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Novel Coordination of a Neutral Borane Adduct to Nickel(0). Formation of $Ni(CO)_2[B_2H_4{\cdot}2P(CH_3)_3]$

Sir:

Recently we reported[1] the synthesis and characterization of Zn(II) and Cu(I) complexes of bis(trimethylphosphine)–diborane(4), $B_2H_4{\cdot}2P(CH_3)_3$. These compounds represented the first examples of metal complexes of a neutral borane adduct and featured coordination of the boron hydride ligand to the metal via two B–H–M bridges. This *bidentate-bridging* mode of coordination had previously been observed primarily in complexes of the BH_4^-,[2] $B_2H_6^{2-}$,[3,4] and $B_3H_8^-$ [5,6] borane anions. Of these complexes of the anions, only a few are known to have the metal center in oxidation state zero.[7] So far there have not been reports of these anions complexing to the Ni(0) center. We now report that the neutral borane adduct $B_2H_4{\cdot}2P(CH_3)_3$ will react with $Ni(CO)_4$ to form a stable, isolable Ni(0) complex, $Ni(CO)_2[B_2H_4{\cdot}2P(CH_3)_3]$, which contains two B–H–M bridge bonds to the Ni(0) center.

The new nickel complex was formed by the direct reaction of $Ni(CO)_4$ and $B_2H_4{\cdot}2P(CH_3)_3$ in dichloromethane at room temperature according to eq 1. To drive the reaction forward, the

$$Ni(CO)_4 + B_2H_4{\cdot}2P(CH_3)_3 \rightleftharpoons Ni(CO)_2[B_2H_4{\cdot}2P(CH_3)_3] + 2CO \quad (1)$$

carbon monoxide had to be removed from the reaction system as it was produced, until approximately 80–85% of the reaction was complete. The product could be isolated by adding pentane to its cold, concentrated toluene solution and thus precipitating it as a green-yellow solid that was reasonably air stable at room temperature. Dichloromethane solutions of the isolated compound, however, decompose above −10 °C to unidentifiable products. Attempts to force reaction 1 to completion by further removal of carbon monoxide beyond the extent indicated above resulted in the sudden decomposition of the product, with deposition of nickel metal in the reaction system.

The reaction stoichiometry (observed: CO evolved:complex formed = 2:1) and the elemental analysis of the compound (Anal. Found: Ni, 19.9. Calcd: Ni, 20.1) supported the formula $Ni(CO)_2[B_2H_4{\cdot}2P(CH_3)_3]$ for the new nickel complex. The ^{11}B NMR spectrum of the compound features a broad signal at −44.1 ppm [$BF_3{\cdot}O(C_2H_5)_2$ standard] with a triplet structure, which is similar to the ^{11}B NMR signal of the previously characterized $CuI[P(C_6H_5)_3][B_2H_4{\cdot}2P(CH_3)_3]$ complex.[1] The ^1H (^{11}B-spin decoupled) spectrum shows three signals in a 18:2:2 relative intensity ratio. The most intense signal, at +1.26 ppm, is a doublet ($^2J_{PH}$ = 8.5 Hz) and is assignable to the methyl protons of the trimethylphosphine groups. The signal at −0.21 ppm is assigned to the terminal hydrogens bound to boron and that at −2.42 ppm to the hydrogens in the two B–H–Ni bridges. Thus, the NMR data support the structure shown in Figure 1, in which the $B_2H_4{\cdot}2P(CH_3)_3$ ligand is complexed in the bidentate-bridging mode similar to that in the Zn(II) and Cu(I) complexes previously characterized.[1]

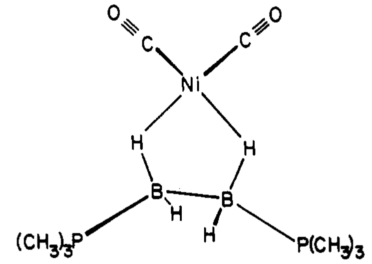

Figure 1. Proposed structure of $Ni(CO)_2[B_2H_4{\cdot}2P(CH_3)_3]$.

The infrared and mass spectral data gave further support to the above structural assignment. The major features of the infrared spectrum include a sharp, strong absorption at 2322 cm^{-1} (terminal B–H stretch), a broad strong absorption at 1895 cm^{-1} (B–H–M), and two CO bands at 1933 and 1909 cm^{-1}. The distribution and intensities of absorptions below 1700 cm^{-1} are very similar to those of the Zn(II) and Cu(I) complexes of $B_2H_4{\cdot}2P(CH_3)_3$.[1] In the mass spectrum, the parent ion cluster is seen centered at m/z = 292 with separate clusters for successive losses of CO at m/z = 264 and 236.

When $Ni(CO)_2[B_2H_4{\cdot}2P(CH_3)_3]$ was treated with anhydrous hydrogen chloride, the B–B bond of the borane ligand was cleaved, producing $BH_3{\cdot}P(CH_3)_3$ and $BH_2Cl{\cdot}P(CH_3)_3$. Treatment of a dichloromethane solution of the compound with excess carbon monoxide at room temperature caused rapid displacement of the $B_2H_4{\cdot}2P(CH_3)_3$ ligand, reaffirming the equilibrium nature of the $Ni(CO)_4$–$B_2H_4{\cdot}2P(CH_3)_3$ reaction system. Furthermore, the reactions of the complex with a series of phosphines of different coordinative strength gave an insight into the strength of binding of the $B_2H_4{\cdot}2P(CH_3)_3$ ligand to the Ni(0) center: The ligand is displaced rapidly and completely by PF_3 at −80 °C, rapidly by $P(C_6H_5)_3$ at −40 °C, and slowly by PH_3 at −20 °C. Thus, the bidentate coordinative bond of this borane ligand is not very strong, and this property can be utilized for the facile, low-temperature preparation of certain Ni(0) complexes with the formula $Ni(CO)_2L_2$. The above reactions yielded $Ni(CO)_2(PF_3)_2$, $Ni(CO)_2[P(C_6H_5)_3]_2$, and $Ni(CO)_2(PH_3)_2$, respectively. Further study

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(1) Snow, S. A.; Shimoi, M.; Ostler, C. D.; Thompson, B. K.; Kodama, G.; Parry, R. W. *Inorg. Chem.* **1984**, *23*, 511.

(2) See, for example: Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

(3) Kaesz, H. D.; Fellmann, W.; Wilkes, G. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1965**, *87*, 2753.

(4) Anderson, E. L.; Fehlner, T. P. *J. Am. Chem. Soc.* **1971**, *93*, 1041.

(5) Gaines, D. F.; Hildebrandt, S. J. In "Metal Interactions with Boron Clusters"; Grimes, R. N., Ed.; Plenum Press: New York, 1982; Chapter 3.

(6) Wegner, P. A. In "Boron Hydride Chemistry"; Muetterties, E. L., Ed.; Academic Press: New York, 1973; Chapter 12.

(7) Klanberg, F.; Guggenberger, L. S. *J. Chem. Soc., Chem. Commun.* **1967**, 1293. Klanberg, F.; Muetterties, E. L.; Guggenberger, L. S. *Inorg. Chem.* **1968**, *7*, 2272. Guggenberger, L. S. *Inorg. Chem.* **1970**, *9*, 367. See also ref 2, p 266.

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on the complexes of the $B_2H_4{\cdot}2P(CH_3)_3$ ligand involving other metals in oxidation state zero and their reaction chemistry is in progress, and the results will be reported elsewhere at a later date.

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Registry No. $Ni(CO)_2[B_2H_4{\cdot}2P(CH_3)_3]$, 94890-80-9; $Ni(CO)_4$, 13463-39-3; $BH_3{\cdot}P(CH_3)_3$, 1898-77-7; $BH_2Cl{\cdot}P(CH_3)_3$, 64160-46-9; $Ni(CO)_2(PF_3)_2$, 13859-78-4; $Ni(CO)_2[P(C_6H_5)_3]_2$, 13007-90-4; $Ni(CO)_2(PH_3)_2$, 83365-30-4.

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An Imido-Capped Tungsten Cluster: $W_3(\mu_3\text{-NH})(O\text{-}i\text{-}Pr)_{10}$

Sir:

A variety of triangular molybdenum and tungsten clusters have been discovered within the past few years.[1,2] These are either bicapped or hemicapped by groups such as O, S, and CR and have M_3X_{17}, M_3X_{16}, M_3X_{13}, M_3X_{11}, and M_3X_{10} skeletons. We report here our preparation and characterization of the first example of an imido-capped triangulo tungsten cluster, $W_3(\mu_3\text{-NH})(O\text{-}i\text{-}Pr)_{10}$.

Following our discovery of the comproportionation of d^0 tungsten–oxo and –alkylidyne alkoxides with M≡M bonds in $M_2(OR)_6$ compounds (M = Mo, W) to give, respectively, oxo-[3] and alkylidyne-capped[4] trinuclear compounds, $M_2W(\mu_3\text{-O})(OR)_{10}$ and $M_2W(\mu_3\text{-CR}')(OR)_9$, where R = *i*-Pr and CH_2-*t*-Bu and R′ = Me, Et and Ph, we sought to prepare a nitrido cluster. The attempted one-pot synthesis failed to yield the desired nitride but provided instead the imido cluster, $W_3(\mu_3\text{-NH})(O\text{-}i\text{-}Pr)_{10}$, as blue crystals in ca. 30% yield, according to eq 1.[5]

$$W_2(O\text{-}i\text{-}Pr)_6(py)_2 + (t\text{-}BuO)_3W{\equiv}N \xrightarrow[\text{hexane}/i\text{-PrOH}]{22\ °C} W_3(\mu\text{-NH})(O\text{-}i\text{-}Pr)_{10} + 3\,t\text{-BuOH} + 2py \quad (1)$$

The reaction pathway leading to the formation of the imido-capped cluster in (1) is presently not known. Of particular interest is whether or not the imido group is formed prior to or subsequent to the assembly of the trinuclear unit.

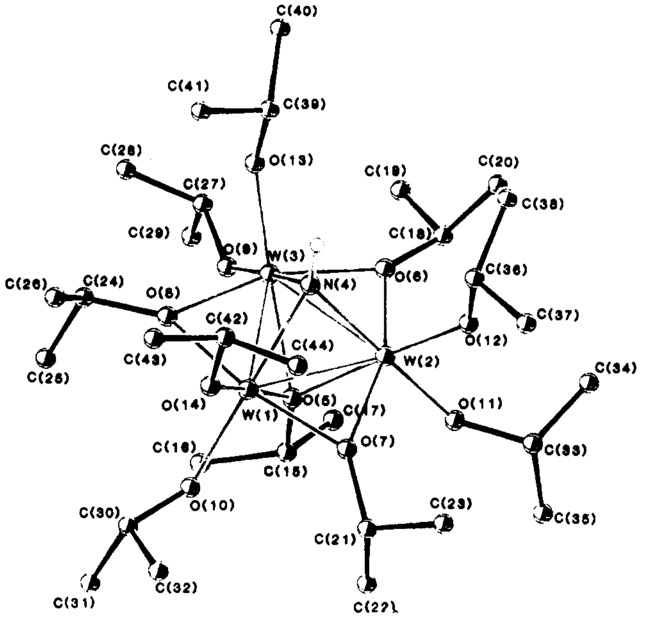

Figure 1. Ball and stick drawing of the $W_3(\mu_3\text{-NH})(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6$ molecule. The hydrogen atom on N(4) was not located crystallographically but is drawn in its calculated position to show its influence on the neighboring oxygen atoms O(12), O(13), and O(14) (see text).

The new blue crystalline compound isolated from (1) was found[6] to be isomorphous with $W_3(\mu_3\text{-O})(O\text{-}i\text{-}Pr)_{10}$, which, like its molybdenum analogue, adopts the M_3X_{11} skeletal geometry as shown in Figure 1. The unit cell dimensions were, however, larger by up to 30σ than those for the oxo capped compound. Also, the W–W distances were longer, 2.556 [2] Å (averaged) vs. 2.541 [3] Å (averaged), by 0.015 Å in the imido-capped compound. The W–N distances 2.08 (2) Å (averaged) were, however, indistinguishable from the W–O(μ_3-oxo) distances. The occupancy factor for the capping group of interest consistently favored N relative to O, but the hydrogen atom was not located crystallographically. Further crystallographic evidence for its presence is available from the relative positions of the *i*-Pr groups in the imido-capped molecule, as they are twisted further away from the capping position, relative to the oxo-capped molecule, in order to accommodate the imido hydrogen atom. Superposition of the three metal atom positions for the two different molecules using a least-squares procedure[6] reveals that the three oxygen positions for these groups (O(12), O(13), and O(14) of Figure 1) lie further from the pseudo-three-fold axis of the molecule by over 0.10 Å compared to corresponding atoms in the oxo-capped species. The oxygen atoms for the remaining *i*-Pr groups are superimposable within experimental error (average Δ*d* = 0.028 Å for the 14 crystallographically independent positions).

Aside from the crystallographic evidence in favor of a capping NH group, there is chemical evidence. (1) The analytical data show the presence of nitrogen in the expected amount. (Anal. Found (calcd) for $W_3O_{10}NC_{30}H_{71}$: C, 30.30 (31.13); H, 6.07 (6.18); N, 1.34 (1.21).) Note crystallography shows that the crystalline samples do not contain solvent molecules of inclusion such as pyridine. (2) The ^{1}H NMR spectrum shows, in addition

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(1) See ref 1–10 in: Ardon, M.; Cotton, F. A.; Dori, Z.; Fang, A.; Kapon, M.; Reisner, G. M.; Shaia, M. *J. Am. Chem. Soc.* **1982**, *104*, 5394.

(2) Muller, A.; Jostes, R.; Cotton, F. A. *Angew Chem.* **1980**, *104*, 5394.

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(4) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 3683. Chisholm, M. H.; Conroy, B.; Hoffman, D. M.; Huffman, J. C., results to be submitted for publication.

(5) All reactions were carried out with dry and oxygen-free atmospheres (N_2) and solvents. For the preparations of $W_2(OPr)_6(py)_2$ and $(t\text{-}BuO)_3W{\equiv}N$ see: Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266. Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2903.

(6) Crystal data for $W_3(NH)(O\text{-}i\text{-}Pr)_{10}$: $a = 21.478\ (10)$ Å, $b = 21.981\ (9)$ Å, $c = 10.131\ (3)$ Å, $\alpha = 98.57\ (2)°$, $\beta = 92.50\ (2)°$, $\gamma = 118.34\ (2)°$, $Z = 4$, $d_{calcd} = 1.863$ g cm^{-3}, space group $P\bar{1}$. Using 9014 reflections having $F > 3.00\sigma(F)$ yielded $R(F) = 0.051$ and $R_w(F) = 0.051$. The program BMFIT was described in: Uyen, Pui Sum; Nyburg, S. C. *J. Appl. Crystallogr.* **1978**, *12*, 258. In the present study, with use of Mo Kα radiation (λ = 0.71069 Å) with $6° \leq 2\theta \leq 45°$, the temperature was −158 °C and the dimensions of the crystal were 0.10 × 0.10 × 0.11 mm. The facility, instruments, and programs have been previously described: Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

(7) ^{1}H NMR data recorded at 360 MHz, 21 °C in benzene-d_6: δ(OCH*Me*$_2$) 1.16 (18 H), 1.39 (6 H), 1.55 (18 H), 1.63 (18 H) (d, J_{HH} = 6 Hz); δ(OC*H*Me$_2$) 5.35 (3 H), 5.60 (sept, J_{HH} = 6 Hz), 4.37 (4 H) (overlapping septets, J_{HH} = 6 Hz); δ(NH) 9.87 (1 H, br, s).

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