a (formation of H(COOEt)C≡C≡NCy). Major peaks are HMB, eluting at 7.745, HOR decomposition product (8.462), and ketenimine (11.229) (see Figures B.79–B.81 for details).

Figure B.79. MS of HMB (m/z of 163) eluting at 7.745.
**Figure B.80.** MS of ROH – tBu (m/z of 162) eluting at 8.462.

**Figure B.81.** MS of ketenimine (m/z of 195) eluting at 11.229.
Figure B.82. $^1$H NMR of 20 mol% catalytic reaction between ethyl diazoacetate and cyclohexyl isocyanide (Table 2, entry 12b). Red asterisks denote ethyl diazoacetate starting material.
Figure B.83. $^1$H NMR of 10 mol% catalytic reaction between ethyl diazoacetate and benzyl isocyanide (Table 2, entry 13). Only the aliphatic region is shown as protons e were hidden under the toluene signals.

Figure B.84. GC-MS of reaction mixture of Table 2, entry 13, that formed H(COOEt)C=C=NBn. The peaks correspond to TMB (7.746), HOR decomposition product (8.456), and ketenimine (8.851) (see Figures B.85 – B.86 for details).
Figure B.85. MS of TMB (m/z of 163), eluting at 7.757.

Figure B.86. MS of ROH – 'Bu (m/z of 163), eluting at 8.464.
Figure B.87. MS of ketenimine (m/z of 203), eluting at 8.51. Major peak refers to benzyl ion.
**Figure B.88.** $^1$H NMR of the isolated H(COOEt)C=CNAd obtained using 1:10 ether:hexane fraction from reaction in Table 2, entry 11.
Figure B.89. $^{13}$C NMR of the isolated H(COOEt)C=C=Na obtained using 1:10 ether:hexane fraction from reaction in Table 2, entry 11.
4. IR spectra

Figure B.90. IR of Co(OR)$_2$(CN(2,6-Me$_2$C$_6$H$_3$))$_2$ (4).
Figure B.91. IR of Co(OR)$_2$(CNAd)$_2$ (8).
Figure B.92. IR of Co(OR)$_2$(CN(4-MeOC$_6$H$_4$))$_2$ (9).
5. UV-vis spectra

Figure B.93. UV-Vis of Co(OR)$_2$(CN(2,6-Me$_2$C$_6$H$_3$))$_2$ (4).
Figure B.94. UV-Vis of Co(OR)$_2$(CNAd)$_2$(8).
Figure B.95. UV-Vis of Co(OR)$_2$(CN(4-MeOC$_6$H$_4$)$_2$) (9).
**Figure B.96.** UV-Vis spectra showing decomposition of the proposed carbene product obtained from the reaction of Co(OR)$_2$(THF)$_2$ and methyl phenyldiazoacetate. The peak at 560 nm disappears over time.
6. Computational Data

The doublet for the N-bound diazoalkane species is 2.1 kcal/mol higher in energy than the quartet. Alternative isomers that involve C=N binding (denoted 17a) is higher in energy by 37.8 and 27.9 kcal/mol on the doublet and quartet surfaces. The N=N bound isomer (17b) is higher in energy by 10.5 kcal/mol on the quartet surface.

![Diagram of isomers](image)

**Figure B.97.** Proposed ketenimine isomers of the ketenimine bound cobalt complex.

**Figure B.98** shows the relative energy of the doublet and quartet surfaces along the IRC path connecting 13-12-TS\(_D\) and 12\(_D\). Though this is not a proper MECP search, this reinforces our suggestion that the doublet/quartet crossing occurs after the rate-limiting step on the doublet surface.

![Graph of relative electronic energies](image)

**Figure B.98.** Relative electronic energies (kcal/mol) of the doublet (blue) and quartet (red) along the IRC path between 13-12-TS\(_D\) (x=0) and 12\(_D\) (x=1).
Table B.3. Electronic I and Gibbs free (G) energies at the OPBE/6-31G(d) (DZ) and OPBE-APFD-SMD(benzene)/def2-TZVP (TZ) levels of theory in hartrees. $G_{TZ} = G_{DZ} - E_{DZ} + E_{TZ}$.

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1. Crystal Structures Not Shown in Chapter 3

Figure C.1. X-ray structure (50% probability ellipsoids) of 21.
Table C.1. Crystal data and structure refinement for 21.

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2. Evans Method Formula and Procedure

The procedure for the Evans method is the same as that reported in Appendix B.

**Table C.2.** Spin-only magnetic moments calculated for 20 using the Evans method.

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3. NMR and GC-MS Spectra

Figure C.2. $^1$H NMR spectrum of $[\text{Co(OR)}_2(C\text{Ph}_2)][\text{CoCp}^*_2]$ (20).

Figure C.3. $^1$H NMR spectrum of $\text{Co}_2(\text{CN}(2,6-\text{Me}_2\text{C}_6\text{H}_3))_8$ (21).
Figure C.4. $^1$H NMR spectrum of 22.
Figure C.5. $^1$H-$^1$H COSY NMR spectrum of 22.
Figure C.6. $^1$H NMR spectrum (CD$_2$Cl$_2$) of [Co(OR)$_2$(CPh$_2$)][K(18-crown-6)] (23).
Figure C.7. $^1$H NMR spectrum of the reaction between $[\text{Co(OR)}_2(\text{CPh}_2)][\text{K}(18\text{-crown-6})]$ and $\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ to form $\text{Ph}_2\text{C}=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ and $\text{Co}_2(\text{CN}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_8$. 
Figure C.8. $^1$H NMR spectrum of the reaction between $[\text{Co(OR)}_2(C\text{Ph}_2)][\text{CoCp}^*_2]$ and CNAd to form ketenimine. Purple asterisks denote free isocyanide and red asterisks denote HOR.
Figure C.9. GC-MS of the filtered (silica plug) products mixture of the reaction between 20 and CNAd showing formation ketenimine (MS in Figure C.10 below).
Figure C.10. MS of the product eluting at 12.239 consistent with Ph$_2$C=C=NA (calculate mass 327).
4. IR Spectra

Figure C.11. IR spectrum of \([\text{Co(OR}_2\text{(CPh}_2\text{)}][\text{CoCp}^*\text{]}\) (20).
Figure C.12. IR spectrum of 22.
Figure C.13. IR spectrum of [Co(OR)$_2$(CPh$_2$)][K(18-crown-6)] (23).
5. UV-Vis Spectra

Figure C.14. UV-Vis spectrum of [Co(OR)₂(CPh₂)][CoCp*₂] (20).
Figure C.15. UV-Vis spectrum of 22.
Figure C.16. UV-Vis spectrum of [Co(OR)$_2$(CPh$_3$)][K(18-crown-6)] (23).
6. SQUID Measurements

Figure C.17. Magnetic moment of 20 estimated as $2.827(\chi_M T)^{1/2}$. 
7. DFT Calculations

Two sets of states were optimized; a singlet and triplet whose initial guess wavefunctions correspond to low-spin Co(II) anti- or ferromagnetically coupled to carbene radical ($20' S = 0$ and $20' S = 1$) and a triplet and quintet corresponding to high-spin Co(II) anti- or ferromagnetically coupled to carbene radical ($20' S = 1'$ and $20' S = 2$). As evidenced by Table C.4, the Mulliken spin analysis at the cobalt ion and carbene carbon for each of these states confirms these states though the higher energy triplet state has slightly more spin at Co and slightly less spin at C, suggesting more intermediate-spin Co(III) alkylidene character. The two lowest-energy states both demonstrate high-spin Co(II) character, consistent with the inferences from the crystallographic structures.

<table>
<thead>
<tr>
<th></th>
<th>Co spin</th>
<th>C spin</th>
<th>$\Delta E$(SCF)</th>
<th>$\Delta G$(gas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$20'$ ($S = 0$)</td>
<td>1.06</td>
<td>-0.70</td>
<td>16.96</td>
<td>16.11</td>
</tr>
<tr>
<td>$20'$ ($S = 1$)</td>
<td>1.40</td>
<td>0.26</td>
<td>15.23</td>
<td>14.55</td>
</tr>
<tr>
<td>$20'$ ($S = 1'$)</td>
<td>2.67</td>
<td>-0.63</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$20'$ ($S = 2$)</td>
<td>2.71</td>
<td>0.65</td>
<td>4.52</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Because the quintet was so close in energy to the lowest energy state ($20', S = 1'$), a more detailed analysis of the electronic structure of $20', S = 2$ (beyond Mulliken spins) was performed. As shown in Figure C.18, the singly occupied molecular orbitals of this quintet state confirm the AF/F-coupled nature of these two lowest-energy states. We repeated the analysis of the Mulliken spins assuming this state is lowest in energy due to the nearly isoenergetic nature of these triplet/quintet states. Mulliken spin analysis of the [Co(OR)$_2$] and [CPh$_2$] fragments shows spins of 2.97 and 1.03, in contrast to 1.89 and -0.89 for $2$. Thus, consistent with the conclusions for the antiferromagnetic state presented in the paper, other than the spin flip from the AF- to F-coupled
state, the magnitude of the spin at the carbene carbon only changes by ~0.1 whereas the spin at cobalt changes by ~1.1, consistent with metal-centered reduction.

![Orbital isosurface plots](image)

**Figure C.18.** Orbital isosurface plots (iso = 0.05 au) of the SOMOs of $20'$, $S=2$.

<table>
<thead>
<tr>
<th>Species</th>
<th>E(SCF)</th>
<th>H(gas)</th>
<th>G(gas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$20' (S = 0)$</td>
<td>-3205.394009</td>
<td>-3204.460570</td>
<td>-3204.593084</td>
</tr>
<tr>
<td>$20' (S = 1)$</td>
<td>-3205.396773</td>
<td>-3204.463075</td>
<td>-3204.595569</td>
</tr>
<tr>
<td>$20' (S = 1')$</td>
<td>-3205.421043</td>
<td>-3204.487265</td>
<td>-3204.618762</td>
</tr>
<tr>
<td>$20' (S = 2)$</td>
<td>-3205.413833</td>
<td>-3204.480576</td>
<td>-3204.617222</td>
</tr>
</tbody>
</table>

**Table C.4.** Energies ($E_n$) for the optimized species.

8. Quinoidal Distortion

Figure C.19. Scheme demonstrating quinoidal distortion of 2 and 20.
APPENDIX D

SUPPLEMENTARY MATERIAL FOR CHAPTER 4

1. Evans Method Formula and Procedure

The procedure for the Evans method is the same as that reported in Appendix B.

Table D.1. Spin-only magnetic moments calculated for 26-27 using the Evans method.

<table>
<thead>
<tr>
<th></th>
<th>26</th>
<th>27</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.71</td>
<td>7.32</td>
</tr>
<tr>
<td>2</td>
<td>7.32</td>
<td>7.10</td>
</tr>
<tr>
<td>3</td>
<td>7.39</td>
<td>7.37</td>
</tr>
<tr>
<td>Average</td>
<td>7.47</td>
<td>7.26</td>
</tr>
<tr>
<td>standard deviation</td>
<td>0.21</td>
<td>0.14</td>
</tr>
<tr>
<td>$\mu_{calc} ,(\mu B)$</td>
<td>8.37</td>
<td>8.37</td>
</tr>
</tbody>
</table>
2. NMR spectra

Figure D.1. $^1$H NMR spectrum demonstrating catalytic formation of Ph$_2$CNNCP$_2$ from 24. The peaks at 6.26 and 3.32 ppm correspond to trimethoxybenzene (TMB) used as an internal standard.
Figure D.2. $^1$H NMR spectrum of 26.
Figure D.3. $^1$H NMR spectrum of 27.
Figure D.4. $^1$H NMR spectrum of 28.
3. GC-MS spectra

Figure D.5. GC taken after stirring 26 at 50 °C overnight.

Figure D.6. MS of peak at 11.455 in the chromatogram above showing formation of azine.
4. IR Spectra

Figure D.7. IR of \((\text{Fe}({\text{OR}})_2)_2[\mu-\kappa^2:\kappa^2-(\text{OC}(\text{OMe})\text{C(Ph)}\text{NN})_2]\) (26).

Figure D.8. IR of \((\text{Fe}({\text{OR}})_2)_2[\mu-\kappa^2:\kappa^2-(\text{OC}(\text{OEt})\text{C(Ph)}\text{NN})_2]\) (27).
Figure D.9. IR of \( (\text{Fe(OR)}_2)_2[\mu-\kappa^2: \kappa^2-(\text{OC(OEt)}C(4-\text{Br-Ph})\text{NN})] \) (28).
5. UV-Vis Spectra

Figure D.10. UV-Vis of (Fe(OR)$_2$)$_2$[μ-κ$^2$:κ$^2$-(OC(OMe)C(Ph)NN)$_2$] (26).
Figure D.11. UV-Vis of (Fe(OR)$_2$)$_2$[μ-κ$_2$:κ$_2$-(OC(OEt)C(Ph)NN)$_2$] (27).
Figure D.12. UV-Vis of \( \text{Fe(OR)}_2[\mu-\kappa^{2}:\kappa^{2}-(\text{OC(\text{OE}t)C(4-\text{Br-Ph})NN})_2 \] (28).
Figure D.13. Changes in the UV-Vis spectrum of 26 at RT over 5 days (sampled once a day).
Figure D.14. Zero-order plot for the decomposition of 26 monitored by UV-Vis (Figure D.13).

Figure D.15. First order plot for the decomposition of 26 monitored by UV-Vis (Figure D.13).
Figure D.16. Changes in the UV-Vis spectrum of 26 at RT over 5 days (sampled several times a day).
**Figure D.17.** First order plot for the decomposition of 26 monitored by UV-Vis (Figure D.16).

8. Computational Details

Singlet, triplet, quintet, and septet states were probed for the diazoester iron adduct. The metallacycle with the ester coordinated in addition to the diazo moiety ($\kappa^2$) was favored. The quintet was found to be lowest in energy ($\Delta G = 0.0$ kcal/mol), followed by the septet ($\Delta G = 11.1$ kcal/mol), triplet ($\Delta G = 23.6$ kcal/mol), and singlet ($\Delta G = 38.3$ kcal/mol). Analysis of the spin density of the quintet state is presented in Figure D.18 and, when combined with the Mulliken spins in Table D.2, shows this species is best described as a high-spin Fe$^{III}$ ion antiferromagnetically coupled to a diazoester radical anion. An alternative isomer with only the ester coordinated ($\kappa^1$) was also calculated for the quintet state. This monodentate form is higher in free energy by 1.34 kcal/mol and is best described as a high-spin Fe$^{II}$ species.
Figure D.18. Spin density isosurface plot (iso = 0.002 au) of the lowest energy, $S = 2$ state of the iron diazoester complex at the BP86-D3/def2-SVP level of theory.
Table D.2. Mulliken spins for iron diazoester adducts at the BP86-D3/def2-SVP level of theory.

<table>
<thead>
<tr>
<th>State</th>
<th>Fe</th>
<th>O\textsubscript{OR}</th>
<th>O\textsubscript{OR}</th>
<th>N\textsubscript{1}</th>
<th>N\textsubscript{2}</th>
<th>C\textsubscript{1}</th>
<th>C\textsubscript{2}</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\kappa^2 S = 0)</td>
<td>0.06</td>
<td>0.10</td>
<td>-0.09</td>
<td>0.03</td>
<td>-0.01</td>
<td>-0.03</td>
<td>-0.01</td>
<td>-0.03</td>
</tr>
<tr>
<td>(\kappa^2 S = 1)</td>
<td>2.10</td>
<td>0.09</td>
<td>0.00</td>
<td>-0.12</td>
<td>-0.09</td>
<td>0.00</td>
<td>-0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>(\kappa^2 S = 2)</td>
<td>3.45</td>
<td>0.32</td>
<td>0.26</td>
<td>-0.20</td>
<td>-0.13</td>
<td>0.09</td>
<td>0.00</td>
<td>0.07</td>
</tr>
<tr>
<td>(\kappa^1 S = 2)</td>
<td>3.58</td>
<td>0.21</td>
<td>0.18</td>
<td>-0.04</td>
<td>-0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.03</td>
</tr>
<tr>
<td>(\kappa^2 S = 3)</td>
<td>3.93</td>
<td>0.37</td>
<td>0.33</td>
<td>0.63</td>
<td>0.28</td>
<td>0.12</td>
<td>0.02</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Singlet through septet states were calculated for the iron carbene resulting from \(\text{N}_2\) loss. The quintet was found to be lowest in energy \((\Delta G = -11.35 \text{ kcal/mol})\) vs. quintet diazoester adduct, followed by the septet \((\Delta G = -10.98 \text{ kcal/mol})\), triplet \((\Delta G = -8.06 \text{ kcal/mol})\), and finally the singlet \((\Delta G = 22.18 \text{ kcal/mol})\). Given the sensitivity of density functionals for predicting spin states and the tendency of B3LYP to overstabilize higher spin states,\(^{93}\) we cannot say conclusively whether the quintet or triplet is favored without experimental verification. Formation of the quintet carbene can occur through two transition states: (i) from the \(\kappa^2\) diazoester \((\Delta G^\ddagger = 27.09 \text{ kcal/mol})\) or (ii) from the \(\kappa^1\) diazoester \((\Delta G^\ddagger = 29.33 \text{ kcal/mol})\). Loss of \(\text{N}_2\) from the \(\kappa^2\) form is slightly lower in energy, consistent with the equilibrium for this species that slightly favors the \(\kappa^2\) form over the \(\kappa^1\) form by 1.3 kcal/mol.

Singlet through undecet states were probed for tetrazene product formed by coupling of two of these iron diazoester adducts. The undecet was predicted to be lowest in energy followed by the singlet, nonet, triplet, quintet, then septet. The undecet and singlet were much lower in energy than the other spin states. Quantitative relative energies of these species, as well as the Mulliken spins at each iron center, are
shown in Table D.3. Based on these Mulliken spins we assign the undecet and singlet as ferro- and antiferromagnetically coupled species with two high-spin Fe$^{III}$ ions. The higher energy states involve spin flips at one or more of the iron centers, with the nonet and triplet corresponding to ferro- and antiferromagnetic coupling between one high-spin and one intermediate-spin Fe$^{III}$ ions. The quintet has one high-spin Fe$^{III}$ antiferromagnetically coupled to a low-spin Fe$^{III}$ ion. The septet has two ferromagnetically coupled intermediate-spin Fe$^{III}$ ions. Figure D.19 shows spin density plots for the two lowest energy states. These spin densities highlight the significant spin polarization in the atoms directly attached to the metal centers, which leads to lower Mulliken spins than might be expected. It is clear from these results that the two magnetic states with high-spin Fe$^{III}$ ions are much more favorable in the low-coordination environment in this product.

The singlet and undecet states are nearly isoenergetic at the BP86-D3/def2-SVP ($\Delta E = 0.24$ kcal/mol) and B3LYP-D3(SMD)/def2-TZVP ($\Delta E = 0.01$ kcal/mol) levels of theory, even though BP86 is known to overstabilize low-spin states while B3LYP overestabilizes high-spin states. The near degeneracy predicted for these states may explain the low magnetic moment observed experimentally since both would be expected to have significant thermal population, but more precise magnetic measurements than Evans’ method would be needed to determine this precisely. Because of this we focus our attention on the ferromagnetically coupled states.

Table D.3. Relative Gibbs free energies (in kcal/mol) and Mulliken spins for each spin state calculated for the tetrazene coupled product.

<table>
<thead>
<tr>
<th>State</th>
<th>$\Delta G$</th>
<th>Fe$_1$</th>
<th>Fe$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S = 0$</td>
<td>0.57</td>
<td>3.88</td>
<td>-3.88</td>
</tr>
<tr>
<td>$S = 1$</td>
<td>26.01</td>
<td>3.90</td>
<td>-2.62</td>
</tr>
<tr>
<td>$S = 2$</td>
<td>41.95</td>
<td>3.89</td>
<td>-0.81</td>
</tr>
<tr>
<td>$S = 3$</td>
<td>45.43</td>
<td>2.76</td>
<td>2.76</td>
</tr>
<tr>
<td>$S = 4$</td>
<td>24.72</td>
<td>3.87</td>
<td>2.74</td>
</tr>
<tr>
<td>$S = 5$</td>
<td>0.00</td>
<td>3.89</td>
<td>3.89</td>
</tr>
</tbody>
</table>
Figure D.19. Spin density isosurface plots (iso = 0.002 au) of the antiferromagnetically coupled $S = 0$ (left) and ferromagnetically coupled $S = 5$ (right) states of the iron tetrazene complex at the BP86-D3/def2-SVP level of theory.
Figure D.20. Potential energy scan along the N–N coordinate showing no enthalpic barrier for bond formation on the $S = 5$ surface. Red dots correspond to final SCF energies for constrained geometry optimizations except for the minimum (fully optimized structure) and completely dissociated species (listed at 4.0 Å here, corresponds to twice the $S = 2$ iron diazoester energy). The black curve is a Morse curve fit with $D_e = 47.94$ kcal/mol, $r_e = 1.357$ Å, and $a = 2.25$.

Figure D.21. Calculated IR spectra for the $S = 0$ and $S = 5$ states of the reductively coupled iron product at the BP86-D3/def2-SVP level of theory. Unsurprisingly, both produce remarkably similar IR spectra. Line spectra were generated in Gaussian then fit using the default parameters in GaussView.\textsuperscript{92}
To understand the contrasting reactivity of this new iron complex with our previously reported work with cobalt and diazoester,\textsuperscript{47} we ran similar calculations of the cobalt diazoester and cobalt reductively coupled products. These results are reported below.

Doublet, quartet, and sextet states for the cobalt diazoester adduct were run. In the $\kappa^2$ form the quartet is lowest in energy ($\Delta G = 0.00$ kcal/mol), followed by the sextet ($\Delta G = 17.02$ kcal/mol) and the singlet ($\Delta G = 20.88$ kcal/mol). Unlike iron, however, the $\kappa^1$ form is favored by 5.30 kcal/mol over the $\kappa^2$ form for the quartet. Similar to iron, the $\kappa^2$ quartet is best described as high-spin Co\textsuperscript{III} antiferromagnetically coupled to the reduced diazoester, while the $\kappa^1$ quartet is best described as a high-spin Co\textsuperscript{II} species. Table\textsuperscript{D.4} summarizes the Mulliken spin densities of these species.

**Table D.4.** Mulliken spins for cobalt diazoester adducts at the BP86-D3/def2-SVP level of theory. The numbering in the diazoester is the same as for the iron adduct (Table D.2).

<table>
<thead>
<tr>
<th>State</th>
<th>Co</th>
<th>O$_{OR}$</th>
<th>O$_{OR}$</th>
<th>N$_1$</th>
<th>N$_2$</th>
<th>C$_1$</th>
<th>C$_2$</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa^2$ S = $1/2$</td>
<td>1.03</td>
<td>0.14</td>
<td>-0.08</td>
<td>-0.11</td>
<td>-0.07</td>
<td>0.06</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>$\kappa^2$ S = $3/2$</td>
<td>2.40</td>
<td>0.37</td>
<td>0.35</td>
<td>-0.22</td>
<td>-0.16</td>
<td>0.04</td>
<td>0.01</td>
<td>0.07</td>
</tr>
<tr>
<td>$\kappa^1$ S = $3/2$</td>
<td>2.44</td>
<td>0.26</td>
<td>0.20</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>$\kappa^2$ S = $5/2$</td>
<td>2.74</td>
<td>0.42</td>
<td>0.38</td>
<td>0.68</td>
<td>0.17</td>
<td>0.21</td>
<td>0.01</td>
<td>0.11</td>
</tr>
</tbody>
</table>

We calculated the doublet, quartet, and sextet carbene species. Unsurprisingly, the doublet was found to be lowest in energy ($\Delta G = -3.54$ kcal/mol vs. $\kappa^1$ cobalt diazoester adduct), followed by the sextet ($\Delta G = -2.06$ kcal/mol) then the quartet ($\Delta G = 0.60$ kcal/mol). This is consistent with our extensive calculations and spectroscopy of the electronic structure of this compound.\textsuperscript{39,47} Transition states for N$_2$ loss from both the $\kappa^2$ diazoester ($\Delta G^\ddagger = 38.67$ kcal/mol) and $\kappa^1$ diazoester ($\Delta G^\ddagger = 37.02$ kcal/mol) were located. In contrast to iron, for cobalt the k$^1$ transition state is favored presumably due to the equilibrium favoring that form over the k$^2$ form with reduced diazoester.
For the reductively coupled cobalt species, only the singlet and nonet states were calculated. Similar to iron these were found to feature two high-spin Co$^{III}$ ions antiferromagnetically and ferromagnetically coupled to one another. The nonet state is slightly favored in free energy by 2.11 kcal/mol. The driving force to form this reductively coupled species is markedly lower than for iron, with DFT predicting this to only be exergonic by 1.45 kcal/mol. Figure D.22 shows the spin densities for these two species, which are found to have Mulliken spins at the cobalt atoms of 2.71/–2.71 and 2.73/2.73, respectively. Similar to iron, significant spin polarization to the atoms attached to cobalt lowers these values from the ideal of 4.0/–4.0 and 4.0/4.0.

**Figure D.22.** Spin density isosurface plots (iso = 0.002 au) of the antiferromagnetically coupled $S = 0$ (left) and ferromagnetically coupled $S = 4$ (right) states of the cobalt tetrazene complex at the BP86-D3/def2-SVP level of theory.
### Table D.5. BP86-D3/def2-SVP SCF energies, enthalpies, and free energies, and B3LYP-D3/def2-TZVP (+SMD) single point energies, of all optimized species. All energies are listed in hartrees.

<table>
<thead>
<tr>
<th>Species</th>
<th>Spin</th>
<th>E(SCF)BP86</th>
<th>HBP86</th>
<th>GPBP86</th>
<th>E(SCF)B3LYP</th>
<th>G3B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>diazoester</td>
<td>0</td>
<td>-607.288937</td>
<td>-607.122520</td>
<td>-607.175786</td>
<td>-607.961327</td>
<td>-607.848176</td>
</tr>
<tr>
<td>Fe(OR)₂(k²-diazoester)</td>
<td>0</td>
<td>-3191.641586</td>
<td>-3190.761678</td>
<td>-3190.890634</td>
<td>-3193.740625</td>
<td>-3192.989673</td>
</tr>
<tr>
<td>Fe(OR)₂(k²-diazoester)</td>
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<td>-3193.762256</td>
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</tr>
<tr>
<td>Fe(OR)₂(k²-diazoester)</td>
<td>2</td>
<td>-3191.664509</td>
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<td>-3193.799213</td>
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</tr>
<tr>
<td>Fe(OR)₂(k¹-diazoester)</td>
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<td>-3191.645831</td>
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<td>-3193.793684</td>
<td>-3193.048591</td>
</tr>
<tr>
<td>Fe(OR)₂(k²-diazoester)</td>
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<td>-3190.750073</td>
<td>-3190.884598</td>
<td>-3193.777309</td>
<td>-3193.032927</td>
</tr>
<tr>
<td>Fe(OR)₃(carbene)</td>
<td></td>
<td>-3082.178879</td>
<td>-3081.309113</td>
<td>-3081.441885</td>
<td>-3084.171686</td>
<td>-3083.434692</td>
</tr>
<tr>
<td>Fe(OR)₃(carbene)</td>
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<td>-3082.208534</td>
<td>-3081.340476</td>
<td>-3081.468497</td>
<td>-3084.222917</td>
<td>-3083.482880</td>
</tr>
<tr>
<td>Fe(OR)₃(carbene)</td>
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<td>-3082.194471</td>
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</tr>
<tr>
<td>Fe(OR)₃(carbene)</td>
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<td>-3082.183566</td>
<td>-3081.317521</td>
<td>-3081.446647</td>
<td>-3084.224445</td>
<td>-3083.487526</td>
</tr>
<tr>
<td>Fe(OR)₂(k²-diazoester)</td>
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<td>-3191.596904</td>
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<td>-3190.856335</td>
<td>-3193.748138</td>
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<tr>
<td>N₂ loss TS</td>
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<td>-3191.602721</td>
<td>-3190.725117</td>
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<td>-3193.744235</td>
<td>-3193.004000</td>
</tr>
<tr>
<td>Fe(OR)₂(k¹-diazoester)</td>
<td></td>
<td>-3191.628980</td>
<td>-3190.750073</td>
<td>-3190.884598</td>
<td>-3193.777309</td>
<td>-3193.032927</td>
</tr>
<tr>
<td>N₂ loss TS</td>
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<td>-6381.641108</td>
<td>-6381.875901</td>
<td>-6387.671660</td>
<td>-6386.141768</td>
</tr>
<tr>
<td>2e</td>
<td></td>
<td>-6383.391240</td>
<td>-6381.623592</td>
<td>-6381.857914</td>
<td>-6387.634557</td>
<td>-6386.101231</td>
</tr>
<tr>
<td>2e</td>
<td></td>
<td>-6383.380472</td>
<td>-6381.613920</td>
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<td>( \text{N}_2 \text{ loss TS} )</td>
<td>( \text{Co(OR)}_2(\text{k}^1\text{-diazoester}) )</td>
<td>( \text{N}_2 \text{ loss TS} )</td>
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9. Mössbauer data

Figure D.23. Zero-field Mössbauer spectra recorded at 80 K for 27 (top) and 28 (bottom). The solid red lines are simulations obtained using the parameters listed in Table D.6.

Table D.6. Zero-field Mössbauer parameters obtained at 80 K for complex 26, 27, and 28.

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<th>Complex</th>
<th>$\delta$ [mm/s]</th>
<th>$\Delta E_Q$ [mm/s]</th>
<th>$\Gamma_L$ [mm/s]</th>
<th>$\Gamma_R$ [mm/s]</th>
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REFERENCES


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ABSTRACT

REACTIONS OF FIRST-ROW TRANSITION METAL COMPLEXES IN BIS(ALKOXIDE) LIGAND ENVIRONMENTS WITH DIAZOALKANES: FORMATION OF CARBENES VERSUS REDUCTIVE COUPLING TO FORM BRIDGING TETRAZENES

by

AMANDA GRASS

August 2020

Advisor: Dr. Stanislav Groysman
Major: Chemistry (Inorganic)
Degree: Doctor of Philosophy

This dissertation focuses on the design and reactions of novel late transition metal carbene complexes featuring alkoxide ligand environments. The high-valent cobalt carbene Co(OR)₂(=CPh₂) (OR = OC'Bu₂Ph), featuring short Co=C bond of 1.773(3) Å, was previously reported from the reaction of Co(OR)₂(THF)₂ with diphenyl diazoalkane. Magnetic and spectroscopic (EPR) studies demonstrated Co(OR)₂(=CPh₂) to be a low-spin $S = \frac{1}{2}$ complex. Computational studies, in agreement with experimental data, suggested that the electronic structure of Co(OR)₂(=CPh₂) lies between intermediate spin Co(III) antiferromagnetically coupled to a carbene radical and a Co(IV) alkylidene. This dissertation began with investigation of this complex in carbene transfer reactivity. Stoichiometric ketenimine formation occurs upon reaction with various isocyanides CNR′ (CNR′ =2,6-dimethylphenyl isocyanide, 4-methoxyphenyl isocyanide, 2-chloro-6-methylphenyl isocyanide, adamantyl isocyanide). The reaction is accompanied by the formation of a cobalt bis(alkoxide) bis(isocyanide) complexes Co(OR)₂(CNR)₂, which were independently synthesized and characterized. Excess isocyanide was required to form ketenimine due to formation of the bis(isocyanide) complex. DFT calculations suggest the mechanism proceeds through isocyanide binding to cobalt, in contrast to nucleophilic attack at the carbene carbon. This is followed by intramolecular insertion into the Co-carbene bond to form the ketenimine complex. Dissociation of free ketenimine from cobalt then leads to the bis(isocyanide) complex. Catalytic formation of ketenimines was
investigated at room temperature by exposing the mixtures of the carbene precursors and isocyanides to Co(OR)$_2$(THF)$_2$. The carbene precursors investigated included both diazoalkane (diphenyldiazomethane) and diazoesters (methyl phenyldiazoacetate, and ethyl diazoacetate). Both aryl isocyanides (2,6-dimethylphenyl isocyanide, 4-methoxyphenyl isocyanide) and alkyl isocyanides (adamantyl isocyanide, cyclohexyl isocyanide, and benzyl isocyanide) differing in their steric bulk were investigated. While no catalytic reactivity was observed for diphenyldiazoalkane, the use of diazoester demonstrated catalytic turnover. The highest yields were obtained with the bulkier aliphatic substituent on the isocyanide: adamantyl and cyclohexyl isocyanide. Mechanistic studies suggested that the lack of catalytic reactivity involving diphenyldiazomethane results from the inability of Co(OR)$_2$(CNR)$_2$ to undergo carbene formation upon reaction with N$_2$CPh$_2$. In contrast, facile reaction is observed between Co(OR)$_2$(CNR)$_2$ and diazoesters, enabling the overall catalytic reactivity.

The Co(OR)$_2$(=CPh$_2$) species demonstrated several well-defined quasi-reversible reduction events in cyclic voltammetry experiments. Therefore, its chemical reduction was explored by exposing Co(OR)$_2$(=CPh$_2$) to chemical reductants. Reduction with decamethylcobaltocene or potassium graphite resulted in the anionic carbene products [Co(OR)$_2$(CPh$_2$)](CoCp*) and [Co(OR)$_2$(CPh$_2$)](K(18-crown-6)), respectively. In contrast to the low-spin electronic structure of the neutral carbene, [Co(OR)$_2$(CPh$_2$)]$^-$ was demonstrated by magnetic and computational experiments to be a high-spin Co(II) species. The $S = 1$ state with a high-spin Co(II) antiferromagnetically coupled to a carbene radical was found to be 1 kcal/mol more stable than the $S = 2$ high-spin Co(II) ferromagnetically coupled state. The low-spin Co(II) state was found to be significantly higher in energy. Reactivity with isocyanides was explored to see if ketenimine formation was feasible with the anionic species. Treating [Co(OR)$_2$(CPh$_2$)](CoCp*) with 2,6-dimethylisocyanide formed two new C-C bonds resulting in the imine-Cp*-Co(I) fulvene complex. The formation of the complex likely took places via the initial deprotonation of the decamethylcobaltacene counterion, which then attacked transient ketenimine. Un-derivatized ketenimine was formed by treating
[Co(OR)₂(CPh₂)](CoCp*) with adamantyl isocyanide or [Co(OR)₂(CPh₂)](K(18-crown-6)) with 2,6-dimethylisocyanide.

Following the investigation of the chemistry of Co(OR)₂(THF)₂ with diazoalkanes, the analogous chemistry was investigated with the iron analogue, Fe(OR)₂(THF)₂. While treatment of Fe(OR)₂(THF)₂ with diphenyldiazoalkane resulted in azine formation, utilizing diazoesters as the carbene precursor led to unprecedented reductive coupling of a transition-metal through the terminal nitrogens. The resulting reductively-coupled products were characterized by X-ray diffraction, elemental analysis, UV-Vis, IR, and Mössbauer spectroscopies. The complexes were formulated as high-spin Fe(III) with the tetrazene-bridged bis(diazenylacetate) serving as a novel dinucleating ligand. In contrast to facile azine formation with diphenyldiazoalkane, azine formation from the isolated reductively-coupled complexes was sluggish. DFT calculations were performed to explore why carbene chemistry is observed with cobalt whereas reductive coupling of diazoalkanes is observed with iron. The calculations suggest that the reductive coupling takes place via a κ² diazoester intermediate which induces significant radical character on the terminal nitrogen and consists of a high-spin M(III) center. Reductive coupling of two of these species is essentially barrierless for iron. However, this intermediate is less stable than the high-spin M(II) κ¹ diazoester intermediate with cobalt. Thus, carbene formation occurs from the κ¹ intermediate upon N₂ extrusion, explaining the carbene chemistry observed with cobalt.
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