Zirconium-Cobalt Heterobimetallic Complexes: Synthesis and Analysis of Reactivity Toward the Activation of Small Molecules

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ABSTRACT

Heterobimetallic complexes containing an early transition metal directly interacting with a late transition metal have been shown to have various degrees of reactivity with small molecules. The differences in the electron donating and receiving abilities between the two metals and the ligand substituents coordinated cause the M-M interaction to be highly polarized, which in turn allows tuning of the potentials required to reduce the complexes. Our group has synthesized Zr-Co heterobimetallic species containing phosphinoamide ligands, which we have shown to reduce at potentials ~1 V more positive than their analogous homometallic species. The 2 electron reduction of the synthesized complexes induced the coordination of a N$_2$(g) adduct on the terminal end of the Co center. Due to the stabilization imparted by the phosphinoamide ligands the shortest early/late heterobimetallic interatomic distance has been produced along with the stabilization of an unprecedented open axial coordination site around a trigonal pyramidal Zr geometry. The species were found to be highly reactive toward small molecules especially CO$_2$, showing the ability to activate and cleave one of the C—O bond producing a bridging µ-O and a terminal CO. This research shows promise in the use of CO$_2$ as a feedstock for synthesis and more specifically the design of a catalytic cycle for the rWGS reaction.
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Chapter 1: The Importance of Alternative Energy

A) Climate Change and Environmental Significance

The world’s climate has been changing rapidly ever since the Industrial revolution. The ability to convert fossil fuels into usable energy was the start of an industry that supplied the general populous with machines, vastly changing our way of life. Coupled with the population boom brought about by the Haber–Bosch process, society was shortly thereafter inundated by power plants and automobiles rapidly burning fossil fuels releasing greenhouse gases into the atmosphere. The primary greenhouse gases in the Earth's atmosphere deemed as environmentally hazardous by the Kyoto Protocol are: carbon dioxide (CO$_2$), methane (CH$_4$), nitrous oxide (N$_2$O), perfluorocarbons (PFCs), sulphur hexafluoride (SF$_6$), and chlorofluorocarbons (CFCs). The amount of CO$_2$ in the atmosphere can be directly related to the amount of fossil fuels society burns and considering the number of automobiles in the world, the amount of CO$_2$ has been increasing rapidly. The NOAA has monitored atmospheric CO$_2$ levels since 1960 and over the past 50 years there has been a steady increase of CO$_2$ levels at a research lab in Mauna Loa, Hawaii (Figure A1 of the Appendix). Separately, as shown in Figure 1, the United States EPA compiled data on the amount of carbon dioxide emitted in 2006.
Carbon dioxide accounts for 84.8% of all atmospheric emissions, fossil fuels being the number one source. To further analyze fossil fuels carbon dioxide emissions, they collected data on the amounts released by the various sources. The data show that the two main contributors (by around 1000 Tg of CO\(_2\)) are transportation and the generation of electricity. The three fossil fuels measured were petroleum, coal, and natural gas; with petroleum and coal consumed the majority of the time. As of 2006 the United States was the country producing the second highest amount of CO\(_2\) in total metric tons, China being in first place.\(^2\)

The statistic is quite misleading because it does not take into account the country’s economic status. When the data is analyzed in amount of CO\(_2\) emissions per capita, the United States blows China out of the water by almost 16 tons of CO\(_2\) per capita.\(^3\) Surprisingly enough Australia was the closest contender to the United States, followed closely by Canada. This data can be viewed graphically in figures A5-2 and A5-3 of the appendix. In 1998 governments around the world decided to discuss what actions could, and should, be taken to decrease society’s overall emissions.\(^2\)

The topic of global warming has consistently been a hot topic with highly qualified individuals on both sides of the argument. There are many who believe that CO\(_2\) concentrations do not contribute significantly enough to global warming and that rather than limit CO\(_2\) emissions, countries should increase them.\(^4\) Regardless, whether or not global warming is harmful to the environment is not the topic of this research. The fact of the matter is that there is a large abundance of CO\(_2\) in the atmosphere, and it is just waiting for researchers to discover an efficient way to catalytically break it down.
The steady increase in atmospheric CO\textsubscript{2} concentrations has been hypothesized to effect the environment in ways such as; the extinction of susceptible organisms, increased global average temperature, and ocean acidification. Scientists have observed and analyzed many of the environmental consequences of increased atmospheric CO\textsubscript{2} concentrations, however there are likely effects we haven’t witnessed or even imagined yet. One significant effect, due to the ocean’s ability to sequester CO\textsubscript{2}, is the acidification of the water. Dissolution of greater amounts of CO\textsubscript{2} in the oceans causes an increase in the partial pressure of CO\textsubscript{2} (P\textsubscript{CO2}), a decrease in the carbonate ion concentration ([CO\textsubscript{3}\textsuperscript{2−}]), and an increase in the ocean acidity, which in turn decreases the bioavailability of dissolved Iron to phytoplankton, not to mention any other species that take up dissolved iron.

![Graph showing 2006 CO\textsubscript{2} Emissions and CO\textsubscript{2} Emissions from Fossil Fuel Combustion]

**Figure 1-1.** EPA compiled data on CO emissions from 2006.\textsuperscript{2}

The pH of seawater has been (historically) 8.15, however since we have increased the CO\textsubscript{2} emissions over the past 150 years or so, the pH of the surface waters has
decreased to around 8.00.\textsuperscript{5} This may not seem like a large decrease, but it is exponential in nature and if the trend remains unchanging, the pH could drop as low as 7.80 in the next 50 years. Biological systems are extremely sensitive to small changes in chemistry and even though a 0.35 pH drop may seem insignificant, the affects to ocean life would be drastic and would directly affect our society.

Judging by these documented environmental effects of carbon dioxide emission, how could we as a society not make an attempt to stifle the current rate of increase of carbon dioxide emissions? Unfortunately, the impact that industrial use of carbon dioxide as a feedstock for synthesis would have on the current carbon dioxide concentrations in the atmosphere is minimal. The synthetic breakdown of carbon dioxide is limited by the need for a suitable catalyst. The carbon dioxide molecule is a highly stable molecule at room temperature ($\Delta H^o_f = -94.1$ cal/mol, $\Delta S^o_f = +50.9$ cal/mol, $\Delta G^o_f = -94.3$ cal/mol)$^6$ and has $D_{\infty h}$ symmetry. The thermodynamic parameters of CO$_2$ lead to a molecule that’s hard to activate, especially catalytically, even though it has diverse coordinative capabilities.$^7$ These parameters lead to a limit in both the ability to scrub CO$_2$ from the atmosphere and our ability to make systems that will efficiently break down the molecule.

Over the past millions and billions of years, nature has evolved elegant systems with the ability to efficiently both reduce and oxidize CO$_2$. Two principle types of these systems are found in the family of enzymes known as carbon monoxide dehydrogenases (CODHs). One type comes from anaerobic hydrogenogenic bacteria and contains, in the active site, the Acetyl–Coenzyme A Synthase/CODH, which has a [Ni–Fe–S] cluster.$^8$–$^{10}$
The other type comes from aerobic carboxidotrophic bacteria and contains a [CuSMoO$_2$] cluster in the active site.$^{11,12}$ The knowledge of nature’s ability to efficiently perform an energetically uphill reaction has lead to the field of Biomimetic Chemistry, in which scientists attempt to synthesize small molecule enzyme analogues to perform similar tasks. There are two main branches of biomimetic chemistry, in one structural analogues are synthesized and in the other functional analogues are synthesized. Structural analogues are made to look as close to the enzymatic structure regardless of function, while functional analogues are solely focused on imitating the performance of the enzyme and consider the structural similarities of less importance.

The structure of the active site of the Acetyl−CoA Synthase/CODH with a coordinated carbon dioxide molecule is shown in figure 2. Carbon dioxide binds μ$_2$η$^2$− to the oxygen sensitive metal centers while being stabilized through hydrogen bonds from neighboring amino acids. Through the interaction of the Ni(II) and Fe(II) metal centers with the iron−sulfur cluster the enzyme is able to stabilize the CO$_2$ molecule in a way that allows activation of the C—O bond bridging the two metals. Resulting from the simultaneous coordination to both metal centers, the symmetry of the CO$_2$ molecule decreases as it assumes a bent geometry (C$_{2v}$). Normally the bent geometry is unstable, however the hydrogen bonding interactions with the surrounding amino acids stabilize the electronics and stericities of the system.
Figure 1-2. The active site of the anaerobic Acetyl−CoA Synthase/CODH. The $\mu_2-\eta^2$ coordination of CO$_2$ to the metal centers is stabilized by hydrogen bonding to histidine−93 and lysine−563. Histidine−261 and cysteine−295 both coordinate the the iron(II) center while only cysteine−526 is coordinated to the nickel(II) center. The full enzyme catalyzed cycle is located in the Appendix.

The aerobic bacteria differ from the anaerobic bacteria in that the active site contains different metals that are not as sensitive to the presence of oxygen in the system (Mo and Cu). The structure of the active site and the full enzyme catalyzed cycle are shown in figures A5 and A6 respectively. Just like the aforementioned aerobic active site, the [Mo−Cu−S] site is specifically formed to enable the activation of the CO$_2$ molecule. The beauty of these systems is that the energy difference between the oxidized state and reduced state is minimal, allowing for the highly efficient catalysis. Each active site contains late, low valent, first row transition metals (Cu(I) and Ni(0)) coupled to a redox reservoir (Mo(IV)−S and Fe−S clusters) that supplies electrons for the reduction of the CO$_2$. The overall reaction of both enzymatic cycles (as drawn in figures A4 and A6) is known as the water gas shift reaction (WGS). Synthetic mastery of the WGS and design of an efficient catalytic cycle is one of the holy grails of synthetic chemistry.
B) THE WATER GAS SHIFT REACTION

It is important to take a step back and look at the complexities of reversing the water gas shift reaction (Scheme 1-1) in order to reduce CO₂ to CO.¹ The activation of the pertinent small molecules involved in the WGS (CO₂ and H₂O) share common reaction steps that require multi-electron transfers coupled with proton transfers. The WGS uses CO(g) as a reductant to activate H₂O(g) in order to produce H₂(g) and CO₂(g), which is thermodynamically unfavorable at low temperatures because of the negative entropy change of the overall reaction. The reaction is spontaneous and exothermic (ΔG° = −25.5 kJ/mol·K, ΔH° = −41.18 kJ/mol·K, ΔS° = −42.1 J/mol·K) and due to the moderate exothermic nature of the reaction it does not proceed readily at higher temperatures.

This is seen experimentally when the free energy change of the system increases pseudo-linearly with an increase in temperature, crossing the X-axis (ΔG = 0) at 783°C (T = 1056K). Also seen experimentally are the changing values of the equilibrium constant over varying temperatures; the reaction proceeds slowly at low temperatures (T < 300K) due to the negative entropy and doesn’t achieve a laboratory time scale until ca. 300K, when it exponentially decreases to a limiting value. The data compiled in figure 1-3 show the change in the free energy (top) and equilibrium constant (bottom) of the system as a function of temperature.¹³ The reaction again becomes unfavorable, however, this time non-spontaneous.

What does all this mean? Primarily, it means that the reaction is too slow to be useful at room temperature without a catalyst. The equilibrium constant at room temperature...
temperature indicates that the first order reaction has a half−life of 47.7 years, which is lowered to appreciable values by adjusting the temperature in the reaction chamber. In a Fischer−Tropsch process, hydrocarbons are produced from syngas which uses the WGS to fine−tune the ratio of [H₂]/[CO] flowing into the hydrocarbon production reactor. The WGS is performed twice, once at temperatures ca. 500°C (HTS) and then ca. 190°C – 230°C (LTS), decreasing the concentration of poisonous CO and maximizing the amount of desirable hydrogen gas flowing into the reactor.

Figure 1-3. Thermodynamic equilibrium (K_{eq} and ΔG) of the WGS reaction as a function of temperature (K). At temperatures below 1056K (783°C) the WGS is spontaneous (ΔG_{rxn} < 0).^{13}
Even though we have been successful in manipulating the reaction parameters to allow us to perform the WGS, the catalysts used do not lower the activation energy enough to produce syngas in a manner that efficiently satisfies our growing demand for synthetic fuels. Also, what about all the carbon dioxide produced as a byproduct of the fuel combustion reactions? Much of it is emitted into the atmosphere as exhaust (cars, factories, etc.), attributing to the aforementioned climate change issues. Research is being done industrially and academically that looks into ways of catalyzing the reverse water gas shift reaction (rWGS). If successful, industry would be able to recycle the carbon dioxide produced from the WGS for re–use as carbon monoxide.
C) **REVERSING THE WATER GAS SHIFT: CARBON DIOXIDE REDUCTION**

The thermodynamic considerations of the rWGS system are very similar to those of the reaction in the forward direction; in fact they are exactly opposite. The reaction is endothermic and shows the opposite spontaneity trend as the forward reaction indicating that it will be spontaneous at higher rather than lower temperatures ($\Delta G^\circ = 25.5$ kJ/mol·K, $\Delta H^\circ = 41.18$ kJ/mol·K, $\Delta S^\circ = 42.1$ J/mol·K). The kinetics of the rWGS reaction have been studied thoroughly at temperatures below 873K and the reaction is used industrially but at a significantly lower efficiency than is ideal. The actual reverse water shift reaction is not what research efforts should be focusing on, instead looking into efficient ways to decrease the energy cost of CO$_2$ reduction would be more useful. Scheme 1-1 shows a possible cycle for the reduction of carbon dioxide allowing recycling of the carbon dioxide, which would also prevent release of a possibly harmful greenhouse gas.
Scheme 1-1. An example of a possible catalytic cycle utilizing the WGS and emphasizing the reduction of CO₂ by a transition metal. Note energy is still required to drive the reduction of the transition metal catalyst.

There are various ideas and methods that researchers are pursuing in hopes of finding a way to reduce CO₂ at both low energy input and low temperature. One promising avenue of thought pursues synthetic inorganic catalyst designs in which the goal is to produce a compound (most commonly transition metal based) that will activate the C–O bond in CO₂ without the need for high temperatures or pressures. Various metals have been used to activate carbon dioxide and one even produced a cyclic system. Sadighi’s cycle may be able to achieve a TON = 100 h⁻¹ (which really isn’t very high considering enzymes achieve TON = 700h⁻¹), but the cycle required a stoichiometric amount of a diborane species, which can be expensive both economically and energetically. One similarity each designed system has is that there is always some sort of
polarized moiety that draws substrates and then steals their electrons for its own personal gain.

Figure 1-4. The basic molecular orbital diagram showing the interaction between a, Lewis basic, late transition metal and an electron poor, Lewis acidic, early metal center.

In that vein, our research is focused on the synthesis and reactivity of heterobimetallic complexes with three phosphinoamide ligands caging in a highly polarized M—M interaction. Early transition metals are perfect to substitute with previously used metaloboratran complexes which have a three coordinate boron atom that is flexible enough to allow reversible coordination of the attached metal center. Figure 1-4 shows the basic molecular orbital interaction between an electron deficient,
Lewis acidic, early transition metal and an electron rich, Lewis basic, late transition metal. The empty orbital on the early metal is able to accept donations from the rich late metal center allowing them both to be happy and comfortable in tandem, at least until a small molecule gets too close for its own good.

The really useful thing about the early/late metal–metal interaction is that the highly polarized bond makes it easier (~1V more positive) for the metal complex to accept electrons from a reductant. Electrons can be stored in between the metal centers because of the near–frustrated nature of the atoms when they are in such close proximity to each other. Another helpful characteristic of these complexes is to provide them with a scaffold that allows dynamic movement of the ligand system. This makes it easier for the complex to distort its geometry in a manner that will favor the bimetallic’s reactivity with whatever substrate it is having for dinner.

The following is an account of the research our group has been pursuing toward the goal of someday producing a compound that will solve all of society’s energy problems.
Chapter 2: Multi-Electron Redox Activity Facilitated by Metal-Metal Interactions in Early/Late Heterobimetallics\(^1\)

A) Why Heterobimetallics?

In recent years, dinuclear complexes containing two different transition metal centers have received increasing interest owing to the presumption that their reactivity should vary substantially from that of monometallic complexes or homobimetallic complexes.^15,16^ Heterobimetallic complexes featuring interactions between a Lewis-acidic, hard, early metal center and a Lewis-basic, soft, late metal center are particularly interesting targets in light of their vastly different reaction sites. These early/late heterobimetallic complexes have potential applications as bifunctional catalysts for the activation of small molecule substrates and homogeneous catalysis. While a number of early/late heterobimetallic complexes have been synthesized, the nature of the metal–metal interactions in these complexes and the effect of these interactions on redox behavior and reactivity remain largely unexplored.

\(^1\) Chapter reproduced from [1] with permission from the American Chemical Society.
The metal-metal interactions in early/late heterobimetallics are analogous to metal→borane interactions that have received recent attention in metalloboratrane complexes.\textsuperscript{17-21} These Z-type bonding interactions, in which a metal center datively donates an electron-pair to a ligand atom, are intriguing in that the effective oxidation state of the metal center is higher than that predicted as the formal oxidation state, resulting from electron withdrawal by the Z-type ligand.\textsuperscript{22,23}

Early/late heterobimetallic complexes linked by alkoxyalkylphosphines \([\text{Ph}_2\text{PCH}_2\text{O}]^-\) were synthesized by Wolczanski and coworkers several decades ago in an effort to model the interactions between electron-rich late metals and early metal oxide surfaces.\textsuperscript{24-27} More recently, Nagashima et al. have utilized titanium and zirconium complexes supported by phosphinoamides, \([\text{Ph}_2\text{PNR}]^-\) (where \(R = {^i}\text{Pr} \) or \( {^t}\text{Bu} \)), as metalloligands for late transition metal centers.\textsuperscript{28-31} The disubstituted titanium complex \((\text{Ph}_2\text{PN}^i\text{Bu})_2\text{TiCl}_2\) was utilized as a bidentate ligand in Ni\textsuperscript{II}, Pd\textsuperscript{II}, and Pr\textsuperscript{II} allyl complexes, and it was found that the M→Ti interactions in these complexes reduced the electron density at the late transition metal and, in turn, greatly enhanced the electrophilicity of the M-bound allyl moiety.\textsuperscript{31} In addition, the trisubstituted zirconium complexes \((\text{Ph}_2\text{PNR})_3\text{ZrCl}\) were coordinated to Mo\textsuperscript{0}(CO)\(_3\) and Cu\textsuperscript{I}Cl fragments in a tridentate, tripodal fashion. Nagashima and coworkers found that in the \((\text{CO})_3\text{Mo}(\text{Ph}_2\text{PN}^i\text{Pr})_3\text{ZrCl}\) complex, the CO stretching frequencies are shifted 50–70 cm\(^{-1}\) higher than comparable \((\text{CO})_3\text{Mo(triphos)}\) complexes as a result of weaker back-bonding into CO \(\pi^*\)-orbitals.\textsuperscript{30} In light of this, we were curious to ascertain what effect coordination of a Lewis-acidic early transition metal would have on a potentially redox-active late transition metal. Such a
dative $M_1 \rightarrow M_2$ interaction would be expected to reduce the electron density at $M_1$, thereby facilitating reduction and small molecule activation at milder potentials. In a related study, Berry and coworkers have examined heterobimetallic interactions in $\text{Cr}≡\text{Cr}−\text{Fe}$ complexes, and found that the metal−metal multiply-bonded moieties donate electron density to the iron center, resulting in a $trans$-influence and significantly lowering the Fe$^{III/II}$ potential in these complexes.$^{32,33}$
B) Synthesis of Zr/Co Complexes Supported by Phosphinoamide Ligands

For this investigation, we chose to explore heterobimetallics with a series of phosphinoamide ligands of differing electronic properties. The phosphinoamine precursors Ph$_2$PNH$i$Pr, $^i$Pr$_2$PNHMes, and $^i$Pr$_2$PNH$i$Pr were prepared using modifications of literature procedures.\textsuperscript{34,35} In a procedure similar to that previously described, deprotonation of the phosphinoamines with 1 eq of $^n$BuLi at $-78^\circ$C, followed by treatment with 1/3 equiv of ZrCl$_4$, led to isolation of the zirconium metalloligands (Ph$_2$PN$i$Pr)$_3$ZrCl (1), ($^i$Pr$_2$PNMes)$_3$ZrCl (2), and ($^i$Pr$_2$PN$i$Pr)$_3$ZrCl (3) in moderate to good yield.\textsuperscript{30} Previously, Nagashima and coworkers showed through X-ray crystallography and variable temperature $^1$H NMR that the phosphines in complex 1 are unequivocally bound to the Zr center at low temperature and in the solid state, while reversible phosphine dissociation occurs in solution at room temperature.\textsuperscript{30}

![Scheme 2-1](image_url)

**Scheme 2-1.** Synthesis of the three zirconium–cobalt heterobimetallic derivatives.

Although only one $^{31}$P NMR signal is observed at all temperatures, variable temperature $^1$H NMR spectra of complexes 2 and 3 confirm that these complexes exhibit
the same dynamic behavior, making them viable metalloligands as well. Accordingly, treatment of complexes 1, 2, and 3 with 1 eq of CoI₂ led to isolation of heterobimetallic Zr/Co complexes as shown in Scheme 2-1. Surprisingly, the cobalt centers in the green paramagnetic products ICo(Ph₂PN₂Pr)₃ZrCl (4), ICo(Pr₂PNMes)₃ZrCl (5), and ICo(Pr₂PN₂Pr)₃ZrCl (6), respectively, had been formally reduced from CoII to CoI. The oxidation states of complexes 4, 5, and 6 were confirmed by their solution magnetic moments corresponding to S = 1 (μeff = 2.92, 2.87, and 3.10 μB, respectively). Evidence for Co→Zr interactions in complexes 4–6 provided by structural characterization using X-ray crystallography, computational studies using DFT, and dramatic effects on redox activity will be discussed later in this chapter.

Scheme 2-2. Synthesis of monometallic Coₙ⁺⁻¹(PrNHPPh₂)ₙIₙ for comparison against the redox abilities of the heterobimetallic derivatives.

* Additional experimental details are included in Appendix.
In attempts to synthesize derivatives featuring other metal combinations, we found that reactions of complexes 1–3 with metal salts with a less accessible M^{II/I} redox potential such as FeCl$_2$, FeI$_2$, and ZnCl$_2$ did not lead to heterobimetallic complexes. In addition, CoCl$_2$ was an ineffective starting material for the preparation of mixed metal derivatives. In light of this halide dependence, it is likely that the reducing agent is I$^-$, and the resulting I$_2$ is subsequently consumed via reaction with the phosphines in complexes 1–3.$^{††}$ Nonetheless, it is evident that the close proximity of the Lewis-acidic Zr center enforced by the phosphinoamide ligand geometry necessitates reduction of the late transition metal center to a more Lewis-basic +1 oxidation state upon or prior to coordination.

To provide further evidence that the reduction to Co$^+$ in complexes 4–6 is unequivocally a result of the Zr’s presence, the reaction of CoI$_2$ with the phosphinoamine Ph$_2$PNH$i$Pr was examined in the absence of a tethered Zr center (Scheme 2-2). As expected, treatment of CoI$_2$ with excess Ph$_2$PNH$i$Pr led exclusively to the red

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$^{†}$ I$_2$ reacts stoichiometrically with LiN(PPh$_2$)$_2$ to effect PP coupling: Braunstein, P., Hasselbring, R., Tiripicchio, A. and Ugozzoli, F. J. Chem. Soc., Chem. Commun. 1995, 37–38. We have also confirmed that I$_2$ is consumed quantitatively by both our phosphinoamines and our zirconium phosphinoamide complexes. Stoichiometric reaction of Ph$_2$PNH$i$Pr with I$_2$ in C$_6$D$_6$ leads to complete consumption of both I$_2$ (based on disappearance of the diagnostic purple color) and Ph$_2$PNH$i$Pr (based on disappearance of its $^{31}$P NMR signal) to form a highly insoluble red/orange material. Likewise, stoichiometric reaction of complex 2 with I$_2$ leads to complete consumption of both materials and appearance of new phosphorus-containing products.

$^{‡}$ Preliminary data suggests that the reaction of complex 2 with CoCl$_2$ indeed leads to a heterobimetallic product in the presence of an external reductant such as NaBH$_4$, based on the similarity of $^1$H NMR features to those of complex 5 in the crude NMR of this reaction,
disubstituted Co$^{II}$ product (Ph$_2$PNH$i$Pr)$_2$CoI$_2$ (7), as confirmed structurally and spectroscopically. The Co$^{I}$ trisubstituted complex (Ph$_2$PNH$i$Pr)$_3$CoI (8) could be synthesized, but only in the presence of elemental Zn as a reducing agent. Much like complexes 4−6, complex 8 is green and paramagnetic with a solution magnetic moment indicative of high spin Co$^{I}$ ($\mu_{\text{eff}} = 2.89$ $\mu_B$).

* Additional experimental details are included in the Appendix.
C) Structural Characterization of Heterobimetallic Complexes

Single crystals of complexes 4, 5, and 6 were grown and subjected to X-ray diffraction structural analysis. The molecular structures of complexes 4–6 are shown in Figure 2-1 and relevant interatomic distances and angles are shown in Table 2-1. All three complexes have C₃ᵥ symmetry with a mildly distorted tetrahedral geometry at the Co center. The P–Co–P angles in all three complexes are within 5° of the expected 109.5° angle between ligands in an ideal tetrahedron. Furthermore, the average P–Co–P angles in complexes 4–6 are only slightly expanded (~2–4°) from the P–Co–P angles in monometallic complex 8. This indicates that the distortion from tetrahedral geometry to trigonal bipyramidal geometry at the Co center in complexes 4–6 resulting from the interactions between Co and Zr is insignificant. However, the geometry about Zr clearly indicates a structural distortion toward trigonal bipyramidal geometry in all three complexes.

The average N–Zr–N angles in complexes 4–6 are very close to 120° (118.6°, 119.5°, and 119.5°, respectively) and the sum of the three N–Zr–N angles is 356–359°, as would be expected for the angles in an ideal trigonal bipyramid. In addition, the average N–Zr–Co angles in complexes 4–6 are close to 90° (83.2°, 86.2°, and 86.3°, respectively), consistent with Co occupying the axial position of the trigonal bipyramidal Zr coordination sphere. Notably, a search of the CSD indicated that this sort of geometry about Zr, (3 L–Zr–L angles of 120° ± 2°) is unprecedented in the absence of a fifth donor ligand.
As shown in Figure 2-1 and Table 2-1, complexes 4, 5, and 6 have Zr–Co interatomic distances of 2.7315(5), 2.6280(5), and 2.6309(5) Å, respectively. While large variations in reported covalent radii for Zr and Co exist in the literature, the Zr–Co interatomic distances in complexes 4–6 are shorter than the sum of the covalent radii of Zr and Co determined using most methods. More explicit evidence for a bond comes from comparison of the Zr–Co distances in complexes 4–6 with those in the only two Zr–Co bonds that have been structurally determined to date, 2.705(1) and 2.617(1) Å in complexes [SiMe2N(4-CH3C6H4)]3Zr–Co(CO)3L (L = CO and PPh3, respectively), indicate that the Zr–Co distances in complexes 4–6 are within the range of unsupported Zr–Co bonds.37

Examples of discrepancies in covalent radii reported in the literature: (a) 1.75 Å +1.26 Å = 3.01 Å (for l.s. Co) or 1.75 Å + 1.50 Å = 3.25 Å. (Cordero, B., et. al. Dalton Trans. 2008, 2832.) (b) 1.54 Å + 1.11 Å = 2.65 Å. (Pyykkö, P. and Atsumi, M. Chem.—Eur. J. 2009, 15, 186.) (c) 1.45 Å + 1.16 Å = 2.61 Å. (Pauling, L. The Nature of the Chemical Bond, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.) (d) 1.56 Å + 1.33 Å = 2.89 Å. (CSD, http://www.ccdc.cam.ac.uk/products/csd/radii/table.) (e) If the Co–Co (2.506 Å) and Zr–Zr (3.179 Å) distances in elemental Co and Zr metal are divided by 2 to extract a typical covalent radius in a metal–metal bond, we obtain 1.59 Å + 1.25 Å = 2.84 Å. (Table of Interatomic Distances and Configuration in Molecules and Ions, Supplement 1956–1959, Special publication No. 18; Sutton, L. E., Ed.; Chemical Society:London, U.K., 1965.)
Figure 2-1. Displacement ellipsoid (50%) representations of complexes 4, 5, and 6. Hydrogen atoms and substituents on all but one phosphinoamide ligand have been omitted for clarity.

It is worth noting that these previously characterized Zr–Co bonds, unlike those in complexes 4–6, are not supported or enforced by a ligand framework. In complexes 4–6, it is possible that the close proximity of the Zr and Co atom is enforced by ligand geometry and is not the result of orbital overlap between Zr and Co; however, electrochemical consequences and DFT calculations, discussed later in this chapter, suggest that Zr–Co interactions exist in complexes 4–6 and are dative in nature, with the electron-rich, formally Co$^{1}$ center donating electrons to the Lewis-acidic Zr$^{IV}$ center. The shorter Co–Zr interatomic distances in complexes 5 and 6 compared to that in complex 4 can be attributed to the more electron-rich iPr-phosphine substituents that impart more electron density on the Co center, strengthening its donation into Zr’s d-orbitals.
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<td>82.60(6)</td>
<td>86.51(6)</td>
<td>86.5(3)</td>
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**Table 2-1.** Relevant Interatomic Distances (Å) and Angles (°) in Complexes 4–6 and 8.
D) Analysis of Redox Behavior Using Cyclic Voltammetry

As interatomic distances determined by X-ray crystallography suggest a Co→Zr interaction, which is expected to decrease the electron density at the Co center in complexes 4, 5, and 6. The effect of this interaction on the redox properties of the Co center in the complexes was probed using CV. Interestingly, the CVs of complexes 4–6 showed reductive events, although the nature of these reductions was different for each species (Figure 2-2B). These reductions are assigned as cobalt-based, since CVs of the Zr complexes 1–3 did not contain any features within the THF solvent window. Complex 4 showed a fully reversible reduction at −1.65 V. Although this appears to be a single reduction, even by DPV techniques, bulk electrolysis of a sample of complex 4 at −1.77 V required ~2 electrons per molecule of complex 4 (1.94 e⁻). Thus, the reversible reduction in the CV of complex 4 is assigned as a 2e⁻ process, as confirmed by bulk chemical reduction (vide infra).

The CV of complex 5 also possessed a reversible reduction at −1.64 V; however, in this case the reduction was followed by an immediate, irreversible reduction at −1.87 V. This can best be explained by an EEC mechanism, in which the first one-electron reduction is reversible, but upon addition of a second electron, a chemical process occurs to generate a new species that cannot be re-oxidized. Since electrochemical experiments were performed under an N₂ atmosphere, we propose that the features in the CV of complex 5 are attributed to rapid, irreversible N₂ binding upon reduction by 2e⁻. This proposal is confirmed by a distinct dinitrogen stretching frequency in the infrared
Interestingly, we find that while the phosphine substituents on complexes 4 and 5 should vary in electron-donating ability enough to affect the reduction potential of these Co centers, the reduction potentials for the first reductive events are identical. It seems likely that this is a direct consequence of the stronger Zr–Co interaction in complex 5 based on the ~0.1 Å shorter Zr–Co interatomic distance. The CV of complex 6, which has a Zr–Co distance identical to that of complex 5, shows quasi-reversible reductions at −1.86 and −2.07 V. In this case, the reductions are presumably shifted to more negative potentials than those of complex 5 as a result of the more electron-releasing $^i$Pr-amide substituents.
Figure 2-2. Full CV of complex 4 (A) and reductive portion of the CVs of complexes 4, 5, 6, and 8 (B) (2 mM in 0.4 M [\text{Bu}_4\text{N}][\text{PF}_6] in THF; scan rate = 100 mV/s).

To compare the reduction potentials of complexes 4–6 with a similar compound lacking an electron-withdrawing Zr center, the CV of complex 8 was obtained. As observed for the heterobimetallic complexes, complex 8’s CV showed two irreversible reductive events (Figure 2-2B). However, these reductions occurred at −2.46 and −2.65 V, nearly 1 V more negative than the reduction potentials of the corresponding Co/Zr complex 4. In light of this, it can be concluded that in complex 4 the electron density on cobalt is significantly diminished with respect to complex 8, thermodynamically favoring

* Additional experimental details can be found in the Appendix.
the reduced product and raising the reduction potential. Thus, dative donation from Co to Zr has a dramatic effect on the redox activity of the Co, allowing further reduction of the Co$^1$ center at milder potentials.

In addition, it is worth noting that the CVs of complexes 4–6 in THF show only irreversible Co$^{II}$/Co$^I$ oxidation events, consistent with the inability to isolate Zr$^{IV}$/Co$^{II}$ species prior to reduction (Table 2-2).* For example, the CV of complex 4 has only irreversible oxidative features at 0.32 and 0.53 V, implying that a Co$^{II}$ species is unstable (Figure 2-2A).

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<td>Co$^{III}$/Co$^{II}$</td>
<td>0.53 V$^d$</td>
<td>0.60 V$^d$</td>
<td>0.25 V$^d$</td>
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<tr>
<td>Co$^{II}$/Co$^I$</td>
<td>0.32 V$^d$</td>
<td>0.47 V$^d$</td>
<td>−0.07 V$^d$</td>
<td>0.57 V$^d$</td>
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<td>Co$^I$/Co$^{II}$</td>
<td>−1.65 V$^b$</td>
<td>−1.64 V$^b$</td>
<td>−1.86 V$^c$</td>
<td>−2.49 V$^c$</td>
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<td>Co$^0$/Co$^{I}$</td>
<td>−1.65 V$^b$</td>
<td>−1.87 V$^c$</td>
<td>−2.07 V$^c$</td>
<td>−2.66 V$^c$</td>
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</table>

Table 2-2. Oxidation and Reduction Potentials of Complexes 4, 5, 6, and 8 as Determined Using Cyclic Voltammetry.$^a$ $^a$2 mM analyte in 0.4 M [$^n$Bu$_4$N][PF$_6$] in THF; scan rate = 100 mV/s. $^b$E$_{1/2}$ (reversible). $^c$E$_{pc}$ (irreversible or quasireversible). $^d$E$_{pa}$ (irreversible).
E) Two–Electron Reduction of Complex 5 Under N$_2$(g)

As predicted by cyclic voltammetry, bulk samples of complexes 4–6 can be chemically reduced with excess Na/Hg in THF solution, resulting in a color change from green to red/brown. Notably, in all three complexes, addition of just 1 eq of Na/Hg led to a 1:1 mixture of starting material and reduced product, indicating that reduction by two electrons is favored. As shown in Scheme 2-3, the product generated upon treatment of complex 5 with excess Na/Hg is diamagnetic and contains a dinitrogen moiety bound to the Co center, as indicated by IR spectroscopy (ν(N$_2$) = 2023 cm$^{-1}$).

The structure of this complex, [N$_2$-Co($^{1}$Pr$_2$PNMes)$_3$ZrX][Na(THF)$_5$] (9, X = a mixture of Cl and I) was determined via X-ray crystallography and is shown in Figure 2-3. Upon reduction, the halide remaining on Zr exchanges with the NaI in solution, leading to significant crystallographic disorder between Cl$^-$ and I$^-$ which has been modeled adequately with occupancies of 73% I and 27% Cl in the structure of complex 9. In addition to halide loss and dinitrogen binding, some noteworthy structural changes occur upon reduction of complexes 5 to 9. Most interestingly, the Zr–Co distance in complex 9 is 2.4112(3) Å, more than 0.2 Å shorter than the 2.6280(5) Å distance in complex 5. This contraction of the intermetallic distance suggests that the increase in electron density upon reduction of Co leads to a stronger dative donation from Co to the Lewis-acidic Zr center. The geometry about the Zr center continues to be trigonal bipyramidal, as was observed in the structure of complex 5. While the Co center is still best described as tetrahedral, the P–Co–P angles are slightly expanded upon strengthening the Co–Zr interaction (avg. P–Co–P angles are 108° and 113°
in complexes 5 and 9, respectively), indicative of a distortion toward a trigonal bipyramid.

Scheme 2-3. Reduction of a Zr−Co heterobimetallic using 2.5 equivalents of 0.5 wt% Na/Hg amalgam as the reductant under an N\(_2\)(g) atmosphere.

Both the relatively short N−N distance of 1.120(2) Å (in free N\(_2\), N−N = 1.0975 Å) and the relatively high ν(N\(_2\)) (2023 cm\(^{-1}\) vs 2331 cm\(^{-1}\) in free N\(_2\)) suggest very little activation of the N\(_2\) unit in complex 9 despite the seemingly low formal oxidation state of the Co center (Co\(^{1}\)). Moreover, in comparing the N−N distance and ν(N\(_2\)) stretch for complex 9 with parameters for previously reported Co−N\(_2\) complexes, it is found that the degree of N\(_2\) activation in complex 9 is most consistent with Co\(^{1}\)−N\(_2\) complexes, which have N−N distances ranging from 1.08 Å to 1.15 Å and ν(N\(_2\)) bands in the 2024–2125 cm\(^{-1}\) range. In contrast, Co−N\(_2\) complexes in the formal −1 or 0 oxidation state typically have lower ν(N\(_2\)) stretching frequencies (1830–1910 cm\(^{-1}\)) and longer N−N distances (1.15 Å to 1.19 Å).

We attribute this to the involvement of the filled Co d-orbitals in both σ- and π-donation to Zr, disfavoring back-bonding into the N−N anti-bonding orbitals of coordinated N\(_2\), as supported by DFT calculations (vide infra). Bourissou and coworkers
note a similar shift to higher stretching frequency as a result of a dative Rh→B interaction in their complex RhCl(CO)(diphosphineborane).\textsuperscript{49} It is also noteworthy that the Zr–X distance (in both the case of Cl and I) is significantly elongated from that observed in typical Zr halide complexes. While this is due, at least in part, to the strong interaction with the Na\textsuperscript{+} countercation, it is also likely that the electron rich Co center exerts a strong trans-influence on Zr. Reduction of complexes 4 and 6 with Na/Hg also leads to diamagnetic red/brown products with dinitrogen bound to Co (ν(N\textsubscript{2}) = 2019 and 1992 cm\textsuperscript{-1}, respectively), and the structures and characterization of these products will be reported in Chapter 3.

\textbf{Figure 2-3.} Displacement ellipsoid (50\%) representation of complex 9. Hydrogen atoms have been omitted for clarity. Relevant bond distances (Å) and angles (deg): Zr1–Co1, 2.4112(3); Co1–N4, 1.8186(16); N4–N5, 1.120(2); Zr1–I1, 2.9722(7); Zr1–Cl1, 2.690(7); Na1–I1, 3.2695(12); Co1–P1, 2.1209(5); Co1–P2, 2.2153(5); Co1–P3, 2.2098(5); Zr1–N1, 2.1524; Zr1–N2, 2.1559(15); Zr1–N3, 2.1639(15); I1–Zr1–Co1, 178.560(17); N4–Co1–Zr1, 179.33(5); N1–Zr1–N2, 117.80(6); N2–Zr1–N3, 121.16(6);
N1–Zr1–N3, 119.82(6); N1–Zr1–Co1, 96.35(4); N2–Zr1–Co1, 86.73(4); N3–Zr1–Co1, 85.93(4); P1–Co1–P2, 112.404(19); P2–Co1–P3, 113.80(2); P3–Co1–P1, 113.24(2).
F) **Theoretical Investigation of Metal–Metal Interactions in Co/Zr Heterobimetallics using DFT**

To better understand the interaction between the cobalt and zirconium atoms in this series of complexes, theoretical calculations were performed on an analogue of compound 5 and the reduced dinitrogen adduct, complex 9. Geometry optimization and frequency calculations were carried out using the BP86 functional and a mixed basis set consisting of LANL2TZ(f) (Co,Zr), 6311+G(d) (Cl, N, P), and D95V (C, H) basis sets (Gaussian03-E.01). Although the full molecules were used for our computational analyses starting from coordinates determined via X-ray crystallography, the Iodine atom in complex 5 was replaced with Chlorine for simplicity.

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<tr>
<td>Co–P3</td>
<td>2.3806(8)</td>
<td>2.38</td>
</tr>
<tr>
<td>Zr–N1</td>
<td>2.129(2)</td>
<td>2.136</td>
</tr>
<tr>
<td>Zr–N2</td>
<td>2.131(2)</td>
<td>2.147</td>
</tr>
<tr>
<td>Zr–N3</td>
<td>2.133(2)</td>
<td>2.132</td>
</tr>
<tr>
<td>Cl2–Zr–Co</td>
<td>178.95(2)</td>
<td>178.75</td>
</tr>
</tbody>
</table>

**Table 2-3.** Selected Bond Lengths (Å) and Angles (deg) of complex 5 as Determined by Crystallography and Theoretical Calculations. *Gaussian ’03: BP86/LANL2TZ(f)/6311+G(d)/D95 V.

The results of geometry optimization of complex 5 using DFT are in excellent agreement with the experiment results, as shown in Table 2-3. In accordance with our assignment of the Co atom as existing in the +1 oxidation state, the unpaired spin density resides almost exclusively on the Co atom and Mulliken population analysis predicts a spin density of 1.87 on the Co atom in complex 5. Visualization of the frontier molecular
orbits of complex 5 reveals several interesting features relating to the interaction between the Co and Zr atoms (Figure 2-4). Rather than the three–over–two usual d-orbital splitting pattern that would be predicted for a tetrahedral Co center, theory predicts a significant lowering of the energy of the Co d_{z^2}-orbital in complex 5. This stabilization appears to result from substantial orbital overlap between the Co and Zr d_{z^2}-orbitals. Thus, donation of electron density from the filled Co d_{z^2}-orbital to the empty Zr d_{z^2}-orbital results in a net bonding interaction. In addition to this σ-bonding orbital, close inspection of the frontier orbitals also reveals two orbitals corresponding to the Co d_{xz}- and d_{yz}-orbitals that exhibit π-type bonding interactions with the Zr center. Furthermore, Mayer population analysis reveals a Co–Zr bond index of 0.73 as a result of these three interactions. Thus, electron density is clearly drawn away from the Co center by the Lewis-acidic Zr atom, and it is to this dative-like interaction that we attribute the facile two-electron reduction of complex 5.

In computational studies of complex 9, it was necessary to include the THF-coordinated Na^+ countercation to obtain a geometry consistent with that determined using X-ray diffraction data. The calculated Co–Zr interatomic distance agrees well with the experimental value (2.41 Å vs. 2.42 Å, respectively), as does the N–N bond distance of the ligated dinitrogen moiety (1.12 Å vs. 1.14 Å, respectively). Moreover, the dinitrogen stretching frequency of 2025 cm^{-1} derived from the frequency calculation is nearly identical to the 2023 cm^{-1} frequency observed in the IR spectrum of complex 9.

The 0.23 Å reduction in the Co–Zr distance that accompanies the two-electron reduction of complex 5 to form complex 9 is intriguing, as it suggests that a stronger
bonding interaction is forming between the two metal centers. Accordingly, the Co−Zr Mayer bond index is increased to 1.23 in complex 9. As with complex 5, visualization of the frontier orbitals reveals a discrete σ-bonding interaction between the two metal centers mediated by the Co and Zr \( d_z^2 \)-orbitals as well as two π-type bonding interactions originating from the \( d_{xz} \) and \( d_{yz} \)-orbitals on Co (Figure 2-5). In addition to these interactions, examination of the HOMOs, to which the two additional electrons have been added, reveals a noticeably greater bonding contribution between Co and Zr which was not present in complex 5. We attribute the significantly higher Zr−Co bond order and shorter Zr−Co distance to this new bonding contribution.
With respect to the bonding interactions between Co and N\textsubscript{2}, the elongation and diminished stretching frequency of the dinitrogen bond with respect to gaseous N\textsubscript{2} suggests activation of the N–N bond upon binding to the metal center, but to a far lesser extent than is typically seen in such low valent late transition metal dinitrogen complexes. The results of the theoretical investigation of complex 9 give some insight into the nature of this phenomenon. As evident in the molecular orbital surfaces in Figure 2-5, the molecular orbitals that house the Co–N\textsubscript{2} back–bonding interactions are also involved in the π-type interactions between Co and Zr, and it appears that this
diminishes the amount of electron density available for back-bonding into the N\textsubscript{2}'s π*-
orbitals.

**Figure 2-5.** Calculated MO diagram of the frontier orbitals of complex 9 with visualizations of the corresponding MOs. The [Na(THF)]\textsuperscript{3+} unit has been omitted for clarity.\textsuperscript{50}
G) Summary

In summary, we have shown that tethering a Lewis-acidic early transition metal such as Zr in close proximity to an electron-rich late transition metal leads to metal–metal interactions which are dative in nature. Evidence for Co→Zr interactions in complexes 4–6 is provided by structural characterization data and computational studies using DFT. DFT calculations reveal that the interaction between Co and Zr occurs through both σ- and π-overlap of the metal d-orbitals. Donation of electron density from Co to Zr has dramatic effects on the redox activity of Co, causing shifts of nearly 1 V to milder reduction potentials. The Zr center in these complexes plays the role of a Z-type metalloligand, rendering these complexes analogous to recently reported “metallaboratranes” featuring M→B dative bonds. Much like transition metal boranes, the assignments of a formal oxidation to the metal centers in complexes 4–6 and 9 is not informative. This is particularly evident in complex 9, which would traditionally be assigned an oxidation state of Co−I but has structural and spectroscopic features more consistent with a CoI center. The polarized nature of dative metal–metal interactions such as those presented in this chapter may prove advantageous in the activation of small molecule substrates, which will be addressed in Chapter 3. Furthermore, the ability of dative interactions in heterobimetallic complexes to facilitate multi-electron redox activity at significantly milder potentials is a promising lead in the design of catalysts for redox transformations.
**H) Experimental Section**

**I. General Considerations**

Unless otherwise noted, all syntheses reported were carried out using standard glovebox and Schlenk techniques in the absence of water and dioxygen. C\textsubscript{6}H\textsubscript{6}, pentane, Et\textsubscript{2}O, THF, CH\textsubscript{2}Cl\textsubscript{2} and toluene were degassed and dried by sparging with N\textsubscript{2} gas followed by passage through an activated alumina column. Ethanol was dried over CaH\textsubscript{2} and distilled, followed by sparging with N\textsubscript{2} prior to use. All solvents were stored over 3 \textdegree molecular sieves. Deuterated benzene and toluene were purchased from Cambridge Isotope Laboratories, Inc., degassed via repeated freeze–pump–thaw cycles, and dried over 3 \textdegree molecular sieves. THF-d\textsubscript{8} was dried over Na/K alloy, vacuum-transferred, and degassed via repeated freeze–pump–thaw cycles. Solvents were frequently tested using a standard solution of sodium benzophenone ketyl in THF to confirm the absence of oxygen and moisture. Ph\textsubscript{2}PNHiPr\textsuperscript{34,35} and complex I\textsuperscript{30} were synthesized using literature procedures. All other chemicals were purchased from Aldrich, Strem, or Alfa Aesar and used without further purification. NMR spectra were recorded at ambient temperature unless otherwise stated on a Varian Inova 400 MHz instrument. 1H and 13C NMR chemical shifts were referenced to residual solvent. 31P NMR chemical shifts were referenced to 85\% H\textsubscript{3}PO\textsubscript{4}. IR spectra were recorded on a Varian 640IR spectrometer controlled by Resolutions Pro software. UV–Vis spectra were recorded on a Cary 50 UV–Vis spectrophotometer using Cary WinUV software. Elemental microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA. Solution magnetic moments were measured using Evans’ method\textsuperscript{51,52}. 

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II. Xray Crystallography Procedures

All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated Mo Kα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.\textsuperscript{53} Preliminary cell constants were obtained from three sets of 12 frames. Structures were solved using SIR92,\textsuperscript{54} and refined (full-matrix-least-squares) using the Oxford University Crystals for Windows program.\textsuperscript{55} All ordered non-hydrogen atoms were refined using anisotropic displacement parameters; hydrogen atoms were fixed at calculated geometric positions and allowed to ride on the corresponding carbon atoms. Crystallographic parameters for all structures reported are summarized in Tables 2.4 and 2.5. Further crystallographic details may be found in the Appendix.

III. Electrochemistry

Cyclic voltammetry measurements were carried out in a glovebox under a dinitrogen atmosphere in a one-compartment cell using a CH Instruments electrochemical analyzer. A glassy-carbon electrode and platinum wire were used as the working and auxiliary electrodes, respectively. The reference electrode was Ag/AgNO\textsubscript{3} in THF. Solutions (THF) of electrolyte (0.40 M [nBu\textsubscript{4}N][PF\textsubscript{6}]) and analyte (2 mM) were also prepared in the glovebox.
A standard H-type bulk electrolysis cell was used for bulk electrolysis measurements. The cathodic chamber was charged with crystalline complex 4 (20.6 mg, 0.0168 mmol) and both chambers were filled with 10 mL of a 0.1 M [nBuN₄][PF₆] solution in THF. Controlled potential electrolysis commenced at −1.77 V until the solution current was less than 0.5% of the initial value (3.14 C passed, in 62 min). This corresponds to 1.94 electron equivalents if you take into account the presence of three toluene solvent molecules per molecule in crystals of complex 4.

IV. Computational Details

All calculations were performed using Gaussian03E.01 for the Linux operating system. DFT calculations were carried out using a combination of Becke’s 1988 gradient-corrected exchange functional and Perdew’s 1986 electron correlation functional (BP86). For open shell systems, unrestricted wave functions were used in energy calculations. A mixed-basis set was employed, using the LANL2TZ(f) triple-ζ basis set with effective core potentials for Co and Zr, Gaussian03’s internal 6311+G(d) for atoms bonded directly to the metal centers (nitrogen, phosphorus, and chlorine), and Gaussian03’s internal LANL2DZ basis set (equivalent to D95 V) for carbon and hydrogen. Using crystallographically determined geometries as a starting point, when available, the geometries were optimized to a minimum, followed by analytical frequency calculations to confirm that no imaginary frequencies were present. Mayer bond order analysis was performed with the routines included in the Gaussian03 package.
V. MesNHP$^i$Pr$_2$

A solution of MesNH$_2$ (5.00 g, 37.0 mmol) in Et$_2$O (100 mL) was cooled to 0°C in an ice bath. To this was added nBuLi (25.0 mL, 1.6 M in hexanes, 40.7 mmol) drop-wise over 20 min. The resulting solution was allowed to warm slowly to room temperature, resulting in the formation of a white precipitate, then refluxed for 30 min to ensure a complete reaction. The resulting suspension was added drop-wise to a stirring solution of iPr$_2$PCl (5.88 mL, 37.0 mmol) in Et$_2$O (100 mL) at −78°C. Upon warming slowly to room temperature, the mixture became slightly yellow with a white LiCl precipitate. After stirring for 1 h, the reaction mixture was filtered through a pad of Celite, and solvent was removed from the filtrate in vacuo. The resulting oily residue was redissolved in Et$_2$O and filtered through a plug of silica gel. Removal of the solvent in vacuo yielded analytically pure product as a yellow oil (7.64 g, 82.2%). 1H NMR (400 MHz, C$_6$D$_6$): δ = 6.79 (s, 2H, Mes), 3.16 (d, 1H, 2J$_{H−P}$ = 9.2 Hz, NH), 2.38 (s, 6H, Mes), 2.21 (s, 3H, Mes), 1.57 (m, 2H, CH(CH$_3$)$_2$), 1.04 (m, 12H, CH(CH$_3$)$_2$). 31P NMR (161.8 MHz, C$_6$D$_6$): δ = 57.7 (br, s). 13C NMR (100.5 MHz, C$_6$D$_6$): δ = 142.0 (2J$_{C−P}$ = 9.9 Hz), 130.4, 129, 127.8, 28.3 (1J$_{C−P}$ = 16.8 Hz), 20.4, 19.0, 18.8, 17.3. Anal. Calcd for C$_{15}$H$_{26}$NP: C, 71.68; H, 10.43; N, 5.57. Found: C, 71.75; H, 10.66; N, 5.55.

VI. iPr2PNHiPr

A solution of iPrNH$_2$ (4.29 g, 72.5 mmol) in C$_6$H$_6$ (100 mL) was cooled to 0°C. To this was added iPr$_2$PCl (4.25 mL, 29.0 mmol) drop-wise while stirring. The resulting
solution was allowed to warm to room temperature over 1 h to ensure completion of the reaction. Upon warming to room temperature the solution became viscous. After completion, the viscous solution was filtered through a plug of silica gel. Removal of the solvent in vacuo yielded analytically pure product as a clear colorless liquid (4.43 g, 87.2%). 1H NMR (400 MHz, C6D6): δ 2.99 (m, NiPr, 1H), 1.33 (m, PiPr, 2H), 0.95 (d, NiPr, 3H), 0.92 (m, PiPr, 6H), 0.56 (s, NH, 1H). 31P NMR (161.8 MHz, C6D6): δ 57.6 (br, s). 13C NMR (100.5 MHz, C6D6): δ 49.0 (2JC−P = 34 Hz), 26.4 (1JC−P = 15.1), 26.2 (2JC−P = 7.1), 19.4 (3JC−P = 25.18), 17.2 (2JC−P = 10.07). Owing to the increased oxygen sensitivity of this ligand, repeated elemental analysis samples analyzed as the oxidized form (iPr2P(=O)NHiPr). Anal. Calcd for C9H22NPO: C, 56.52; H, 11.59; N, 7.32. Found: C, 56.29; H, 11.76; N, 7.15.

VII. (iPr2PNMes)3ZrCl (2)

A solution of MesNHPiPr2 (1.046 g, 4.162 mmol) in Et2O (50 mL) was cooled to −78°C. To this was added nBuLi (2.6 mL, 1.6 M in hexanes, 4.2 mmol) drop-wise over 10 min. The resulting yellow/orange solution was warmed to room temperature and stirred for 2 h. The solution was then cooled again to −78°C, and ZrCl4 (0.323 g, 1.39 mmol) was added portion-wise as a solid. The reaction mixture was warmed to room temperature and stirred for 12 h. Volatiles were removed from the solution in vacuo, and the resulting solids were extracted with CH2Cl2 (30 mL) and filtered through a pad of Celite to remove LiCl. The volume of the filtrate was reduced to 10 mL in vacuo. The resulting supersaturated solution was layered with pentane and cooled to −35°C to yield
analytically pure colorless crystals of complex 2 (0.772 g, 63.4%). 1H NMR (400 MHz, C6D6): δ = 6.84 (s, 6H, Mes), 2.48 (s, 18H, Mes), 2.34 (m, 6H, CH(CH3)2), 2.19 (s, 9H, Mes), 1.30 (m, 18H, CH(CH3)2), 1.16 (m, 18H, CH(CH3)2). 31P NMR (161.8 MHz, C6D6): δ = 9.49 (s). 13C NMR (100.5 MHz, C6D6): δ = 148.7, 133.3, 131.9, 129.3, 34.5, 21.9, 21.7, 20.8. Anal. Calcd for C45H75ClN3P3Zr: C, 61.58; H, 8.61; N, 4.79. Found: C, 61.09; H, 8.47; N, 4.61.

VIII. (iPr2PNiPr)3ZrCl (3)

A solution of iPr2PNHiPr (2.589 g, 10.06 mmol) in Et2O (100 mL) was cooled to −78°C. To this was added nBuLi (6.33 mL, 1.6 M in hexanes, 10.1 mmol) drop-wise over 10 min. The resulting yellow/orange solution was warmed to room temperature and stirred for 3 h. The solution was then cooled back to −78°C, and ZrCl4 (0.800 g, 3.43 mmol) was added portion-wise as a solid. This reaction mixture was then warmed to room temperature and stirred for 12 h. Volatiles were removed from the solution in vacuo, and the resulting solids were extracted with CH2Cl2 (20 mL) and filtered through a pad of Celite to remove LiCl. The volume of the filtrate was reduced to 5 mL in vacuo. The resulting supersaturated solution was layered with pentane and cooled to −35°C for 12 h. The mother liquor was decanted to yield analytically pure colorless crystals of complex 3. The decanted mother liquor was removed in vacuo, and the resulting solid was repeatedly washed with pentane to precipitate a pure colorless solid (0.727 g, 32.7%). 1H NMR (400 MHz, C6D6): δ = 3.95 (m, 3H, NCH), 2.06 (m, 6H, PCH), 1.60
(d, 18H, NC(CH3)2), 1.17 (m, 36H, PC(CH3)2). 31P NMR (161.8 MHz, C6D6): δ = 1.5 (br, s). 13C NMR (100.5 MHz, C6D6): δ = 52.7, 29.0, 26.9, 21.6, 19.1. Owing to the increased oxygen sensitivity of this complex, repeated elemental analysis samples analyzed as the mono-oxidized compound (iPr2P(=O)NiPr)(iPr2PNiPr)2ZrCl. Anal. Calcd for C27H63ClN3P3ZrO: C, 48.74; H, 9.54; N, 6.31. Found: C, 48.41; H, 9.69; N, 6.15.

IX. ICo(Ph2PNiPr)3ZrCl (4)

Solid complex 1 (1.502 g, 1.76 mmol) and solid CoI2 (0.551 g, 1.76 mmol) were combined in THF (15 mL) and stirred for 4 h at room temperature. The resulting dark green reaction solution was filtered through Celite, and solvent was removed from the volatiles in vacuo. The remaining green solids were extracted with toluene (10 mL) and filtered through Celite. The filtrate was cooled to −35°C overnight to yield complex 4 as dark green crystalline solids. (1.137 g, 62.2%). Crystals for X-ray diffraction were grown by cooling a toluene/pentane solution to −35°C. 1H NMR (400 MHz, C6D6): δ = 14.22 (br s, Ph), 3.45 (br, (CH(CH3)2), 1.66 (br s, (CH(CH3)2), −5.57 (br, Ph), −7.01 (br s, Ph). UV−Vis (C6H6) λmax, nm (ε): 588 (190), 689 (140), 709 (130), 800 (240), 872 (610). Evans’ method (C6D6): 2.92 μB. Anal. Calcd for C45H51ClCoIN3P3Zr: C, 52.00; H, 4.95; N, 4.04. Found: C, 51.17; H, 4.99; N, 3.94.
X.  ICo(iPr2PNMes)3ZrCl (5)

Solid complex 2 (1.641 g, 1.87 mmol) and solid CoI2 (0.585 g, 1.87 mmol) were combined in CH2Cl2 and stirred for 48 h at room temperature. The resulting bright green solution was filtered through Celite, and solvent was removed from the filtrate in vacuo. The remaining green solids were washed with copious amounts of pentane and dried in vacuo to yield analytically pure complex 5 as a bright green solid (1.571 g, 79.0%). Crystals suitable for X-ray diffraction were grown via slow evaporation of a concentrated CH2Cl2 solution. 1H NMR (400 MHz, C6D6): δ = 12.98 (br s, iPrMe), 7.01 (s, MesMe), 2.54 (br s, iPrMe), 1.95 (s, MesMe), −1.92 (br, MesAr). UV−Vis (C6H6) λmax, nm (ε): 654 (190), 894 (350). Evans’ method (C6D6): 2.87 μB. Anal. Calcd for C45H75ClCoIN3P3Zr: C, 50.82; H, 7.11; N, 3.95. Found: C, 49.69; H, 7.09; N, 3.79.

XI.  ICo(iPr2PNiPr)3ZrCl (6)

Solid complex 3 (0.637 g, 9.81 mmol) and solid CoI2 (0.307 g, 9.81 mmol) were combined in CH2Cl2 and stirred for 15 h at room temperature. The resulting green solution was filtered through Celite, and the solvent was removed from the filtrate in vacuo. The remaining green solids were repeatedly washed with Et2O and dried in vacuo to yield analytically pure product as a green solid (0.382 g, 46.5%). Crystals suitable for X-ray diffraction were grown via slow diffusion of pentane into a concentrated toluene solution. 1H NMR (400 MHz, C6D6): δ = 70.6 (s br, PCH), 8.05 (s br, PiPrMe), 3.26 (s br, N−CH), 1.92 (s br, NiPrMe), −1.68 (s br, PiPrMe). UV−Vis (C6H6) λmax, nm (ε): 691.0 (180), 724.9 (210), 744.0 (230), 767.9 (290), 873.9 (240). Evans’ method (C6D6):
3.10 μB. Anal. Calcd for C27H63ClCoIN3P3Zr: C, 38.83; H, 7.60; N, 5.03. Found: C, 38.77; H, 7.62; N, 5.00.

XII. (Ph2PNHiPr)2CoI2 (7)

Solid CoI2 (0.176 g, 0.562 mmol) and Ph2PNHiPr (0.410 g, 1.69 mmol) were combined in THF (15 mL), and the resulting brick red solution was stirred for 4 h at room temperature. Solvent was removed from this solution in vacuo, and the resulting red solids were extracted into benzene (5 mL) and filtered through Celite. The brick red filtrate was then layered with pentane (15 mL) and allowed to sit for 12 h at room temperature to obtain complex 7 as a pure red crystalline product (0.182 g, 40.4%). Crystals of complex 7 suitable for X-ray diffraction were grown via vapor diffusion of pentane into a concentrated C6H6 solution. 1H NMR (400 MHz, C6D6): δ = 15.94 (br s, Ph), 4.66 (br s, Ph), 4.86 (br s, CH(CH3)2), −10.0 (br, CH(CH3)2), −10.8 (br s, Ph). UV−Vis (C6H6) λmax, nm (ε): 486 (1600), 677 (1040), 715 (1390), 782 (1100). Evans’ method (C6D6): 4.38 μB. Anal. Calcd for C30H36CoI2N2P2: C, 45.08; H, 4.54; N, 3.50. Found: C, 45.34; H, 4.46; N, 3.48.

XIII. (Ph2PNHiPr)3CoI (8)

Solid CoI2 (0.582 g, 1.86 mmol) and Ph2PNHiPr (1.583 g, 6.51 mmol) were combined in THF (15 mL) at room temperature, initially generating a brick red solution of complex 7. To this vigorously stirred mixture was added Zn powder (0.608 g, 9.30
mmol). After 4 h of vigorous stirring, the resulting green solution was filtered away from
the excess Zn. The solvent was removed from the filtrate in vacuo, and the resulting
green residue was extracted into toluene (10 mL) and filtered to remove Zn salts. The
green toluene solution was concentrated to 5 mL and layered with pentane (15 mL). After
storage for 12 h at −35°C, complex 8 was isolated as green crystals (1.129 g, 66.4%).
Note: Over time in solution, complex 8 disproportionates to form complex 7 even at low
temperature. Thus, the yield reported above corresponds to material that is only ~85–90%
pure, with red/brown powder of complex 7 present. Spectroscopic and elemental analysis
data was collected on crystals of complex 8 that were mechanically separated from this
mixture. Crystals suitable for X-ray diffraction were grown via layering a concentrated
C6H6 solution with pentane. 1H NMR (400 MHz, C6D6): δ = 79.5 (br, Ph), 11.17 (br s, Ph), 7.03 (br s, CH(CH3)2) 2.96 (br s, CH(CH3)2), 0.64 (br s, Ph). UV–Vis (C6H6)
λmax, nm (ε): 611 (130), 683 (150), 955 (280). Evans’ method (C6D6): 2.89 μB. Anal.
Calcd for C45H54CoIN3P3: C, 59.02; H, 5.94; N, 4.59. Found: C, 58.94; H, 5.94; N,
4.58.

XIV. [N2Co(iPr2PNMes)3ZrX][Na(THF)5] (9)

A 0.5% Na/Hg amalgam was prepared from 0.0057 g Na (0.25 mmol) and 1.1 g
Hg. To this vigorously stirred amalgam in 10 mL of THF was added a solution
of complex 5 (0.1056 g, 0.0993 mmol) in THF (5 mL). The solution immediately began
to change color from green to red. After 2 h, the resulting red solution was filtered away
from the amalgam, and the solvent was removed from the filtrate in vacuo. Solvent was
extracted back into THF and filtered through Celite. Layering the resulting concentrated red solution with pentane and cooling to −35°C resulted in red crystals of 9 (0.0879 g, 61.5%). Crystals suitable for X-ray diffraction were grown via vapor diffusion of pentane into a concentrated THF solution of complex 9 at −35°C. 1H NMR (400 MHz, C6D6): δ = 6.77 (s, 6H, Mes), 3.36 (br m, 20H, THF), 3.03 (m, 6H, CH(CH3)2), 2.51 (s, 18H, MesMe), 2.13 (s, 9H, MesMe), 1.79 (m, 18H, CH(CH3)2), 1.57 (m, 18H, CH(CH3)2), 1.24 (br m, 20H, THF). 31P64 NMR (162 MHz, C6D6): δ = 43 ppm (br s). IR (KBr solution cell, THF): 2024 cm−1. UV–Vis (C6H6) λmax, nm (ε): 509 (410), 676 (sh). The lability of the dinitrogen ligand and the overall instability of complex 9 precluded the collection of satisfactory combustion analysis data. Repeated samples consistently analyzed low for %N, as well as %C.
Chapter 3: Characterization and Reactivity Analysis of Zirconium-Cobalt Heterobimetallics with Small Molecules

A) Reduction of Zirconium–Cobalt Heterobimetallics

The highly polarized Zr–Co bonds in the early/late heterobimetallic complexes present a unique platform to use for tuning redox potentials and small molecule activation processes.\textsuperscript{15,65} For example, Casey and co-workers targeted early/late heterobimetallic dihydrides featuring a hydridic early metal hydride and an acidic late metal hydride as potential small molecule reducing agents.\textsuperscript{66-68} While a number of early/late heterobimetallic complexes have been reported, there are few accounts of reactivity in which both metals are involved\textsuperscript{31,69-71} and limited reports of metal–metal multiple bonds between early and late transition metals.\textsuperscript{27,72-74} Wolczanski and co-workers reported several alkoxyphosphine–linked heterobimetallic complexes, namely Ti(OCMe\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2})\textsubscript{3}Rh and Cp\textsuperscript{*}Zr(OCH\textsubscript{2}PPh\textsubscript{2})\textsubscript{2}RhMe\textsubscript{2}, featuring triple and double M–Rh bonds, respectively.\textsuperscript{26,72}

\footnote{Portions reproduced from [1] with permission from the American Chemical Society.}
In light of this, we chose to incorporate more reactive first row transition metals into new early/late heterobimetallic complexes. Herein, is reported the synthesis of Co/Zr heterobimetallic complexes featuring Co–Zr multiple bonds and the ability of these metal–metal interactions to support coordinatively unsaturated species, including an unprecedented trigonal monopyramidal Zr complex.
B) Reduction Under a $N_2$ Atmosphere

In chapter 2, the synthesis and characterization of a family of Co/Zr heterobimetallic complexes linked by three derivatives of phosphinoamide ligands, including $\text{ClZr(MesNP}^\text{tPr}_2\text{)}_3\text{CoI}$ (5) and $\text{ClZr(}^\text{tPrNP}^\text{tPr}_2\text{)}_3\text{CoI}$ (6) was reported.\textsuperscript{14} It was found that the dative metal–metal interactions in these complexes facilitated two–electron reduction at potentials ~1 V more positive than expected for analogous monometallic complexes. Complex 5 was chemically reduced with excess Na/Hg, leading to the Co–bound dinitrogen product $(\text{THF})_3\text{Na–X–Zr(NMesP}^\text{tPr}_2\text{)}_3\text{Co–N}_2$ (9).

Scheme 3-1. Reduction of Zr–Co heterobimetallic derivatives under inert glovebox atmospheres.
Complex 9 shows a 0.22 Å decrease in the distance between the two metal centers in comparison with complex 5 (2.4112(3) Å vs 2.6280(5) Å), indicating a substantial increase in Co–Zr bond order upon two–electron reduction. Interestingly, the solid state structure revealed a strong Na–X interaction and a weakly bound Zr halide resulting from a trans–influence imparted on zirconium by the electron–rich cobalt center, suggesting the likelihood of Na–X extrusion from complex 9.

As shown in Scheme 3-1, extraction of complex 9 into benzene leads to precipitation of the labile NaX moiety, producing a red diamagnetic complex $(\text{THF})\text{Zr(MesNP}^\text{iPr}_2)_3\text{Co–N}_2$ (10), in which a bound THF molecule occupies the axial coordination site on zirconium. Replacement of the NaX with THF leads to a subtle increase in the $\nu(\text{N}_2)$ from 2023 cm$^{-1}$ in complex 9 to 2026 cm$^{-1}$ in complex 10. X–ray quality crystals of complex 10 were obtained, and the solid state structure is shown in Figure 3-1. The Zr–Co distance in complex 10 is 2.36 Å (avg. of two molecules in asymmetric unit), showing a slight contraction of the Zr–Co bond compared to 9 (2.4112(3) Å) and a 0.27 Å decrease in the Co–Zr distance from the dihalide heterobimetallic precursor 5 (2.6280(5) Å).14

Similarly, reduction of complex 6 with excess Na/Hg, followed by subsequent benzene extraction, leads to a neutral dinitrogen adduct, $\text{Zr(PrNP}^\text{iPr}_2)_3\text{Co–N}_2$ (11, Scheme 3-1). In contrast to the mesityl derivative, we were unable to isolate a NaX–bound product similar to complex 9, presumably due to the lability of the NaX
moiety. The IR stretch corresponding to the bound N₂ moiety of complex 10 was 2056 cm⁻¹, showing a dramatic increase in the N₂ vibrational frequency with respect to complex 11.

The structure of compound 11 is analogous to that of complex 10; however, rather than binding THF, the axial coordination site of complex 11 remains open (Figure 3-1). The geometry about Zr is trigonal monopyramidal, an unprecedented geometry for Zr,† with all three N–Zr–N bond angles within 0.1° of 120° (120.0°, 119.9°, and 120.0°) and N–Zr–Co angles of 89.7°. The Zr–Co distance in complex 11 is moderately shorter than that of complex 10 (avg. Zr–Co distance in three independent molecules in asymmetric unit of complex 11 = 2.33 Å). We attribute the drastic decrease in back-bonding from Co to N₂ in complex 11, as indicated by the increase in the ν(N₂) by 30 cm⁻¹ with respect to complex 10, to stronger involvement of the dₓz- and dᵧz-orbitals in the Co–Zr bonding interaction in the absence of sigma donation from THF to Zr.

* An IR spectrum of the crude product prior to C₆H₆ extraction showed multiple ν(N₂) bands: 2056, 2003, 1992 cm⁻¹.
† Based on a 2009 search of the CSD.
Figure 3-1. Displacement ellipsoid (50%) representations of complexes 10, 11, and 12. Zr–Co distances of complexes 10, 11, and 12 are 2.36(1), 2.33(1), and 2.14(1) Å, respectively (averages of two (complexes 10 and 12) or three (complex 11) molecules in asymmetric unit). All hydrogen atoms and the isopropyl methyl groups have been omitted for clarity.

Interestingly, reduction of complex 5 in an argon–filled glovebox in the absence of N₂ leads to an isolable diamagnetic green product, (THF)Zr(MesNPiPr₂)₃Co (12, Scheme 3-1). The solid state structure reveals that complex 12 features an open Co coordination site and a trigonal monopyramidal Co center (Figure 3-1). The absence of an apical ligand at Co appears to dramatically strengthen the bonding between Co and Zr: the Co–Zr bond length contracts to 2.14(1) Å.
C) **Analysis of Reduced N₂−Bound Complexes Via DFT**

To better understand the nature of the metal–metal bonds and the factors that maintain the open coordination sites on both the Zr and Co centers, electronic structure calculations were performed on complexes 10–12. Examination of the highest occupied molecular orbitals of complexes 10 and 11 (Figure 3-2A) reveals substantial Co–Zr bond character manifested in both σ− and π−bonding interactions through overlap of the d_{z^2}-orbitals (σ) and the d_{xz}- and d_{yz}-orbitals (π) of Co and Zr. Alternatively, the metal–metal interaction in the dihalide precursor, complex 5, was composed predominately of σ−character. A comparison of the orbitals of complexes 10 and 11 reveals the nature of their most notable differences: the coordination number of the Zr atom and the Δν(N₂) = 30 cm⁻¹.

Indeed, the orbitals involved in the stronger Co–Zr π−bond are the same orbitals participating in back–bonding to the N₂ π*−orbitals (Figure 3-2A), and competition with Zr for the electron density from the Co’s d_{xz}- and d_{yz}-orbitals leads to a higher ν(N₂). It can likewise be inferred that some of the electron density involved in binding to N₂ might have otherwise been involved in more pronounced Co–Zr bonding. To assess this hypothesis, the electronic structure of complex 12, the N₂−free analogue of complex 10, was determined (Figure 3-2B). Particularly striking in the frontier orbitals of complex 12 is the degree to which the three lowest energy orbitals exhibit Co–Zr bonding interactions, clearly forming one σ− and two π−bonds between the metal centers. This increase in M–M multiple bonding character is reflected in the contraction of the Co–Zr distance by ca. 0.2 Å between complexes 10 and 12.
Regarding the assessment of bond distances while making sure to take differences in atomic size into account, Cotton defined the “formal shortness ratio”:

\[ \text{FSR}_{AB} = \frac{D_{AB}}{R_1^A + R_1^B}, \]

where \( D_{AB} \) is the interatomic distance and the \( R_1 \) values are the radii of the two atoms (Co: 1.152 Å, Zr: 1.454 Å).\(^{75,76}\) Applying this method, we find the FSR of complexes \( 10, 11, \) and \( 12 \) to be 0.902, 0.891, and 0.818, respectively. For comparison, the FSR of complexes \( 5 \) and \( 6 \) are 1.00.\(^{14}\) Thus, complex \( 12 \) unequivocally holds the record for the shortest M–M distance in an early/late heterobimetallic complex in both absolute distance and FSR,\(^*\) greatly surpassing the Ti–Rh complex of Wolczanski et al. (FSR = 0.860)\(^ {72} \) and the Mo–Ru complexes of Collman et al. (FSR = 0.869, 0.857).\(^ {74} \)

\( ^* \) Based on a 2009 search of the CSD.
Figure 3-2. Depictions and energies of the frontier molecular orbitals of complexes 11 (A) and 12 (B). Note the presence of one σ–bond and two π–bonds strengthening the M–M interaction. Reduction Under a CO Atmosphere
Figure 3-3. Displacement ellipsoid (50%) representations of complexes 13 and 14 (A) and the linear, through-space, intramolecular interactions in a unit cell of complex 14 (B). Hydrogen atoms and substituents on all but one ligand have been omitted for clarity. Two Na\textsuperscript{+}-bound THF molecules per sodium have been omitted for visual clarity.

Complexes 10 and 11 showed no reactivity when reacted with various equivalents of CO (stoichiometries ranging from < 1 to excess). Rather than reacting the reduced complex directly with CO, complexes 5 and 6 were chemically reduced with 2.5 equivalents of Na/Hg under a CO atmosphere (Scheme 3-2). This lead to the terminally-bound cobalt–carbonyl products (THF)$_3$Na–X–Zr(MesNP\textsuperscript{i}Pr$_2$)$_3$Co–CO (13) and X–Zr(PrNP\textsuperscript{i}Pr$_2$)$_3$Co–CO–Na(THF)$_4$ (14) (Figure 3-3A), containing a carbonyl bound through the less electronegative carbon atom. Complexes 13 and 14 show...
decreased inter-metallic bond distances with values of 2.4677(3) Å and 2.5057(8) Å respectively (originally 2.6280(5) Å and 2.6309(5) Å in compounds 5 and 6), indicating a noteworthy increase in Zr–Co bond order upon reduction.

**Scheme 3-2. Synthesis of Zr/Co complexes 13–17.**

In comparison to the aforementioned Zr-Co complexes 10 and 11 reduced under N_2 (complex 10, d_{Zr-Co} = 2.36(1) Å and complex 11, d_{Zr-Co} = 2.33(1) Å), complexes 13
and 14 show slightly higher Zr-Co distances indicating a weaker bond between the two metals due to CO being a stronger π-acid than N₂. Competing with the Zr-Co orbital interactions, a halide coordinated apical to the Zr draws electron density away from the d₅²-orbital while a [Na(THF)ₙ]⁺ adduct ionically-coordinates to the halide or the CO’s oxygen atom, thus decreasing the σ-character of the Zr-Co bond. Interestingly, the Na(THF)ₙ⁺ adduct coordinates to different ends in each molecule, one to the terminal halide, Zr—X—Na(THF)ₙ (complex 13), and the other to the terminal oxygen atom of the carbonyl, Co—CO—Na(THF)ₙ (complex 14). The presence of the Na⁺ countercation interaction on the terminal carbonyl decreases the bond order, consequently making the CO more electrophilic in terms of its ligation to the Co center. This leads to increased π-character in the Co-CO bond and, contrasting the Co-N₂ interaction, more back-bonding into the π*-orbitals of the CO.

Analogous to the reduced N₂-containing complex 9, there is a Na−X interaction along with a Zr-bound halide, suggesting the likely displacement of Na−X from complex 13. Contrary to our expectation, Na−X extrusion from complex 13 did not occur readily at room temperature. Instead heat was required to drive precipitation of the sodium salt (Scheme 3-2). Analogous heating of complex 14 did not effectively extract the Zr-Co away from the sodium salt, producing a mixture of crude products which were not easily separable. The differing aptitudes toward extrusion between complexes 13 and 14 are most likely a result of the higher electron-donating ability of the iPr-P substituents

coordinated to the Co center. With a larger reservoir of electron density, the already electron-rich Co center is able to donate superfluous electron density into the LUMO of the carbonyl, adding stability to the highly electronegative oxygen atom.

In his review, Hughes\textsuperscript{78} suggests that CO preferentially binds to electron-rich Lewis-basic metal centers because of the stability imparted by the metal center’s electron-donation into the ligand’s $\pi^*$-orbitals.\textsuperscript{78-80} Therefore it is not unexpected that the resulting decrease in available electron density led to a larger Zr-Co bond distance, a lower Zr-Co bond order, and superior back-bonding contrasting with the analogous reduced-$\text{N}_2$ complexes. The extent of back-bonding in each complex can be measured by the amount of energy needed for vibration of the C-O bond, ergo, IR spectroscopy is a technique commonly used to measure bond activation and confirm the presence and type of CO interaction. Extrusion of Na–X into C\textsubscript{6}H\textsubscript{6} from complex 13 was successful when at elevated temperatures, producing a diamagnetic red solution of (THF)$\text{Zr(MesNPPr}_2)_3\text{Co−CO}$ (15).\textsuperscript{*} Table 3-2 lists the measured and calculated $\nu$(CO) stretching frequencies for the each major product’s axial coordinated carbonyl ligand, specifics of the IR stretches will be discussed vida infra.

The solid state structure of complex 13 (Figure 3-3A) shows a Zr–Co distance of 2.4677(3) Å, indicating a lower bond order than any of the N\textsubscript{2} bound species,\textsuperscript{14} but a higher bond order than either of the aforementioned carbonyl-bound moieties. The M-M distance measured from the solid state structure of complex 14 indicates that the Zr–Co

\textsuperscript{*} Complex Complex 15 can also be synthesized directly by the addition of CO\textsubscript{(g)} to a frozen solution of complex 12.
bond is weaker than the analogous interaction in complex 13. Other than the amide substituents, the structures differ in both their crystal packing orientation and the atom to which the Na$^+$ counteraction is coordinated. Complex 14’s crystal packing indicates an intramolecular interaction between the Na of one molecule and the halide of another, causing the crystals to line up along the axis containing the Zr-Co bond (Figure 3-3).

The through space distance between the Na$^+$ and the next molecule’s halide is too great for the possibility of a full σ- or π-type bonding interaction (Na—I = 3.6468(27) Å, Na—Cl = 4.0818(66) Å). It was first hypothesized that, perhaps, the Na—X distances were within the covalent radius, which would indicate a bonding interaction; Regardless of the methods used, the Na-X interactions are always greater than the sum of the covalent radii which indicates the absence of a bond. The most likely explanation for the intramolecular interactions is electrostatic forces which cause coordination and lead to the molecules orientating to maximize stability.
Complexes 16 and 17 were synthesized directly by stoichiometrically adding AgOTf, leading to oxidation by one-electron (Scheme 3-2). The solid state structures of complexes 15 and 16 show co-crystallization of two different molecules in a 1:1 ratio. This means that there are two molecules in the same unit cell, differing solely by the axial substituent bound to the Zr center (either THF or Cl). Interestingly, both complexes crystallized in the same THF/Cl ratio and the Zr–Co distance was identical in both co-crystallized complexes. The solid state structure of complex 17 has not yet been obtained.
D) Reactivity of Reduced Species with CO$_2$

Due to the differences in electronegativity between oxygen and carbon atoms, CO$_2$ has polarized bonds, which cause dipoles along each bond. The dipole means, the carbon atom has a positive charge and is more electrophilic than the outer, negatively charged oxygen atoms. The rich variety of CO$_2$ binding modes is a result of the charge distribution caused by the presence of the dipoles, although binding does not guarantee CO bond activation or cleavage.$^{6,7,81-87}$ The resonance and $\pi$-bond character of the molecule aid in the stability of the molecule, which can be seen in the thermodynamic parameters (Table 3-1). The various binding modes of CO$_2$ to homobimetallic and monometallic complexes (Figure 3-5) lead to very complicated product mixtures that have been extensively studied and characterized.$^{6,7,81,82,84-88}$ In stark contrast, few studies focusing specifically on the reactivity of early/late heterobimetallic complexes have been conducted.$^{89}$

<table>
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<td>- 26.4</td>
<td>- 57.8</td>
</tr>
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<td>+ 0.0509</td>
<td>+ 0.0472</td>
<td>+ 0.0451</td>
</tr>
<tr>
<td>$\Delta G_f^a$</td>
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<td>- 169.4</td>
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<th>Bending$^c$</th>
<th>Asym$_{C=O}^c$</th>
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<td>-</td>
<td>2342</td>
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<tr>
<td>Solid</td>
<td>-</td>
<td>660 and 653</td>
<td>2344</td>
</tr>
</tbody>
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Table 3-1. Standard Thermodynamic parameters for selected molecules and the vibrational frequencies associated with free CO$_2$.$^6$ $^a$Units of all thermodynamic parameters are in kcal/mol. $^b$Symmetric stretches can only be measured with Raman spectroscopy.$^{80}$ $^c$All vibration and bending frequencies are reported in cm$^{-1}$. 

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Complexes 10 and 11, when reacted with 1 eq of CO$_2$(g) (scheme 3-3), produced a mixture of products, the main being an orange–red complex that is sparingly THF soluble (Complexes 18 and 19). The product of complex 11 and CO$_2$ shows significant insolubility,* especially as the higher purity is achieved.† Full purification of the product was difficult to obtain due to similar product and byproduct solubility; however v(CO) stretches of the most pure samples† indicate labile substituents in the molecule and the $^1$H NMR spectra indicate lowering of the molecular symmetry. The reaction products are shown in Scheme 3-3, and significant v$_{\text{asym}}$(CO) stretching frequencies are shown in Table 3-2.

![Diagram of Scheme 3-4](image)

**Scheme 3-4.** Reaction of CO$_2$ with both derivatives of the reduced, dinitrogen–bound, Zr–Co.

The reaction of complex 11 with CO$_2$, much like its reduction under CO$_2$(g), has competing mechanisms that vie for preferential product formation. The crude reaction contains two major peaks one corresponding to pure complex 18 and the other signifying

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* Solvents attempted: THF, C$_6$H$_6$, pentane, Et$_2$O, and toluene. No solvent showed significant solubility of the product.
† Purity was assumed by analysis of $^1$H NMR.
what is most likely a labile coordination mode (1930 cm$^{-1}$ and 1882 cm$^{-1}$, respectively). Carbon monoxide, as well as CO$_2$, vibrational frequencies have been well documented.$^{7,80}$ Free CO(g) shows an asymmetric stretch at 2143 cm$^{-1}$, while free CO$_2$(g) shows an asymmetric stretch at 2349 cm$^{-1}$.\textsuperscript{6} Carbonyl stretching frequencies typically exhibit sharp ν(CO) bands between 2100 cm$^{-1}$ and 1800 cm$^{-1}$, although bands have been found to appear as low as 1600 cm$^{-1}$.\textsuperscript{80} Lower frequencies are indicative of how extensively the metal is able to back-bond into the carbonyl ligand because as the carbonyl becomes more electron-rich the oxygen atom needs less electron density to feel stable. As the oxygen becomes more electronically stable the CO bond weakens causing lengthening and requiring less energy for vibration.

![Diagram of CO$_2$ binding modes](image)

**Figure 3-4.** Examples of the variation in possible binding modes of CO$_2$ to metal centers.$^{7,87,90}$
The carbonyl of purified complex 18 has a vibrational frequency of 1926 cm\(^{-1}\), which correlates with the calculated value of 1912 cm\(^{-1}\). The bridging \(\mu\)-O group donates an electron pair to the Co’s orbitals which would help activate the carbonyl; however one of the \(\eta_2\)-phosphinoamide ligands dissociates from the Co center to lie solely coordinated to the Zr center. The \(^3\)Pr-P substituents coordinated to the Co center are highly electron donating and the absence of one counteracts the ability of the \(\mu\)-O to activate the CO. This effect can be seen when the \(\nu\)(CO) stretches of complex 18 are compared to the stretches obtained from the reactions of the bimetallic species with CO\(_{\text{g}}\) (Table 3-2).

The \(\nu\)(CO) stretches of the terminal carbonyls in complexes 13 and 16 present just lower than 1910 cm\(^{-1}\), showing small variation from the activation of complex 18. Complex 15, on the other hand, has a \(\nu\)(CO) = 1886 cm\(^{-1}\), showing the greatest activation of all complexes containing the MesNP\(^3\)Pr\(_2\) ligand derivative. The greater activation in complex 15 is due to the L-type ligand interaction the coordinated THF molecule has with the Zr center. The other complexes have X-type ligand interactions from halides (complexes 13 and 16) or an amide (complex 18), which share an electron with the Zr center, drawing away electron density rather than donating an electron pair like an L-type ligand. The subtle differences in the electronic interactions on the apical side of the Zr center are significant enough to affect the activation of the terminal CO.
Table 3-2. Calculated and experimentally collected ν(CO) bands for selected reactions. Terminal ligands (L) are coordinated η^2- to the Zr center. Bridging phosphinoamide ligands have been omitted for clarity. X represents either a Cl or I atom.

The reaction of complex 12 with CO₂ most likely produces an analogous structure to complex 18; however it has not yet been confirmed. Lacking a solid state structure, the characterization of complex 19 relies heavily on the ν(CO) bands and their comparison to analogous complexes. The spectrum of complex 19 exhibits a sharp ν(CO) band at 1880 cm⁻¹ indicating a greater activation of the carbonyl moiety than complex 18. While the rest of the complexes show single sharp ν(CO) stretches, complex 14 exhibits a second sharp stretch at 1752 cm⁻¹. A similar situation occurred in the vibrational spectra before the extraction of complex 10 into C₆H₆, which was caused by the lability of the coordinated Na⁺ counteraction.

In the case of complex 14, the extra ν(CO) band can be attributed to the coordination of a Lewis acid onto the oxygen atom of the terminal carbonyl, as seen in the crystal structure (Figure 3-3). Lewis-acidic species coordinating to terminal carboxyls cause a 100 cm⁻¹ – 200 cm⁻¹ decrease in the ν(CO) stretching frequency,⁸⁰ which would
explain the second $\nu$(CO) band at 1752 cm$^{-1}$. The $\nu$(CO) bands in the $\text{^{1}PrNP^{3}Pr_2}$ ligand derivative complexes do not exhibit frequencies above 1900 cm$^{-1}$ and show little variation except for complex 14. The difference from complex 13 is due to the differences in the electronic interactions caused by having more electron donating substituents on the amides bound to the Zr center in complex 14.

Complex 19 has one other vibrational characteristic which distinguishes it as most likely being analogous to complex 18, the bridging oxygen atom between the two metal centers. In 1976, Sniadoch and co-workers analyzed the vibrational spectra of various $\mu$–O species, discovering that as the M–O–M angle decreases, there will be an impressive increase in the symmetric vibrational band and a slight decrease in the asymmetric band.$^{91}$ A compound with a bridging $\mu_2$–O angle of $\theta \approx 100^\circ$ will have an asymmetric stretch $ca.$ $\sim750$ cm$^{-1}$ and a symmetric stretch $ca.$ $\sim560$ cm$^{-1}$. In comparison, both compounds 18 and 19 have bridging $\mu_2$–O angles $ca.$ 98$^\circ$. Complex 19 shows stretching bands at $\nu$(CO)$_{\text{asym}} = 763$ cm$^{-1}$ and $\nu$(CO)$_{\text{sym}} = 545$ cm$^{-1}$ which agree with the trends proposed by literature sources.$^{80,91,92}$ While the $\nu$(CO) bands are not fully conclusive, they provide substantial information about the expected structure and electronics of the complexes.

* DFT Calculations were used to analyze the M-O-M angle in complex 19 due to lack of a solid state structure.
**E) Experimental Section**

**I. General Considerations**

All syntheses reported were carried out using standard glovebox and Schlenk techniques in the absence of H₂O and O₂, unless otherwise noted. Benzene, pentane, Et₂O, THF, and toluene were degassed and dried by sparging with N₂ gas followed by passage through an activated alumina column. All solvents were stored over 3 Å molecular sieves; THF used in the reductions of complexes 5 and 6 was dried over alumina before use. Deuterated benzene was purchased from Cambridge Isotope Laboratories, Inc., degassed via repeated freeze−pump−thaw cycles, and dried over 3 Å molecular sieves. Solvents were frequently tested using a standard solution of sodium benzophenone ketyl in THF to confirm the absence of oxygen and moisture. Complexes 5, 6, and 9 were synthesized using literature procedures.¹⁴ All other chemicals were purchased from commercial vendors and used without further purification. NMR spectra were recorded at ambient temperature on a Varian Inova 400 MHz instrument. ¹H and ¹³C NMR chemical shifts were referenced to residual solvent. ³¹P NMR chemical shifts were referenced to 85% H₃PO₄. IR spectra were recorded on a Varian 640−IR spectrometer controlled by Resolutions Pro software. UV–Vis spectra were recorded on a Cary 50 UV–Vis spectrophotometer using Cary WinUV software. Elemental microanalyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ.
II. X-ray Crystallography Procedures

All operations were performed on a Bruker−Nonius Kappa Apex2 diffractometer, using graphite−monochromated Mo Kα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software. Preliminary cell constants were obtained from three sets of 12 frames. Structures were solved using SIR−92, and refined (full−matrix−least−squares) using the Oxford University Crystals for Windows program. All ordered non−hydrogen atoms were refined using anisotropic displacement parameters; hydrogen atoms were fixed at calculated geometric positions and allowed to ride on the corresponding carbon atoms. Fully labeled diagrams and data collection and refinement details are included in the appendix of the Supporting Information file. Further crystallographic details may be found in the accompanying CIF files.

III. Computational Details

All calculations were performed using Gaussian03−E.01 for the Linux operating system. Density functional theory calculations were carried out using a combination of Becke’s 1988 gradient−corrected exchange functional and Perdew’s 1986 electron correlation functional (BP86). A mixed−basis set was employed, using the LANL2TZ(f) triple zeta basis set with effective core potentials for cobalt and zirconium, Gaussian03’s internal 6−311+G(d) for heteroatoms (nitrogen, phosphorus, and oxygen), and Gaussian03’s internal LANL2DZ basis set (equivalent to D95V) for carbon and hydrogen. Using crystallographically determined geometries as a starting
point, the geometries were optimized to a minimum, followed by analytical frequency
calculations to confirm that no imaginary frequencies were present.

IV. (THF)Zr(NMesPiPr2)3Co–N2 (10)

Solid complex 314 (0.085 g, 0.06 mmol) was dissolved in C6H6 (5 mL) and
filtered through Celite. Solvent was removed from the filtrate in vacuo to yield
spectroscopically pure product as a maroon solid (0.061 g, ~100%). 1H NMR (400 MHz,
C6D6): δ 6.77 (s, 6H, Mes), 3.02 (br m, 4H, THF), 2.51 (m, 24 H, Mes–Me + CH(CH3)2
overlapping), 2.12 (s, 9H, Mes–Me), 1.78 (m, 18H, CH(CH3)2), 1.56 (m, 18H,
CH(CH3)2), 0.49 (br m, 4H, THF). 31P64 NMR (161.8 MHz, THF–d8): δ 44.4 (br s). 13C64
NMR (100.5 MHz, C6D6): δ 149.5 (ipso–Mes), 134.8 (Mes), 131.1 (Mes), 129.4 (Mes),
70.0 (THF), 45.6 (PC(CH3)2), 24.5 (THF), 23.6 (PC(CH3)2), 23.5 (PC(CH3)2 + Mes–Me
overlapping), 21.0 (Mes–Me). IR: 2026 cm−1 (KBr solution cell, THF); 2028 cm−1 (KBr
pellet). UV–Vis (C6H6, λ(nm) (ε, M−1 cm−1)): 360 (4000), 510 (sh), 669 (sh) 856 (130).
Repeated elemental microanalysis results were consistently low in %N, suggesting that
the lability of the N2 moiety precludes characterization using this method.

V. Zr(iPrNPiPr2)3Co–N2 (11)

A 0.5% Na/Hg amalgam was prepared in THF (10 mL) from 17.8 mg Na (0.775
mmol) and 3.6 g Hg. After vigorously stirring the amalgam a solution of complex 614
(0.259 g, 0.310 mmol) in THF (2 mL) was added. After three hours of stirring, the
resulting red/brown solution was filtered away from the amalgam and the volatiles were removed in vacuo. The resulting solid was extracted into C₆H₆ and filtered through Celite. Removal of volatiles from the filtrate in vacuo yielded complex 11 as an analytically pure red/brown solid (0.0963 g, 44.5%). Crystals suitable for X–ray diffraction were grown by vapor diffusion of pentane into a concentrated THF solution.

¹H NMR (400 MHz, C₆D₆): δ 3.60 (m, 3H, NCH), 2.70 (m, 6H, PCH), 1.37 (m, 36H, PC(CH₃)₂), 1.08 (d, 18H, NC(CH₃)₂). ³¹P (161.8 MHz, C₆D₆): δ 39.0 (br, s).

¹³C NMR (100.5 MHz, C₆D₆): δ 48.5 (NC(CH₃)₂), 32.0 (PC(CH₃)₂), 31.1 (NC(CH₃)₂), 21.4 (PC(CH₃)₂), 20.0 (PC(CH₃)₂). UV−Vis (THF, λ(nm) (ε, M⁻¹ cm⁻¹)): 359 (630), 499 (80).


VI. (THF)Zr(MesNPᵢPr₂)₃Co (12)

A 0.5% Na/Hg amalgam was prepared in THF (10 mL) from 7.0 mg Na (0.30 mmol) and 1.4 g Hg. After vigorously stirring the amalgam a solution of complex 5¹⁴ (6) (0.129 g, 0.121 mmol) in THF (2 mL) was added. The solution gradually changed color from a light green to an intense dark green. After two hours of stirring, the resulting green solution was filtered away from the amalgam and the volatiles were removed in vacuo. The remaining green solids were extracted into pentane (5 mL) and filtered through Celite. Removal of volatiles from the filtrate resulted in analytically pure complex 12 as a green microcrystalline solid (0.097 g, 83.2%). Crystals suitable for X–ray diffraction were grown by slow evaporation of a concentrated Et₂O solution of 6 at −35°C. ¹H NMR
(400 MHz, C₆D₆): δ 6.83 (s, 6H, Mes), 3.22 (m, 6H, CH(CH₃)₂), 2.79 (br s, 4H, THF)
2.58 (s, 18 H, Mes–Me), 2.15 (s, 9H, Mes–Me), 1.63 (m, 18H, CH(CH₃)₂), 1.52 (m, 18H,
CH(CH₃)₂), 0.72 (br m, 4H, THF). ³¹P⁶⁴ NMR (161.8 MHz, C₆D₆): δ 34.6 (br s). ¹³C⁶⁴
NMR (100.5 MHz, C₆D₆): δ 150.6 (ipso–Mes), 134.8 (Mes), 130.4 (Mes), 129.3 (Mes),
70.2 (THF), 43.0 (PC(CH₃)₂), 24.9 (THF), 24.2 (PC(CH₃)₂), 22.8 (Mes–Me), 22.3
(PC(CH₃)₂), 21.1 (Mes–Me). UV–Vis (C₆H₆, λ (nm) (ε, M⁻¹ cm⁻¹)): 367 (2800), 634
H, 7.99; N, 4.30

VII. (THF)₅Na–X–Zr(MesNPⁱPr₂)₃Co–CO (13)

A 0.5% Na/Hg amalgam was prepared in a Schlenk tube in THF (10 mL) from 18
mg Na (0.79 mmol) and 3.7 g Hg. The solution was frozen and a cold solution of
complex 5¹⁴ (0.170 g, 0.159 mmol) in THF (5 mL) was carefully layered on top of the
frozen Na/Hg amalgam in the Schlenk tube, allowing it to freeze without reacting with
the compounds in the other layers. Once the two–layer mixture was frozen, the
headspace of the flask was evacuated and backfilled with 1 atm CO. The tube was sealed
and the mixture was allowed to thaw and warm to room temperature with vigorous
stirring over the course of 3 hours, at which point the color of the solution changed from
green to orange. The orange solution was filtered through Celite and volatiles were
removed from the filtrate in vacuo. The resulting solids were re–dissolved in minimal
THF, layered with pentane, and stored at −35°C, resulting in orange crystalline product which could be isolate by filtration (0.0857 g, 38.1%).

VIII. \([\text{X−Zr}^{\text{iPrNP}_{2}}\text{Co−CO−Na(THF)}_{4}]_{n}\) (14)

A 0.5% Na/Hg amalgam was prepared in THF (10 mL) in a Schlenk tube from 18 mg Na (0.79 mmol) and 3.7 g Hg. The solution was frozen and a cold solution of complex 6\textsuperscript{14} (0.170 g, 0.159 mmol) in THF (5 mL) was carefully layered on top of the frozen Na/Hg amalgam in the Schlenk tube, allowing it to freeze without reacting with the other layers. Once the two-layer mixture was frozen, the headspace of the flask was evacuated and backfilled with 1 atm CO. The tube was sealed and the mixture was allowed to thaw and warm to room temperature with vigorous stirring over the course of 2 hours, at which point the color of the solution changed from green to orange. The orange solution was filtered through Celite and volatiles were removed from the filtrate in vacuo. The resulting solids were redissolved in minimal THF and stored at −35°C, resulting in an orange crystalline product that could be isolate by filtration (0.0857 g, 38.1%). \(^1\)H NMR (400 MHz, \(\text{C}_6\text{D}_6\)): IR. UV−Vis \(\lambda(\text{nm}) (\varepsilon, \text{M}^{-1}\text{cm}^{-1})\).

IX. \((\text{THF})\text{Zr(MesNP}_{2})\text{Co−CO} (15)\)
A 0.5% Na/Hg amalgam was prepared in THF (10 mL) in a Schlenk tube from 18 mg Na (0.79 mmol) and 3.7 g Hg. The solution was frozen and a cold solution of 5 (0.170 g, 0.159 mmol) in THF (5 mL) was in the Schlenk tube on top of the frozen Na/Hg amalgam. Once the two-layer mixture was frozen, the headspace of the flask was evacuated and backfilled with 1 atm CO. The tube was sealed and the mixture was allowed to thaw and warm to room temperature with vigorous stirring over the course of 3 hours, at which point the color of the solution changed from green to orange. The orange solution was filtered through Celite and volatiles were removed from the filtrate in vacuo. The resulting solids were redissolved in minimal THF, layered with pentane, and stored at −35°C, resulting in orange crystalline product which could be isolate by filtration (0.0857 g, 38.1%).

X. \((\text{THF})\text{Zr} (\text{MesNP}^i\text{Pr}_2)_3\text{Co−CO} (16)\)

A solution of \((\text{THF})\text{Zr} (\text{MesNP}^i\text{Pr}_2)_3\text{Co} (g, \text{mmol})\) in THF (mL) was placed in a Schlenk tube equipped with a stir bar and sealed with a Teflon valve. The solution was frozen, then the headspace of the flask was evacuated and backfilled with 1 equivalent of CO using a known-volume gas bulb and partial pressure methods. The Schlenk tube was sealed and the solution was allowed to warm to room temperature and stir for 30 minutes as the color rapidly changed from green to red. Solvent was removed from the resulting mixture in vacuo. $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ 6.77 (s, 6H, Mes), 2.73 (m, 6H, $CH(CH_3)_2$), 2.57 (m, 4H, THF), 2.47 (s, 18H, Mes-Me), 2.13 (s, 9H, Mes-Me), 1.85 (m, 18H, $CH(CH_3)_2$), 1.53 (m, 18H, $CH(CH_3)_2$), 0.56 (m, 4H, THF). $^{31}$P NMR (162 MHz,

Found: C, 59.82; H, 8.19; N, 4.14.
Zirconium–Cobalt heterobimetallics species have been synthesized using Lewis-acidic early transition metals acting as Z-type ligands, drawing electron density away from an electron–rich, Lewis-basic late transition metal. The highly-polarized dative Co→Zr interaction provided a shift in the reduction potential of the complex allowing reduction to occur at a more positive potential, thus requiring less energy to drive the reduction. The electron deficient Zr center’s trans–Co positioning, effectively allows it to compete with π–acid type ligand, such as N₂ or CO, bound to the opposite side of the Co atom. In the absence of a π–acid ligand, the Zr center is able to pull a greater amount of electron density away from the Co center, thereby strengthening the Zr-Co interaction and increasing the bond order.

The metals have a significant amount of influence over how effectively a ligand is able to bind to the opposing metal center due to the orbital interactions producing the trans-effect. For example, the trans–influence imparted by Co’s dₓ²-orbital on the opposite coordination site in the Zr center of Zr(PrNPPr₂)₃Co-N₂ (complex 11) is so strong in σ-character, it stabilizes the apical coordination site of the Zr center enough to preserve the unoccupied coordination site, resulting in an unprecedented Zr coordination geometry. In contrast, trans-effect imparted on the Co center via the Zr’s dₓz- and dᵧz-orbitals decreases the amount of back-bonding that Co can provide to the π*-orbitals of the coordinated ligand, diminishing the activation and weakening the Co-L interaction.
This tandem cooperation between the electronics of the two metal centers allows the bimetallic complex to react with a large number of molecules and the flexible nature of the ligand system allows for geometric distortions at the metal centers to better allow coordination and reactivity. Confirmed via solid state structure determination and spectroscopic techniques, reduced early/late Zr-Co heterobimetallics can activate and fully cleave an oxygen atom from CO$_2$ at room temperature and pressure. Carbon dioxide, while moderately reactive in terms of coordination to metals, is highly thermodynamically stable and strongly resists full activation and consecutive cleavage of its bonds. The tunable redox potential and exceptional reactivity toward small molecule substrates make early/late heterobimetallics excellent candidates for the production of alternative fuel sources from small molecule sources.
Chapter 5: Appendix: Supporting Figures and Tables

Figure A5-1. Carbon dioxide trend over the last 50 years. Data gathered from the Mauna Loa laboratory.
Scheme A51. The top 20 countries and their total 2006 carbon dioxide emissions (million metric tons).
Figure A5-2. Carbon dioxide emissions per capita of selected countries in 1990 (blue), 2000 (red), and in 2006 (green).
Scheme A5-2. Catalytic cycle of anaerobic Acetyl–CoA Synthase/CODH showing the oxidation of carbon monoxide and the reduction of H₂O to H₂.
Figure A5-3. The proposed structure of the active site of the aerobic [Mo−Cu−S] containing CODH when CO$_2$ has coordinated between the metals. Notice the geometry around the copper center has deviated from the typical linear geometry expected for a 2 coordinate metal center. Also, a sulfur atom is bridging the Mo(IV) and the central carbon, stabilizing CO$_2$ coordination and aiding in the activation of the C—O bond.
Scheme A5-3. Catalytic cycle of the aerobic [Mo–Cu–S] enzyme showing the oxidation of CO and the reduction of H₂O to H₂.
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Table A5-1. X-ray Diffraction Experimental Details for ICo(Ph₂PN/Pr)₃ZrCl (4), ICo(Pr₂PNMes)₃ZrCl (5), and ICo(Pr₂PN/Pr)₃ZrCl (6).

*R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \quad wR2 = [\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}]^{1/2}
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**Table A5-2.** Xray Diffraction Experimental Details for (Ph₂PNHPr)₂CoI₂ (7), (Ph₂PNHPr)₃CoI (8), and [N₂Co(Pr₂PNMes)₃ZrX][Na(THF)₅] (9).
Figure A5-4. Crystal structure of reduced complex A. Reduction under a CO atmosphere rather than N2 affords a two electron reduced carbonyl product with a halide coordinated linearly between a Na atom and the Zr center.
Figure A5-5. Co–crystallized structures of Co–bound carbonyl complexes 10 and 11. A THF molecule and a halide are competing for coordination and were found to be in approximately a 50:50 crystallization ratio.
Figure A5-6. Crystal structure of \([\text{ClZr}^\text{II}(\text{PrNPPr})_3\text{Co}−\text{CO−}]_2−\text{Na(THF)}_4\).
Figure A5-7. Crystal structure of \((\text{iPr}_2\text{PNMes})\text{Zr(MesNPr}_2\text{µO)}\text{Co−CO).}
Chapter 6: References

(2) EPA, U. S.; United States Environmental Protection Agency; Vol. 2011.