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Synthesis and C−C Coupling Reactivity of a Dinuclear Ni^I-Ni^I Complex Supported by a Terphenyl Diphosphine

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Reactions involving multielectron transfers between metal centers and substrates are at the core of many important transformations in biology and chemistry.[1,2] While biological redox reactions are commonly performed by multimetallic enzyme active sites, the majority of synthetic homogeneous catalysts are monometallic, despite significant advances in cluster chemistry over the last few decades.[2,3] For example, group 10 monometallic complexes have been used for a wide variety of catalytic organometallic transformations involving redox cycling, whereas bimetallic complexes have found fewer applications in catalysis. This may be due to the use of multidentate ligands, which hinder reactivity by saturating the metal coordination sphere.[4,5]

Recently, monophosphine bimetallic Pd^I-Pd^I complexes have been shown to be efficient initiators for catalytic redox coupling reactions, presumably by providing access to a low-coordinate reactive monometallic species.[6] The intriguing ability of dinuclear complexes of palladium to catalyze C−H bond functionalization via intermediates involving $Pd^{III}-Pd^{III}$ bonds has been documented.[7] These reports raise the interesting possibility of alternate mechanistic pathways for known reactions and new catalytic reactions based on group 10 bimetallic species displaying metal−metal bonds. We report herein an entry into bimetallic Ni^I-Ni^I complexes stabilized by metal−arene interactions. Their reactivity with CO and CH_2Cl_2 is indicative of redox chemistry accessing both higher- and lower-oxidation-state nickel intermediates.

A *p*-terphenyl diphosphine, **1** (Figure 1), was designed [see the Supporting Information (SI) for the synthesis] to take advantage of potential metal−arene interactions.[8] Interactions of group 10 elements with aromatic systems are often transient but have been invoked in the stabilization of intermediates in catalytic processes.[4,9] Compound **1** reacted smoothly with 1 equiv of $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) to generate a red species, **2** (Figure 1). The solid-state structure of the isolated product shows a Ni^0 center coordinated to the two phosphine donors and to a double bond of the aromatic system [Ni−C bond lengths of 1.992(1) and 2.002(1) Å]. Chelation of the nickel center bends the peripheral aryl rings 14° inward relative to *p*-terphenyl (see the SI for angle definitions). Though two-coordinate homoleptic Ni(0) phosphine complexes are generally not isolable, this moiety can be stabilized by intermolecular coordination of arenes.[9c] The present Ni−arene interactions in **2** provide intramolecular stabilization of the Ni^0P_2 unit.

Comproportionation of **2** and $NiCl_2$(dme) (dme = 1,2-dimethoxyethane) led to a dark-green species that displays sharp peaks in the diamagnetic region of the ^1H NMR spectrum consistent with a Ni^I-Ni^I bonding interaction. A single-crystal X-ray diffraction (XRD) study of **3** (Figure 2) revealed that the targeted Ni_2 moiety is coordinated by the phosphines in a nearly linear PNiNiP arrangement. To accommodate the coordination of the two phosphines to the dinickel unit, the peripheral aryl rings are bent 16° outward. The metal centers are bridged by chlorides and interact with a vicinal diene moiety of the central ring of the terphenyl framework (Ni−C distance of 2.05−2.10 Å). These metal−arene interactions likely are important for the stability and isolation of **3**. Dinuclear complexes stabilized by inter- and intramolecular interactions between an arene and the Ni^I-Ni^I moiety have recently been reported.[10]

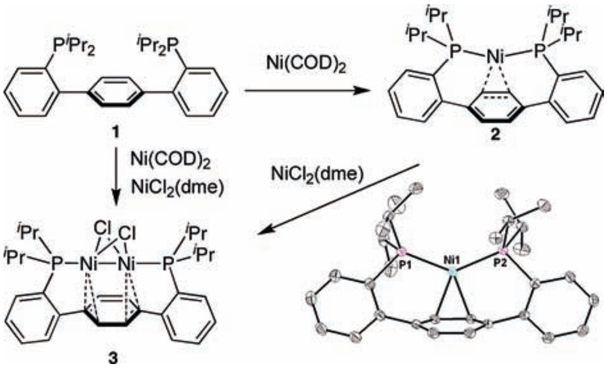

Figure 1. Preparation, reactivity, and solid-state structure of **2**.[11]

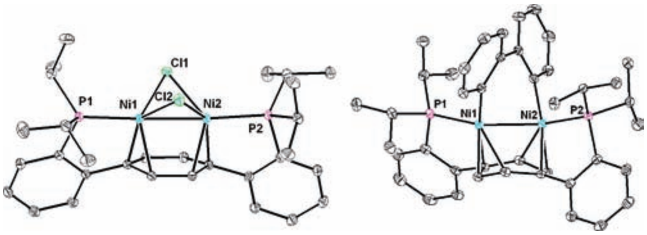

Figure 2. Solid-state structures of (left) **3** and (right) **4**.[11]

In an effort to document redox organometallic reactivity at the dinuclear core of **3**, derivatives displaying hydrocarbyl ligands were targeted. Such complexes are expected to provide examples of reductive elimination or oxidative addition at a bimetallic nickel complex. Attempts to make a diphenyl complex by treating **3** with PhMgBr led to the formation of biphenyl, presumably by reductive elimination from the in situ-generated $Ni^I_2Ph_2(PR_3)_2$ target. Reaction of **3** with *o,o′*-biphenyldiyl Grignard afforded an isolable dinickel biphenyldiyl complex (**4**, Scheme 1), probably because of a lack of facile decomposition pathways such as reductive or β-H elimination. A single-crystal XRD study of **4** revealed a μ-η^1:η^1 binding mode for the biphenyldiyl ligand and again a strong interaction between the metal centers and the central aryl ring of the terphenyl unit (Figure 2). Each nickel center interacts primarily with two nonvicinal double bonds (Ni−C distance of 1.98−2.06 Å) and with a third carbon at a longer distance (2.20−2.30 Å).[12] Compound **4** shows a significant distortion of the plane of the central ring toward a boat conformation.

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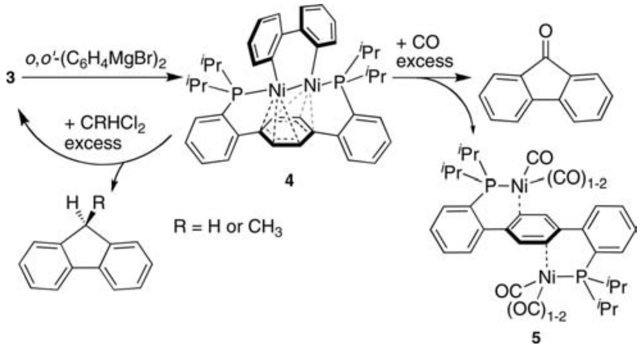
Diverse Ni−arene interactions are present in the solid state for all of the reported complexes, substantiating the potential of pendant arenes to act as versatile supporting ligands for nickel. The C−C bond lengths of the central arene indicate a partial loss of aromaticity. Solution NMR spectroscopic data for **2**−**4** are consistent with species that have C_{2v} symmetry on average, in contrast to the solid-state structures, which are pseudo-C_s (**2**, **3**) or pseudo-C_2 (**4**). These observations suggest that fluxional processes occur in solution that allow for the exchange of metal−arene bonds.

Reactivity studies were performed with **4** to address the potential for metal−carbon bond elaboration at a bimetallic moiety. Treatment with excess CO at room temperature led to the generation of fluorenone (Scheme 1).[13] While fluorenone formation from a mononickel biphenyldiyl complex has been reported previously, the functionalization of a diaryl fragment bound across two metal centers is rare.[12b,c] A possible mechanism (see the SI) involves the formal reduction of the dinickel fragment by two electrons. In agreement, dinuclear Ni^0−Ni^0 carbonyl complexes, **5**, were observed in the resulting mixture (see the SI).

Scheme 1



Reaction of **4** with geminal dichloroalkanes caused a color change from brown to green. Analysis of the mixture using GC-MS and ^{1}H NMR spectroscopy indicated the formation of fluorene derivatives and **3** as the major products (Scheme 1). Nickel-catalyzed C−C coupling reactions have been proposed to occur via intermediates in diverse oxidation states (from Ni^I to Ni^{IV}) by radical or nonradical mechanisms.[14] Stoichiometric intramolecular C−C couplings have been reported for Ni^I−Ni^I dinuclear complexes;[12b,c] in those cases, the metal centers are reduced to Ni^0. In contrast, the present cases provide examples of intermolecular C−C couplings with dichloroalkanes, suggesting dinickel intermediates in higher oxidation states. A possible mechanism (see the SI) involves oxidative addition of C−Cl bonds to generate Ni^{II}−Ni^{II} intermediates that reductively eliminate C−C bonds and produce Ni^I−Ni^I species. A radical mechanism involving partially oxidized dinickel (Ni^I−Ni^{II}) species can be envisioned as well. In these reaction pathways, electrons from the Ni−Ni bond are utilized for substrate reduction. While a mechanism involving both metal centers is appealing, an alternative involving fast dissociation of a mononickel biphenyldiyl moiety followed by reactivity at this monometallic species may be possible.[15] Mechanistic investigations are required for further insight.

In summary, mono- and bimetallic diphosphine complexes of nickel have been isolated by employing stabilizing metal−arene interactions with an ancillary terphenyl framework. The present bimetallic complexes perform redox transformations relevant to organic methodology in both oxidative and reductive directions. Applications of these complexes and related multimetallic systems to small-molecule activation and new reaction development are under study.

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Supporting Information Available: Detailed experimental procedures, characterization data, crystallographic details for **2**−**5** (CIF), and drawings of proposed mechanisms. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) H atoms have been omitted for clarity. Displacement ellipsoids are depicted at the 50% probability level.
(12) The Ni−Ni distances in **3** [2.3658(2) Å] and **4** [2.4426(2) Å] are similar to reported Ni(I)−Ni(I) bonds lengths. For examples, see ref 10 and: (a) Keen, A. L.; Doster, M.; Johnson, S. A. *J. Am. Chem. Soc.* **2007**, *129*, 810–819. (b) Ramakrishna, T. V. V.; Sharp, P. R. *Organometallics* **2004**, *23*, 3079–3081. (c) Eisch, J. J.; Piotrowski, A. M.; Han, K. I.; Krüger, C.; Tsay, Y. H. *Organometallics* **1985**, *4*, 224–231.
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(15) **3** and $NiCl_2$(dme) catalyzed the formation of fluorene from *o,o'*-biphenyldiyl Grignard and CH_2Cl_2 with similar yields.

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