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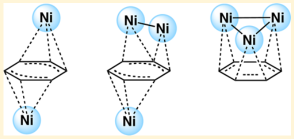
Trinuclear Nickel Complexes with Metal–Arene Interactions Supported by Tris- and Bis(phosphinoaryl)benzene Frameworks

Sandy Suseno, Kyle T. Horak, Michael W. Day, and Theodor Agapie*

Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Boulevard,
MC 127-72, Pasadena, California 91125, United States

Supporting Information

ABSTRACT: Triphosphine and diphosphine ligands with backbones designed to facilitate metal–arene interactions were employed to support multinuclear Ni complexes. Di- and trinuclear metal complexes supported by a triphosphine containing a triarylbenzene linker display diverse metal–arene binding modes. Multinuclear Ni halide complexes were isolated with strongly interacting metal centers bound to opposite faces of the coordinated arene. Upon reaction of the trinickel diiodide complex **2** with disodium tetracarbonylferrate, a cofacial triangulo nickel(0) complex, **4**, was isolated. The Ni^0_3 cluster motif can also be supported by a *para*-terphenyl diphosphine, where a terminal carbon monoxide ligand replaces the third phosphine donor. All multinuclear complexes feature strong metal–arene interactions, demonstrating the use of an arene as a versatile ligand design element for small clusters.

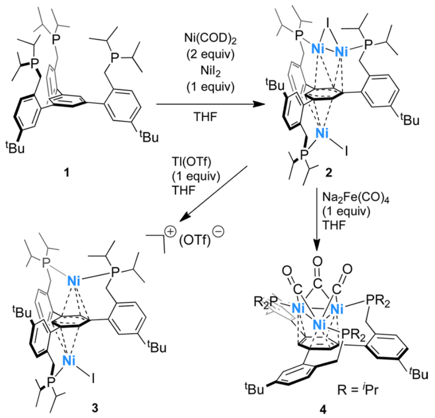


Multinickel complexes have been employed for a variety of transformations.[1] Di- and trinickel complexes have been reported to activate, cleave, and electrochemically reduce CO_2.[1a−e,g] C–C cross-coupling chemistry has been reported at dinuclear sites as well.[1f] To further develop the reactivity of multinuclear Ni complexes, the design of new coordination motifs is of interest. A wide variety of multidentate ligands have been utilized to support dinuclear transition metal chemistry.[2] Ligand design strategies for the controlled synthesis of trinuclear complexes are less developed. Several approaches have been reported recently for targeting trinuclear complexes of Mn, Fe, Co, Cu, and Zn.[3]

We have employed multidentate phosphines linked by aryl–benzene bridges to support mono- and dinuclear complexes stabilized by strong metal–arene interactions.[1f,4] The central arene in these systems serves both as a spacer to facilitate the coordination of multiple metals by the phosphines and as a site of metal coordination with a variety of possible binding modes. The rigid aryl–aryl linkages facilitate coordination of the metals in positions prone to interaction with the central arene and also enforce a relatively large distance between donors, depending on ring substitution, favoring coordination of multiple metals. Further exploring the potential of phosphinoaryl-benzene frameworks to support discrete metal clusters with unusual bonding motifs, herein we present the synthesis and characterization of trinuclear Ni complexes displaying metal–metal bonds and strong metal–arene interactions.

Comproportionation reactions between Ni^0 and Ni^{II} precursors have offered facile access to dinuclear Ni^I_2 complexes.[1f] A similar strategy was employed toward multinuclear complexes. Treatment of a tris(phosphinoaryl)benzene species, **1**, with 2 equiv of $Ni(COD)_2$ (COD = cyclooctadiene) followed by 1 equiv of NiI_2 afforded the trinickel species **2** (Scheme 1). A single-crystal X-ray diffraction (XRD) study of complex **2** reveals a trimetallic complex with one phosphine arm coordinated per Ni center (Figure 1). Two metal centers (Ni1, Ni2) are bridged by an iodide and coordinated cofacially relative to the central arene. The third Ni (Ni3) is located on the opposite face relative to the central arene ring and coordinated by a terminal iodide. Complex **2** exhibits a short Ni1–Ni2 distance (2.3907(2) Å) similar to previously reported bonding Ni^I–Ni^I motifs[1f,i,4a,5] or metal–metal distances in $[Ni_3]^{2+}$ species.[6] Additionally, strong metal–arene interactions to the central ring are observed, with Ni–C distances ranging between 1.95 and 2.11 Å.[5a] The solution ^1H nuclear magnetic resonance spectrum of **2** shows peaks only in the diamagnetic region with significantly upfield shifted proton signals that correspond to the central ring at 4.61 and 3.35 ppm in 2:1 ratio, indicative of strong metal–arene interactions, as shown by the crystal structure. The ^{31}P NMR spectrum of **2** in C_6D_6 at room temperature displays two phosphorus signals: a triplet at 11.66 ppm and a broad multiplet at 67.71 ppm in 1:2 ratio.

Scheme 1. Synthesis of Di- and Trinickel Complexes Supported by a Triphosphine–Arene Framework (1)



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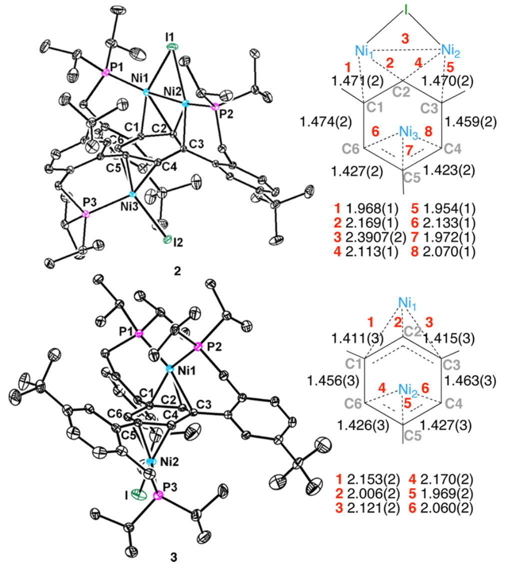


Figure 1. Solid-state structures with thermal ellipsoids at the 50% probability level (left) and selected C−C and Ni−C bond distances (Å, right) of **2** (top) and **3** (bottom). Hydrogen atoms and anions are omitted for clarity.

The upfield peak is assigned to the mononickel site, while the second peak corresponds to the dinuclear site. The presence of two rather than three peaks for the phosphines (^{31}P NMR) and the hydrogen atoms of the central arene (^{1}H NMR) suggests that although the solid-state structure has C_1 symmetry, the solution structure is fluxional. An exchange process consistent with the observed spectra involves shifting of the iodide and phosphine coordinated to Ni3 across a reflection plane perpendicular to the central ring and containing C2 and C5.

Previous studies of a dinuclear Ni complex supported by a related triphosphine demonstrated the reversible interconversion of isomers with the two metal centers coordinated to the same face vs opposite sides of the central arene.[4a] Halide abstraction induced formation of the cofacial isomer with a Ni^{I}−Ni^{I} bond and a bridging halide. Analogously, complex **2** was treated with Tl(OTf) (OTf = triflate) in an attempt to generate a cationic triangulo trinickel cluster capped by a μ_3-iodide. However, a dinuclear complex **3** (Scheme 1) was isolated as the major product, as revealed by XRD (Figure 1). Formation of **3** likely results from loss of an equivalent of Ni^{0} following halide abstraction, consistent with the black precipitate observed during reaction. Attempts to regenerate **2** by addition of a third Ni center with Ni(COD)$_2$ in the presence of a halide do not lead to the trinuclear complex, suggesting that the formation of **3** is irreversible. The solid-state structure of **3** shows the two metal centers on opposite faces of the central arene. Ni1 is coordinated by two phosphines, and Ni2 by one phosphine and a terminal iodide. As with complex **2**, both metal centers interact strongly with the π system of the central ring, indicated by the short Ni−C$_{\text{arene}}$ distances of 1.97−2.17 Å. The ^{1}H NMR spectrum shows broad peaks in the diamagnetic region. Three upshifted signals for the central ring protons in a 1:1:1 ratio (4.5−6 ppm) are observed, consistent with the short Ni−C$_{\text{arene}}$ distances. Consistent with the low symmetry suggested by the ^{1}H NMR spectrum, the ^{31}P NMR spectrum displays three peaks in a 1:1:1 ratio. The NMR data are consistent with the solid-state structure of **3** having C_1 symmetry. The fluxional process exchanging the sides of the molecule as described for **2** is slower for **3**, although the broad peaks observed at room temperature approach coalescence.

Complexes **2** and **3** represent unusual cases of electronic interactions between Ni centers and arenes. Previous examples of dinickel complexes with metal−arene interactions are of three types. Complexes with cofacial Ni^{I} centers display the metals in close proximity (2.3−2.6 Å) consistent with a Ni^{I}−Ni^{I} bonding interaction.[1f,4a,5b,7] The metal−arene interactions in these complexes are typically supported by pendant donors, although a tetraphenylborate was reported to coordinate the Ni$^{I}_2$ moiety without additional ligands.[7a] A second type of Ni$_2$−arene complex involves two Ni^{0} centers ligated to opposite sides of the arene.[5a,8] A third class includes dinickel complexes with metals coordinated on opposite faces of the arene, but in higher oxidation states.[4a,7b,9] A common metal−arene binding mode in these complexes is μ-η^3:η^3, with structural distortions of the ring away from planarity and elongation of the C−C bonds between the two η^3 metal coordination sites.[7b,9a−c] This binding mode and the diamagnetism of these complexes have been interpreted as a formal reduction of the ring by Ni^{I} to result in a diallyl moiety and two Ni^{II} centers. For a related μ-η^1:η^3 binding mode, the two unpaired electrons of the Ni^{I} centers couple via a back-bonding interaction with an empty arene δ^* orbital different from the diallyl case, as supported by computation and the shortened C−C bonds adjacent to the η^3-coordinated moiety.[4a] Trinuclear complexes of Ni supported by interactions with an arene have not been structurally characterized to the authors' knowledge.[10] Compounds **2** and **3** both show distortion of the coordinated arene suggestive of a diallyl structure, with the elongated C−C bonds linking the allyl moieties (C1−C6 and C3−C4 *ca.* 1.46 Å). One allyl moiety coordinates to a monophosphine-mononickel site, and the second binds either a diphosphine-mononickel (**3**) or a diphosphine-dinickel site (**2**). Compound **3**, binding the arene μ-η^3:η^3, belongs to the third class of compounds described above. Compound **2**, binding the arene μ_3-η^3:η^3, displays two metals instead of one coordinated to one of the allyl moieties. There is one other complex that has been structurally characterized with a μ_3-η^3:η^3-arene coordinated to three ruthenium centers.[11] In the limiting case of a doubly reduced arene, the mononuclear site corresponds to a Ni^{II} and the binuclear site to a Ni^{I}−Ni^{I} moiety. The Ni$^{I}_2$ motif with bridging allyl ligands has been structurally characterized.[12] The strong interactions between the metal centers and the arene are supported not only by the short distances in the solid state but also by NMR spectroscopy. ^{31}P−^{31}P coupling through five bonds is observed in both **2** and **3**, indicating electronic communication across metals coordinated to opposite faces of the arene.

While halide abstraction results in the loss of Ni^{0}, a cofacial trinickel complex (**4**) can be isolated from the reaction of complex **2** with Na$_2$Fe(CO)$_4$ (Scheme 1). The hexanes-soluble fraction from this reaction shows one singlet in the ^{31}P NMR spectrum at 61.90 ppm. The ^{1}H NMR spectrum displays the central arene proton signal at 5.77 ppm, again indicative of strong metal−arene interactions and also suggesting a high-symmetry structure. The solution infrared spectrum of **4** shows intense bands at 1846 and 1796 cm^{-1}, consistent with μ_2-CO ligation. In agreement, the XRD study of **4** reveals a pseudo-C_3-symmetric structure, displaying a triangulo-trinickel core with each metal center coordinated by a phosphine donor, the arene moiety, and bridging μ_2-CO ligands (Figure 2). The electron-rich Ni$^{0}_3$ core is stabilized by back-bonding to CO and arene. The solid-state structure of **4** shows different metal−arene interactions than **2**. In contrast to the μ_3-η^3:η^3 arene binding mode of **2**, complex **4** displays μ_3-η^2:η^2:η^2 metal coordination to localized olefin

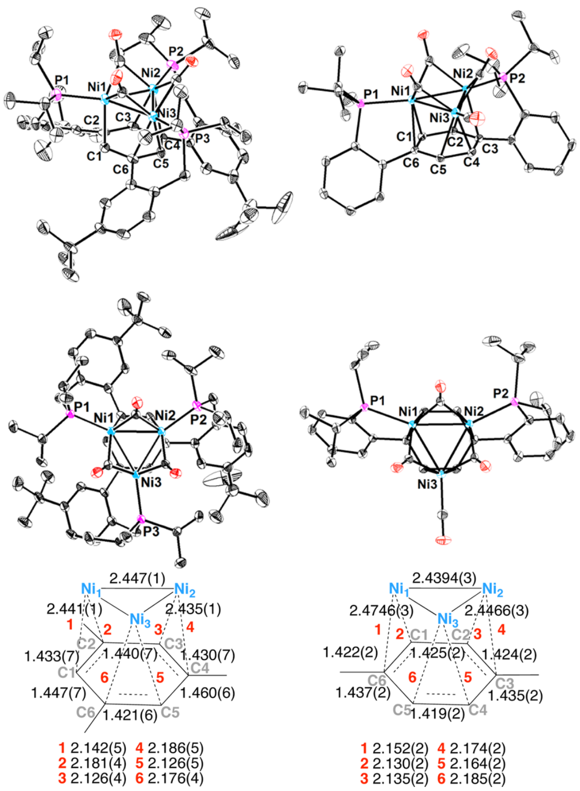
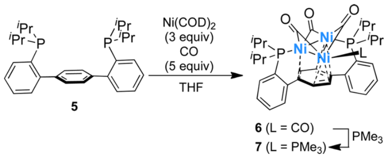


Figure 2. Solid-state structures with thermal ellipsoids at the 50% probability level (top: side view; middle: top view) and selected C−C and Ni−C bond distances (Å, bottom) of **4** (left) and **6** (right). Hydrogen atoms are omitted for clarity.

Scheme 2. Synthesis of Triangulo-trinickel Complexes Supported by a Diphosphine Ligand



moieties of the central arene. The bridging CO ligands likely provide additional stabilization to the Ni_3 core that is not accessible from **2** by iodide abstraction, albeit in a different oxidation state. To generate **4**, $Na_2Fe(CO)_4$ acts as both a reducing agent and CO source. A more direct route to **4** employing a Ni^0 precursor was attempted. Treatment of **1** with $Ni(COD)_2$ and appropriate amounts of CO resulted only in the formation of a trinickel nonacarbonyl complex with each phosphine arm coordinating a $Ni(CO)_3$ unit rather than the arene-supported trinuclear cluster with Ni−Ni contacts (see SI). Compound **4** represents the first structurally characterized example of an arene-supported triangulo-nickel complex. A Ni_3 cluster supported by the cyclooctatetraenyl dication has been reported.[10] Higher oxidation state Ni_3 moieties are typically supported by cyclopentadienyl or κ^2-bridging ligands.[13] A notable difference compared to the majority of reported Ni_3 species is the lack of a μ_3-capping ligand besides the arene.

Typically, the Ni_3 core is coordinated by two μ_3-ligands such as alkyne,[14] CO,[13a] alkylidyne,[15] benzyne,[16] halide,[6c] chalcogenide,[6d] or hydride moieties. Beyond nickel, trimetallic complexes supported by μ_3-arene donors are known for Os,[17] Co,[18] Rh,[19] Ru,[11] and Pd.[20] Given the unusual binding mode for Ni in the trimetallic complex **4**, the versatility of such coordination mode was investigated with fewer phosphine donors linked by a central arene. A *para*-terphenyl diphosphine was employed as supporting ligand (Scheme 2).[1f] Metalation of **5** with 3 equiv of $Ni(COD)_2$ in the presence of a slight excess of carbon monoxide provided access to the desired trinickel complex, **6** (Scheme 2), in 74% yield. Control of carbon monoxide stoichiometry is necessary, as a large excess results in the excessive coordination of carbon monoxide to generate previously characterized transfacial dinuclear $Ni(CO)_n$ ($n = 2-3$) complexes.[1f] An XRD study reveals that complex **6** has similar structural features to **4** in terms of the trinuclear core (Figure 2). Instead of a third phosphine arm, Ni3 binds a terminal CO ligand. Consistent with the solid-state structure, the solution IR spectrum of **6** shows bands at 1985, 1864, and 1817 cm^{-1} indicative of terminal and bridging carbon monoxide coordination.[21] The facile over carbonylation with the triphosphine ligand (**1**) suggests that the more flexible methylene-linked phosphine arms do not stabilize the intermediates and metal−arene interactions that facilitate formation of the Ni_3 core to the same extent as **5**. Complexes **4** and **6** exhibit average Ni−Ni distances of 2.44 and 2.45 Å, respectively, which are similar to a previously reported Ni^0−Ni^0 motif (2.47−2.50 Å) in a $Ni_4(CO)_6(PMe_3)_4$ cluster.[22] The Ni−Ni distances of **4** and **6** are also similar to those of the $Ni_3(dppm)_3$ (dppm = $Ph_2PCH_2PPh_2$) clusters, which are more oxidized.[6c,23]

The terminal carbon monoxide ligand of complex **6** is readily substituted upon addition of trimethylphosphine (PMe_3) to yield complex **7** (Scheme 2). While single crystals suitable for X-ray diffaction studies have not been obtained to date due to the compound's high solubility, spectroscopic characterization of the complex indicates an intact triangulo-trinickel core. The C_s symmetry of complex **6** has not been perturbed by PMe_3 substitution, as two ^1H NMR resonances corresponding to the methine protons are observed (2.41 and 2.24 ppm). The ^{31}P NMR spectrum of **7** displays the terphenyl phosphines as a doublet at 51.49 ppm and the PMe_3 as a triplet at −6.61 ppm; the observed multiplicity is consistent with the assigned structure. Strong metal−arene interactions are also maintained based on the upfield-shifted ^1H NMR resonances at 5.12 and 4.67 ppm. The substitution of the terminal CO ligand is supported by the IR spectrum showing only bands indicative of bridging CO ligands (1854, 1783 cm^{-1}) and the disappearance of the peak at 195.08 ppm (^{13}C NMR) observed for complex **6**. The increased electron density of Ni3 induced by the ligand substitution is reflected in the 0.53 upfield shift of the arene C−*H* ^1H NMR peak compared to **6** and the lower stretching energy of the bridging CO ligands. The coordination sphere of the Ni_3 cluster is identical in complexes **4** and **7**. In agreement, the CO stretching frequencies observed for the two compounds are almost identical (1847, 1795 cm^{-1} for **4**). The lability of this terminal CO ligand suggests that coordination and activation of other molecules at the Ni_3 unit in **6** may be possible.

In summary, bi- and trinuclear Ni complexes have been synthesized by employing phosphine ligand architectures that facilitate metal−arene interactions. Two complexes with metal centers coordinated transfacially show structural features consistent with a diallyl motif for the bridging arene. $^{31}P-^{31}P$ NMR coupling across five bonds spanning the bridging arene is indicative of the strong interactions with the metals. Cofacial trinuclear Ni_3 complexes have been isolated as well and exhibit μ_3-η^2:η^2:η^2 arene binding, a novel coordination mode for nickel. The triangular Ni_3 moiety was supported by the diphosphine **5**, in addition to the triphosphine **1**, suggesting that the arene-Ni_3 motif does not require pendant donors for each Ni center. Facile ligand substitution was observed for the terminal CO ligand of the Ni_3 species **6**. The present complexes demonstrate the utility of a coordinating arene as a versatile multidentate ligand design element for the synthesis of new types of metal clusters.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, characterization data, and crystallographic details for complexes **2**, **3**, **4**, and **6** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: agapie@caltech.edu.

Notes

The authors declare no competing financial interest.

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