

1,4-Phosphaboratabenzene: A Heteroaromatic π -Ligand Containing Boron and Phosphorus

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Summary: The reaction of 1,4-dihydro-4-(diisopropylamino)-2,6-dimethyl-1-phenyl-1,4-phosphaborin (**6**) with $Mn_2(CO)_{10}$ affords **7**, the $Mn(CO)_3$ complex of 4-(diisopropylamino)-2,6-dimethyl-1,4-phosphaboratabenzene. Reaction of **6** with Li followed by $[Cp^*RuCl]_4$ gives the ruthenium(II) complex **8**. Crystal structures of **6–8** have been determined.

We have been interested in preparing new organometallic compounds by replacing Cp groups of metallocenes with anionic heterocyclic ligands.^{1–7} It is hoped to thereby adjust the electronic environment of the metal so that metal-based reactivity can be modulated. For example boratabenzene–zirconium complexes have a different and more controllable reactivity than does Cp_2ZrCl_2 in Ziegler–Natta olefin polymerization.^{1bc} Recent work has indicated that certain phospholyl zirconium complexes have good reactivity as Ziegler–Natta catalysts.^{8,9} 1,4-Phosphaboratabenzene (**4**) might be expected to have ligand properties intermediate between those of boratabenzene (**2**) and phospholyl (**3**), and we felt it was of interest to explore its chemistry. Although a synthesis of derivatives of **4** was reported

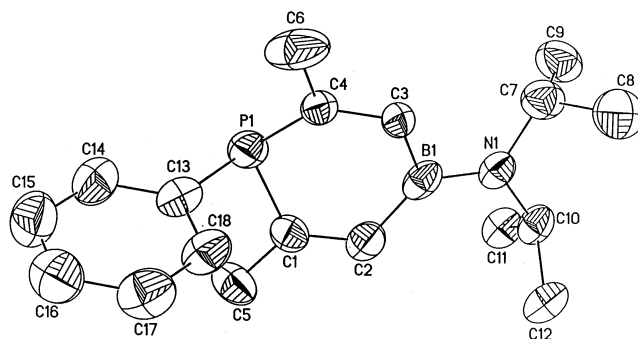
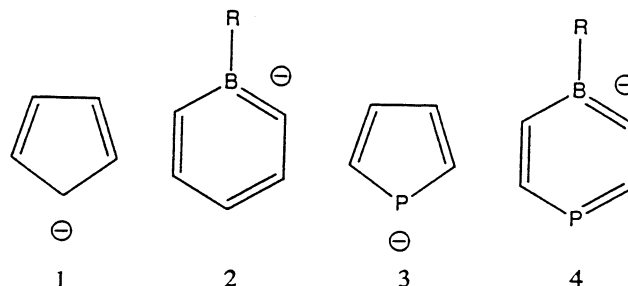


Figure 1. Solid-state structure of **6**. Selected distances (Å): B–N, 1.407(3); B–C(2), 1.561(3); B–C(3), 1.584(4); C(3)–C(4), 1.352(6); C(1)–C(2), 1.345(3); C(1)–P, 1.811(2); C(4)–P, 1.782(3); C(13)–P, 1.838(2).



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(6) For reviews of 1,2-azaborolyl, see: (a) Schmid, G. *Comments Inorg. Chem.* **1985**, *4*, 17. (b) Schmid, G. In *Comprehensive Heterocyclic Chemistry II*; Shinkai, I., Ed.; Pergamon: Oxford, U.K., 1996; Vol. 3, p 739.

(7) For recent work on 1,2-azaborolyl, see: (a) Liu, S. Y.; Lo, M. M. C.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 174. (b) Liu, S. Y.; Hills, I. D.; Fu, G. C. *Organometallics* **2002**, *21*, 4323.

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(9) However, see: (a) Janiak, C.; Lange, K. C. H.; Versteeg, U.; Lentz, D.; Budzelaar, P. H. M. *Chem. Ber.* **1996**, *129*, 1517. (b) de Boer, E. J. M.; Gilmore, I. J.; Korndorffer, F. M.; Horton, A. D.; van der Linden, A.; Royan, B. W.; Ruisch, B. J.; Schoon, L.; Shaw, R. W. *J. Mol. Catal. A* **1998**, *128*, 155. (c) Janiak, C.; Versteeg, U.; Lange, K. C. H.; Weimann, R.; Hahn, E. *J. Organomet. Chem.* **1995**, *501*, 219.

by Nöth and Berger in 1983,¹⁰ the coordination chemistry of **4** remains completely unexplored. We report here that **4** can be converted to late transition metal complexes which closely resemble those of the related boratabenzene and phospholyl.

Our synthesis of **4** (Scheme 1) is closely based on the Nöth–Berger synthesis¹⁰ but features a B-pendant *i*-Pr₂N group so that compounds in the series could be easily compared with the corresponding boratabenzenes. The reaction of 1-propynyllithium with *i*-Pr₂NBCl₂ affords *i*-Pr₂NB(C≡CCH₃)₂ (**5**) in 52% yield.^{11a} The reaction of **5** with PhPH₂ under radical-generating conditions gave **6**, in 68% yield, as a pale yellow viscous oil which slowly crystallized.^{11b} The molecular structure of **6**,¹² illustrated in Figure 1, shows the expected B,P-heterocyclic ring, which features a pyramidal phosphorus atom and a largely coplanar aminoboradienyl unit. The ¹H NMR spectrum of **6** in CDCl₃ at ambient temperature shows two nonequivalent *i*-Pr methyl signals. When the compound is heated to 68 °C, these signals coalesce, indicating a barrier of 17.5 ± 0.5 kcal/mol. The magnitude of the barrier suggests that it corresponds to slow rotation about the B–N π -bond.¹³

(10) Berger, H.-O.; Nöth, H. *J. Organomet. Chem.* **1983**, *250*, 33.

However, an alternative process involving inversion of the pyramidal phosphorus cannot be excluded.¹⁴

The *P*-phenyl group of **6** is easily cleaved. The reaction of **6** with $\text{Mn}_2(\text{CO})_{10}$ in xylene at 140 °C gave the $\text{Mn}(\text{CO})_3$ complex **7** as pale yellow crystals in 71% yield.^{11c} Also, the reaction of **6** with lithium powder in ether affords a deep red solution of the lithium salt **4a**, which

(11) Procedures for the preparation of new compounds are as follows. (a) **5**: a solution of (diisopropylamino)boron dichloride (5 g, 27.5 mmol) in 50 mL of hexane was added dropwise to 1-propynyllithium (2.53 g, 54.9 mmol) in 50 mL of hexane at -78 °C. The reaction mixture was warmed slowly to 25 °C with stirring for 12 h. The mixture was filtered, and the precipitate was washed with excess hexane. The combined filtrate and organic washings were distilled, affording 2.7 g (52%) of product (bp 70 °C at 0.01 Torr), which slowly solidified (mp 49–50 °C). ¹H NMR (CDCl_3 , 300 MHz): δ 1.22 (d, $J = 6.9$ Hz, 12H, *i*-Pr), 1.96 (s, 6H, Me), 3.89 (br, 2H, *i*-Pr). ¹¹B NMR (CDCl_3 , 160.5 MHz): δ 20.2. ¹³C NMR (CDCl_3 , 100.6 MHz): δ 5.1 (Me), 22.9 (*i*-Pr), 48.7 (*i*-Pr), 85.5 (brCB), 104.1 (C). HRMS (EI): m/z calcd for $\text{C}_{12}\text{H}_{20}^{11}\text{BN}$, 189.1689; found, 189.1692. Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{BN}$: C, 76.21; H, 10.66; N, 7.40. Found: C, 76.01; H, 10.40; N, 7.35. (b) **6**: a hexane solution of **5** (20 g, 106 mmol), phenylphosphine (12.9 g, 117 mmol), and 2,2'-azobis(2-methylpropionitrile) (AIBN; 100 mg) was heated to reflux for 3 h. An additional 100 mg of AIBN was added, and the mixture was refluxed for 3 h more. The mixture was filtered through Celite, and the solvent was evaporated. Distillation at 140 °C at 0.01 Torr gave 21.6 g (68%) of product, which slowly solidified (mp 60–62 °C). ¹H NMR (CDCl_3 , 300 MHz): δ 1.28 (d, $J = 6.6$ Hz, 6H, *i*-Pr), 1.29 (d, $J = 6.6$ Hz, 6H, *i*-Pr), 1.88 (dd, $J = 10.4, 0.8$ Hz, 6H, Me), 3.92 (br, 2H, *i*-Pr), 6.69 (d, $J = 16.4$ Hz, 2H, CH), 7.34 (m, 3H, Ar H), 7.47 (m, 2H, Ar H). ¹³C NMR (CDCl_3 , 100.6 MHz): δ 23.8 (*i*-Pr), 24.1 (*i*-Pr), 25.8 (d, $J = 25.9$ Hz, Me), 47.1 (*i*-Pr), 128.55 (d, $J = 8.4$ Hz), 129.45 (d, $J = 1.4$ Hz), 135.1 (d, $J = 19.8$ Hz) (Ph), 135.2 (d, $J = 15.3$ Hz), 155.1 (d, $J = 8.4$ Hz). ¹¹B NMR (CDCl_3 , 160.5 MHz): δ 31.0. ³¹P NMR (CDCl_3 , 121.5 MHz): δ -11.5. HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{27}^{11}\text{BNP}$, 299.1974; found, 299.1965. Anal. Calcd for $\text{C}_{18}\text{H}_{27}^{11}\text{BNP}$: C, 72.19; H, 9.00; N, 4.60. Found: C, 71.79; H, 9.04; N, 4.18. (c) **7**: a solution of **6** (1.0 g, 3.34 mmol) and $\text{Mn}_2(\text{CO})_{10}$ (1.3 g, 3.35 mmol) in 25 mL of xylene was heated to reflux for 10 h, during which time the color changed from yellow to deep orange. The mixture was filtered through Celite, and the solvent was evaporated. The residue was taken up in pentane, filtered, and evaporated, leaving 0.86 g (72%) of orange-yellow crystals. Recrystallization from pentane gave pure product (mp = 118 °C). ¹H NMR (CDCl_3 , 300 MHz): δ 1.24 (d, $J = 7.0$ Hz, 6H, *i*-Pr), 1.28 (d, $J = 7.0$ Hz, 6H, *i*-Pr), 1.96 (d, $J = 12.6$ Hz, 6H, Me), 3.70 (sept, $J = 7.0$ Hz, 2H, *i*-Pr), 4.06 (d, $J = 6.6$ Hz, 2H, CH). ¹¹B NMR (CDCl_3 , 160.5 MHz): δ 25.0. ¹³C NMR (C_6D_6 , 100.6 MHz): δ 22.6 (*i*-Pr), 26.6 (d, $J = 34.3$ Hz, Me), 46.2 (*i*-Pr), 84 (br, CH), 134.6 (d, $J = 62.6$ Hz, C), CO not observed. ³¹P NMR (CDCl_3 , 121.5 MHz): δ -37.8. IR (hexane): 2023, 1952, 1934 cm^{-1} (CO). HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{22}^{11}\text{BMnNO}_3\text{P}$, 361.0811; found, 361.0819. Anal. Calcd for $\text{C}_{15}\text{H}_{22}^{11}\text{BMnNO}_3\text{P}$: C, 49.85; H, 6.09; N, 3.80. Found: C, 49.70; H, 6.02; N, 3.63. (d) **8**: a solution of **6** (1 g, 3.3 mmol) in THF was treated with excess lithium powder for 12 h at 25 °C. The initially colorless solution turned red after several minutes. The excess Li was removed by filtration through Celite. The byproduct PhLi was removed by cooling to -78 °C and flushing with excess anhydrous NH_3 gas for 5 min. After the mixture was warmed to 25 °C, the solvent was removed to afford the lithium salt **4a** as an oil: ³¹P NMR ($\text{THF}-d_8$, 121.5 MHz) δ 38.5. The lithium salt was taken up in 20 mL of THF and added to $[\text{Cp}^*\text{RuCl}]_4$ (1.22 g, 1.13 mmol) at -78 °C. The resulting mixture was warmed slowly to 25 °C and was stirred for 12 h at 25 °C. The solvent was removed under reduced pressure, leaving a residue which was taken up in toluene. After filtration and partial removal of the solvent, **8** (1.38 g, 67%) was obtained as brown-yellow crystals (mp 142 °C). ¹H NMR (C_7D_8 , 400 MHz): δ 1.39 (d, $J = 6.6$ Hz, 12H, *i*-Pr), 1.77 (s, 15H, Cp*), 1.91 (d, $J = 12.8$ Hz, 6H, Me), 3.50 (br, 2H, *i*-Pr), 3.83 (d, $J = 8$ Hz, 2H, CH). ¹¹B NMR (C_6D_6 , 160 MHz): δ 20.4. ¹³C NMR (C_7H_8 , 100.6 MHz): δ 11.0 (Cp*), 23.5 (*i*-Pr), 25.2 (d, $J = 36.6$ Hz, Me), 46.0 (*i*-Pr), 73.0 (br, CH), 88.6 (Cp* (C)), 110.0 (d, $J = 59.8$ Hz, C). ³¹P NMR (C_7D_8 , 121.5 MHz): δ -41.9. HRMS (EI): m/z calcd for $\text{C}_{22}\text{H}_{37}^{11}\text{BNP}^{102}\text{Ru}$, 459.1800; found, 459.1805. Anal. Calcd for $\text{C}_{22}\text{H}_{37}^{11}\text{BNP}^{102}\text{Ru}$: C, 57.64; H, 8.07; N, 3.05. Found: C, 57.76; H, 8.23; N, 3.02.

(12) Crystal data for **6**: $\text{C}_{18}\text{H}_{27}^{11}\text{BNP}$, monoclinic, $P2_1/n$, $a = 6.0415$ (7) Å, $b = 15.1912$ (16) Å, $c = 19.986$ (2) Å, $\beta = 95.550$ (2)°, $V = 1825.7$ (3) Å³, $Z = 4$, $D_c = 1.089$ g cm^{-3} , $T = 150$ (2) K, $\lambda(\text{Mo K}\alpha) = 0.710$ 73 Å. Data were collected on a Siemens SMART CCD diffractometer. Final R indices ($I > 2\sigma(I)$): $R_1 = 0.0524$, $wR_2 = 0.1248$, R indices (all data): $R_1 = 0.0949$, $wR_2 = 0.1441$.

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(14) The related phospholes have a relatively low inversion barrier. See: Egan, W.; Tang, R.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1971**, *93*, 6205.

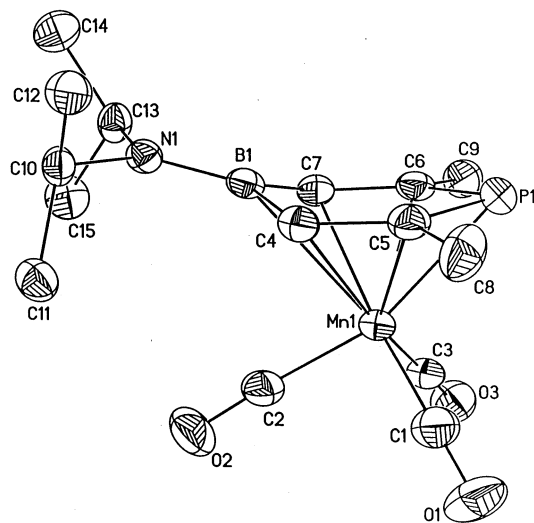


Figure 2. Solid-state structure of **7**. Selected distances (Å): B–N, 1.408(3); B–C(4), 1.547(3); B–C(7), 1.556(3); C(4)–C(5), 1.396(3); C(6)–C(7), 1.392(3); C(5)–P, 1.780(3); C(6)–P, 1.778(2); B–Mn, 2.605(3); C(4)–Mn, 2.274(2); C(5)–Mn, 2.223(2); C(6)–Mn, 2.225(2); C(7)–Mn, 2.262(2); P–Mn, 2.4051(7).

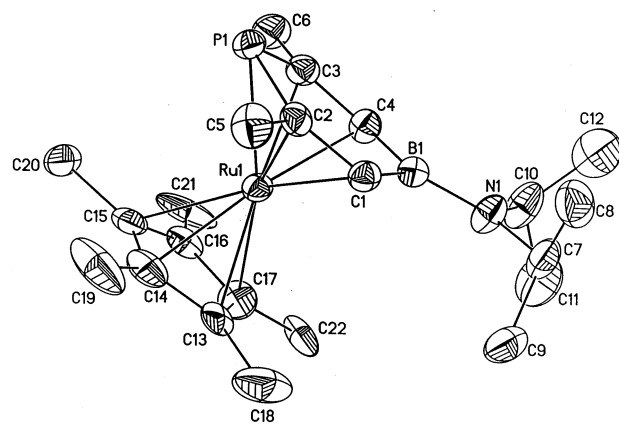


Figure 3. Solid-state structure of **8**. Selected distances (Å): B–N, 1.442(3); B–C(1), 1.535(4); B–C(4), 1.542(4); C(1)–C(2), 1.408(3); C(3)–C(4), 1.413(3); C(2)–P, 1.779(3); C(3)–P, 1.775(3); B–Ru, 2.546(3); C(1)–Ru, 2.257(2); C(2)–Ru, 2.233(2); C(3)–Ru, 2.236(2); C(4)–Ru, 2.266(2); P–Ru, 2.4286(9).

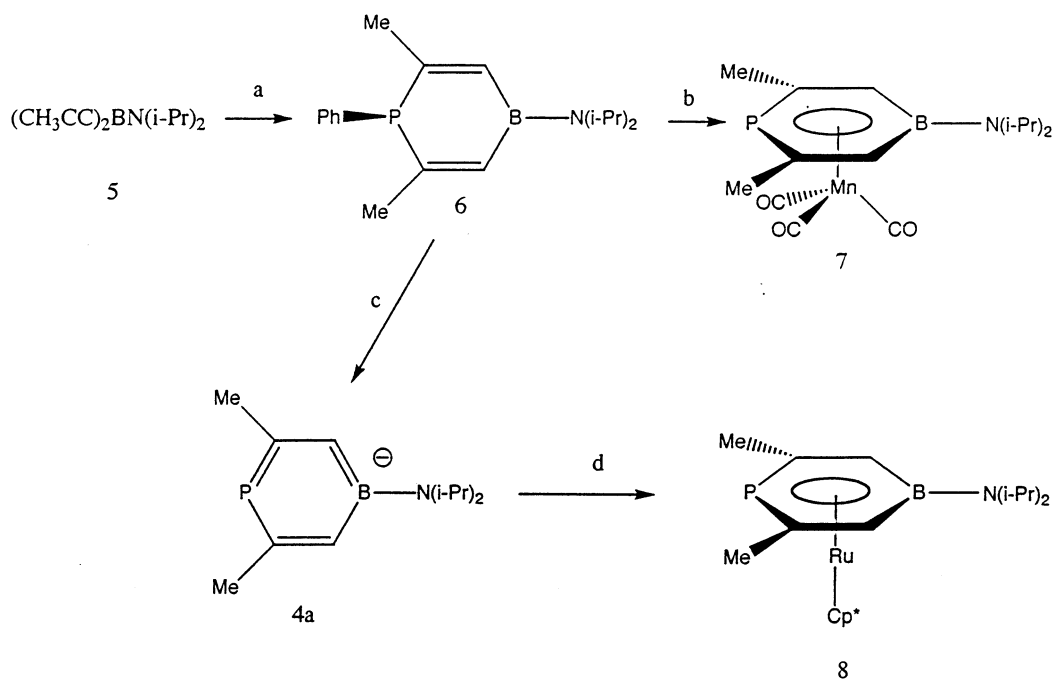
is readily detectable by ³¹P NMR spectroscopy. The downfield shift on the conversion of **6** (δ -11.5) to **4a** (δ 38.5) is characteristic for the formation of phosphorus π -coordinated anions.¹⁵ Reaction of **4a** with $[\text{Cp}^*\text{RuCl}]_4$ gives a good yield of the $\text{Cp}^*\text{Ru}^{\text{II}}$ complex **8** as deep yellow crystals.^{11d}

The molecular structures of **7**¹⁶ and **8**¹⁷ are illustrated in Figures 2 and 3, respectively. In **7**, the heterocyclic

(15) (a) Mathey, F. *Chem. Rev.* **1988**, *88*, 429. (b) Mathey, F. *Coord. Chem. Rev.* **1994**, *94*, 1.

(16) Crystal data for **7**: $\text{C}_{15}\text{H}_{22}^{11}\text{BMnNO}_3\text{P}$, orthorhombic, $Pbca$, $a = 15.678$ (3) Å, $b = 11.785$ (2) Å, $c = 18.819$ (4) Å, $V = 3477.3$ (12) Å³, $Z = 8$, $D_c = 1.379$ g cm^{-3} , $T = 150$ (2) K, $\lambda(\text{Mo K}\alpha) = 0.710$ 73 Å. Data were collected on a Siemens SMART CCD diffractometer. Final R indices ($I > 2\sigma(I)$): $R_1 = 0.0345$, $wR_2 = 0.0808$. R indices (all data): $R_1 = 0.0630$, $wR_2 = 0.0913$.

(17) Crystal data for **8**: $\text{C}_{22}\text{H}_{37}^{11}\text{BNP}^{102}\text{Ru}$, monoclinic, $P2_1/c$, $a = 18.876$ (4) Å, $b = 12.132$ (2) Å, $c = 10.304$ (2) Å, $\beta = 103.29$ (3)°, $V = 2296.4$ (8) Å³, $Z = 4$, $D_c = 1.326$ g cm^{-3} , $T = 150$ (2) K, $\lambda(\text{Mo K}\alpha) = 0.710$ 73 Å. Data were collected on a Siemens SMART CCD diffractometer. Final R indices ($I > 2\sigma(I)$): $R_1 = 0.0324$, $wR_2 = 0.0727$. R indices (all data): $R_1 = 0.0564$, $wR_2 = 0.0815$.

Scheme 1^a

^a Key: (a) PhPH₂, AIBN; (b) Mn₂(CO)₁₀; (c) Li; (d) [Cp^{*}RuCl]₄.

ring is π -coordinated to the Mn(CO)₃ group in a piano-stool fashion. One of the CO groups eclipses the boron atom, which is a typical feature of metal tricarbonyl complexes of boron heterocycles and which indicates weaker metal bonding to boron than to the other ring atoms.¹ Although the four carbon atoms of the BC₄P ring are coplanar, the boron and phosphorus atoms are displaced out of this plane away from Mn by 0.336(4) and 0.061(3) Å, respectively, which gives the ligand a boatlike geometry. There is also a strong slip distortion away from boron so that the bonding of the metal to the ring approaches η^5 . These structural features are strongly reminiscent of those of metal complexes of aminoboratabenzenes, which show a similar distortion toward η^5 coordination.¹ The coordination of the C₂PC₂ unit of the ring to the metal resembles that shown by phospholylmetal complexes.¹⁹ The B–N distance (1.408(3) Å) is short and indicates strong B–N π -bonding.²⁰ The slow rotation about this bond at 25 °C is also indicated by the H NMR spectrum, which shows two doublets (δ 1.25, 1.28) for the diastereotopic *i*-Pr methyl groups. These signals coalesce at 72 °C, which corresponds to a barrier of 18.1 \pm 0.5 kcal/mol for rotation about the B–N bond. This barrier is identical within experimental error with that shown for the B–N rotational barrier for **6** and for (1-(diisopropylamino)-boratabenzene)Mn(CO)₃.^{1a} It is likely that the B–N π -bonding is very similar for the three compounds.

The molecular structure of **8** is that of a classical sandwich compound. The heterocyclic ligand is little changed by coordination to Ru(II) relative to Mn(I), since the corresponding intra-ring distances in **7** and **8** differ by less than ± 0.02 Å. The juxtaposition of the metal with the heterocyclic ring is similar for **7** and **8**. Again, the boron is strongly displaced out of the plane of the four carbon atoms (0.284(3) Å) while phosphorus is only displaced by 0.052(3) Å. However, the B–N bond (1.443(2) Å) is somewhat longer in **8** than in **7**, indicating weaker B–N π -bonding. Weaker B–N π -bonding for **8** is consistent with a smaller electron withdrawal by the ruthenium relative to the Mn(CO)₃ group of **7**.^{1a,21} At 25 °C the H NMR spectrum of **8** shows only a single doublet for the four *i*-Pr methyl groups, which is consistent with a low barrier to rotation about the B–N bond.²²

In summary, the 1,4-phosphaboratabenzene is good six- π -electron ligand toward late transition metals. Its complexes closely resemble those of the boratabenzenes.

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Supporting Information Available: Tables of crystallographic data for **6–8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(18) (a) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (b) Albright, T. A.; Hoffmann, R. *Chem. Ber.* **1978**, *111*, 1578. (c) Albright, T. A. *Acc. Chem. Res.* **1982**, *15*, 149.

(19) Mathey, F.; Mitschler, A.; Weiss, R. *J. Am. Chem. Soc.* **1978**, *100*, 5748.

(20) Paetzold, P. *Adv. Inorg. Chem.* **1987**, *31*, 123.

(21) This order of electron withdrawal is analogous to the change from Cp₂Ru to CpMn(CO)₃; see: Watts, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 8, p 1016.

(22) These signals broaden on cooling to –12 °C. However, it was not possible to unambiguously determine the rate of coalescence, since peaks did not separate well at lower temperatures.