

Synthesis, Structure, and Reactivity of a Dinuclear Metal Complex with Linear M–H–M Bonding

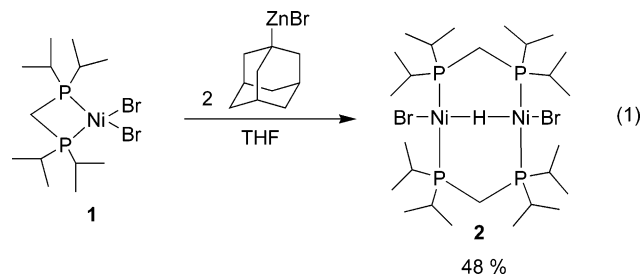
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A number of years ago, the X-ray crystal structure of the unsupported bridging hydride complex $[\text{HCr}_2(\text{CO})_{10}]^-$ was reported by Dahl and co-workers.^{1,2} The structural data was quite intriguing, as it detailed what would have been the first linear hydride of a simple dinuclear metal complex. The position of the bridging hydride could only be inferred to have a linear relationship with the two chromium atoms on the basis of the D_{4h} symmetry of the anion and the eclipsed positions of the equatorial carbonyl groups. The same argument was later used to postulate a linear Re–H–Re bridge in $\text{HRe}_2\text{Mn}(\text{CO})_{14}$.³ However, the description of the bonding in $[\text{HCr}_2(\text{CO})_{10}]^-$ was later discovered to be much more complex than originally believed. It was revealed by neutron diffraction studies that, because of the presence of a crystallographic center of inversion in the middle of the anion, the hydrogen atom did not lie at the predicted position but rather was disordered over two bent Cr–H–Cr positions.⁴ Low-temperature neutron diffraction analysis of the $[\text{K}(\text{crypt-222})]^+$ salt (which has no symmetry-imposed restraints) later confirmed the bent nature of the Cr–H–Cr bond.⁵ Since then, a plethora of neutron diffraction studies on transition metal hydrides suggest that the M–H–M linkage is inherently bent (Table 1 shows the largest M–H–M bond angles thus far reported in single hydrogen-bridged systems).^{6,7} Here we report a dinuclear nickel complex containing a single bridging hydride that was found to lie collinearly with the two metal centers and showed no disorder in the neutron diffraction studies.

Reaction of two equiv of 1-adamantylzinc bromide with (dippm)- NiBr_2 (**1**, dippm = bis(di-isopropylphosphino)methane) in THF solution led to the formation of the mixed-valent nickel dimer **2** in moderate yield (eq 1).⁸ Compound **2** is an air-sensitive, dark green



solid that slowly turns orange when exposed to oxygen. Comparison of the X-ray data of **2** to those of the related compound $[(\text{dcpm})_2\text{Ni}_2\text{Cl}_2](\mu\text{-H})$ (**3**, dcpm = bis(dicyclohexylphosphino)methane) revealed some interesting structural differences that warranted further investigation. The halides in **2** were found to lie on the same axis as the two metal centers, whereas the halides in **3** conform to the more conventional “A-frame” structure imposed by the bridging hydride ligand. Additionally, despite the similarity between the

Table 1. M–H–M Bond Angles of Bimetallic Compounds Characterized by Neutron Diffraction

compound	$\angle\text{M–H–M}$	ref
$[(\text{dippm})_2\text{Ni}_2\text{Br}_2](\mu\text{-H})$	177.9(10)	this work
$[\text{Cr}_2(\mu\text{-H})(\text{CO})_{10}][\text{NEt}_4]$	158.9(6)	4
$[\text{Cr}_2(\mu\text{-D})(\text{CO})_{10}][\text{PPN}]$	155.8(9)	10
$[\text{Cr}_2(\mu\text{-H})(\text{CO})_{10}][\text{K}(\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6)]$	145.2(3)	5
$(\text{CO})_5\text{Re}(\mu\text{-H})\text{Mn}(\text{CO})_4\text{Mn}(\text{CO})_5$	138.5(3)	11
$[\text{W}_2\text{H}(\text{CO})_{10}][\text{NEt}_4]$	137.1(10)	6
$\text{W}_2\text{H}(\text{CO})_8\text{NO}[\text{P}(\text{OMe})_3]$	129.4(3)	12
$\beta\text{-W}_2\text{H}(\text{CO})_9\text{NO}$	125.4(4)	13
$\alpha\text{-W}_2\text{H}(\text{CO})_9\text{NO}$	125.0(2)	13
$[\text{W}_2\text{H}(\text{CO})_{10}][\text{PPh}_4]$	123.4(5)	14
$[\text{MoCp}(\text{CO})_2]_2\text{H}[\text{PMe}_2]$	122.9(2)	15

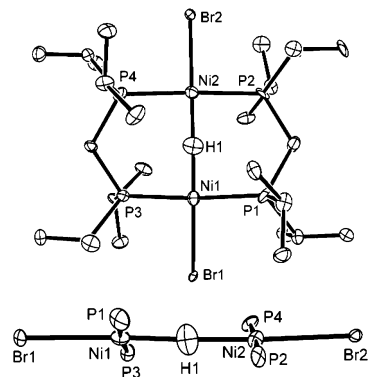


Figure 1. (Top) Anisotropic displacement ellipsoid view of **2** derived from neutron diffraction data. All hydrogens except H1 are omitted for clarity. (Bottom) View of the bridging hydride with all carbon and hydrogen atoms except H1 omitted for clarity. All ellipsoids shown at the 50% level.

phosphine ligands, the $\text{Ni}\cdots\text{Ni}$ separation in **2** was found to be more than 0.31 \AA longer than that in **3**. Once a spectroscopic handle has been developed for **2** and **3**, differences in the solid-state and solution structures can be more rigorously pursued. However, it was first necessary to carry out a single-crystal neutron diffraction analysis¹⁶ of **2** to indeed determine if a linear bridging hydride was present in the solid-state structure.

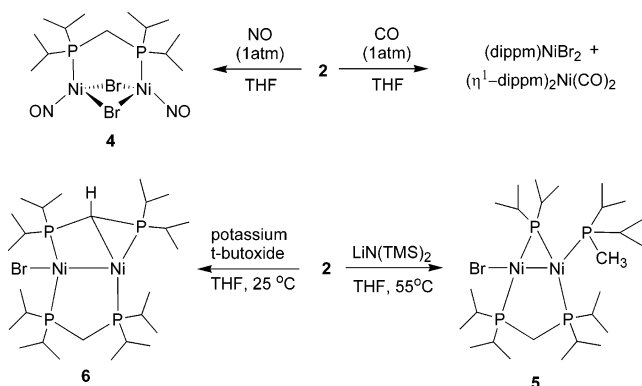
The ORTEP diagram of **2** is provided in Figure 1, and shows the position of the hydride ligand relative to the two nickel centers. The Ni–H–Ni angle was found to be $177.9(10)^\circ$ (Table 2), almost 20° larger than that found for $[\text{HCr}_2(\text{CO})_{10}]^-$. The bromide ligands lie almost at right angles to the Ni–P bonds and do not adopt a cisoid conformation that might be expected for an A-frame conformation. The dramatic differences in geometry for **2** relative to **3** are currently being investigated by computational methods. Possibly the difference between Cl and Br affects the occupancy of the Ni antibonding orbital, leading to a longer Ni–Ni distance and a linear Ni–H–Ni bond in the case of the Br analogue.

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Table 2. Selected Bond Lengths and Angles for **2**

selected bond lengths (Å)		selected bond angles (°)	
Ni1–Ni2	3.205(5)	Br1–Ni1–Ni2	178.22(20)
Br1–Ni1	2.374(6)	Br1–Ni1–P1	93.38(25)
Br2–Ni2	2.361(6)	Br1–Ni1–P3	91.11(25)
Ni1–P1	2.208(8)	Br1–Ni1–H1	177.7(6)
Ni1–P3	2.217(8)	P1–Ni1–P3	175.49(31)
Ni1–H1	1.588(13)	P1–Ni1–H1	87.8(5)
Ni2–H	1.618(13)	P3–Ni1–H1	87.7(5)
Ni2–P2	2.231(8)	Br2–Ni2–H1	177.7(5)
Ni2–P4	2.211(7)	Ni1–H1–Ni2	177.9(10)

Scheme 1. Solution Reactivity of **2**

A preliminary description of the reactivity of this unique hydride is shown in Scheme 1 (compounds **4**–**6** all characterized by X-ray crystallography). Reaction with 1 atm CO led mainly to decomposition, with the disproportionation products (dippm)NiBr₂ and (η¹-dippm)Ni(CO)₂ as the only identifiable species. Reaction of **2** with 1 atm NO, on the other hand, afforded the blue, symmetric dimer **4** in nearly quantitative yield. The reaction with NO appears to be quite a complicated transformation, as loss of both a phosphine and a hydride ligand occurs (perhaps as HNO), along with rotation of the bromide ligands to adopt a bridging conformation.

The hydrido complex **2** was also found to be extremely sensitive to basic reagents. Reaction with two equiv of LiN(TMS)₂ in THF solution at 55 °C led to cleavage of the methylene unit of the phosphinomethane ligand to afford the bridging phosphido complex **5**. A similar reaction has been reported in which [(dcpm)₂Ni₂Cl₂](μ-H) was found to react with excess LiH at 90 °C to afford the doubly cleaved product [Ni₂(μ-PCy₂)₂(PCy₂Me)₂],⁹ and other nickel complexes containing bridging phosphido ligands are known.^{17–19} The use of potassium *tert*-butoxide allowed conversions to be run at even lower temperatures, and when monitoring by ³¹P{¹H} NMR spectroscopy, a new product can be observed. An X-ray crystallographic analysis revealed that this new product was the result of a deprotonation reaction²⁰ at the methylene unit of the phosphinomethane bridge to afford **6** and, in this instance, also revealed that the overall skeleton of the phosphine ligand remains intact. It is

unclear at this point if **6** is a precursor to **5**, as further studies are still underway. An important lesson, however, is that such susceptibility of the bis(dialkylphosphino)methane ligand to basic reagents is an important consideration if one desires to replace the bromide ligands in this dimer with other functionalities.

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Supporting Information Available: General methods and neutron data for compound **2** (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- Neutron diffraction data were obtained using the time-of-flight Laue single-crystal diffractometer (SCD). A crystal of **2** was covered in a fluorocarbon grease in a glovebag and mounted on the cold stage of a closed-cycle helium refrigerator operating at 20 ± 0.1 K for data collection. Space group P2₁/a, *a* = 14.662(5), *b* = 14.817(6), and *c* = 16.080(5) Å, β = 94.06(3)°. In the final refinement, all non-hydrogen atoms and the H bridging atom were refined with anisotropic displacement parameters. All other hydrogen atoms were refined with an isotropic displacement parameter. The refinement on F² of 600 variables using 5244 reflections with a minimum *d* spacing of 0.7 Å converged to R_w(F) = 0.081 and R(F) = 0.121. For a more complete protocol of a typical analysis, see: Schultz, A. J.; Srinivasan, K.; Teller, R. G.; Williams, J. M.; Lukehart, C. M. *J. Am. Chem. Soc.* **1984**, *106*, 999–1003.
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