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Dinickel Complexes

Reversible Halide-Modulated Nickel–Nickel Bond Cleavage: Metal–Metal Bonds as Design Elements for Molecular Devices**

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The synthesis and study of basic molecular devices are areas of research aimed toward understanding the fundamental design and functional parameters required for the construction of complex molecular machines.[1] Transition metals have been used extensively in this context in conjunction with elegantly designed ligand frameworks.[2] Typically, transition metals bind to different sets of donors in these frameworks, inducing large molecular motions, as a function of changes in pH value,[3] redox processes,[4] excitation by light,[5] heating,[5] introduction of additional ligands,[3] and removal or addition of different metal ions.[6] We report herein strategies based on chloride-mediated Ni–Ni bond cleavage and thermally accessible Ni–P bond cleavage to construct molecular analogues of hinge and mechanical crank mechanisms.

A previous report from our group shows that a *p*-terphenyl platform can act as an axis for rotation of two metals with respect to each other upon reduction of a bonded cofacial Ni^{I}–Ni^{I} moiety to a non-bonded transfacial Ni^{0}–Ni^{0} species.[7] In that context, the chemical reaction is irreversible; a species that allows better chemical control over molecular motion was sought. Inspired by the ability of related triarylbenzene architectures with pyridine and alkoxide donors to support robust trinuclear transition-metal complexes, we developed a triphosphine variant, **1**.[8] Addition of a single equivalent each of $[Ni(COD)_2]$ (COD = 1,5-cyclooctadiene) and $[NiCl_2(dme)]$ (dme = 1,2-dimethoxyethane) to **1** generates a dark brown species, **2** (Figure 1a). A single crystal X-ray diffraction (XRD) study of **2** reveals a dinuclear complex of nickel (Figure 2). One metal center coordinates two phosphines and one chloride and interacts with one carbon (C18) of the central arene ((Ni1–C18) = 2.047(2) Å). Notably, C18 comes out of the plane of the five other carbon atoms of the central ring by approximately 18°. The second nickel center is located on the opposite face of the central ring and binds one phosphine, one chloride and the π system of the central ring. The binding of the two nickel centers on opposite faces of the central ring contrasts with the related *p*-terphenyl and 2′,3′-dihydro-*p*-terphenyl diphosphine dinickel systems in which the dinickel dichloride moiety is cofacially bound by the central ring.[7,9] For compound **2**, a similar binding mode would lead to a higher metal coordination number, likely leading to steric repulsions between the chloride and phosphine ligands.

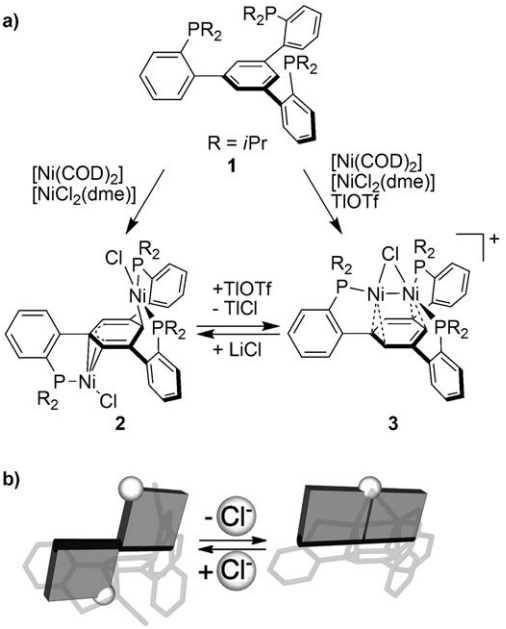

Figure 1. a) Preparation and interconversion of **2** and **3**. b) Schematic representation of the corresponding molecular hinge motion.

Attempting to open a coordination site on nickel in **2**, chloride abstraction was performed with TlOTf (OTf = triflate). A new species (**3**, Figure 1a) was formed based on ^{1}H and ^{31}P NMR spectra, which display broad peaks at room temperature. The same product can be obtained in a one-pot procedure by treating **1** with $[Ni(COD)_2]$ and $[NiCl_2(dme)]$ followed by TlOTf. An XRD study reveals that the two metal centers are on the same face of the central arene; both interact with the π system of the central ring and are bridged by the remaining μ^2-chloride (Figure 2). The Ni–Ni distance (2.5248(3) Å) in **3** is longer than the distance observed for the Ni^{I}–Ni^{I} moiety supported by a *p*-terphenyl diphosphine system (2.3658(2) Å)[7] but comparable to distances observed for other dinickel(I) moieties supported by bridging arenes[10] or by only bridging halides.[11] Treatment of **3** with a chloride source leads to the clean regeneration of **2** (^{1}H NMR spectroscopy). To our knowledge, this is an unprecedented example of reversible metal–metal bond formation/cleavage mediated by halide. Moreover, due to the geometrical

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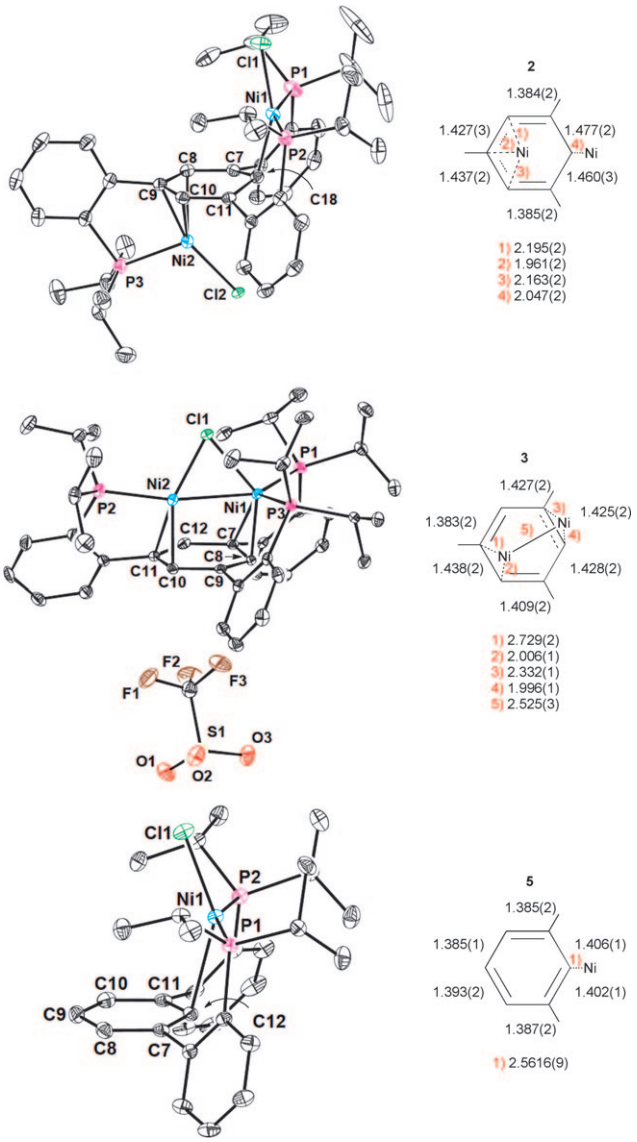

Figure 2. Left: Solid-state structures of **2**, **3**, and **5** (H atoms omitted for clarity). Right: C···C distances and selected Ni···C, Ni···Ni distances (numbered 1–5) of the central arene unit.

constraints of the ligand framework, the molecular movement induced by the above process is large and discrete (ca. 180° rotation around an aryl–aryl bond), and can be described as a molecular hinge mechanism (Figure 1b). Previously reported molecular hinges pivot about linkers, such as hexose,[12] methylene,[13] alkynyl,[14] triptycene-aryl,[15] and biaryl moieties,[16] or photo-switchable azobenzene[19] and olefinic cores.[1c, 17] The present system represents a reversible hinge that is controlled by metal–metal and metal–arene interactions and that can be switched by chloride.

The propensity of chloride to break the metal-metal bond is probably due to a combination of the weak, elongated nickel–nickel bond of **3** and a stabilization of **2** by strong interactions with the aromatic π system. To further interrogate the nature of the Ni–arene interactions in **2**, a homologous *m*-terphenyl diphosphine was prepared (**4**, see Figure 3). Treatment of **4** with a half equivalent each of

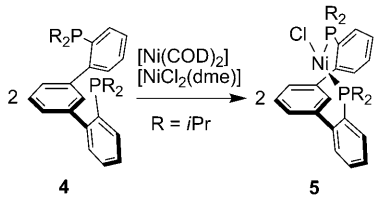

Figure 3. Preparation of **5**.

$[Ni(COD)_2]$ and $[NiCl_2(dme)]$ leads to a new species (**5**) with broad peaks in the ^1H NMR spectrum and an EPR spectrum consistent with a comproportionation reaction to generate a mononuclear Ni^I species. In agreement, an XRD study of **5** shows the metal center bound to two phosphines and one chloride (Figure 2), similar to Ni1 in **2**. The Ni1–C distance is much larger in **5** than in **2**, indicating that the two nickel centers synergistically bind the central arene in **2**.

Computation studies on models of **2** and **5**, with methyl groups substituted for isopropyl (**2**-Me and **5**-Me, respectively), support this notion (Figure 4). Model **5**-Me shows a

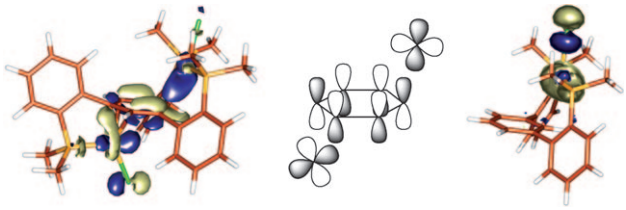

Figure 4. Computed (left) and schematic representation (center) of HOMO of **2**-Me, and computed SOMO of **5**-Me (right).

singly occupied molecular orbital (SOMO) that has antibonding character between the metal center and the P and Cl donors; little contribution from the central ring is observed. In contrast, the highest occupied molecular orbital (HOMO) of **2**-Me has a backbonding interaction between the nickel centers and an empty δ* orbital of the bridging arene. Corroborating this calculated interaction, the crystal structure of **2** shows the C7–C8 and C10–C11 distances to be shorter than the other C–C bonds of the central arene. Bifacial η^3,η^3-bridging of an arene between two metal centers has been previously observed in dinuclear Ni,[10a,18] Pt,[19] and Co complexes.[20] In contrast, in compound **2**, the arene bridges in η^3,η^1-fashion, probably due to the steric constraints of the triphosphine.

Compounds **2** and **3** were studied by variable temperature NMR spectroscopy. At −85 °C, the ^{31}P NMR spectrum of **3** displays three multiplets. Upon warming to −40 °C, two of the peaks coalesce, and above room temperature only one peak is observed. Across the same temperature range, similar coalescence of three distinct central arene protons is observed by ^1H NMR spectroscopy.[21] The low-temperature behavior is consistent with a C_1 symmetric structure as observed in the solid state. At −40 °C, the two phosphines coordinated to the same metal center are proposed to exchange on the NMR timescale due to a twist of the dinickel moiety and phosphine arms about an axis perpendicular to the central arene (**A** to **B**

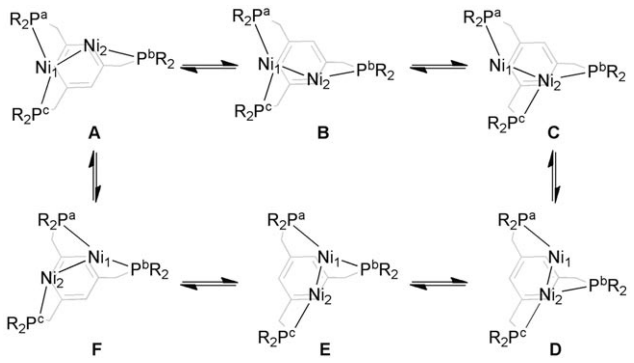

Figure 5. Proposed mechanism of rotation of the Ni_2 core in **3** (bridging chloride omitted for clarity). See text for details.

in Figure 5). This step does not require any Ni–P bond cleavage. Above room temperature, all phosphines exchange on the NMR time scale. This exchange involves phosphine (for example P^c, in the conversion of **B** into **C** in Figure 5) dissociation from the diphosphine-ligated nickel center (Ni1) and coordination to the monophosphine-ligated nickel center (Ni2). In contrast, **2** does not show similar exchange processes on the ^{1}H NMR spectroscopy time scale.[22] The exchange processes involving the dinickel unit of **3** resemble the motion of a mechanical crank (see Supporting Information). Related processes, albeit without metal–metal interactions, involving silver ions supported by arene-connected heterocyclic ligands have been reported.[23,24]

In summary, a dinuclear nickel system supported by a tris(phosphinoaryl)benzene ligand shows unusual molecular dynamics with potential applications in molecular devices. Reversible Ni–Ni bond cleavage that induces 180° rotation around an aryl–aryl bond occurs in response to chloride addition. A dinickel moiety was found to rotate around the bridging arene by a mechanism proposed to involve breaking and forming Ni–P bonds. All the accessed dinickel compounds are stabilized by strong metal–arene interactions. Further studies are focused on exploring the potential of the present architecture for more complex molecular devices and chemical reactivity.

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[21] Central arene protons were assigned based on isotopic labeling and a variety of NMR spectroscopy experiments (see Supporting Information).

[22] Variable temperature NMR spectroscopy studies of **2** show large changes of the chemical shifts of the signals assigned to hydrogen atoms on the central arene and the isopropyl methine positions (^{1}H NMR). However, the central arene and isopropyl methine signals, respectively, do not coalesce. Compound **3** also shows significant chemical shift dependence for nuclei close to nickel at higher than room temperature. The observed temperature-dependent shifts of the signals corresponding to nuclei close to the metal centers are proposed to be caused by population of paramagnetic excited states. In agreement, Evans' method magnetic susceptibility measurements give small, but non-zero values. Although smaller, variations of the ^{31}P chemical shift with temperature have been previously reported for other organometallic compounds. This phenomenon has been interpreted in terms of the temperature dependence of the ^{31}P shielding parameter. a) C. J. Jameson, A. C. De Dios, A. K. Jameson, *J. Chem. Phys.* **1991**, *95*, 9042; b) C. J. Jameson, D. Rehder, M. Hoch, *J. Am. Chem. Soc.* **1987**, *109*, 2589; c) E. T. Singewald, X. Shi, C. A. Mirkin, S. J. Schofer, C. L. Stern, *Organometallics* **1996**, *15*, 3062.

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