Arene non-innocence in dinuclear complexes of Fe, Co, and Ni supported by a para-terphenyl diphosphine†

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Cofacial Fe₂, Co₂, and Ni₂ complexes supported by a para-terphenyl diphosphine ligand were prepared. Central arene deplanarization and a μ₂(η²,η²) coordination mode suggest partial bisallyl character in the Fe₂ and Co₂ complexes. An oxidation induced shift in Fe₂–arene binding highlights the non-innocent nature of the arene ligand.

Dinuclear metal complexes have the potential to act in a cooperative fashion in small molecule activation and multi-electron processes. In particular, low-valent Fe₂, Co₂, and Ni₂ complexes have been shown to participate in a variety of transformations, including proton reduction, Pauson-Khand-type cycloadditions, C–C coupling, group transfer, and carbon dioxide activation. The development of novel dinucleating ligand scaffolds and complexes capable of both undergoing redox processes and facilitating novel chemical transformations is currently a topic of active research. Our group has recently utilized bis- and tris(phosphinoaryl)benzene ligands as multinucleating scaffolds for Ni and Pd complexes, where the central arene participates as a flexible donor ligand. Herein, we describe a series of dinuclear, first-row transition metal complexes supported by a para-terphenyl diphosphine, compound 1 (Scheme 1), and the changes in Fe₂–arene coordination upon one-electron redox chemistry.

After multiple days of ultraviolet irradiation, a tetrahydrofuran (THF) solution of compound 1 and Fe₃(CO)₁₂ yielded a Fe₂ complex, 2, in 11% isolated yield (Scheme 1). Refluxing a toluene (PhMe) solution of compound 1 and Co₂(CO)₈ at 110 °C cleanly afforded a Co₂ complex, 3, in 54% isolated yield (Scheme 1). The analogous cofacial Ni₂ complex was prepared by the reduction of a previously synthesized Ni I–NiI dichloride complex, 5, with Na[Co(CO)₄], which served as a source of both reducing equivalents and carbon monoxide (CO) ligands. The Ni₂ complex, 4, was isolated in 11% yield (Scheme 1). An alternative synthesis of complex 4 involved the addition of four equivalents of CO to two equivalents of Ni(COD)₂ (COD = 1,5-cyclooctadiene) and compound 1 (Scheme 1). However, this method was lower yielding and not used as the primary synthetic route. The low yields for compounds 2 and 4 are due to purification procedures, which require isolation of crystalline material. The reaction mixtures for the syntheses of these complexes display the desired compounds as the major species by ³¹P NMR spectroscopy.

Single crystal X-ray diffraction (XRD) studies of complexes 2, 3, and 4 confirmed the stabilization of dinuclear fragments by metal–arene interactions (Fig. 1). The dinuclear core of complex 2 and 3 coordinate in a μ₂(η²,η²) fashion to the central arene. In 2, the phosphines coordinate roughly along the Fe–Fe vector, resulting in a structure of pseudo-C₂₃ symmetry. The zig-zag arrangement of the P₂Co moiety in 3, imposed by the bridging and terminal CO ligands on Co, effects the overall pseudo-C₂₃ symmetry of the dicobalt complex. In complex 2, the planes...
represented unusual examples of cofacially coordinated and C4–C5 in complex 3. The Fe–Fe distance in complex 2 (2.7563(2) Å) is comparable to a cofacial μ2[(η3,η3)芳]iron complex at 2.746(1) Å,12 but shorter than typical bisallyl diiron compounds which range between 2.927(3) and 3.138(3) Å.4ab–d The Co–Co distance (2.6035(2) Å) in 3 is in the range for a formal single Co–Co bond.7

In contrast to the Fe2 and Co2 systems, the Ni2 core of 5 binds μ2[(η2,η2)芳] to adjacent C–C bonds of the central arene. In the solid-state, 4 shows partial localization of single bond character at C1–C6, C2–C3, and C4–C5 indicative of disrupted aromaticity. No deplanarization of the central arene ligand is observed, suggesting that bisallyl character is not present. While transficial μ2[(η3,η3)芳] arene NiNi3 complexes are known,8 4 displays the first structurally characterized cofacial μ2[(η3,η3)芳] binding mode. The coordination sphere of Ni in 4 is reminiscent of NiNi(CO)(dpmm),10 with a phosphine donor replaced by an arene double bond for each metal center (dpmm = bis(diphenylylphosphino)methane).10a

The 1H NMR chemical shifts of the central arene protons of complex 2, 3, and 4 are shifted upfield in comparison to the parent ligand, as a singlet at 4.39 ppm, a pair of 1:1 singlets at 4.29 and 3.95 ppm, and a singlet at 5.85 ppm, respectively, indicating that strong metal–arene interactions and disruption of aromaticity are preserved in solution. The NMR spectra of 2 are consistent with the high symmetry observed in the solid-state structure. Variable temperature (VT) 1H NMR experiments with 3 show broadening of the central arene and methine protons upon heating, with coalescence observed around 80 °C (Fig. S11, ESI†). The fluxional process consistent with the observed NMR features involves the interconversion of the two pseudo-C2 isomers by partial rotation of the CO unit around the central arene ring. VT 1H NMR studies with complex 4 show decoalescence of the central arene protons into a pair of doublets at −20 °C (Fig. S12, ESI†). Further cooling to −78 °C was not sufficient to resolve the central arene protons into four separate resonances indicating the complex was not locked out as the C1 solid-state structure due to partial rotation of Ni3 unit. In agreement, the 31P NMR spectrum shows a single peak, even at −78 °C. The lower energetic barrier for the fluxional process in 4 versus 3 may be due to a smaller molecular distortion, particularly of the central ring, necessary for partial rotation of the M2 unit of 4.

The IR spectrum of complex 2 displays peaks corresponding to terminal CO stretches at 1966, 1914, 1903, and 1880 cm−1, with CO stretches at 1972, 1933, 1897, and 1882 cm−1, comparable to an asymmetrically substituted [FeFe]-hydrogenase model complex, (μ-pdt)[Fe3(CO)12(PMe3)][Fe3(CO)12(IMes)] (pdt = 1,3-propanedithiolate, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), with CO stretches at 1972, 1933, 1897, and 1882 cm−1.9 Complex 3 shows peaks consistent with the presence of two terminal (1946 and 1928 cm−1) and one bridging (1771 cm−1) CO ligands, as observed in the solid-state.10 Similarly, complex 4 shows IR absorptions for two terminal (1972, 1952 cm−1) and one bridging (1803 cm−1) CO ligands.10

Cyclic voltammetry (CV) studies of complex 2 revealed a quasi-reversible oxidation at −0.44 V versus the ferrocene (Fc) and ferrocenium couple (Fig. S13, ESI†). Complexes 3 and 4 did not show reversible redox events in CV studies, and chemical oxidations led to decomposition. The addition of one equivalent of [FeCl2(dppm)] to a THF solution of complex 2 resulted in a color

![Fig. 1 Solid-state structures as 50% thermal ellipsoids of complexes (from top to bottom) 2, 3, and 4. Hydrogen atoms, solvents, and counterions have been omitted for clarity. Selected bond distances for each complex are shown on right.](image-url)
change from orange-red to green. The one-electron oxidized complex, \(2[\text{PF}_6]\), was isolated in 41% yield, but was found to be unstable in solution at ambient temperatures. However, crystals of complex \(2[\text{PF}_6]\) grown at \(-35\) °C are stable for weeks in the solid-state and proved suitable for XRD analysis.

Oxidation of complex \(2\) results in significant structural changes to both the coordination mode of the \(\text{Fe}_2\) core to the central arene and the nature of the central arene deplanarization (Fig. 1). The diiron core binds in an \(\mu_2:([\eta^5,\eta^5])\) fashion, consistent with a distorted neutral ene-diene assignment for the arene. The longest C–C distances are C1–C2 and C3–C4 (average of 1.467 Å), which correspond to the bonds separating the metal-bound olefin and diene fragments. This is an unusual structural motif for an arene coordinated to a dinuclear unit. The Fe–Fe bond of \(2[\text{PF}_6]\) has contracted to 2.6320(3) Å, over 0.12 Å shorter than the Fe–Fe bond of complex \(2\), suggestive of a strengthened metal–metal bonding interaction. The IR spectrum of \(2[\text{PF}_6]\) shows peaks at 2010, 1972, 1938, and 1917 cm\(^{-1}\) for an arene coordinated to a dinuclear unit. The Fe–Fe bond of which correspond to the bonds separating the metal-bound IMes ligand from an apical to a basal position. Given CO stretching frequencies at 2036, 1997, and 1987 cm\(^{-1}\), these values are indicative of weaker terminal CO stretches. These values are consistent with a formal oxidation state assignment of \(\text{Fe}^{2+}\). Such ambiguity in formal oxidation results in significant structural shifts of \(\text{Fe}_2:([\eta^5,\eta^5])\) compared to \(2\), consistent with a higher formal oxidation state in the former.

The aforementioned [FeFe]-hydrogenase model complex has been employed in the redox-induced reorganization of the central arene to accommodate electron transfer chemistry. Future work will focus on employing the redox non-innocence and coordination flexibility of \(\eta^5\)-bound aromatic systems for reactivity.

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Notes and references


6. A CSD search of dinuclear Co or Fe complexes bound to a cyclic ene-diene assignment of the central arene challenges a formal oxidation state assignment of \(\text{Fe}^{2+}\). Such ambiguity in formal oxidation results in significant structural shifts of \(\text{Fe}_2:([\eta^5,\eta^5])\) compared to \(2\), consistent with a higher formal oxidation state in the former.

In summary, the compounds presented here show that the combination of pendant donors surrounding an arene moiety provides a versatile multidentate platform to support a variety of dinuclear complexes of first-row transition metals. Beyond the intriguing structural aspects, the redox-induced reorganization of the arene highlights its flexible coordination modes and the ability to accommodate electron transfer chemistry. Future work will focus on employing the redox non-innocence and coordination flexibility of \(\eta^5\)-bound aromatic systems for reactivity.

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