Communications to the Editor

Synthesis and Structure of a Dinuclear Cobalt Complex Bridged by Nonsubstituted Borylene−Trimethylphosphine

Mamoru Shimoi,* Sachiko Ikubo, and Yasuro Kawano

Department of Basic Science
Graduate School of Arts and Sciences
University of Tokyo, Meguro-ku, Tokyo 153, Japan

Kinji Katoh and Hiroshi Ogino*

Department of Chemistry
Graduate School of Science
Tohoku University, Aoba-ku, Sendai 980-77, Japan

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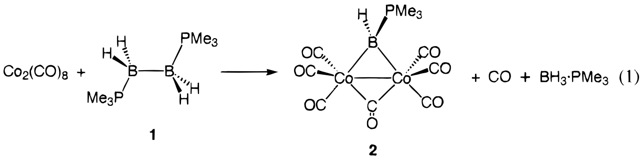
The chemistry of transition metal dinuclear complexes bridged by a methylene has been extensively studied.[1] Several examples of base-free borylene-bridged dinuclear complexes were reported recently, in which the borylene works as a tricoordinated planar ligand and is stabilized by a π donor amino group, alkoxy group, chlorine, or a bulky *tert*-butyl group.[2] Borylene-capped trinuclear complexes $[(Cp^*Co)_3(\mu\text{-}H)_2(\mu_3\text{-}BX)_2]$ (X = H, Cl),[3] $[(Cp^*Co)_3(\mu\text{-}H)_2(\mu_3\text{-}BH)(\mu_3\text{-}BX)]$ (X = Cl, OH),[3b] and $[(CpCo)_3(\mu_3\text{-}BPh)(\mu_3\text{-}PPh)]$[4] are also known. In sharp contrast to this, no chemistry has been known for dinuclear complexes bridged by nonsubstituted borylene−Lewis base adducts BH·L, which are the isoelectronic boron counterparts to methylene. We have found that $B_2H_4{\cdot}2PMe_3$[5] (**1**) is fragmented into $BH_3{\cdot}PMe_3$ and $BH{\cdot}PMe_3$ in the reaction with $Co_2(CO)_8$ and the generated $BH{\cdot}PMe_3$ fragment acts as a bridging ligand in the product $[\{Co(CO)_3\}_2(\mu\text{-}CO)(\mu\text{-}BH{\cdot}PMe_3)]$ (**2**).

Treatment of $Co_2(CO)_8$ with ca. 2-fold excess of **1** at −15 °C in hexane afforded a yellow-orange solution, from which **2** was isolated as yellow crystals in 66% yield.[6] The amount of evolved CO was estimated to be 0.8 equiv to the precursor $Co_2(CO)_8$ with use of a Toepler pump. During the reaction, $BH_3{\cdot}PMe_3$ was generated and removed by sublimation. Thus, the reaction occurs as shown in eq 1. Complex **2** is moderately stable at room temperature under a nitrogen atmosphere in the pure state.



Bis(trimethylphosphine)diborane(4), **1**, has been known to coordinate to a metal center through the vicinal H(B) atoms to produce chelate compounds or through one M−H−B bond to form unidentate complexes: $[ZnCl_2(B_2H_4{\cdot}2PMe_3)]$,[7] $[Ni(CO)_2(B_2H_4{\cdot}2PMe_3)]$,[8] $[CuI(B_2H_4{\cdot}2PMe_3)]$,[7] $[Cu(B_2H_4{\cdot}2PMe_3)_2]X$ (X = Cl, I),[9] and $[M(CO)_n(B_2H_4{\cdot}2PMe_3)]$ ($n = 4$, M = Cr, Mo, W; $n = 5$, M = Cr, W).[10] In these complexes, however, **1** is included, retaining the original form in the coordination sphere. The present work is the first example of the degradation of **1** in the reaction with transition metal complexes.

An ORTEP diagram of **2** is shown in Figure 1.[11] The two $Co(CO)_3$ moieties are symmetrically bridged by the carbonyl and borylene ligands. The dihedral angle between the two three-membered rings, B−Co(1)−Co(2) and C(4)−Co(1)−Co(2), is 110°. Coordination of the lone electron pair of the phosphorus atom of trimethylphosphine to the boron atom in the borylene ligand induces boron to adopt a pyramidal geometry. The angle between the B−P bond and the B−Co(1)−Co(2) three-membered ring is 130.4° while the angle between the B−H(B) bond and the three-membered ring is 118.1°. The former is enlarged and the latter is narrowed from the calculated value for the ideal tetrahedron (125.3°), probably due to the steric demand of PMe_3. The Co(1)−B and Co(2)−B bond lengths are 2.112(9) and 2.108(11) Å, respectively. These are considerably shorter than that found in the boryl complex $[Co(CO)_2(\eta^1\text{-}dppm)(\mu\text{-}dppm{\cdot}BH_2)]$ (2.227(6) Å).[12] However, they are longer than those in cobaltaborane clusters with μ_3-borylene ligands, $[(Cp^*Co)_3(\mu\text{-}H)_2(\mu_3\text{-}BH)_2]$ (2.013(8) and 1.985(6) Å)[3a] and $[(CpCo)_3(\mu_3\text{-}PPh)(\mu_3\text{-}BPh)]$ (2.018(8)−2.065(8) Å).[4] The interatomic distance Co(1)−Co(2) of 2.486(2) Å clearly indicates the existence of a single bond between the cobalt atoms. This distance is slightly longer than that in the μ-carbene dicobalt complex $[\{Co(CO)_3\}_2(\mu\text{-}CO)(\mu\text{-}C_4H_2O_2)]$ (2.451 Å)[13] but shorter than those in germylene-bridged

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[6] Freshly sublimed $Co_2(CO)_8$ (39 mg, 0.11 mmol) and **1** (47 mg, 0.26 mmol) were combined in dry hexane (6.0 mL) under a high vacuum at 77 K and the resulting mixture was gradually warmed to −15 °C. During stirring at −15 °C, evolution of a gas which is noncondensable at 77 K was observed. The amount of the gas collected over 8 h was determined to be 0.09 mmol by using a Toepler pump. The solvent was then removed and the residue was recrystallized from pentane (8.5 mL) to give yellow crystals with coproduced $BH_3{\cdot}PMe_3$. Removal of $BH_3{\cdot}PMe_3$ by sublimation from the solid afforded **2** (29 mg, 0.07 mmol, 66%) as a pure product. Data for **2**: ^{1}H NMR (500 MHz, C_6D_6) δ 0.61 (d, $^2J_{PH} = 10.5$ Hz, 9H, PMe_3), 4.59 (q br, $^1J_{BH} \cong 125$ Hz, 1H, BH); ^{11}B NMR (160.35 MHz, toluene-d_8) δ 17.5 (br); $^{31}P\{^1H\}$ NMR (202.35 MHz, toluene-d_8) δ −6.2 (q br, $^1J_{PB} \cong 90$ Hz); IR (KBr) ν 2395 (m) (BH), 2080 (s), 2050 (sh), 2040 (vs), 2002 (sh), 1980 (vs), 1970 (sh), 1940 (sh) (CO_{term}), 1795 cm^{-1} (m) (CO_{brid}); MS (70 eV) *m/z* (%) 402 (M^+, 15), 374 ($[M - CO]^+$, 25), 346 ($[M - 2CO]^+$, 38), 318 ($[M - 3CO]^+$, 290 ($[M - 4CO]^+$, 25), 262 ($[M - 5CO]^+$, 83), 234 ($[M - 6CO]^+$, 100), 206 ($[M - 7CO]^+$, 48). Anal. Calcd for $C_{10}H_{10}BCo_2O_7P$: C, 29.89; H, 2.51. Found: C, 29.78; H, 2.52.

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[11] Crystallographic data for **2**: yellow crystals, crystal size 0.5 × 0.15 × 0.1 mm, monoclinic, space group $P2_1/n$ (variant of No. 14); $a = 11.365(1)$ Å, $b = 17.028(2)$ Å, $c = 8.543(2)$ Å, $\beta = 93.31(1)°$; $V = 1650.7(4)$ Å^3; $Z = 4$. Data collection: Mo Kα, 1.25 kW, 293 K, $2\theta = 3−55°$, 3915 independent reflections. The structure was solved by the heavy atom method (UNICS-III).[19] 195 parameters. Positions of non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms bound to boron were determined by difference Fourier synthesis and refined isotropically. The other hydrogens were not found. $R = 0.061$ for 1792 reflections having $|F_o| > 3\sigma(F_o)$.

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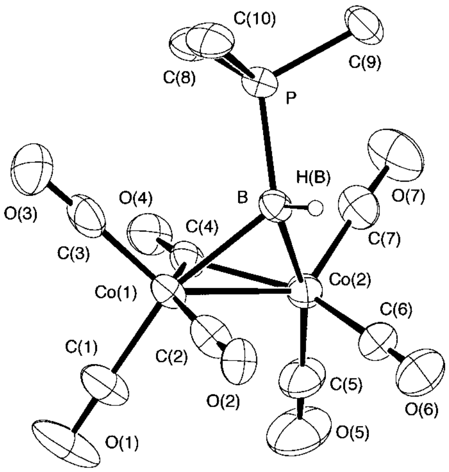

Figure 1. ORTEP diagram of [{Co(CO)$_3$}$_2$(μ-CO)(μ-BH•PMe$_3$)] (**2**) with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Co(1)−Co(2) 2.486(2), Co(1)−B 2.112(9), Co(2)−B 2.108 (11), B−P 1.921 (10), B−H(B) 1.02(7); Co(1)−B−Co(2) 72.2(3), B−Co(1)−Co(2) 53.8(3), B−Co(2)−Co(1) 54.0(3), Co(1)−C(4)−Co(2) 81.8(4), P−B−Co(1) 119.9(5), P−B−Co(2) 123.2(5), H(B)-B−Co(1) 122(4), H(B)−B−Co(2) 117(4), P−B−H(B) 102(4).

complexes [{Co(CO)$_3$}$_2$(μ-CO)(μ-GeRR′)] (2.491−2.587 Å; av 2.55 Å)[14] and the tricobalt complex capped by a borylene and a phosphinidene [(CpCo)$_3$(μ_3-PPh)(μ_3-BPh)] (2.473(2)−2.561(1) Å; av 2.53 Å).[4] These differences are attributable to the size of the bridging atoms. The Co−Co distance in [(Cp*Co)$_3$(μ-H)$_2$(μ_3-BH)$_2$] is 2.507(1) Å;[3a] however, a comparison of **2** with this trinuclear complex is rather difficult because of the existence of two borylene bridges as well as bridging hydrido ligands.[3b]

In the ^{11}B NMR spectrum of **2**, the bridging borylene resonates at considerably lower field (17.5 ppm) than the precursor **1** (−37.4 ppm) and BH$_3$•PMe$_3$ (−37.0 ppm). Similarly, the chemical shift of **2** is also higher (lower field) compared to that of a boryl complex Cp*W(CO)$_3$BH$_2$•PMe$_3$ (−27.6 ppm).[15] This phenomenon is parallel to the fact that the signal of the carbene ligand in μ-carbene complexes is observed at remarkably low field in ^{13}C NMR spectroscopy.[1,16] It should be noted that base-free μ-borylene complexes [{(η-C$_5$H$_4$R)Mn(CO)$_2$}$_2$(μ-BX)] (R = H, Me; X = NMe$_2$, NHR′, OR′, Cl, *t*-Bu) recently reported by Braunschweig and co-workers exhibit the ^{11}B signals at extremely low field (97.6−107.6 ppm for X = NMe$_2$, NHR′, OR′; 133.5 ppm for X = Cl, and 170 ppm for X = *t*-Bu).[2] The ^{1}H NMR signal of B-*H* in **2** is also found at low field (4.59 ppm).

Kodama and Kameda previously reported borane-cage expansion reactions using **1**. In the reactions, the frameworks of boranes are expanded by the introduction of BH•PMe$_3$ derived from the fragmentation of **1**. Thus, diborane(6) reacts with **1** to give B$_3$H$_7$•PMe$_3$ releasing BH$_3$•PMe$_3$ via an ionic intermediate [B$_3$H$_6$•2PMe$_3$][B$_2$H$_7$] (eq 2).[17]

$$\mathrm{B_2H_6 + B_2H_4{\cdot}2PMe_3 \longrightarrow B_3H_7{\cdot}PMe_3 + BH_3{\cdot}PMe_3} \quad (2)$$

Some boranes release a Lewis base during the reaction (eq 3).[18]

$$\mathrm{B_3H_7{\cdot}THF + B_2H_4{\cdot}2PMe_3 \longrightarrow B_4H_8{\cdot}PMe_3 + BH_3{\cdot}PMe_3 + THF} \quad (3)$$

In the present case, **1** gives the dicobalt framework a BH•PMe$_3$ moiety to afford **2**, which can be regarded as a trinuclear metallaborane. In this aspect, the reaction reported here corresponds to the borane expansion reactions with **1**.

Complex **2** undergoes ligand substitution with 2 equiv of PPh$_3$ to afford [{Co(CO)$_2$(PPh$_3$)}$_2$(μ-CO)(μ-BH•PMe$_3$)].[20] Investigation of reactions of **2** with other substrates is in progress toward syntheses of new compounds containing a boron moiety.

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Supporting Information Available: Experimental details and tables of crystallographic data, positional parameters, anisotropic temperature factors, bond distances, and bond angles for **2** (8 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[20] NMR data for [{Co(CO)$_2$(PPh$_3$)}$_2$(μ-CO)(μ-BH•PMe$_3$)]: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 0.88 (d, $^2J_{\mathrm{PH}}$ = 10.5 Hz, 9H, PMe$_3$), 4.85 (q br, $^1J_{\mathrm{BH}} \cong$ 140 Hz, 1H, BH), 7.05, 7.75 (m, 30H, PPh$_3$); ^{11}B NMR (160.35 MHz, C$_6$D$_6$) δ 18.5 (br); ^{31}P{^{1}H} NMR (202.35 MHz, C$_6$D$_6$) δ 7.1 (br, PMe$_3$), 57.3 (br, PPh$_3$).