

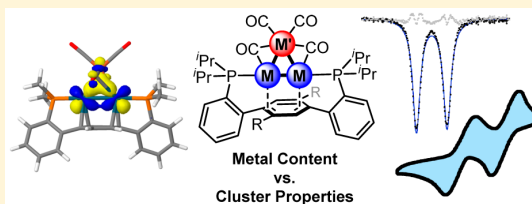
Heterometallic Effects in Trinuclear Complexes Supported by *p*-Terphenyl Diphosphine Ligands

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S Supporting Information

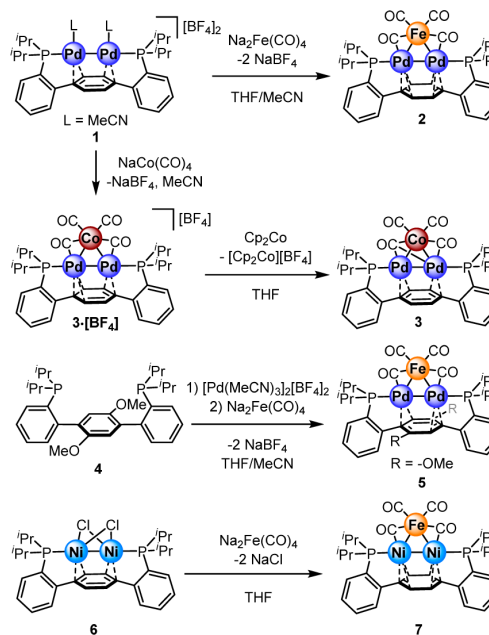
ABSTRACT: A series of isostructural trinuclear complexes of metal composition Pd_2Fe , Pd_2Co , and Ni_2Fe was synthesized in a stepwise fashion. Using dinuclear precursors (Pd_2^{I} and Ni_2^{I}) supported by *p*-terphenyl diphosphine ligands allowed for the selective incorporation of a single additional metal center. The effects of both metal composition and ligand electronics on cluster properties were studied. These results highlight the importance of metal–metal interactions in mixed-metal sites of structurally analogous clusters.



Discrete mixed-metal complexes have been studied for molecular-level insight into the structural and electronic factors that influence cluster properties.¹ As the performance of heterogeneous catalysts, in terms of activity, durability, selectivity, or cost, can be improved upon inclusion of cometals, an understanding of the underlying metal–metal interactions is needed.² To gain insight into such interactions, the study of well-defined, homogeneous, multinuclear heterometallic complexes has been pursued. Heterometallic dinuclear complexes are an active area of current research.³ Additionally, heterometallic trinuclear complexes in triangular geometries are particularly appealing as the simplest model clusters displaying major and minor metal components and direct interactions between all metals, similar to the case for heterogeneous catalysts. Although many advances have been made in the synthesis of multinuclear complexes containing isolated triangular heterometallic motifs,^{2,4} systematic access to related, isostructural clusters suitable for structure–property studies is limited. Triangular trinuclear motifs are common in multinuclear heterometallic complexes, but differences in nuclearity, supporting ligands, or cluster oxidation state make systematic comparisons challenging.² Herein we report the rational synthesis of a series of isostructural, low-oxidation-state heterometallic complexes of the $\text{M}_2\text{M}'$ type, supported by *p*-terphenyl diphosphine ligands.

We have previously reported the chemistry of homometallic clusters coordinated by multidentate phosphinoarene ligands.⁵ With heterometallic trinuclear clusters as the target, dinuclear Pd_2 (**1**) and Ni_2 (**6**) precursors were treated with the tetracarbonyl anions of Fe and Co (Scheme 1). $\text{Na}_2[\text{Fe}(\text{CO})_4]$ reacts with **1** and **6** to yield $[\text{Pd}_2\text{Fe}]^0$ (**2**) and $[\text{Ni}_2\text{Fe}]^0$ (**7**) cores, respectively, while $\text{Na}[\text{Co}(\text{CO})_4]$ generates the $[\text{Pd}_2\text{Co}]^+$ (**3**· $[\text{BF}_4]$) core upon reaction with **1**. Reactions of **6** and $\text{Na}[\text{Co}(\text{CO})_4]$ have been previously reported to form a $\text{Ni}_2^0(\text{CO})_3$ cluster rather than a $[\text{Ni}_2\text{Co}]^+$ core.^{5e} These complexes represent rare examples of triangular clusters, with

Scheme 1. Synthesis of Trinuclear Complexes



only two Pd_2Co , four Ni_2Fe , and no Pd_2Fe species structurally characterized previously.^{4a,b,e–g,i} Spectroscopic and structural parameters of these reported clusters are challenging to compare, due to differences in oxidation state and the identity of supporting ligands. The present series maintains the same ligand environment while varying the major and minor metal

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components. To analyze the effect of ligand electronics on cluster properties, a diphosphine variant with *p*-methoxy substitution of the central arene, **4** (Scheme 1, see the Supporting Information for detailed synthesis), was employed to support a $[\text{Pd}_2\text{Fe}]^0$ cluster (**5**). Multiple techniques have been utilized to compare the reported compounds: electrochemical measurements, NMR spectroscopy, Mössbauer spectroscopy, and IR spectroscopy in addition to structural comparisons from solid-state structures.

Single-crystal X-ray diffraction (XRD) studies were performed for **2**, $3\cdot[\text{BF}_4]$, **5**, and **7** (Figure 1). The homodinuclear moiety (M_2) is bound to the phosphine and arene donors in a manner reminiscent of the precursors.^{5a,c,6} The apical metal (M') displays interactions with the M_2 core and two CO ligands, one bridging each $\text{M}-\text{M}'$ interaction. Despite the variation of apical and dinuclear core metal identity as well as ligand electronics, the clusters remain largely isostructural. The metal–metal distances for Pd_2M clusters are similar among complexes **2**, $3\cdot[\text{BF}_4]$, and **5**, with $\text{Pd}-\text{Pd}$ distances between 2.5653(3) and 2.5753(3) Å and $\text{Pd}-\text{M}'$ distances between 2.5374(3) and 2.5541(6) Å. Complex **7** shows shorter metal–metal distances of 2.3931(8) and 2.4169(6) Å for $\text{Ni}-\text{Ni}$ and $\text{Ni}-\text{Fe}$, respectively. Average $\text{Pd}-\text{Pd}$ and $\text{Ni}-\text{Ni}$ distances are both similar to the metal–metal distances in previously reported monoatom-bridged complexes such as the dmdbt-Pd_2 complex ($\text{dmdbt} = 4,6\text{-dimethyldibenzothiophene}$) and complex **6**.^{5a,c} Although diphosphinoarenes have been shown to support Co_2 and Fe_2 moieties with partial reduction of the arene, the structural parameters of the present compounds are not indicative of a bis-allyl motif.^{5e}

The NMR characteristics and the binding mode of the central arene allows for the interrogation of the effects on the M_2 moiety with changes in apical metal identity. The isoelectronic compounds **2** and $3\cdot[\text{BF}_4]$ show slightly different metal–arene interactions, changing from pseudo- $\text{C}_2 \mu_2: (\eta^3, \eta^3)$ to $\mu_2: (\eta^3, \eta^2)$. The closest $\text{Pd}-\text{C}$ contacts are slightly shorter in $3\cdot[\text{BF}_4]$ in comparison to those in **2**, potentially a consequence of the cationic nature of $3\cdot[\text{BF}_4]$ leading to stronger metal–arene interactions. In solution, complexes **2**, $3\cdot[\text{BF}_4]$, and **7** show single resonances (^1H NMR spectroscopy) for central arene protons (δ (ppm): **2**, 5.92; $3\cdot[\text{BF}_4]$, 6.39; **7**, 5.78), indicating fluxional central arene coordination on the NMR time scale. The significantly upfield shifted resonance for the central arene protons in comparison to that for **1** (7.55 ppm) is indicative of metal–arene interactions as observed by XRD.

Solution infrared (IR) spectroscopy was used as a measure of the effect of the identity of the homodinuclear component (M_2) and supporting ligand on the cluster properties. The clusters containing the $\text{Fe}(\text{CO})_4$ moiety display bands corresponding to $\text{C}-\text{O}$ stretches (ν_{CO} (cm^{-1}): **2**, 1901 (s), 1874 (m), 1848 (s), 1843 (w, sh); **5**, 1898 (s), 1867 (m), 1838 (s, likely two overlapping bands given computed frequencies; see the Supporting Information); **7**, 1896 (s), 1874 (m), 1821 (m), 1798 (w, sh)). Complex **7** shows a reduction in average carbonyl stretching frequency (20 cm^{-1}) in comparison to **2**. The effect of the more electron rich central arene of **5** is seen in the average carbonyl stretching frequencies that shift by 7 cm^{-1} to lower energy in comparison to **2**, though the magnitude of the change is smaller relative to **7**. These differences indicate that the moiety in direct contact with Fe (Ni_2 or Pd_2) has a larger effect than the more distant arene ligand, due to the direct interactions with the bridging CO ligands. Mössbauer data were obtained to further to probe the electronic

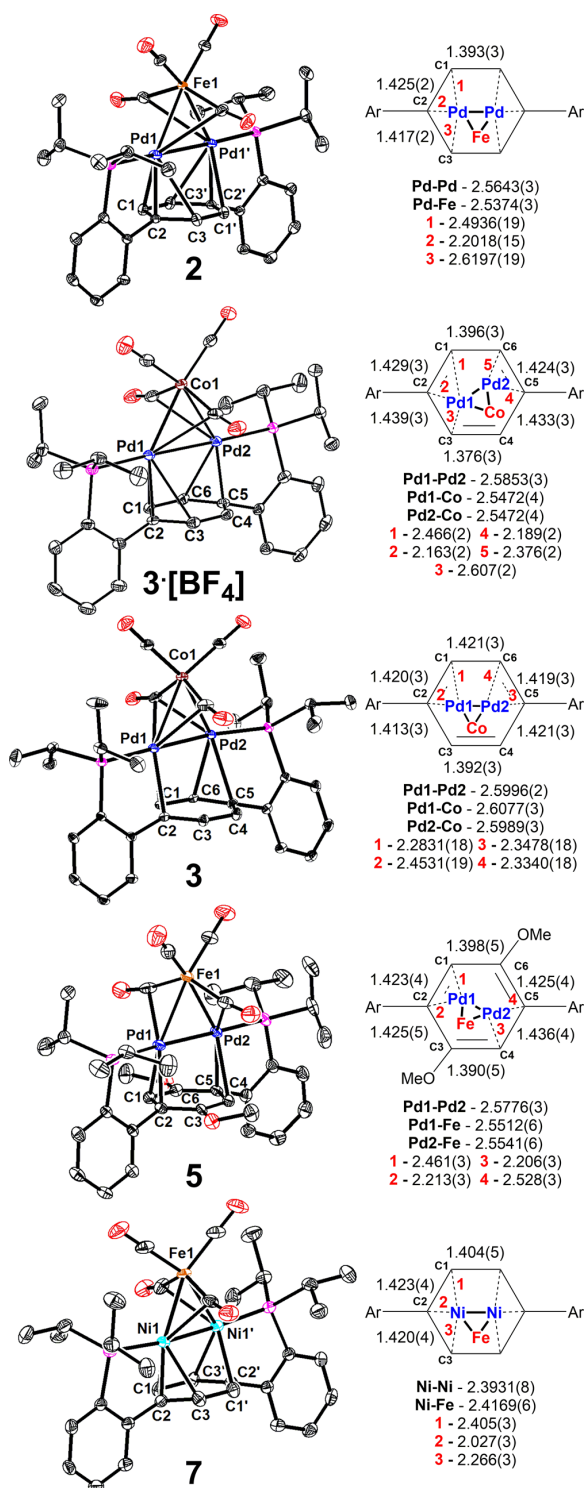


Figure 1. Solid-state structures of (top to bottom) **2**, $3\cdot[\text{BF}_4]$, **5**, and **7** (left) and selected bond distances (right). Hydrogen atoms, solvents, and counteranions have been omitted for clarity.

differences between Fe-containing complexes. The isomer shifts and quadrupole splitting of all complexes (δ (mm s^{-1}))

(Δq (mm s⁻¹)): **2**, -0.10 (1.08); **5**, -0.09 (1.13); **7**, -0.11 (0.83)) within 0.02 and 0.30 mm s⁻¹ ranges, respectively, suggest that the nature of the Fe sites does not change significantly despite the differences observed by IR spectroscopy. Complex **3**·[BF₄] shows IR absorptions at higher energy (2057 (s), 2012 (m), 1915 (m), and 1878 (w, sh) cm⁻¹) in comparison to **2**, consistent with the expected trends for isoelectronic complexes based on higher nuclear charge for Co vs Fe.

Computational studies were performed on simplified models of **2**, **3**·[BF₄], **5**, and **7** (see the Supporting Information for details and representative molecular orbitals for all compounds). Calculated metal–metal distances are in good agreement with solid-state parameters obtained from XRD studies (Table S3 in the Supporting Information), with the largest deviations in M–M and M–M' distances seen for complex **7** at 0.046 and 0.020 Å, respectively. Differences in computed average carbonyl stretching frequencies also largely agree with the experimental differences (Table S2 in the Supporting Information). Select computed MOs are highlighted for a truncated model of **2** (2-Me₂) (Figure 2). The

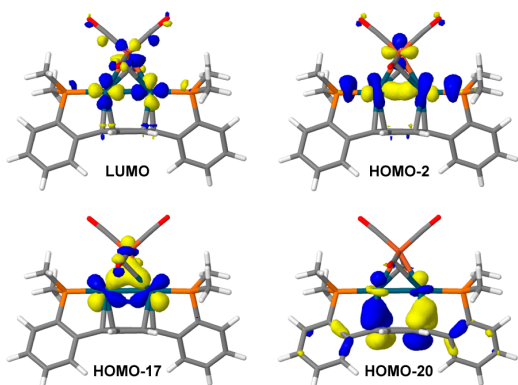


Figure 2. Representative molecular orbitals calculated for a truncated version of **2** that show interactions between (clockwise from LUMO) M–M/M–M', M–M, M–arene, and M–M' moieties.

analysis of Wiberg bond indices (WBIs) is consistent with weak bonds of comparable strength for the M–M (2-Me₂, 0.1647; 3⁺-Me₂, 0.1647; 5-Me₂, 0.1658; 7-Me₂, 0.1647) and M–M' (2-Me₂, 0.2147; 3⁺-Me₂, (0.1758, 0.1753); 5-Me₂, (0.2133, 0.2131); 7-Me₂, 0.2140) interactions in all complexes. Although weak, these M–M' interactions suggest direct electronic communication between M' and the homodinuclear core. Additionally, the bridging CO ligands are found to have significant bonding interactions with the M₂ moiety (see Figure S34 in the Supporting Information). These results are consistent with a previously reported bonding picture with the formally 18-electron M'(CO)₄ fragment donating electron density to the M₂ motif with additional stabilization provided by the bridging ligands.⁷

Cyclic voltammetry (CV) experiments were conducted on complexes of the trinuclear series (see the Supporting Information for experimental conditions). Quasi-reversible reductions for all complexes vs the ferrocene/ferrocenium (Fc^{0/+}) couple were observed as follows: **2**, -2.43 V; **3**·[BF₄], -1.31, -1.81 V; **5**, -2.62 V; **7**, -2.29, -2.75 V (Figure 3). While comparable CV data for Pd₂Fe and Ni₂Fe complexes are absent from the literature to the best of our knowledge, a

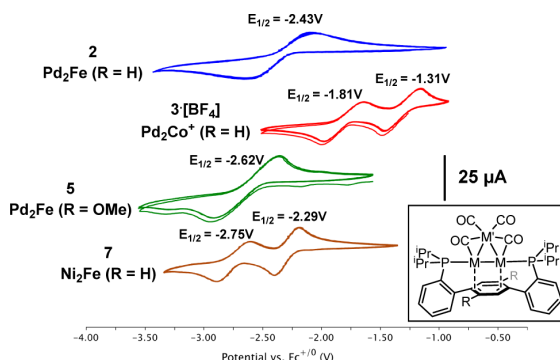


Figure 3. Cyclic voltammograms of reported compounds. Conditions: glassy-carbon working electrode, platinum-wire counter electrode, AgNO₃/Ag⁰ reference electrode, 0.1 M [*n*Bu₄N][PF₆] THF electrolyte, 100 mV/s scan rate.

systematic study of ligand variation in isoelectronic Pd₂Co complexes has been reported.^{4g} The trinuclear complex [Pd₂Co(μ-dppm)₂(μ₃-CO)₂(CO)₂][PF₆] (dppm = 1,1-bis-(diphenylphosphino)methane) was reported to have two one-electron reductions with E_{1/2} potentials comparable to those of **3**·[BF₄] at -1.20 and -1.63 V vs Fc^{0/+} in THF despite significant differences in supporting ligands.

Pd₂Fe complexes **2** and **5** both display CV behavior with only a single two-electron-reduction event (S24) observed at potentials more negative than both peaks for **3**·[BF₄]. The reduction of **5** is ~200 mV more negative than that of **2**, a consequence of the more electron rich supporting arene. The Ni₂Fe complex **7** shows electrochemical behavior similar to that of **3**·[BF₄], with two reduction events, but at potentials ~1 V more negative. The increased charge of the Pd₂Co core relative to the Ni₂Fe or Pd₂Fe complexes likely contributes to the positive shift in the redox events for complex **3**·[BF₄], making the reduction more facile. Overall, the electrochemical data indicate that the metal composition and supporting ligand play a significant role in cluster properties, as the variation of the apical metal (Fe to Co) and dinuclear core (Pd₂ to Ni₂) significantly affects redox behavior.

In light of the electrochemical observations, chemical reductions were performed with **2**, **3**·[BF₄], **5**, and **7**. The Fe-containing complexes led to complex mixtures of products. The neutral Pd₂Co complex **3** was successfully isolated upon treatment of **3**·[BF₄] with 1 equiv of cobaltocene (Scheme 1). While unstable at room temperature, single crystals suitable for XRD analysis were obtained at -35 °C (Figure 1). Coordination to the central arene has shifted to μ₂:(η²,η²), and the bridging CO ligands have adopted a different geometry, with one bound μ₃ across the Pd₂Co core, indicative of increased back-bonding to the π-acidic ligands. In agreement, IR spectra of complex **3** display CO stretching frequencies of 2007 (s), 1920 (m, sh), 1879 (m), and 1837 (m) cm⁻¹, which are shifted to lower energy in comparison to those of **3**·[BF₄]. Increases in Pd–Co and Pd–Pd bond distances by 0.06 and 0.03 Å, respectively, are consistent with weakened M–M and M–M' interactions. Solution electron paramagnetic resonance (EPR) data for **3** obtained in a toluene glass at 77 K shows a rhombic signal (g = 2.128, 2.032, 1.930) with hyperfine coupling to the Co nucleus (A = 119, 65, 105) and compare well to those of a related literature complex.^{4g} The flexible

coordination of the central arene and CO ligands likely helps stabilize complex 3, allowing for its isolation.

In summary, the synthesis of a new series of heterometallic trinuclear complexes allowed for the systematic study of the effects of changes in metal composition and ligand electronics. The identity of the minor, apical metal significantly affects the C–O stretching frequency, as expected given the direct M'–CO interaction, and the Pd–arene interactions. The identity of the homodinuclear moiety also affects the CO stretching frequency. Ligand electronics were found to affect the spectroscopic features of the clusters, but to a lesser extent than changes in metal identity. Electrochemical behavior varied considerably with the metal composition and nature of the supporting arene. Overall, the present studies provide a quantitative evaluation of the effect of metal identity and supporting ligands in triangular low-oxidation-state metal clusters. Current studies focus on gaining further insight into heterometallic effects on the chemical and physical properties of transition-metal clusters.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00579.

Experimental procedures, characterization data, computational details, and crystallographic details (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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