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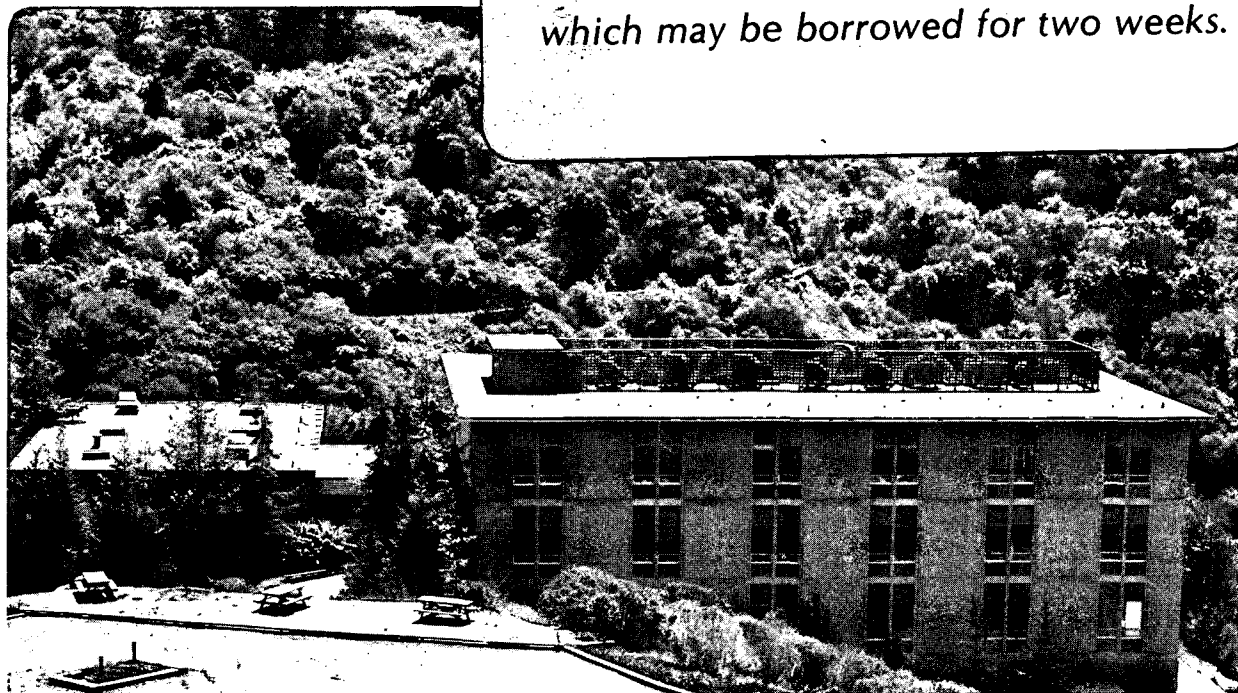
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$(\text{Me}_5\text{C}_5)_2\text{Yb}(\mu\text{-H}_3\text{B})(\text{PMe}_3)$: A Complex with
a Near-Linear BH_3 Bridging Group

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Addition of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ to H_3BPMe_3 gives the 1:1 coordination compound, $(\text{Me}_5\text{C}_5)_2\text{Yb}(\mu\text{-H}_3\text{B})(\text{PMe}_3)$, with BH_3 bridging the Yb and P centers so that $(\text{Me}_5\text{C}_5)_2\text{Yb}$ is a Lewis acid and the borane portion of H_3BPMe_3 is the Lewis base.

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The unusual molecule $(\text{Me}_5\text{C}_5)_2\text{Yb}(\mu\text{-Me})\text{Be}(\text{C}_5\text{Me}_5)$, which contains a near linear $\text{Yb}(\mu\text{-Me})\text{Be}$ unit, has recently been described.¹ The coordination complex may be described as a donor-acceptor complex with $(\text{Me}_5\text{C}_5)_2\text{Yb}$ being the Lewis acid and $\text{MeBe}(\text{C}_5\text{Me}_5)$ being the Lewis base. The molecule, $\text{MeBe}(\text{C}_5\text{Me}_5)$, may be factored into the fragments MeBe^+ and C_5Me_5^- , suggesting that the complex can be viewed as a model for methane coordination, MeBe^+ being isolobal with CH_4 . The beryllium compound was chosen since it is a monomeric, linear molecule with a large dipole moment in the direction of the methyl group. Since MeBe^+ is also isolobal with $\text{H}_3\text{B}(\text{L})$, where L is a two-electron ligand, we thought that H_3BPMe_3 should yield a coordination compound with H_3B bridging the ytterbium and phosphorus centers, as H_3BPMe_3 has a dipole moment of 4.97 D in benzene^{2a} or 4.99D (gas phase)^{2b} with the negative direction towards boron, i.e., $\text{H}_3\text{B}^- \text{-P}^+\text{Me}_3$.

Addition of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ to one molar equivalent of H_3BPMe_3 in hexane gave a light green-yellow solid that was crystallized as bright green crystals by slow cooling of a hot toluene solution to 20°C in 77% yield. The resonance due to the BH_3 group in the ^1H NMR spectrum of the diamagnetic complex could not be observed though the $^{11}\text{B}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show only slight perturbations upon complexation.[‡] The infrared spectrum (Nujol mull) shows that the B-H stretching frequencies in the addition compound increase slightly relative to those in free H_3BPMe_3 . The spectroscopic parameters of orange $(\text{Me}_5\text{C}_5)_2\text{YbH}_3\text{BPh}_3$ also show only slight changes upon coordination.[‡] In the somewhat related compounds, $\text{B}_2\text{H}_4(\text{PMe}_3)_2(\text{ZnCl}_2)$ ^{3a} or $\text{B}_2\text{H}_4(\text{PMe}_3)_2\text{Ni}(\text{CO})_2$ ^{3b} in which there are two terminal BH bonds and two bridging B-H-M (M=Zn or Ni) bonds, the ν_{BH} decreases upon coordination by ca. 150-300 cm^{-1} and J_{BP} increases by ca. 50 Hz relative to $\text{B}_2\text{H}_4(\text{PMe}_3)_2$.^{3c} The spectroscopic features of the H_3BPR_3 portion of $(\text{Me}_5\text{C}_5)_2\text{YbH}_3\text{BPR}_3$ are less perturbed than those of the $\text{B}_2\text{H}_4(\text{PMe}_3)_2$ complexes which is consistent with a weaker $\text{Yb}\cdots\text{H}_3\text{B}$ interaction.

The extent of the geometric perturbation is shown by comparison of the gas phase structure of H_3BPMe_3 as determined by microwave spectroscopy^{2b} with that of $(\text{Me}_5\text{C}_5)_2\text{YbH}_3\text{BPMe}_3$ by room temperature X-ray crystallography (Figure).[†] The 1:1 adduct is formed by an end-on interaction of H_3BPMe_3 with $(\text{Me}_5\text{C}_5)_2\text{Yb}$. The Yb-C distance and the ring centroid-Yb-ring centroid angle are similar to those found in $(\text{Me}_5\text{C}_5)_2\text{Yb}(\mu\text{-Me})\text{BeC}_5\text{Me}_5$.¹ The B-P distance of 1.910(8) Å is not significantly different from that found in H_3BPMe_3 .^{2b} The near linear Yb...B-P angle of 162.3(5)° and the Yb...B distance of 2.764(8) Å may be compared with Yb...C-Be angle of 177.2(3)° and the Yb...C distance of 2.766(4) Å in $(\text{Me}_5\text{C}_5)_2\text{Yb}(\mu\text{-Me})\text{Be}(\text{C}_5\text{Me}_5)$.¹ In addition, the C(14)...C(211) distance is only 3.54(2) Å which presumably prevents further bending of the Yb...B-P bond due to steric effects. Unfortunately, the disorder of some of the methyl groups and our inability to obtain a low temperature data set due to crystal cracking prevented us from locating the hydrogen atoms. However, the small perturbations upon coordination and the similarity between $(\text{Me}_5\text{C}_5)_2\text{Yb}(\mu\text{-Me})\text{BeC}_5\text{Me}_5$,¹ in which the hydrogen atoms on the bridging methyl group were located and refined, and $(\text{Me}_5\text{C}_5)_2\text{Yb}(\mu\text{-H}_3\text{B})\text{PMe}_3$ strongly suggests that the CH_3^- and BH_3 portions are bonded to $(\text{Me}_5\text{C}_5)_2\text{Yb}$ in a similar fashion, i.e., by way of Yb...H-B and Yb...B interactions. The BH_3 portion in the 1:1 coordination compound may be viewed in much the same way as the bridging BH_4^- group (BH_3L is isolobal with BH_4^- and CH_4) in metal tetrahydroborate complexes is viewed.⁴

Only a few transition metal compounds with BH_3 groups bound to them are known.⁵ The anions, $\text{H}_3\text{BRe}(\text{CO})_5^-$ and $\text{H}_3\text{BMn}(\text{CO})_5^-$ are presumably isostructural with the neutral $\text{MeRe}(\text{CO})_5$ and $\text{MeMn}(\text{CO})_5$,^{5b} and $\text{Fe}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-H}_2\text{BH})^-$,^{5c} whose structure is thought to be similar to its isoelectronic counterpart $\text{Fe}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-H}_2\text{CH})$,^{5d} have been described. No BH_3 compounds are known

which are related to the complex described in this paper, viz., neutral BH_3 acting as a bridging ligand like the somewhat more common bridging methyl group in organometallic chemistry.

*All compounds give satisfactory elemental analysis. $(\text{Me}_5\text{C}_5)_2\text{YbH}_3\text{BPM}_3$, m.p. 250-253°C. ^1H NMR (C_6D_6 , 30°C): δ 2.25 (s, 30H), 0.49 (d, $J_{\text{HP}}=10.9$ Hz, 9H). $^{11}\text{B}\{^1\text{H}\}$: δ -35.41 (d, $J_{\text{BP}}=78.2$ Hz). $^{31}\text{P}\{^1\text{H}\}$: δ -1.64 (q, $J_{\text{BP}}=77.7$ Hz). IR: ν_{BH} (Nujol)=2427m, 2363w, 2234 sh, 2302 sh, 2266 m. H_3BPM_3 . $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6 , 30°C): δ -36.71 (d, $J_{\text{BP}}=59.8$ Hz). $^{31}\text{P}\{^1\text{H}\}$: δ -1.59 (q, $J_{\text{BP}}=59.8$ Hz). $\nu_{\text{BH}}=2364\text{s}$, 2339 sh, 2268 sh, 2256w. $(\text{Me}_5\text{C}_5)_2\text{YbH}_3\text{BPPH}_3$, m.p. 155-158°C, ^1H NMR (C_6D_6 , 30°C): δ 7.51 and 6.98 (m, 15 H), 2.20 (s, 30H). $^{11}\text{B}\{^1\text{H}\}$: δ -36.47 (broad, $\nu_{\frac{1}{2}}=170$ Hz). $^{31}\text{P}\{^1\text{H}\}$: δ 22.5 (q, $J_{\text{BP}}=57$ Hz). ν_{BH} (Nujol)=2434m, 2380s, 2345m, 2296w, 2265w, H_3BPPH_3 $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6 , 30°C): δ -37.28 (d, $J_{\text{BP}}=46$ Hz). $^{31}\text{P}\{^1\text{H}\}$: δ 21.5 (q, $J_{\text{BP}}=65$ Hz). $\nu_{\text{BH}}=2378\text{s}$, 2344m, 2253w.

*X-Ray Crystallography: $\text{C}_{23}\text{H}_{42}\text{BPYb}$, $M=533.42$, orthorhombic, space group Pnma, $a=19.778(2)$, $b=13.266(2)$, $c=9.801(1)\text{\AA}$, $U=2630(1)\text{\AA}^3$, $D_c=1.35\text{ g cm}^{-3}$, $Z=4$, Mo- $\text{K}\alpha$ radiation, $\lambda=0.71073\text{\AA}$, $\mu=36.1\text{ cm}^{-1}$. A total of 3793 raw data were collected and after rejection of the systematically absent data the 3421 remaining reflections were averaged. The agreement factors for the averaging (based upon F_{obs}) were 0.011 for all the observed data and 0.033 for all data. The structure was solved from Patterson and electron density maps and refined by full-matrix least squares to a conventional R factor of 0.030 by using 1160 absorption corrected data for which $F_o^2 > 3\sigma(F_o^2)$ against 130 variables. The $R_w = 0.049$, GOF = 2.38, and R for all data was 0.060. The large and highly anisotropic thermal parameters for the methyl groups on the cyclopentadienyl rings indicate that the rings were undergoing librational motion about the pseudo- C_5 axis. The methyl groups on the crystallographic mirror plane were most severely affected, and these were best refined as two half-occupancy carbon positions, C(11) and C(14), lying off the mirror plane. The half-occupancy carbon were refined isotropically, as including anisotropic thermal parameters did not improve the refinement. Attempts to refine the other methyl groups on the ring in a similar manner led to unreasonable values for the C(ring)-C(Me) bond lengths so C(12), C(13), C(15), C(16) were refined anisotropically in single positions. One of the methyl groups on the phosphorus atom, C(211) was also refined in two half-occupancy positions. All other non-hydrogen atoms were anisotropically refined. Examination of difference Fourier maps did not unambiguously reveal the hydrogen atom positions, so they were not included in the structure refinement. Atomic coordinates, bond distances and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, issue No. 1.

Acknowledgments.

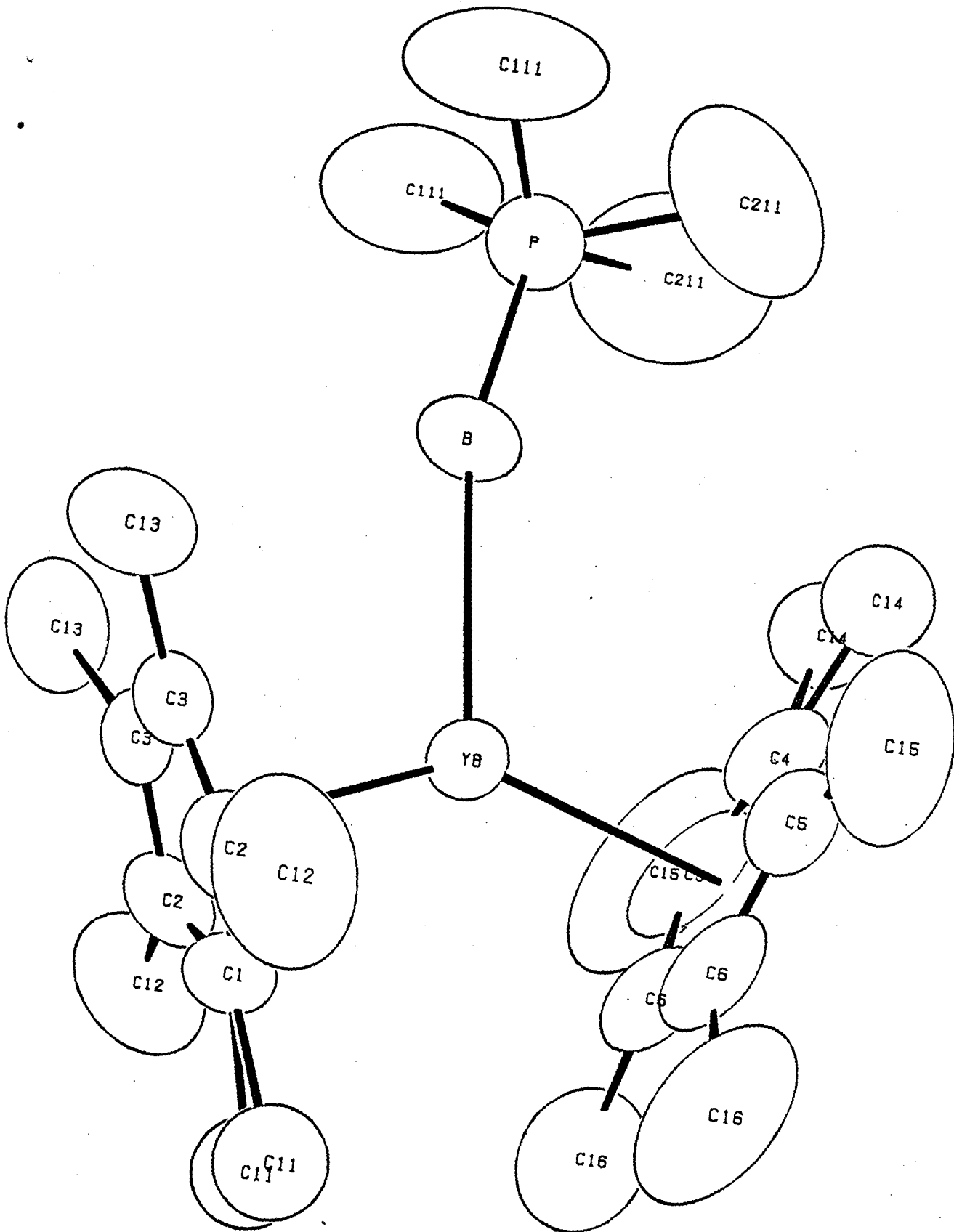
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Figure Captions

An ORTEP diagram of $(\text{Me}_5\text{C}_5)_2\text{Yb}(\mu\text{-BH}_3)(\text{PMe}_3)$. The molecule lies on a crystallographic mirror plane defined by C(1), C(4), Yb, B, and P. The methyl groups C(11) and C(14) on the cyclopentadienyl ring and C(211) on the phosphorous atom are disordered and they are refined in two half-occupancy positions. The averaged Yb-C distance is $2.69 \pm 0.01 \text{ \AA}$, the Yb-ring centroid distance is 2.41 \AA , and the ring centroid-Yb-ring centroid angle is 139° .



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