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Structural Factors Influencing Linear M–H–M Bonding in Bis(dialkylphosphino)methane Complexes of Nickel

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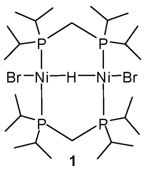
Structural data for four closely related dinuclear nickel hydride complexes have been compared in order to gain insight into the factors governing the Ni–H–Ni geometries. The derivatives $[(dippm)_2Ni_2X_2](\mu\text{-H})$ [dippm = 1,2-bis(diisopropylphosphino)methane] were found to contain a linear Ni–H–Ni bridge, whereas the derivatives $[(dcpm)_2Ni_2X_2](\mu\text{-H})$ [dcpm = 1,2-bis(dicyclohexylphosphino)methane] were found to contain a bent Ni–H–Ni bridge. The number of internal and interatomic CH-to-halide contacts of the former were much shorter and more numerous than the latter, suggesting an important role of external forces in bridging hydride geometries.

It was long believed that the M−H−M linkage in a bridging hydride complex was inherently bent because the bend allows the orbitals of the two supporting metals to be closer in space and potentially interact in a stabilizing fashion.[1] The result of a productive interaction is a bonding situation akin to the three-center, two-electron bonds in diborane.

Two recent reports have challenged the above model of inherent bonding in bridging hydride complexes. We have recently characterized the simple dinuclear metal complex $[(dippm)_2Ni_2Br_2](\mu\text{-H})$ [**1**; dippm = 1,2-bis(diisopropylphosphino)methane] by neutron diffraction[2] and have shown that, unlike the related derivative $[(dcpm)_2Ni_2Cl_2](\mu\text{-H})$ [**2**; dcpm = 1,2-bis(dicyclohexylphosphino)methane],[3] complex **1** indeed contains a linear Ni−H−Ni bond. Shortly after this report, Macchi and co-workers investigated the electronic structure in the bent $[HCr_2(CO)_{10}]$ anion.[4] Interestingly, they found that both the experimental and theoretical charge densities afforded molecular graphs *lacking* a bona fide metal−metal interaction.[4] In fact, their calculated structures of different conformers of $[Cr_2(\mu\text{-H})(CO)_{10}]^-$ at the B3LYP level all refined to a structure with D_{4h} symmetry and a linear bridging hydride.[4] Experimentally, the crystallized $[Cr_2(\mu\text{-H})(CO)_{10}]$ anion only exists in the bent form, so a direct experimental comparison of charge densities in linear and bent forms could not be accomplished. Nevertheless, these above data all imply that a new, more comprehensive model is needed to describe the geometrical preferences in bridging hydride complexes.



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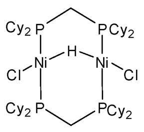

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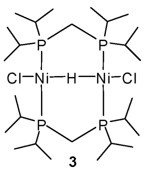

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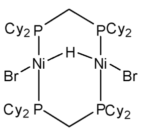

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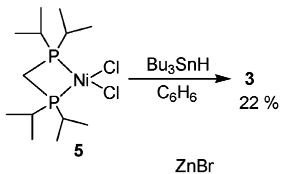
Given that the M−H−M bond angles of **1** and **2** are linear and bent, respectively, we realized the potential to further probe the salient features of these structures experimentally. However, more derivatives were needed in order to separate out the electronic effects arising from the different halogens in **1** and **2** and the steric effects arising from slightly different phosphine ligands. Here, we expand the series by describing the syntheses, solid-state structures, and chemical bonding features of **3** and **4**.



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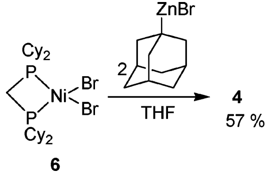

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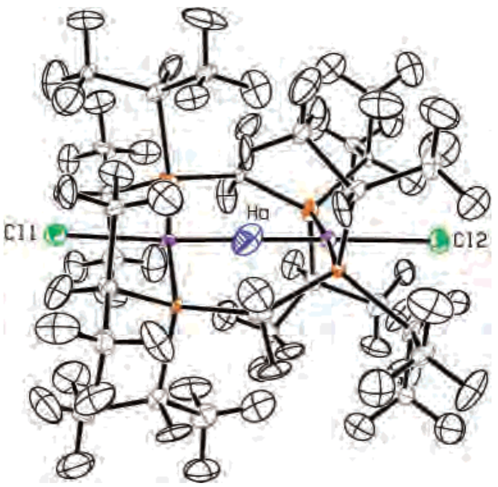

Figure 1. Anisotropic displacement ellipsoid view of **3** derived from neutron diffraction data at 40 K. All ellipsoids are shown at the 50% level. Selected bond lengths (Å): Ni1−Cl1, 2.250(6); Ni2−Cl2, 2.279(6); Ni1−H, 1.594(17); Ni2−H, 1.633(16); Ni1−Ni2, 3.227(5). Selected bond angles (deg): Ni1−H−Ni2, 177.5(11); Cl1−Ni1−P1, 91.65(27); Cl1−Ni1−H, 176.7(6).

Complex **3** was prepared by the reaction of Bu_3SnH with **5** (eq 1) by analogy to the reported methods used to prepare **2**.[3] We found that the reaction of 1-adamantylzinc bromide with **6** was a more reliable and better yielding method to produce **4** (eq 2). The difficulty in preparing 1-adamantylzinc chloride precluded the use of zinc reagents to prepare **3**. The isopropyl chloride derivative **3** was much more crystalline than **4**, which permitted the growth of crystals large enough for a neutron diffraction study. Figure 1 shows the ORTEP diagram of **3** derived from neutron diffraction data and confirms that this derivative also displays the linear Ni−H−Ni bonding previously observed in the bromo derivative **1**.[5]

This experimental result suggests that the sterics of the phosphine ligand and not the electronics of the halides influence the Ni−H−Ni geometry in these unique dimers. Although crystals of **4** large enough for neutron diffraction studies have not yet been obtained, an X-ray analysis (see the Supporting Information) provides a preliminary description of the overall structure. Compound **4** was found to crystallize in the same tetragonal space group as **2** ($I4_1/a$) and exhibits an M−H−M bend of 24(5)° from linearity. Although this value should only be considered as approximate (because the position of the hydride can only be inferred from the X-ray structure), the short Ni−Ni separation of 2.920(2) Å along with the "A-frame-like" cisoid conformation of the halides suggests a substantial deviation from linearity in the Ni−H−Ni bond angle, similar to **2**.

Now that the solid-state structures of all four derivatives **1**−**4** have been obtained, more detailed comparisons of their structures can be made. One of the most interesting features of the dimers is that the isopropyl derivatives exhibit shorter and more numerous CH-to-halide ligand hydrogen bonds than the cyclohexyl counterparts (Table 1). Compound **2**, for instance, contains only one internal hydrogen bond and no interatomic contacts per chloride (Figure 2). The isopropyl derivative **3**, on the other hand, exhibited four much shorter internal contacts (Figure 2) and a total of five interatomic contacts per dimer. These CH interactions to the halide ligands are important to consider when discussing the overall geometries of the complexes because similar hydrogen bonding is known to disrupt metal−metal interactions.[8]

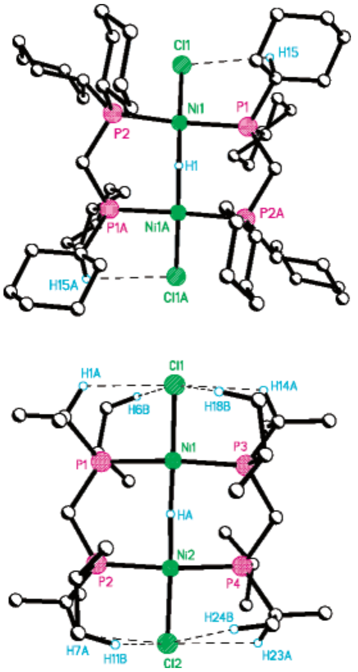

Figure 2. Ball-and-stick diagrams of **2** (top) and **3** (bottom) showing the internal hydrogen-bonding interactions between the alkylphosphine and halide ligands. All hydrogen atoms except the bridging hydrides and those involved in hydrogen bonding have been omitted for clarity.[6]

Table 1. Distances of CH−X Contacts (Å) Shorter than the Sum of the van der Waals Radii (H−Cl = 2.95 Å; H−Br = 3.05 Å)[7]

complex **1**	complex **2**	complex **3**	complex **4**
Intraatomic Distance			
2.850(15) Br1	2.858 Cl	2.705(11) Cl1	2.905 Br
3.042(14) Br1		2.734(14) Cl1	2.999 Br
2.789(14) Br1		2.642(14) Cl1	3.020 Br
2.743(13) Br1		2.866(14) Cl1	
3.003(16) Br1		2.739(13) Cl2	
2.688(14) Br2		2.798(13) Cl2	
2.908(15) Br2		2.726(12) Cl2	
2.715(13) Br2		2.948(14) Cl2	
2.766(15) Br2			
Interatomic Distance			
2.769(13) Br1		2.748(10) Cl1	3.040 Br
2.915(14) Br1		2.858(12) Cl1	
2.841(14) Br2		2.709(13) Cl1	
2.729(13) Br2		2.745(11) Cl2	
2.770(15) Br2		2.931(14) Cl2	

It is known that packing forces can influence the geometry of bridging hydrides and crystal packing forces appear to dominate the many M−H−M bond angles found for the

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(5) Data collection and refinement parameters are summarized in the Supporting Information. 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.

(6) The coordinates for **2** have been downloaded from the Cambridge Structural Database.

(7) The two halides in complexes **2** and **4** are symmetry-related. Because the refinements for **2** and **4** (characterized by X-ray diffraction) used hydrogen atoms on idealized positions, no errors can be reported. No corrections have been made for the fact that idealized C−H distances are inherently shorter than 1.09 Å.

$[Cr_2(\mu\text{-}H)(CO)_{10}]$ anion.[4,9] Here, we show evidence that ligand sterics and hydrogen-bonding interactions may also play a role in the M−H−M geometries.

It thus appears more and more likely that external influences such as sterics, hydrogen bonding, and crystal packing forces largely determine the geometry of the M−H−M bond angle and that bridging hydrides need not inherently possess a *closed* three-center bond containing stabilizing metal−metal interactions.

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Supporting Information Available: X-ray crystallographic data in CIF format and general methods and structural data for compounds **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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