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Metal−Metal Multiple Bonds in Early/Late Heterobimetallics Support Unusual Trigonal Monopyramidal Geometries at both Zr and Co

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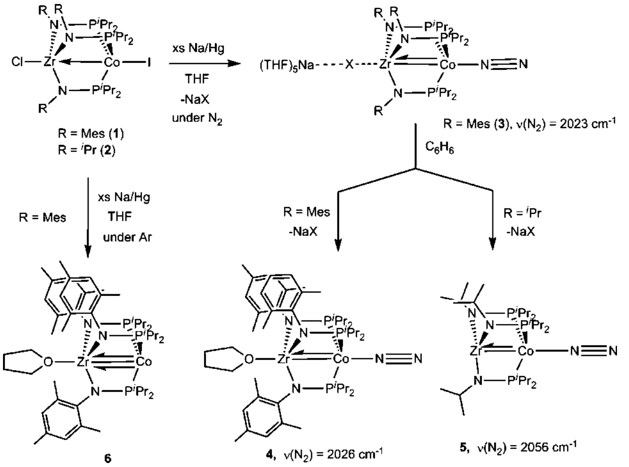
The highly polarized metal−metal bonds in early/late heterobimetallic complexes present a unique strategy for tuning redox potentials and small molecule activation processes.[1] For example, Casey and co-workers targeted early/late heterobimetallic dihydrides featuring a hydridic early metal hydride and an acidic late metal hydride as potential small molecule reducing agents.[2] While a number of early/late heterobimetallic complexes have been reported, there are few accounts of reactivity in which both metals are involved[3] and limited reports of metal−metal multiple bonds between early and late transition metals.[4,5] Wolczanski and co-workers reported several alkoxyphosphine-linked heterobimetallic complexes, namely Ti(OCMe$_2$CH$_2$PPh$_2$)$_3$Rh and Cp*Zr(OCH$_2$PPh$_2$)$_2$RhMe$_2$, featuring triple and double M−Rh bonds, respectively.[4] In light of this, our group has chosen to incorporate more reactive first row transition metals into new early/late heterobimetallic complexes. Herein, we report 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.

We previously reported the synthesis and characterization of a family of Co/Zr heterobimetallic complexes linked by three phosphinoamide ligands, including ICo(MesNP^{i}Pr$_2$)$_3$ZrCl (**1**) and ICo(^{i}PrNP^{i}Pr$_2$)$_3$ZrCl (**2**).[6] 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 **1** was chemically reduced with excess Na/Hg, leading to the Co-bound dinitrogen product (THF)$_5$Na−X−Zr(NMesP^{i}Pr$_2$)$_3$Co−N$_2$ (**3**). Complex **3** shows a 0.22 Å decrease in the distance between the two metal centers in comparison with **1** (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 Zr by the electron-rich Co center, suggesting the likelihood of Na−X extrusion from **3**.

As shown in Scheme 1, extraction of complex **3** into benzene leads to precipitation of the labile NaX moiety, producing a red diamagnetic complex (THF)Zr(MesNP^{i}Pr$_2$)$_3$Co−N$_2$ (**4**), in which a bound THF molecule occupies the axial coordination site on Zr. Replacement of the NaX with THF leads to a subtle increase in the ν(N$_2$) from 2023 cm^{-1} in **3** to 2026 cm^{-1} in **4**. X-ray quality crystals of **4** were obtained, and the solid state structure is shown in Figure 1. The Zr−Co distance in **4** is 2.36 Å (avg. of two molecules in asymmetric unit), showing a slight contraction of the Zr−Co bond compared to **3** (2.4112(3) Å) and a 0.27 Å decrease in the Co−Zr distance from the dihalide heterobimetallic precursor **1** (2.6280(5) Å).[6]

Similarly, reduction of complex **2** with excess Na/Hg, followed by subsequent benzene extraction, leads to a neutral dinitrogen adduct, Zr(^{i}PrNP^{i}Pr$_2$)$_3$Co−N$_2$ (**5**, Scheme 1). In contrast to the mesityl derivative, we were unable to isolate a NaX-bound product similar to **3**, presumably due to the lability of the NaX moiety.[7] The IR stretch corresponding to the bound N$_2$ moiety of **5** was 2056 cm^{-1}, showing a dramatic increase in the N$_2$ vibrational frequency with respect to **4**.

Scheme 1



The structure of compound **5** is analogous to that of **4**; however, rather than binding THF, the axial coordination site of **5** remains open (Figure 1). The geometry about Zr is trigonal monopyramidal, an unprecedented geometry for Zr,[8] 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 **5** is moderately shorter than that of **4** (avg. Zr−Co distance in three independent molecules in asymmetric unit of **5** = 2.33 Å). We attribute the drastic decrease in backbonding from Co to N$_2$ in **5**, as indicated by the increase in the ν(N$_2$) by 30 cm^{-1} with respect to **4**, to stronger involvement of the d$_{xz}$ and d$_{yz}$ orbitals in the Co−Zr bonding interaction in the absence of sigma donation from THF to Zr.

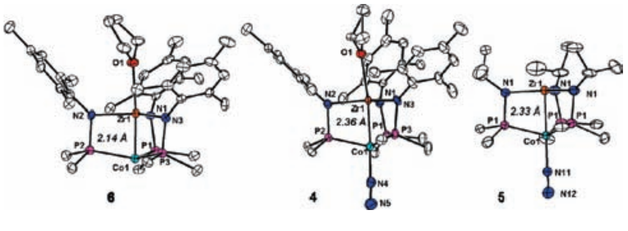


Figure 1. Displacement ellipsoid (50%) representations of **4**, **5**, and **6**. Zr−Co distances of **4**, **5**, and **6** are 2.36(1), 2.33(1), and 2.14(1) Å, respectively (averages of two (**4**, **6**) or three (**5**) molecules in asymmetric unit). All hydrogen atoms and the isopropyl methyl groups have been omitted for clarity.

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Interestingly, we have found that reduction of **1** in an argon-filled glovebox in the absence of N_2 leads to an isolable diamagnetic green product, (THF)Zr(MesNP^{i}Pr$_2$)$_3$Co (**6**, Scheme 1). The solid state structure reveals that **6** features an open Co coordination site and a trigonal monopyramidal Co center (Figure 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 Å.

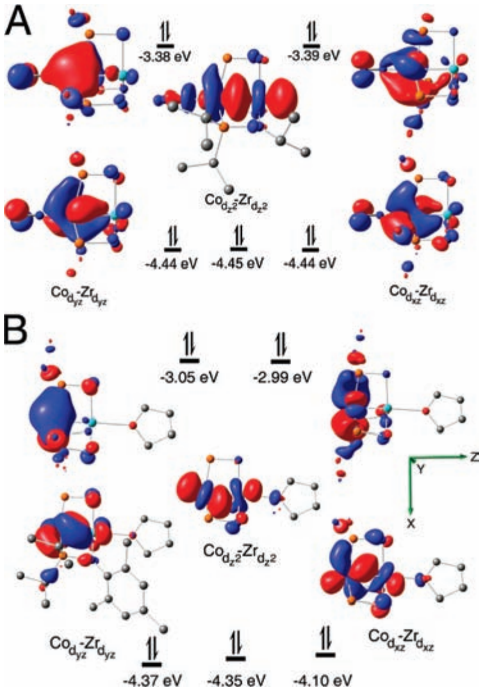

Figure 2. Depictions and energies of the frontier molecular orbitals of complexes **5** (A) and **6** (B).

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 **4**−**6**.[9] Examination of the highest occupied molecular orbitals of **4** and **5** (Figure 2A and Supporting Information) 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. The metal−metal interaction in the dihalide precursor **1**, on the other hand, was composed predominately of σ character.[6] A comparison of the orbitals of **4** and **5** reveals the nature of their most notable differences: the coordination number of the zirconium atom and the 30 cm^{-1} difference in $\nu(N_2)$. Indeed, the orbitals involved in the stronger Co−Zr π-bond are the same orbitals participating in backbonding to the N_2 π^* orbitals (Figure 2A), and competition with Zr for the electron density from the Co d_{xz} and d_{yz} orbitals leads to a higher $\nu(N_2)$. It can likewise be inferred that some of the electron density involved in binding to N_2 might have otherwise been involved in more pronounced Co−Zr bonding. To assess this hypothesis, the electronic structure of **6**, the dinitrogen-free analogue of **4**, was determined (Figure 2B). Particularly striking in the frontier orbitals of **6** 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 **4** and **6**.

To assess bond distances while taking into account differences in atomic size, Cotton defined the "formal shortness ratio": $FSR_{AB} = D_{AB}/R_1^A + R_1^B$, where D_{AB} is the interatomic distance and the R_1 values are the van der Waal's radii of the two atoms (Co: 1.152 Å, Zr: 1.454 Å).[10] By this treatment, we find the FSR of complexes **4**, **5**, and **6** to be 0.902, 0.891, and 0.818, respectively. For comparison, the FSR of complexes **1** and **2** are 1.00.[6] Thus, complex **6** unequivocally holds the record for the shortest M−M distance in an early/late heterobimetallic complex in both absolute distance and FSR,[8] greatly surpassing the Ti−Rh complex of Wolczanksi et al. (FSR = 0.860)[4a] and the Mo−Ru complexes of Collman et al. (FSR = 0.869, 0.857).[5a]

In summary, we have synthesized three heterobimetallic complexes featuring Co−Zr multiple bonds, including two complexes featuring unusual trigonal monopyramidal geometries at either the Zr (**5**) or Co (**6**) center. We anticipate that these highly reduced, coordinatively unsaturated molecules will be reactive toward a wide variety of small molecule substrates and future works will focus on their reactivity.

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Supporting Information Available: Experimental details, crystallographic data for complexes **4**, **5**, and **6** (in CIF format) and additional computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Based on a 2009 search of the Cambridge Structural Database.
(9) See Supporting Information for computational details.
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