

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

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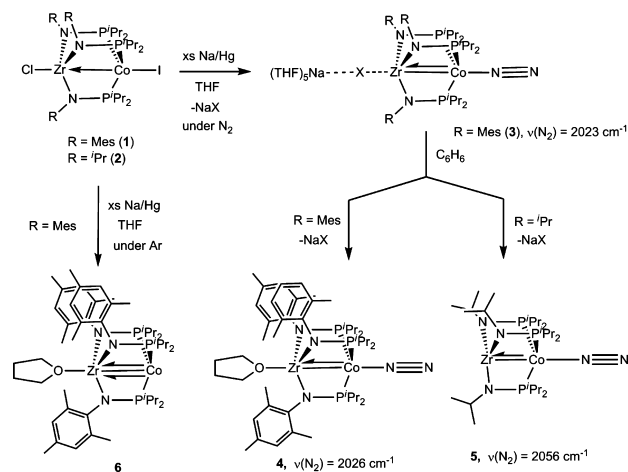
The highly polarized metal–metal bonds in early/late heterobimetallic complexes present a unique strategy for tuning redox potentials and small molecule activation processes.¹ For example, Casey and co-workers targeted early/late heterobimetallic dihydrides featuring a hydridic early metal hydride and 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 involved³ 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 $\text{Ti}(\text{OCMe}_2\text{CH}_2\text{PPh}_2)_3\text{Rh}$ and $\text{Cp}^*\text{Zr}(\text{OCH}_2\text{PPh}_2)_2\text{RhMe}_2$, 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 $\text{ICo}(\text{MesNP}^i\text{Pr}_2)_3\text{ZrCl}$ (**1**) and $\text{ICo}^i(\text{PrNP}^i\text{Pr}_2)_3\text{ZrCl}$ (**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 $(\text{THF})_5\text{Na}-\text{X}-\text{Zr}(\text{NMesNP}^i\text{Pr}_2)_3\text{Co}-\text{N}_2$ (**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 $(\text{THF})\text{Zr}(\text{MesNP}^i\text{Pr}_2)_3\text{Co}-\text{N}_2$ (**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 $\nu(\text{N}_2)$ 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

Scheme 1



adduct, $\text{Zr}^i(\text{PrNP}^i\text{Pr}_2)_3\text{Co}-\text{N}_2$ (**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**.

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 $\nu(\text{N}_2)$ 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.

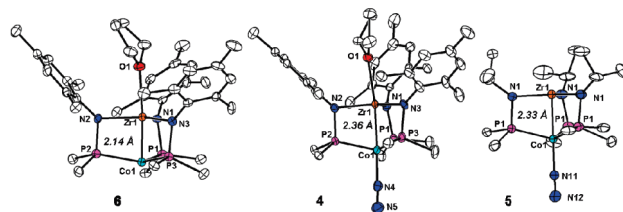


Figure 1. Displacement ellipsoid (50%) representations of **4**, **5**, and **6**. Zr–Co distances of **4**, **5**, and **6** are 2.36(1), 2.33(1), and 2.14(1) Å, respectively (averages of two (**4**, **6**) or three (**5**) molecules in asymmetric unit). All hydrogen atoms and the isopropyl methyl groups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

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, $(THF)Zr(MesNP^iPr)_3Co$ (**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.

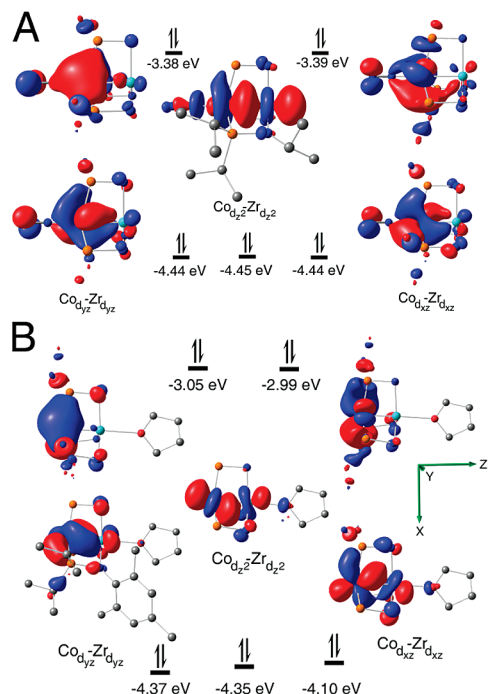


Figure 2. Depictions and energies of the frontier molecular orbitals of complexes **5** (A) and **6** (B).

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 Wolczanski 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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- (9) See Supporting Information for computational details.
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