Published in final edited form as:

Angew Chem Int Ed Engl. 2011 August 8; 50(33): 7529–7532. doi:10.1002/anie.201102797.

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 active 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,^[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 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 Ni⁰-Ni⁰ 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 NiCl₂(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 ca. 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.

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 ¹H and ³¹P

**We thank Lawrence M. Henling for assistance with collection of crystallographic data. We are grateful to NSF GRFP (SL), Caltech, SURF office (NCL), and bp for funding. The Bruker KAPPA APEXII X-ray diffractometer was purchased via an NSF CRIF:MU Award to Caltech (CHE-0639094). The 400 MHz NMR spectrometer was purchased via an NIH award, RR027690.

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Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

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 NiCl₂(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** (¹H NMR spectroscopy). To the authors' knowledge, this is an unprecedented example of reversible metal-metal bond formation/cleavage mediated by halide. Moreover, due to the geometrical constraints of the ligand framework, the molecular movement induced by the above process is large and discrete (~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.^[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**, Figure 3). Treatment of **4** with a half equivalent each of Ni(COD)₂ and NiCl₂(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). **5-Me** shows a 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 π^* 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 π^3, π^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 π^3, π^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 ³¹P 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** 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** to **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 ^1H NMR spectroscopy time scale.^[22] The exchange processes involving the dinickel unit of **3** resemble the motion of a mechanical crank (see SI). 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 triarylbenzene triphosphine 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 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.

Supplementary Material

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References

1. a) Balzani V, Credi A, Raymo FM, Stoddart JF. *Angew Chem Int Ed.* 2000; 39:3348–3391. b) Kay ER, Leigh DA, Zerbetto F. *Angew Chem Int Ed.* 2007; 46:72–191. c) Feringa BL. *Acc Chem Res.* 2001; 34:504–513. [PubMed: 11412087] d) Kottas GS, Clarke LI, Horinek D, Michl J. *Chem Rev.* 2005; 105:1281–1376. [PubMed: 15826014] e) Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines.* Wiley-VCH; Weinheim: 2003. f) Kinbara K, Aida T. *Chem Rev.* 2005; 105:1377–1400. [PubMed: 15826015]
2. a) Champin B, Mobian P, Sauvage J-P. *Chem Soc Rev.* 2007; 36:358–366. [PubMed: 17264936] b) Elhabiri M, Albrecht-Gary A-M. *Coord Chem Rev.* 2008; 252:1079–1092.
3. Amendola V, Fabbrizzi L, Mangano C, Miller H, Pallavicini P, Perotti A, Taglietti A. *Angew Chem Int Ed.* 2002; 41:2553–+.
4. a) Canevet C, Libman J, Shanzer A. *Angew Chem Int Ed.* 1996; 35:2657–2660. b) Zelikovich L, Libman J, Shanzer A. *Nature.* 1995; 374:790–792. c) Livoreil A, Dietrichbuchecker CO, Sauvage JP. *J Am Chem Soc.* 1994; 116:9399–9400.
5. Mobian P, Kern J-M, Sauvage J-P. *Angew Chem Int Ed.* 2004; 43:2392–2395.
6. Jimenez MC, Dietrich-Buchecker C, Sauvage JP. *Angew Chem Int Ed.* 2000; 39:3284–+.
7. Velian A, Lin S, Miller AJM, Day MW, Agapie T. *J Am Chem Soc.* 2010; 132:6296–6297. [PubMed: 20397653]
8. a) Tsui EY, Day MW, Agapie T. *Angew Chem Int Ed.* 2011; 50:1668–1672. b) Tsui EY, Kanady JS, Day MW, Agapie T. *Chem Commun.* 2011; 47:4189–4191.
9. Lin S, Day MW, Agapie T. *J Am Chem Soc.* 2011; 133:3828–3831. [PubMed: 21344904]
10. a) Jones C, Schulten C, Fohlmeister L, Stasch A, Murray KS, Moubaraki B, Kohl S, Ertem MZ, Gagliardi L, Cramer CJ. *Chem Eur J.* 2011; 17:1294–1303. [PubMed: 21243697] b) Ito M, Matsumoto T, Tatsumi K. *Inorg Chem.* 2009; 48:2215–2223. [PubMed: 19235981] c) Chen Y, Sui-Seng C, Zargarian D. *Angew Chem Int Ed.* 2005; 44:7721–7725.
11. a) Laskowski CA, Hillhouse GL. *Chemical Science.* 2011; 2:321–325. b) Dible BR, Sigman MS, Arif AM. *Inorg Chem.* 2005; 44:3774–3776. [PubMed: 15907100]
12. a) Yuasa H, Fujii N, Yamazaki S. *Org Biomol Chem.* 2007; 5:2920–2924. [PubMed: 17728857] b) Yuasa H, Miyagawa N, Nakatani M, Izumi M, Hashimoto H. *Org Biomol Chem.* 2004; 2:3548–3556. [PubMed: 15592612]
13. Koo C-K, Lam B, Leung S-K, Lam MH-W, Wong W-Y. *J Am Chem Soc.* 2006; 128:16434–16435. [PubMed: 17177356]

14. a) Nandy R, Subramoni M, Varghese B, Sankararaman S. *J Org Chem*. 2007; 72:938–944. [PubMed: 17253814] b) Toyota S. *Chem Rev*. 2010; 110:5398–5424. [PubMed: 20521837] c) Jones IM, Hamilton AD. *Angew Chem Int Ed*. 2011:n/a–n/a.d) Jones IM, Hamilton AD. *Org Lett*. 2010; 12:3651–3653. [PubMed: 20669923]
15. a) Kelly TR, De Silva H, Silva RA. *Nature*. 1999; 401:150–152. [PubMed: 10490021] b) Kelly TR, Cai X, Damkaci F, Panicker SB, Tu B, Bushell SM, Cornella I, Piggott MJ, Salives R, Cavero M, Zhao Y, Jasmin S. *J Am Chem Soc*. 2006; 129:376–386. [PubMed: 17212418]
16. a) Lin Y, Dahl BJ, Branchaud BP. *Tetrahedron Lett*. 2005; 46:8359–8362. b) Fletcher SP, Dumur F, Pollard MM, Feringa BL. *Science*. 2005; 310:80–82. [PubMed: 16210531]
17. a) Feringa BL. *Acc Chem Res*. 2001; 34:504–513. [PubMed: 11412087] b) Kulago AA, Mes EM, Klok M, Meetsma A, Brouwer AM, Feringa BL. *J Org Chem*. 2009; 75:666–679. [PubMed: 20030300] c) Koumura N, Zijlstra RWJ, van Delden RA, Harada N, Feringa BL. *Nature*. 1999; 401:152–155. [PubMed: 10490022] d) Vicario J, Walko M, Meetsma A, Feringa BL. *J Am Chem Soc*. 2006; 128:5127–5135. [PubMed: 16608348] e) Wang J, Feringa BL. *Science*. 2011; 331:1429–1432. [PubMed: 21310964]
18. a) Bai G, Wei P, Stephan DW. *Organometallics*. 2005; 24:5901–5908. b) Schneider, Jörg J.; Spickermann, D.; Bläser, D.; Boese, R.; Rademacher, P.; Labahn, T.; Magull, J.; Janiak, C.; Seidel, N.; Jacob, K. *Eur J Inorg Chem*. 2001; 2001:1371–1382.
19. a) Thomas JC, Peters JC. *J Am Chem Soc*. 2003; 125:8870–8888. [PubMed: 12862484] b) Konze WV, Scott BL, Kubas GJ. *J Am Chem Soc*. 2002; 124:12550–12556. [PubMed: 12381199]
20. Jonas K, Koepe G, Schieferstein L, Mynott R, Krüger C, Tsay Y-H. *Angew Chem Int Ed Engl*. 1983; 22:620–621.
21. Note, p. The central arene protons were assigned based on isotopic labeling and a variety of NMR spectroscopy experiments (see SI).
22. Note, pp. Variable temperature NMR spectroscopy studies of 2 show large changes of the chemical shifts of the peaks assigned to hydrogens on the central arene and the isopropyl methine positions (¹H NMR). However, the central arene and isopropyl methine peaks, 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 peaks 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.
23. a) Hiraoka S, Okuno E, Tanaka T, Shiro M, Shionoya M. *J Am Chem Soc*. 2008; 130:9089–9098. [PubMed: 18558686] b) Hiraoka S, Shiro M, Shionoya M. *J Am Chem Soc*. 2004; 126:1214–1218. [PubMed: 14746493] c) Hiraoka S, Yi T, Shiro M, Shionoya M. *J Am Chem Soc*. 2002; 124:14510–14511. [PubMed: 12465941]
24. Okuno E, Hiraoka S, Shionoya M. *Dalton Trans*. 2010; 39:4107–4116. [PubMed: 20390173]

Figure 1.

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

Figure 2. Solid-state structures of **2**, **3**, and **5** (H atoms omitted for clarity) and central arene C—C and Ni—C distances.

Figure 3.
Preparation of 5.

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

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