Early-Late Heterobimetallic Complexes Linked by Phosphinoamide Ligands: Tuning Redox Potentials and Small Molecule Activation

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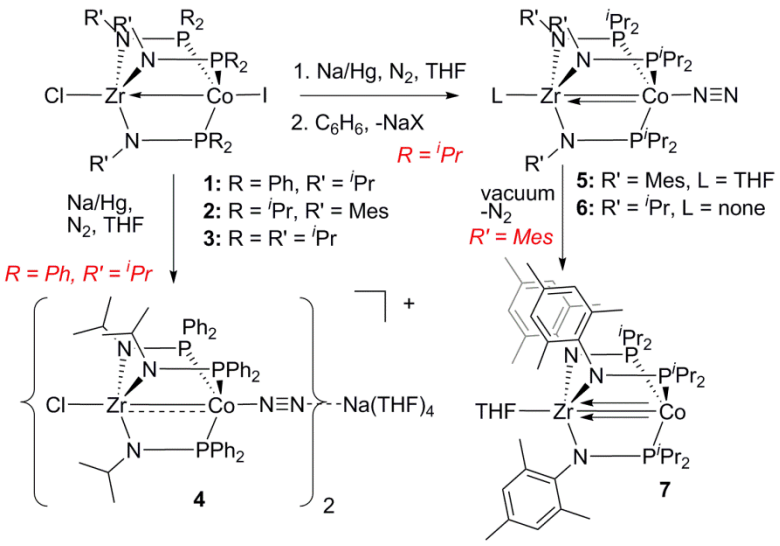
Explicit Description of Specific Objectives Pursued and Results Obtained

(a) Extensive Description of Results

During the 5-year funding period, our research focused on fundamental studies of the nature of metal-metal interactions in our originally reported early/late Zr/Co heterobimetallic complexes,[1] the factors that affect these interactions, the reactivity of Zr/Co complexes towards small molecule activation, the development of catalytic applications of Zr/Co complexes, the extension of the tris(phosphinoamide) framework to new metal-metal combinations containing two first row metals, and the investigation of late transition metal homobimetallics in which each metal center occupies a dramatically different coordination environment. Prior support has resulted in 27 publications in peer-reviewed journals,[2-28] including 3 invited review articles.[7, 9, 23] As detailed below, these studies of C_3-symmetric systems have resulted in a deeper understanding of metal-metal multiple bonding involving first row transition metals, and have provided insight into the key design principles that promote cooperative reactivity with bimetallic systems.

Fundamental Studies of Electronic Structure and Bonding in Heterobimetallic Zr/Co Complexes. For our initial investigation, we chose to investigate a family of Zr/Co complexes - ICo[Ph_2PN^iPr]$_3$ZrCl (**1**), ICo[$^iPr_2PNMes$]$_3$ZrCl (**2**, Mes = 2,4,6-trimethylphenyl) and ICo[$^iPr_2PN^iPr$]$_3$ZrCl (**3**) – modulating steric and electronic properties using variations in alkyl and aryl substituents on both the phosphorus and nitrogen atoms.[1] A computational investigation using density functional theory (DFT) revealed Co→Zr donor-acceptor interactions from the filled d_{z^2} orbital on Co to the empty d_{z^2} orbital on Zr, with stronger interactions in the case of the more electron-rich Co centers in $^iPr_2P$-substituted complexes **2** and **3** that are also manifested in a shorter Co-Zr interatomic distance (2.63 Å for **2** and **3** vs 2.73 Å for **1**). Upon finding that these complexes were ~ 1.0 V easier to reduce than their monometallic Co tris(phosphine) analogues using cyclic voltammetry, the chemical reduction of these complexes was investigated. Chemical reduction of bulk samples of **1**-**3** under N_2 leads to isolation of two-electron reduced dinitrogen-bound species [{N_2Co[Ph_2PN^iPr]$_3$ZrCl}$_2$-(Na(THF)$_4$)]$^+$ (**4**), N_2Co[$^iPr_2PNMes$]$_3$Zr(THF) (**5**) and N_2Co[$^iPr_2PN^iPr$]$_3$Zr (**6**), respectively (Scheme 1).[3] In all of these cases, the increase in electron density upon reduction leads to contraction of the intermetallic Co/Zr distance (e.g. 2.54 Å (**4**); 2.36 Å (**5**); 2.33 Å (**6**)), and in the case of the electron-rich $^iPr_2P$-substituted complexes **4** and **5**, the Zr-bound halide *trans* to the Co is labilized to open a coordination site at Zr.

Scheme 1.



Computational and spectroscopic investigations of metal-metal interactions. Electronic structure calculations on **5** indicate that in addition to the Co-Zr bond resulting from overlap of the d_{z2} orbitals (σ) there is also substantial overlap between the d_{xz} and d_{yz} orbitals (π) of Co and Zr, as shown in Figure 1. Since the orbitals involved in this Co→Zr π-bonding interaction are the same orbitals participating in π-backbonding to N_2, the bond order is best described as 1σ + 2(1/2π) bonds. This phenomenon is also manifested in a relatively high infrared N_2 stretch compared to monometallic Co analogues as the result of weakened π-backbonding. Removal of the coordinated N_2 from **5** leads to the coordinately unsaturated complex Co[^{i}Pr$_2$PNMes]$_3$Zr(THF) (**7**), in which a full Co→Zr triple bond with an intermetallic distance of 2.14 Å is achieved (Scheme 1).[3] While the presence of a Zr-bound halide in complex **4** leads to reactions essentially identical to a reduced monometallic Co complex,[4] the highly reduced, effectively coordinatively unsaturated heterobimetallic molecules **5**-**7** are poised to react with a wide variety of substrates at either metal center. Indeed, diverse examples of reactivity are observed (*vide infra*), but to understand the origin of these transformations, it is important to first understand the nature of the Co-Zr σ bond in **5**. The question of whether this bond is best described as "dative" or "polar covalent" could also be posed in terms of the effective oxidation states of Co and Zr, so to address this question, complex **5** along with a series of structurally similar reference complexes were examined using X-ray Absorption Near Edge Structure (XANES) spectroscopy in collaboration with the research team of Jeff Miller at Argonne National Laboratory. Upon examination of both Zr and Co K-edge XANES spectra of **5** and comparison to compounds of known oxidation state, it was determined definitively that complex **5** is best described as a Zr^{IV}/Co^{-I} zwitterionic complex, as depicted in Figure 2.

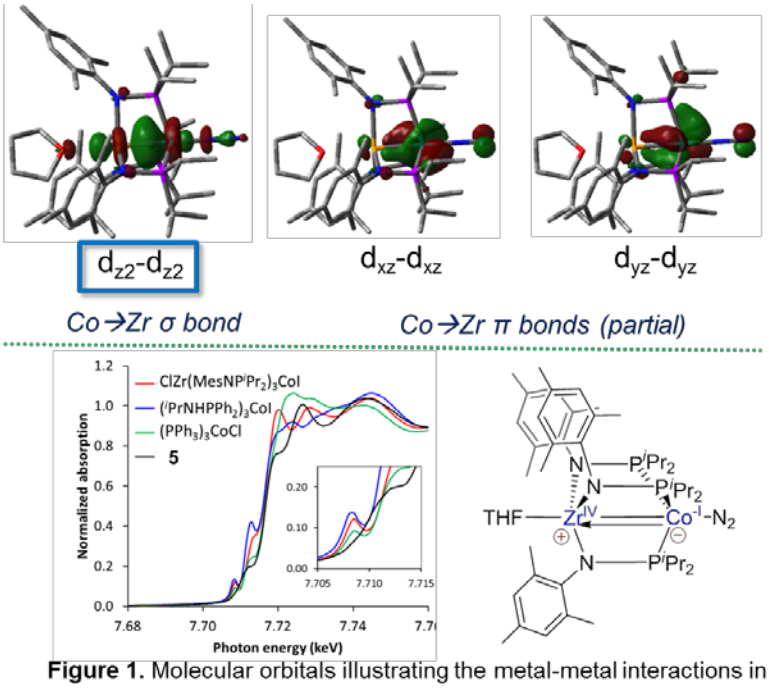


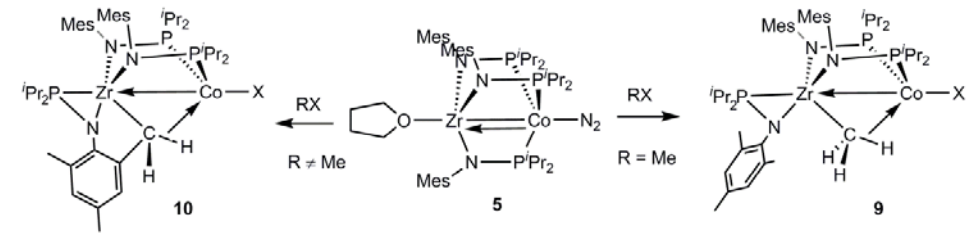
Figure 1. Molecular orbitals illustrating the metal-metal interactions in complex **5** (top), and Co K-edge XANES spectra of complex **5** and reference compounds of known oxidation state, revealing a zwitterionic Zr^{IV}/Co^{-I} description as depicted on the right (bottom).

Sensitivity of metal-metal interaction to ligand variations. Several systematic studies have been undertaken to explore the effect of ancillary ligands on metal-metal interactions. Using a Zr/Pt model system, $X_2Zr(^iPrNPPh_2)_2PtMe_2$, it was found that the identity of the Zr-bound ligands X^- has a substantial effect on the Pt→Zr dative interactions.[2] The Pt-Zr interatomic distance increased with electron-donating ability of X^- in the order $Cl^- < CH_2SiMe_3^- < NMe_2^-$, demonstrating that the Lewis acidity of Zr could be modified using ancillary ligands to tune the strength of the metal-metal interaction. Similarly, we had already shown a dramatic difference in the metal-metal interactions and reactivity of Zr/Co complexes upon varying the

phosphinoamide phosphorus substituent from Ph to ^{i}Pr (*vide supra*), with much stronger metal-metal interactions and more interesting cooperative reactivity in the presence of the more electron-rich alkyl phosphine substituents.[1, 4] Recently, we also demonstrated that variations in the N-aryl amide substituents also lead to dramatic differences in the reactivity of reduced Zr/Co complexes. In a recent publication,[27] we demonstrated that changing the mesityl substituents of complex **5** to *m*-xylyl groups in $N_2Co[^{i}Pr_2PNXyl]_3Zr(THF)$ (**8**, Xyl = 3,5-dimethylphenyl) increases the infrared N_2 stretching frequency from 2026 to 2045 cm^{-1}. This electronic difference also manifests itself in decreased reactivity of **8** compared to **5**.[27]

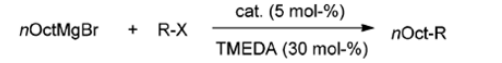
Small Molecule Activation and Catalysis. With a family of heterobimetallic Co/Zr complexes in various redox states already in hand, we examined their utility in small molecule activation reactions and catalysis. Owing to the labile ligands or open coordination sites at both the Co and Zr sites in $^{i}Pr_2P$-substituted reduced complexes **5-7**, these two complexes were the focus of these studies. In most cases, we have found that N_2-free complex **7** reacts similarly to complex **5**, so most of the efforts discussed below have been focused on the reactivity of complex **5**.

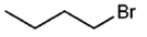
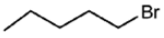
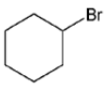
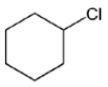
Scheme 2



Reactivity towards C-X Bonds and catalytic cross-coupling. Complex **5** was shown to react rapidly with alkyl halides RX to form either the well-defined oxidative addition product **9** (R = Me) or intramolecular C-H activation products **10** (RX = EtI, ^{i}PrI, chlorocyclohexane), as shown in Scheme 2.[4] We saw this as an opportunity to investigate C-C bond forming cross-coupling reactions, since (1) most cross-coupling reactions are catalyzed by noble metals such as Pd, and Zr and Co are both cheaper and more Earth-abundant, (2) cross-coupling with alkyl halide reactions are rare, given the propensity for 2nd and 3rd row metal alkyls to undergo β-hydride elimination, and (3) organic chloride substrates are known to be the most difficult to activate owing to the strength of the C-Cl bond, but our Zr/Co complexes can very rapidly activate these σ bonds. All three Zr/Co derivatives **1-3** were shown to be catalysts for the coupling of *n*-octylMgBr with a series of primary and secondary alkyl halides (Table 1). Notably, prior to our report there were no previous reports of Co catalysts with activity towards alkyl chlorides, and a monometallic analogue of heterobimetallic complex **1**, $ICo(Ph_2PNH^{i}Pr)_3$, was also inactive towards alkyl chlorides. This result implies that the presence of Zr is unequivocally responsible for the enhanced activity we observed. Preliminary studies into the mechanism of this reaction in an effort to understand the individual roles of both Zr and Co have revealed that

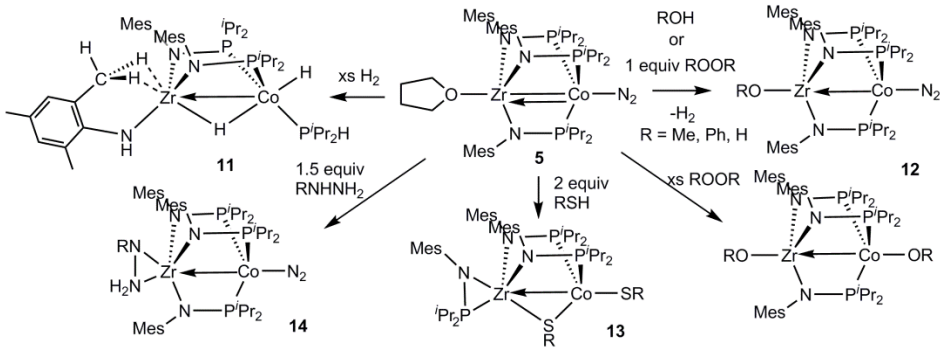
Table 1. Results of Kumada coupling reactions using heterobimetallic Zr/Co catalysts **1-3**.



Entry	R–X	% Yield[a]		
		Cat. **1**	Cat. **2**	Cat. **3**
1		62.9	81.9	83.3
2		28.0	45.8	77.2
3		92.6	95.4	99.1
4		63.7	93.2	99.0
5		37.5	55.9	77.9

the reaction proceeds via a radical pathway, despite the overall two-electron transformations occurring.

Scheme 3

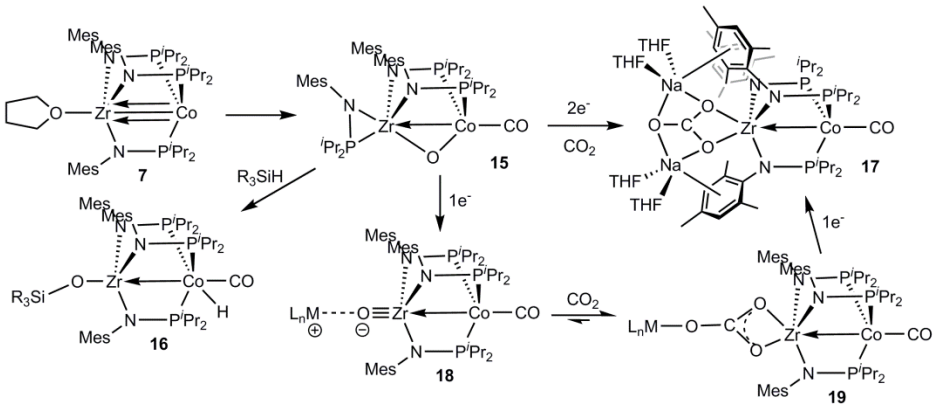


Element-hydrogen bond activation. In light of the ability of **5** to oxidatively add σ bonds across its metal-metal bond, the reactivity of **5** towards dihydrogen was investigated. Unfortunately, while **5** does react with excess hydrogen to cleave two molecules of H_2, H-H activation is also accompanied by P-N bond cleavage to cleanly afford product **11** (Scheme 3).[4] Although this reaction is not productive as it involves ligand decomposition, this result inspired our later work into catalytic hydrosilylation chemistry (*vide infra*). Turning our attention to O-H and S-H bonds, we have recently discovered that the O-H bonds in phenols, alcohols, and even water can be activated readily by **5** at room temperature via a one-electron process, to generate one-electron oxidized complexes of the general form RO-Zr(MesNP^{i}Pr$_2$)$_3$CoN$_2$ (**12**, Scheme 3), with concomitant release of 0.5 equiv H_2.[20] On the other hand, PhSH reacts via a two-electron oxidative addition process, generating the bis(thiolate) complex (MesNP^{i}Pr$_2$)Zr(MesNP^{i}Pr$_2$)$_2$(μ-SPh)CoSPh (**13**, Scheme 3). To further investigate these mechanisms, we have examined similar reactivity using organic peroxides ROOR, confirming that sequential one-electron transfer pathways are at play and that product preferences are dictated by hard/soft acid/base concepts. Similar one-electron dissociative electron transfer reactions were observed when **5** was treated with hydrazine derivatives $RNHNH_2$. As shown in Scheme 3, treatment of **5** with $RNHNH_2$ affords the one-electron oxidized Zr-hydrazido complex (η^2-RNNH$_2$)Zr(MesNP^{i}Pr$_2$)$_3$CoN$_2$ (**14**).

Carbon Dioxide. Perhaps the most interesting small molecule activation reactivity we have uncovered with our Zr/Co systems is the reaction between reduced complex **7** and carbon dioxide. Complex **7** readily reacts with one equivalent of CO_2 at temperatures well below room temperature to cleanly generate complex **15**, in which a thermodynamically stable C-O double bond has oxidatively added across the Co-Zr bond (Scheme 4).[5] While complex **15** reacts readily with both electrophiles (e.g. H^+, TMS^+, Me^+) and silanes (R_3SiH), the resulting products such as **16** (Scheme 4) feature strong Zr-O bonds that are resistant to cleavage under mild conditions,[5] making it very difficult to envision a method to make this stoichiometric CO_2 addition part of a viable catalytic CO_2 reduction cycle. We also ascertained via cyclic voltammetry that the CO_2 activation product **15** could be re-reduced at relatively mild potential (~ -1.8 V vs Fc/Fc^+), prompting us to investigate the chemical reduction of **15** in an effort to understand the stoichiometric steps in a potential electrocatalytic CO_2 reduction cycle. Reduction of **15** with excess Na/Hg results in the doubly-reduced κ^2-CO_3^{2-} dianion **17** (Scheme 4). Contrary to the stoichiometry of the reaction, this product contains an additional CO_2 equivalent and reduction of **15** in the presence of extrinsic CO_2 improves the yield of **17** substantially. More carefully controlled chemical reduction of **15** affords the unusual Zr-oxoanion $^-$[O-Zr(MesNP^{i}Pr$_2$)$_3$Co(CO)] (**18**) in very low yield (Scheme 4).[5] After developing an alternative

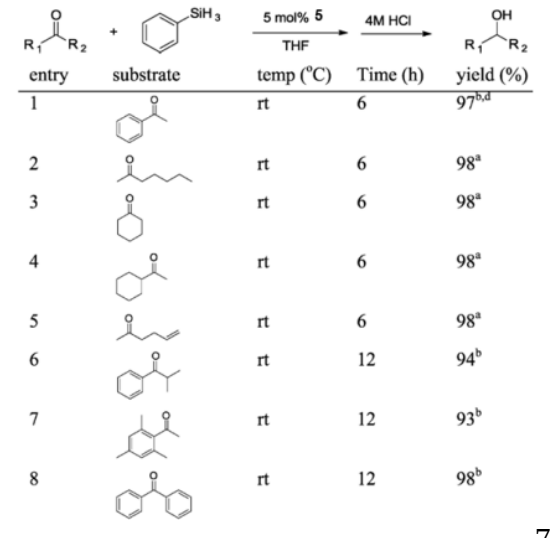
synthetic route to **18**,[13] its reactivity towards an additional equivalent of CO_2 was investigated. Indeed, the oxoanion reacts readily with CO_2 to generate the κ^2-carbonate complex **19**, as shown in Scheme 4, and a ^{13}C labeling experiment reveals that CO_2 binding is reversible.[13] Complex **19** can be further reduced to **17**, demonstrating the stoichiometric steps at play in the formation of **17** from **15** and extrinsic CO_2 under reductive conditions. As would be expected for an early metal oxo anion, the oxo ligand of **18** reacts readily with electrophiles, but in all cases inert Zr-O linkages remain problematic.[13]

Scheme 4



Reactivity towards C=E double bonds and catalytic hydrosilylation. Upon discovering such facile reactivity towards the polar C=O bonds in CO_2, we chose to investigate ketone/aldehyde hydrosilylation chemistry (in hopes of eventually applying this to the hydrosilylation of CO_2 itself). As shown in Table 2, the reduced Zr/Co complex **5** is an active catalyst for the hydrosilylation of ketones.[21] Most interesting to us, however, is that monometallic Zr complexes (e.g. $ClZr(MesNP\textit{i}Pr_2)_3$) are completely ineffective catalysts (0% conversion), and monometallic Co complexes (e.g. $ICo(PPh_3)_3$ or $ICo(Ph_2PNH^{\textit{i}}Pr)_3$) are far less active (30-45% yield with benzophenone under identical conditions). In an effort to further understand the specific roles of Zr and Co in this catalytic process, the mechanism was investigated using stoichiometric reactions. We found that complex **5** does not react with $PhSiH_3$ but does react readily with ketones. Treatment of **5** with benzophenone affords the isobenzopinacol product **20**, resulting from coupling of two benzophenone ketyl radicals through their benzylic and para positions (Scheme 5).[21] Product **20** is a competent precursor to hydrosilylation products suggesting that an equilibrium exists between this coupled product and the ketyl radical monomer.

Table 2. Hydrosilylation of ketones catalyzed by complex **5**.

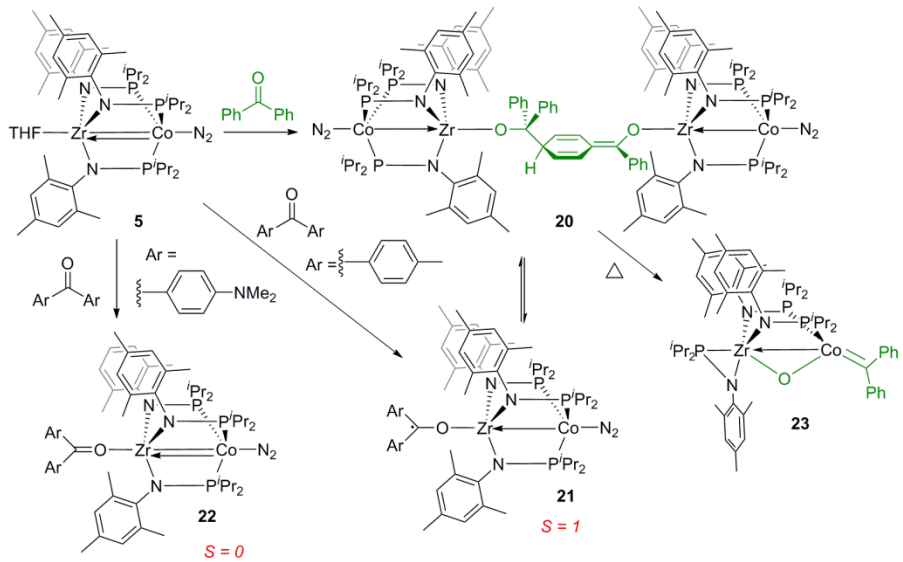


entry	substrate	temp (°C)	Time (h)	yield (%)
1		rt	6	97[b,d]
2		rt	6	98[a]
3		rt	6	98[a]
4		rt	6	98[a]
5		rt	6	98[a]
6		rt	12	94[b]
7		rt	12	93[b]
8		rt	12	98[b]

The stoichiometric reaction between **5** and diarylketones leads us to postulate a hydrosilylation mechanism in which inner-sphere electron transfer from Zr/Co complex **5** forms a Zr-bound ketyl radical which then abstracts an H-atom from $PhSiH_3$, subsequently forming an Si-O bond.[21] In keeping with this mechanism, we have shown that stable ketyl radical complexes such as **21** can be isolated without dimerization when stabilized or sterically-blocked diaryl ketones such as fluorenone or 4,4'-dimethylbenzophenone are used.[26] However, it was found that single-electron transfer does not

occur upon reaction of **5** with electron rich diaryl ketones such as 4,4'-bis((Dimethylamino)benzophenone but rather the diamagnetic ketone adduct complex **22** is isolated. Interestingly, diamagnetic ketone adducts such as **22** do not afford hydrosilylation products upon treatment with $PhSiH_3$, indicating the intermediacy of ketyl radicals in the hydrosilylation mechanism.

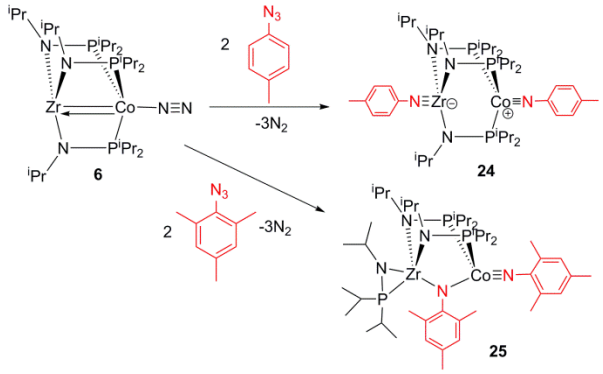
Scheme 5



To explore the equilibrium between **20** and its ketyl radical monomer **21**, complex **20** was heated. Unexpectedly, a new product was formed and identified as the oxo-carbene complex **23** (Scheme 5).[16] While this C-O bond cleavage event is analogous to that we observed for CO_2, the formation of transition metal carbenes via this type of synthetic strategy is quite rare. Moreover, complex **23** represents the first structurally characterized example of a non-heteroatom-stabilized Co-carbene.

Reactivity Towards Oxidative Nitrene Transfer. Given our ability to use heterobimetallic Zr/Co frameworks to undergo multielectron redox transformations, we investigated the reactivity of Zr/Co heterobimetallic complex **6** with respect to oxidative nitrene transfer from aryl azides. In contrast to previously observed one- and two-electron transfer processes, treatment of complex **6** with excess ArN_3 reagents rapidly generates the $Zr^{IV}Co^{III}$ diimido complexes **24** and **25**.[29] This reaction represents a four-electron oxidation reaction with all four electrons originating at the Co center, which cycles between Co^{-I} and Co^{III} in a single step.

Scheme 6



New metal-metal combinations. As described above, the majority of our work with heterobimetallic complexes has been centered on Zr/Co complexes, which have shown remarkable and diverse reactivity towards the activation of both σ and π bonds. In addition to uncovering new facets of metal-metal bonding and new examples of cooperative reactivity, we sought to target heterobimetallic complexes featuring less oxophilic metals in the context of developing more useful and potentially catalytic reactions with carbon dioxide and other oxygenated substrates. Given the paucity of metal-metal bonded complexes containing two different first row metals, we turned our attention to the construction of Cr/M and V/M heterobimetallic complexes.

First row-first row heterobimetallics. Despite the synthetic challenges posed by the 2nd and 3rd row group 5 metals (*vide infra*), the tris(phosphinoamide) vanadium metalloligand $V(^{i}PrNPPh_2)_3$ (**26**) has been successfully synthesized and its coordination chemistry with Fe has been explored (Scheme 7).[15] Coordination of **26** to FeI_2 is possible in the presence of a reductant such as Zn^0 to generate the $V^{III}Fe^{I}$ complex $V(^{i}PrNPPh_2)_3FeI$ (**28**). Further reduction of this complex leads to formation of the diamagnetic reduced $V^{III}Fe^{0}$ complex (**29**). Both complexes feature unprecedented metal-metal distances (~2.05 Å) indicative of V-Fe multiple bonding. Tris(phosphinoamide) Cr complexes such as $Cr(^{i}PrNPPh_2)_3$ (**27**)[30] can also be readily synthesized and used to generate a series of Cr/M complexes (M = Fe, Co, Cu).[24] The $Cr^{III}M^{I}$ (**30**, **32**) and $Cr^{III}M^{0}$ complexes (**31**, **33**) have M-M interatomic distances far longer than the V/Fe analogues,

Scheme 7

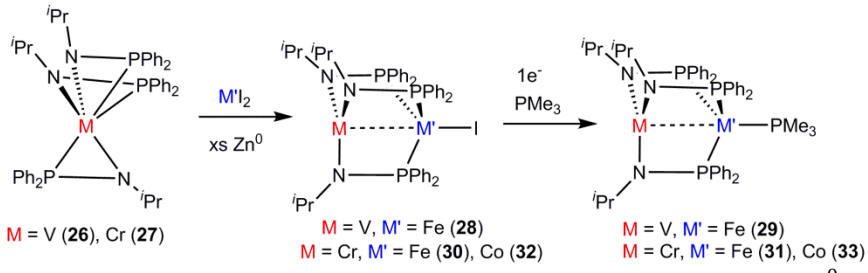
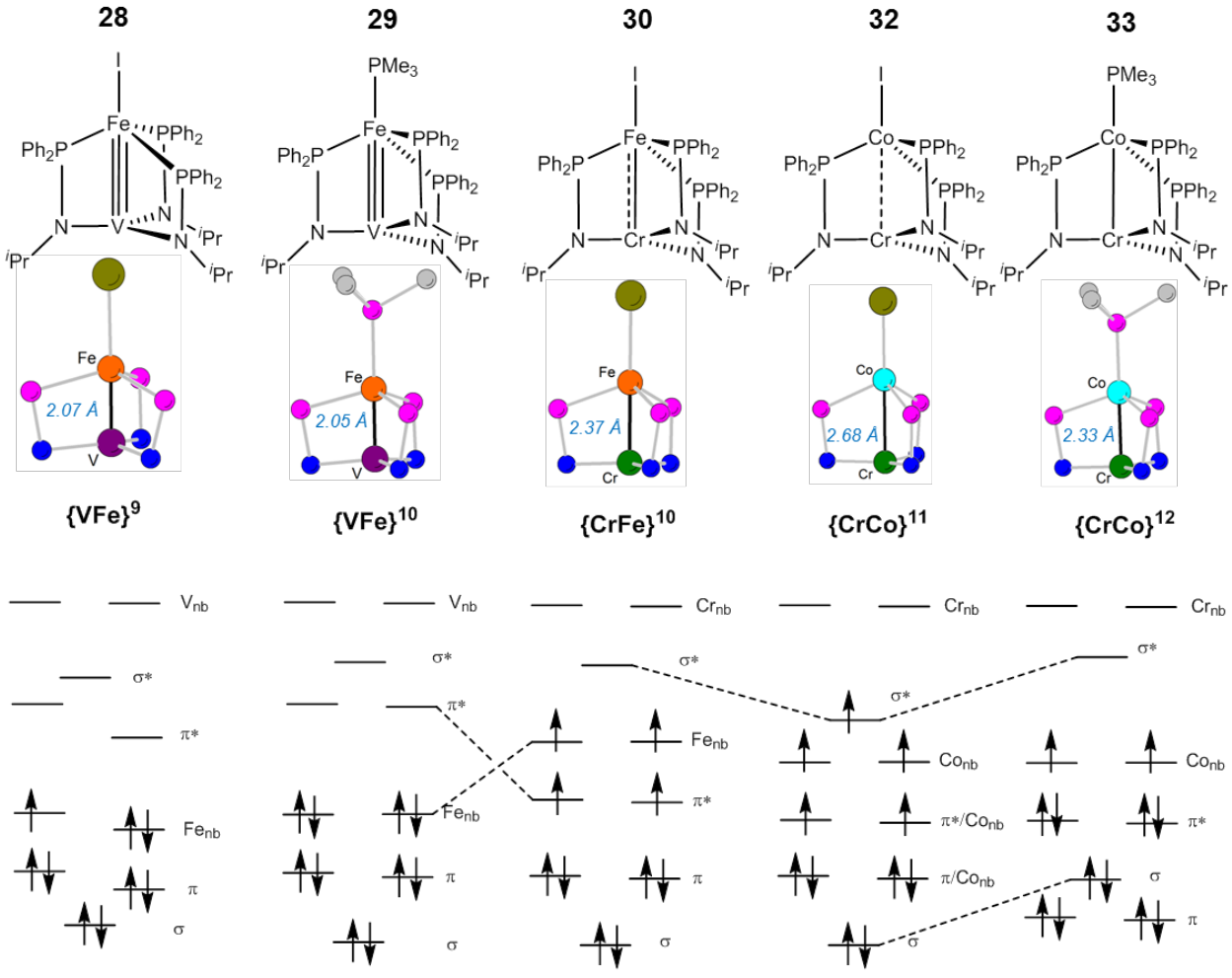


Figure 2. Variations in molecular orbital configurations, spin states, and metal-metal bond order as a function of metal/metal combination, coordination environment, and redox state.

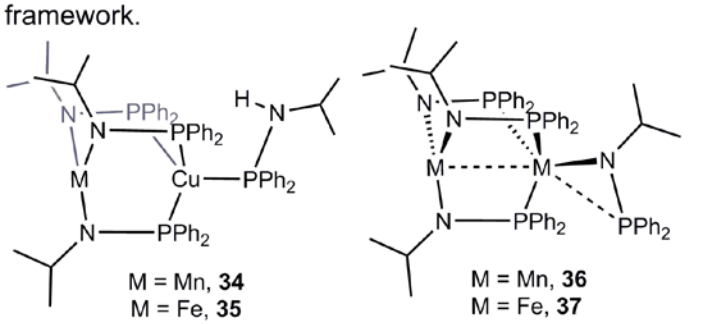


which was initially quite surprising. Moreover, the changes in metal-metal distance and spin state upon changing from Fe to Co or upon reducing **32** to **33**, were difficult to predict. The electronic structures and metal-metal bonding of bimetallic complexes **28**-**33** were examined using magnetic measurements, spectroscopic methods and DFT calculations, revealing that changes in molecular orbital energies as a result of small variations in metal atom, coordination environment and redox state lead to dramatic changes in metal-metal bonding and spin state preferences (Figure 2).[14, 15] Complexes **28**-**33** are among the first examples of metal-metal multiple bonds between two different first row metals.[31, 32]

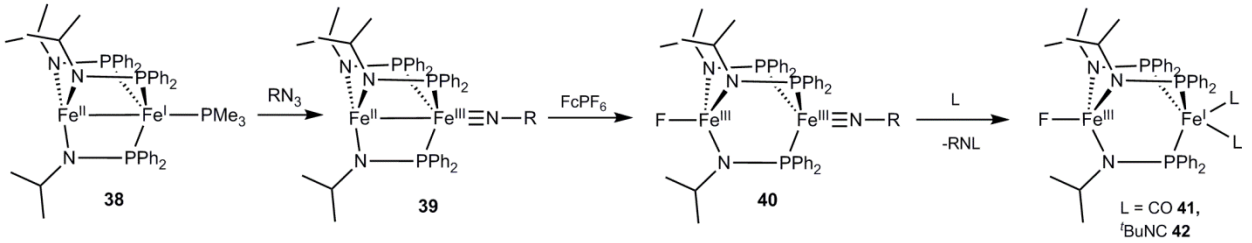
Preliminary studies into the reactivity of first row / first row heterobimetallic Cr/M and V/Fe complexes have revealed sluggish reactions towards small molecules. Our working hypothesis is that the bonding between two similar first row metals is too strong to facilitate reactivity and that combinations of second/third row and first row metals will lead to more facile reactivity.

Late-late homobimetallics. Another facet of this project we have been exploring is the combination of two identical or similar metals in vastly different coordination environments. Utilizing the same phosphinoamide ligand set that has proven useful for early/late heterobimetallic work, we have found in a series of first row late transition metal homo- and heterobimetallic complexes that the phosphinoamide ligands self-assemble such that one metal is in a tris(amide)coordination environment while the second metal is coordinated by the three phosphines. For example complexes **34**-**37** are readily synthesized in a one-pot procedure (Chart 1).[11, 12] While these complexes do involve similar or identical metals, the two different coordination environments may promote polar bond activation similar to that which we have observed in early/late heterobimetallic complexes. Very little is known about high spin non-organometallic homobimetallic complexes and their electronic structure, magnetic properties, and reactivity. Only a handful of complexes of this type have been reported.[33-39] Our work with phosphinoamide ligands adds to these studies, but presents an interesting twist – the absence of symmetrical coordination environments disrupts metal-metal bonding considerably and leads to even more complex bonding and unique properties. Likewise, extensive spectroscopic and computational studies have been carried out on these molecules.[11, 12]

Chart 1. Homo- and hetero-bimetallic late metal complexes supported by the tris(phosphinoamide) ligand framework.



Scheme 8



38 39 40

We have begun to explore the interesting multielectron redox properties and stoichiometric reactivity of our Fe-Fe heterobimetallic complexes. One-electron reduction of **37** affords the reduced $Fe^{II}Fe^{I}$ complex **38** (Scheme 8).[14] We found that compound **38** undergoes oxidative group transfer with organic azides, leading to the $Fe^{II}Fe^{III}$ imido complexes **39**, the first

structurally characterized examples of first row bimetallic complexes featuring both metal-metal and metal-ligand multiple bonds.[14] The electronic structure of this complex has been investigated using SQUID magnetometry, Mössbauer spectroscopy, and DFT calculations, revealing an insightful correlation between metal-metal and metal-ligand bonding. We initially thought that the three-center three-electron Fe-Fe≡NR interaction in these complexes would allow these compounds to be nitrene transfer reagents. However, we found that in contrast to monometallic Fe-imido complexes,[40] our diiron complexes **39** are unreactive towards nitrene transfer to CO or isocyanides even at elevated temperatures. However, one-electron oxidation of **39** leads to disruption of the Fe-Fe interaction, and the resulting oxidized species **40** react readily with CO or ^{t}BuNC to transfer the nitrene functionality and form $Fe^{III}Fe^{I}$ complexes **41** and **42**, respectively (Scheme 8).[25] While oxidation was shown to occur at the tris(amido)Fe center, disruption of the Fe-Fe interaction restores the nucleophilicity of the Fe-imido fragment, allowing it to react with electrophilic substrates in a manner similar to monometallic Fe-imido complexes. The observation that metal-metal interactions actually hinder some stoichiometric reactions in this case is in stark contrast to our previous observations with early/late heterobimetallic systems and further study is warranted to explore the generality of this phenomenon.

References Cited

1. Greenwood, B. P.; Forman, S. I.; Rowe, G. T.; Chen, C.-H.; Foxman, B. M.; Thomas, C. M., "Multielectron Redox Activity Facilitated by Metal-Metal Interactions in Early/Late Heterobimetallics: Co/Zr Complexes Supported by Phosphinoamide Ligands", *Inorg. Chem.* **2009,** *48*, 6251-6260.
2. Cooper, B. G.; Fafard, C. M.; Foxman, B. M.; Thomas, C. M., "Electronic Factors Affecting Metal-Metal Interactions in Early/Late Heterobimetallics: Substituent Effects in Zirconium/Platinum Bis(phosphinoamide) Complexes", *Organometallics* **2010,** *29*, 5179-5186.
3. Greenwood, B. P.; Rowe, G. T.; Chen, C.-H.; Foxman, B. M.; Thomas, C. M., "Metal-Metal Multiple Bonds in Early/Late Heterobimetallics Support Unusual Trigonal Monopyramidal Geometries at both Zr and Co", *J. Am. Chem. Soc.* **2010,** *132*, 44-45.
4. Thomas, C. M.; Napoline, J. W.; Rowe, G. T.; Foxman, B. M., "Oxidative Addition Across Co/Zr Multiple Bonds in Early/Late Heterobimetallic Complexes", *Chem. Commun.* **2010,** *46*, 5790-5792.
5. Krogman, J. P.; Foxman, B. M.; Thomas, C. M., "Activation of CO_2 by a Heterobimetallic Zr/Co Complex", *J. Am. Chem. Soc.* **2011,** *133*, 14582-14585.
6. Setty, V. N.; Zhou, W.; Foxman, B. M.; Thomas, C. M., "Subtle Differences Between Zr and Hf in Early/Late Heterobimetallic Complexes with Cobalt", *Inorg. Chem.* **2011,** *50*, 4647-4655.
7. Thomas, C. M., "Metal-Metal Multiple Bonds In Early/Late Heterobimetallic Complexes: Applications Toward Small Molecule Activation and Catalysis", *Comments Inorg. Chem.* **2011,** *32*, 14-38.
8. Zhou, W.; Napoline, J. W.; Thomas, C. M., "A Catalytic Application of Co/Zr Heterobimetallic Complexes: Kumada Coupling of Unactivated Alkyl Halides with Alkyl Grignard Reagents", *Eur. J. Inorg. Chem.* **2011,** *2011*, 2029-2033.
9. Cooper, B. G.; Napoline, J. W.; Thomas, C. M., "Catalytic Applications of Early/Late Heterobimetallic Complexes", *Cat. Rev. - Sci. Eng.* **2012,** *54*, 1-40.

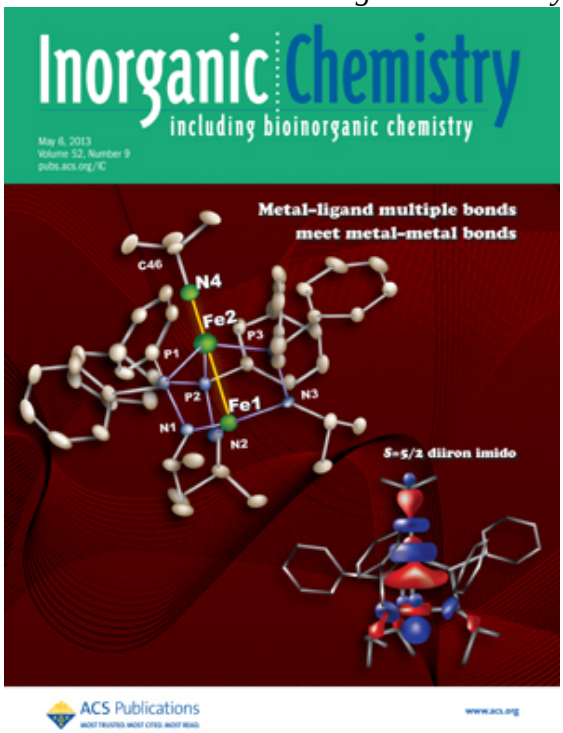
10. Evers, D. A.; Bluestein, A. H.; Foxman, B. M.; Thomas, C. M., "Synthesis and Investigation of the Metal-Metal Interactions in Early/Late Heterobimetallic Complexes Linking Group 5 Imido Fragments to Co(I)", *Dalton Trans.* **2012,** *41*, 8111-8115.
11. Kuppuswamy, S.; Bezpalko, M. W.; Powers, T. M.; Turnbull, M. M.; Foxman, B. M.; Thomas, C. M., "Utilization of Phosphinoamide Ligands in Homobimetallic Fe and Mn Complexes: The Effect of Disparate Coordination Environments on Metal-Metal Interactions and Magnetic and Redox Properties", *Inorg. Chem.* **2012,** *51*, 8225-8240.
12. Kuppuswamy, S.; Cooper, B. G.; Bezpalko, M. W.; Foxman, B. M.; Powers, T. M.; Thomas, C. M., "Synthesis and Structural Characterization of High Spin M/Cu (M = Mn, Fe) Heterobimetallic and Fe/Cu_2 Trimetallic Phosphinoamides", *Inorg. Chem.* **2012,** *51*, 1866-1873.
13. Krogman, J. P.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M., "Synthesis, Structure, and Reactivity of an Anionic Zr-Oxo Relevant to CO_2 Reduction by a Zr/Co Heterobimetallic Complex", *Inorg. Chem.* **2013,** *52*, 3022-3031.
14. Kuppuswamy, S.; Powers, T. M.; Johnson, B. M.; Bezpalko, M. W.; Brozek, C. K.; Foxman, B. M.; Berben, L. A.; Thomas, C. M., "Metal-Metal Interactions in C_3-Symmetric Diiron Imido Complexes Linked by Phosphinoamide Ligands", *Inorg. Chem.* **2013,** *52*, 4802-4811.
15. Kuppuswamy, S.; Powers, T. M.; Krogman, J. P.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M., "Vanadium-Iron Complexes Featuring Metal-Metal Multiple Bonds", *Chem. Sci.* **2013,** *4*, 3557-3565.
16. Marquard, S. L.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M., "Stoichiometric C-O Bond Oxidative Addition of Benzophenone by a Discrete Radical Intermediate To Form a Cobalt(I) Carbene", *J. Am. Chem. Soc.* **2013,** *135*, 6018-6021.
17. Mathialagan, R.; Kuppuswamy, S.; De Denko, A. T.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M., "Metal-Metal Bonding in Low-Coordinate Dicobalt Complexes Supported by Phosphinoamide Ligands", *Inorg. Chem.* **2013,** *52*, 701-706.
18. Napoline, J. W.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M., "N-H activation of hydrazines by a heterobimetallic Zr-Co complex: promotion of one-electron chemistry at Zr", *Chem. Commun.* **2013,** *49*, 4388-4390.
19. Napoline, J. W.; Kraft, S. J.; Matson, E. M.; Fanwick, P. E.; Bart, S. C.; Thomas, C. M., "Tris(phosphinoamide)-Supported Uranium–Cobalt Heterobimetallic Complexes Featuring Co → U Dative Interactions", *Inorg. Chem.* **2013,** *52*, 12170-12177.
20. Napoline, J. W.; Krogman, J. P.; Shi, R.; Kuppuswamy, S.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M., "Activation of E–H and E–E (E = S, O) Bonds by Heterobimetallic Zr/Co Complexes: Evidence for Both One- and Two-Electron Processes", *Eur. J. Inorg. Chem.* **2013,** *2013*, 3874-3882.
21. Zhou, W.; Marquard, S. L.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M., "Catalytic Hydrosilylation of Ketones Using a Co/Zr Heterobimetallic Complex: Evidence for an Unusual Mechanism Involving Ketyl Radicals", *Organometallics* **2013,** *32*, 1766-1772.
22. Krogman, J. P.; Gallagher, J. R.; Zhang, G.; Hock, A. S.; Miller, J. T.; Thomas, C. M., "Assignment of the oxidation states of Zr and Co in a highly reactive heterobimetallic Zr/Co complex using X-ray absorption spectroscopy (XANES)", *Dalton Trans.* **2014,** *43*, 13852-13857.
23. Krogman, J. P.; Thomas, C. M., "Metal-Metal Multiple Bonding in C_3-symmetric Bimetallic Complexes of the First Row Transition Metals", *Chem. Commun.* **2014,** *50*, 5115-5127.

24. Kuppuswamy, S.; Bezpalko, M. W.; Powers, T. M.; Wilding, M. J. T.; Brozek, C. K.; Foxman, B. M.; Thomas, C. M., "A Series of C_3-symmetric Heterobimetallic Cr-M (M = Fe, Co and Cu) Complexes", *Chem. Sci.* **2014,** *5*, 1617-1626.
25. Kuppuswamy, S.; Powers, T. M.; Johnson, B. M.; Brozek, C. K.; Krogman, J. P.; Bezpalko, M. W.; Berben, L. A.; Keith, J. M.; Foxman, B. M.; Thomas, C. M., "One-Electron Oxidation Chemistry and Subsequent Reactivity of Diiron Imido Complexes", *Inorg. Chem.* **2014,** *53*, 5429-5437.
26. Marquard, S. L.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M., "Interaction and Activation of Carbon–Heteroatom π Bonds with a Zr/Co Heterobimetallic Complex", *Organometallics* **2014,** *33*, 2071-2079.
27. Zhou, W.; Saper, N. I.; Krogman, J. P.; Foxman, B. M.; Thomas, C. M., "Effect of Ligand Modification on the Reactivity of Phosphinoamide-Bridged Heterobimetallic Zr/Co Complexes", *Dalton Trans.* **2014,** *43*, 1984-1989.
28. Kuppuswamy, S.; Cass, T. R.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M., "Synthesis and investigation of the metal–metal interactions in heterobimetallic Cr/Rh and Cr/Ir complexes", *Inorg. Chim. Acta*.
29. Wu, B.; Hernandez Sanchez, R.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M., "Formation of Heterobimetallic Zr/Co Diimido Complexes via a Four-electron Transformation ", *Inorg. Chem*, accepted.
30. Thapa, I.; Gambarotta, S.; Korobkov, I.; Duchateau, R.; Kulangara, S. V.; Chevalier, R., "Switchable Chromium(II) Complexes of a Chelating Amidophosphine (N-P) for Selective and Nonselective Ethylene Oligomerization", *Organometallics* **2010,** *29*, 4080-4089.
31. Rudd, P. A.; Liu, S.; Planas, N.; Bill, E.; Gagliardi, L.; Lu, C. C., "Multiple Metal–Metal Bonds in Iron–Chromium Complexes", *Angew. Chem. Int. Ed.* **2013,** *52*, 4449-4452.
32. Clouston, L. J.; Siedschlag, R. B.; Rudd, P. A.; Planas, N.; Hu, S.; Miller, A. D.; Gagliardi, L.; Lu, C. C., "Systematic Variation of Metal-Metal Bond Order in Metal-Chromium Complexes", *J. Am. Chem. Soc.* **2013,** *135*, 13142-13148.
33. Cotton, F. A.; Daniels, L. M.; Murillo, C. A., "Divalent Iron Formamidinato Complexes: a Highly Distorted Dinuclear Compound", *Inorg. Chim. Acta* **1994,** *224*, 5-9.
34. Cotton, F. A.; Daniels, L. M.; Falvello, L. R.; Matonic, J. H.; Murillo, C. A., "Trigonal-Lantern Dinuclear Compounds of Diiron(I,II): the Synthesis and Characterization of Two Highly Paramagnetic $Fe_2(amidinato)_3$ Species with Short Metal-Metal Bonds", *Inorg. Chim. Acta* **1997,** *256*, 269-275.
35. Cotton, F. A.; Daniels, L. M.; Matonic, J. H.; Murillo, C. A., "Highly Distorted Diiron(II, II) Complexes Containing Four Amidinate Ligands. A Long and Short Metal-Metal Distance", *Inorg. Chim. Acta* **1997,** *256*, 277-282.
36. Cotton, F. A.; Feng, X.; Murillo, C. A., "Electronic Structure of Dinuclear Trigonal-Lantern Amidinato Compounds of Iron and Cobalt", *Inorg. Chim. Acta* **1997,** *256*, 303-308.
37. Timmer, G. H.; Berry, J. F., "Jahn-Teller Distortion, Ferromagnetic Coupling, and Electron Delocalization in a High-Spin Fe-Fe Bonded Dimer", *C. R. Chim.* **2012,** *15*, 192-201.
38. Zall, C. M.; Zherebetskyy, D.; Dzubak, A. L.; Bill, E.; Gagliardi, L.; Lu, C. C., "A Combined Spectroscopic and Computational Study of a High-Spin S = 7/2 Diiron Complex with a Short Iron-Iron Bond", *Inorg. Chem.* **2012,** *51*, 728-736.
39. Tereniak, S. J.; Carlson, R. K.; Clouston, L. J.; Young, V. G.; Bill, E.; Maurice, R.; Chen, Y.-S.; Kim, H. J.; Gagliardi, L.; Lu, C. C., "Role of the Metal in the Bonding and Properties of

Bimetallic Complexes Involving Manganese, Iron, and Cobalt", *J. Am. Chem. Soc.* **2013,** *136*, 1842-1855.
40. Brown, S. D.; Betley, T. A.; Peters, J. C., "A Low-Spin d^5 Iron Imide: Nitrene Capture by Low-Coordinate Iron(I) Provides the 4-Coordinate Fe(III) Complex $[PhB(CH_2PPh_2)_3]Fe{\equiv}N$-p-tolyl", *J. Am. Chem. Soc.* **2003,** *125*, 322-323.

(b) Special Recognitions Received by the PI

- Alfred P. Sloan Research Fellowship – 2011
- Kavli Fellow -2012
- *Organometallics* Fellow – 2012
- Michael L. Walzer ’56 Award for Teaching (Brandeis) – 2012
- Alberta Gotthardt and Henry Strage Award for Aspiring Young Science Faculty (Brandeis) – 2013
- *Dalton Transactions* Lectureship, University of California – Berkeley – 2015
- Fellow of the Royal Society of Chemistry (FRSC) – 2014
- Two of the PI’s papers (*Inorg. Chem.* **2013**, *52*, 4802; *Inorg. Chem.* **2013**, *52*, 3022) were chosen for the Virtual Issue on Synthetic Inorganic Chemistry (http://pubs.acs.org/page/vi/2013/synthetic_inorganic.html)
- PI’s work (*Inorg. Chem.* **2013**, 52, 4802-4811) was chosen to be featured on the cover of *Inorganic Chemistry* (May 6, 2013 issue)



(c) List of publications 2010-2015

I. Exclusively funded by this DOE grant

1. Krogman, J. P.; Foxman, B. M.; Thomas, C. M. "Formation and Subsequent Reactivity of a N_2-Stabilized Cobalt Hydride Complex." *Organometallics* **2015**, DOI: 10.1021/acs.organomet.5b00182.
2. Wu, B.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. "A Heterobimetallic Complex Featuring a Ti-Co Multiple Bond and Its Application to the Reductive Coupling of Ketones to Alkenes." *Chem. Sci.* **2015**, *6*, 2044-2049.
3. Lee, K. H.; Napoline, J. W.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. "Probing Substituent Effects in Phosphinoamine Ligands Using $Mo(CO)_5L$ Complexes." *Polyhedron*, **2015**, *87*, 354-360.
4. Wu, B.; Hernandez Sanchez, R.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. "Formation of Heterobimetallic Zirconium/Cobalt Diimido Complexes via a Four-Electron Transformation." *Inorg. Chem.* **2014**, *53*, 10021-10023.
5. Kuppuswamy, S.; Cass, T. R.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. "Synthesis and Investigation of the Metal-Metal Interactions in Heterobimetallic Cr/Rh and Cr/Ir Complexes." *Inorg. Chim. Acta* **2014**, *424*, 167-172.
6. Kuppuswamy, S.; Powers, T. M.; Johnson, B. M.; Brozek, C. K.; Krogman, J. P.; Bezpalko, M. W.; Berben, L. A.; Keith, J. M.; Foxman, B. M.; Thomas, C. M. "One-Electron Oxidation Chemistry and Subsequent Reactivity of Diiron Imido Complexes." *Inorg. Chem.* **2014**, *53*, 5429-5437.
7. Kuppuswamy, S.; Bezpalko, M. W.; Powers, T. M.; Wilding, M. J. T.; Brozek, C. K.; Foxman, B. M.; Thomas, C. M. "A Series of C_3-Symmetric Heterobimetallic Cr/M (M = Fe, Co, Cu) Complexes." *Chem. Sci.* **2014**, 1617-1626.
8. Krogman, J. P.; Thomas, C. M. "Metal-Metal Multiple Bonding C_3-Symmetric Bimetallic Complexes of the First Row Transition Metals." *Chem. Commun.* **2014**, *50*, 5115-5127 (invited *Feature Article* for Emerging Investigators Special Issue).
9. Zhou, W.; Saper, N. I.; Krogman, J. P.; Foxman, B. M.; Thomas, C. M. "Effect of Ligand Modification on the Reactivity of Phosphino-amide-bridged Heterobimetallic Zr/Co Complexes." *Dalton Trans.* **2014**¸*43*, 1984-1989.
10. Kuppuswamy, S.; Powers, T. M.; Krogman, J. P.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M.* "Vanadium-Iron Complexes Featuring Metal-Metal Multiple Bonds." *Chem. Sci.* **2013**, *4*, 3557-3565.
11. Napoline, J. W.; Krogman, J. P.; Shi, R.; Kuppuswamy, S.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M.* "Activation of E-H and E-E (E = S, O) Bonds by Heterobimetallic Zr/Co Complexes: Evidence for both One- and Two-Electron Processes." *Eur. J. Inorg. Chem.* **2013**, *2013*, 3874-3882.
12. Krogman, J. P.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. "Synthesis, Structure, and Reactivity of an Anionic Zr-Oxo Relevant to CO_2 Reduction by a Zr/Co Heterobimetallic Complex." *Inorg. Chem.* **2013**, *52*, 3022-3031.
13. Zhou, W.; Marquard, S. L.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M.* "Catalytic Hydrosilylation of Ketones Using a Co/Zr Heterobimetallic Complex: Evidence for an Unusual Mechanism Involving Ketyl Radicals." *Organometallics* **2013**, *32*, 1766-1772.

14. Kuppuswamy, S.; Powers, T. M.; Johnson, B. M.; Bezpalko, M. W.; Brozek, C. K.; Foxman, B. M.; Berben, L. A.; Thomas, C. M. "Metal-Metal Interactions in C_3-Symmetric Diiron Imido Complexes Linked by Phosphinoamide Ligands." *Inorg. Chem.* **2013**, *52*, 4802-4811.
15. Mathialagan, R.; Kuppuswamy, S.; De Denko, A. T.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M.* "Metal-Metal Bonding in Low-Coordinate Dicobalt Complexes Supported by Phosphinoamide Ligands." *Inorg. Chem.* **2013**, *52*, 701-706.
16. Napoline, J. W.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. "N-H Activaton of Hydrazines by a Heterobimetallic Zr-Co Complex: Promotion of One-electron Chemistry at Zr." *Chem. Commun.* **2013**, *49*, 4388-4390.
17. Kuppuswamy, S.; Bezpalko, M. W.; Powers, T. M.; Turnbull, M. M.; Foxman, B. M.; Thomas, C. M. "Utilization of Phosphinoamide Ligands in Homobimetallic Fe and Mn Complexes: The Effect of Disparate Coordination Environments on Metal-Metal Interactions and Magnetic and Redox Properties." *Inorg. Chem.* **2012**, *51*, 8225-8240.
18. Evers, D. A.; Bluestein, A. H.; Foxman, B. M.; Thomas, C. M. "Synthesis and Investigation of the Metal-Metal Interactions in Early/Late Heterobimetallic Complexes Linking Group 5 Imido Fragments to Co(I)." *Dalton Trans.* **2012**, *41*, 8111-8115 (invited submission for "New Talent: Americas" issue).
19. Kuppuswamy, S.; Cooper, B. G.; Bezpalko, M. W.; Foxman, B. M.; Powers, T. M.; Thomas, C. M. "Synthesis and Structural Characterization of High Spin M/Cu (M = Mn, Fe) Heterobimetallic and Fe/Cu_2 Trimetallic Phosphinoamides." *Inorg. Chem.* **2012**, *51*, 1866-1873.
20. Krogman, J. P.; Foxman, B. M.; Thomas, C. M. "Activation of CO_2 by a Heterobimetallic Zr/Co Complex." *J. Am. Chem. Soc.* **2011**, *133*, 14582-14585.
21. Cooper, B. G.; Napoline, J. W.; Thomas, C. M.* "Recent Progress Towards Catalytic Applications of Early/Late Heterobimetallic Complexes." *Cat. Rev. Sci. Eng*. **2012**, *54*, 1-40.
22. Thomas, C. M. "Metal-Metal Multiple Bonds in Early/Late Heterobimetallic Complexes: Applications Towards Small Molecule Activation and Catalysis." *Comments Inorg. Chem.* **2011**, *32*, 14-38 (invited review).
23. Setty, V. N.; Zhou, W.; Foxman, B. M. Thomas, C. M. "Subtle Differences Between Zr and Hf in Early/Late Heterobimetallic Complexes with Cobalt." *Inorg. Chem.* **2011**, *50*, 4647-4655.
24. Zhou, W.; Napoline, J. W.; Thomas, C. M. "A Catalytic Application of Co/Zr Heterobimetallic Complexes: Cooperative Reactivity Towards Kumada Coupling of Alkyl Halides with Alkyl Grignard Reagents." *Eur. J. Inorg. Chem.* **2011**, *2011*, 2029-2033.
25. Cooper, B. G.; Fafard, C. M.; Foxman, B. M.; Thomas, C. M. "Electronic Factors Affecting Metal-Metal Interactions in Early/Late Heterobimetallics: Substituent Effects in Pt/Zr (Bisphosphinoamide) Complexes." *Organometallics* **2010**, *29*, 5179-5186.
26. Thomas, C. M.; Napoline, J. W.; Rowe, G. T.; Foxman, B. M. "Oxidative Addition Across Co/Zr Multiple Bonds in Early/Late Heterobimetallic Complexes." *Chem. Commun.* **2010**, *46*, 5790-5792.

II. Jointly funded by this and other grants

1. Krogman, J. P.; Gallagher, J. R.; Zhang, G.; Hock, A. S.; Miller, J. T.; Thomas, C. M. "Assignment of the Oxidation States of Zr and Co in a Highly Reactive Heterobimetallic Zr/Co Complex Using X-ray Absorption Spectroscopy (XANES)." *Dalton Trans.* **2014**, *43*, 13852-13857.
2. Marquard, S. L.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M.* "Insertion and Activation of Carbon-Heteroatom π-Bonds with a Zr/Co Heterobimetallic Complex." *Organometallics* **2014**, *33*, 2071-2079.
3. Marquard, S. L.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. "Stoichiometric C=O Bond Oxidative Addition of Benzophenone by a Discrete Radical Intermediate to Form a Cobalt(I) Carbene." *J. Am. Chem. Soc.* **2013**, *135*, 6018-6021.
4. Napoline, J. W.; Kraft, S. J.; Matson, E. M.; Fanwick, P. E.; Bart, S. C.; Thomas, C. M. "Tris(phosphinoamide)-supported Uranium-Cobalt Heterobimetallic Complexes Featuring Co→U Dative Interactions." *Inorg. Chem.* **2013**, *52*, 12170-12177.

III. Not funded by this grant

1. Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. "Use of a Bidentate Ligand Featuring an N-Heterocyclic Phosphenium Cation (NHP^+) to Systematically Explore the Bonding of NHP^+ Ligands with Nickel" *Inorg. Chem.* **2015**, *DOI: 10.1021/acs.inorgchem.5b01363*.
2. Knight, S. E.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. "Coordination of *N*-heterocyclic Phosphine- and Phosphenium-Containing Pincer Ligands to Copper(I): Evidence for Reactive Electrophilic Metal-Phosphenium Intermediates." *Inorg. Chim. Acta* **2014**, *422*, 181-187.
3. Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. "Non-Innocent Behavior of Bidentate Amidophosphido $[NP]^{2-}$ Ligands Upon Coordination to Copper." *Inorg. Chem.* **2013**, *52*, 12329-12331.
4. Pan, B.; Evers-McGregor, D. A.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. "Multimetallic Complexes Featuring a Bridging N-Heterocyclic Phosphido/Phosphenium Ligand: Synthesis, Structure, and Theoretical Investigation." *Inorg. Chem.* **2013**, *52*, 9583-9489.
5. Pan, B.; Pierre, S.; Bezpalko, M. W.; Napoline, J. W.; Foxman, B. M.; Thomas, C. M. "Isolation of N-Heterocyclic Alkyl Intermediates En Route to Transition Metal N-Heterocyclic Carbene Complexes: Insight into the Imidazolinium C-H Activation Mechanism." *Organometallics* **2013**, *32*, 704-710.
6. Depasquale, J.; Nieto, I.; Reuther, L. E.; Herbst-Gervasoni, C. J.; Paul, J. J.; Mochalin, V.; Zeller, M.; Thomas, C. M.; Addison, A. W.; Papish, E. T. "Iridium Dihydroxybipyridine Complexes Show that Ligand Deprotonation Dramatically Speeds Rates of Catalytic Water Oxidation." *Inorg. Chem.* **2013**, *52*, 9175-9183.
7. Pan, B.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. "Heterolytic Activation of E-H Bonds Across Pt-P Bonds in Pt NHP (N-heterocyclic Phosphenium/Phosphido) Complexes." *Dalton Trans.* **2012**, *41*, 9083-9090.

8. Pan, B.; Xu, Z.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. “N-Heterocyclic Phosphenium Ligands as Sterically and Electronically Tunable Isolobal Analogues of Nitrosyls.” *Inorg. Chem.* **2012**, *51*, 4170-4179.
9. Pan, B.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. “Coordination of an N-Heterocyclic Phosphenium-Containing Pincer Ligand to a $Co(CO)_2$ Fragment Allows Oxidation to Form an Unusual N-Heterocyclic Phosphinito Species.” *Organometallics* **2011**, *30*, 5560-5563.
10. Day, G. S.; Pan, B.; Kellenberger, D.; Foxman, B. M.; Thomas, C. M. “Guilty as Charged: Non-Innocent Behavior by A Pincer Ligand Featuring a Central Phosphenium Donor.” *Chem. Commun.* **2011**, *47*, 3634-3636.
11. Huacuja, R.; Graham, D. J.; Fafard, C. M.; Chen, C.-H.; Foxman, B. M.; Herbert, D.; Alliger, G.; Thomas, C. M.; Ozerov, O. “Reactivity of a Pd(I)-Pd(I) dimer with O_2: Monohapto Pd Superoxide and Dipalladium Peroxide in Equilibrium.” *J. Am. Chem. Soc.* **2011**, *33*, 3820-3823.