Diphenylphosphidoboratabenzene: An Anionic Analogue of Triphenylphosphine

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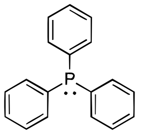
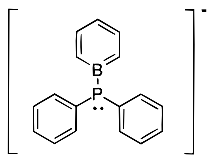
Stimulated by its relationship to the ubiquitous triphenylphosphine ligand (**1**),[1] we have prepared[2] and begun to explore the coordination chemistry of the diphenylphosphidoboratabenzene anion (DPB; **2**). DPB may be viewed as a negatively charged, essentially isosteric, variant of PPh_3; within this context, comparative studies of PPh_3 and DPB complexes, both for a given metal and for metals which are adjacent in the periodic table, could lead to useful new insights into reactivity.[3] In this communication, we report the first stage of our investigation into the chemistry of DPB, specifically, synthetic and structural work which establishes the viability of DPB as a ligand for an array of transition metals.

Triphenylphosphine (**1**)



Diphenylphosphidoboratabenzene (**2**)
DPB



A wide range of DPB adducts can be generated through treatment of transition metal halides with potassium diphenylphosphidoboratabenzene (K-DPB). For example, reaction of Cp_2ZrHCl with K-DPB in the presence of PMe_3 leads to displacement of the chloride ligand and formation of $Cp_2ZrH(DPB)(PMe_3)$ (**3**; eq 1). A single-crystal X-ray diffraction study of this complex (Figure 1a; Table 1a)[4] reveals a structure very similar to that found for $Cp_2ZrH(SiPh_3)(PMe_3)$.[5] The P−C bonds of the DPB ligand are ~0.12 Å shorter than the P−B bond, and the ligand adopts a slightly distorted tetrahedral geometry.

$$\mathrm{Cp_2ZrHCl} + \text{K-DPB} \xrightarrow[\substack{\text{THF, 20 °C} \\ 49\%}]{\text{3 equiv PMe}_3} \underset{\mathbf{3}}{\mathrm{Cp_2ZrH(DPB)(PMe_3)}} \qquad (1)$$

We have also established that the iodide of $CpFe(CO)_2I$ is readily substituted by DPB, producing $CpFe(CO)_2(DPB)$ (**4**, eq 2). The X-ray crystal structure of **4** (Figure 1b; Table 1b)[6] displays a three-legged piano-stool geometry typical of $CpFeL_2X$ complexes, with a nearly staggered conformation about the Fe−P bond (dihedral angle [Cp centroid−Fe(1)−P(1)−C(31)] = −168°).[7] As in the case of zirconium complex **3**, the P−C bonds of the DPB ligand of **4** are shorter than the P−B bond (by ~0.13 Å).

Table 1. Selected Bond Distances (Å) and Angles (deg) for (a) $Cp_2ZrH(DPB)(PMe_3)$, (b) $CpFe(CO)_2(DPB)$, and (c) $Rh(PMe_3)_3(DPB)$

	(a) $Cp_2ZrH(DPB)(PMe_3)$		
Zr−Cp (average Zr−C)	2.506	P(1)−Zr−H	58(2)
		P(1)−Zr−P(2)	115.09(5)
Zr−P(1)	2.738(1)	P(2)−Zr−H	57(2)
Zr−P(2)	2.657(2)	C(17)−P(1)−C(11)	100.1(2)
Zr−H	1.81(5)	C(17)−P(1)−Zr	111.8(2)
P(1)−C(17)	1.841(5)	C(17)−P(1)−B	106.6(2)
P(1)−C(11)	1.848(6)	C(11)−P(1)−Zr	118.5(2)
P(1)−B	1.966(6)	C(11)−P(1)−B	104.4(3)
		Zr−P(1)−B	114.0(2)
	(b) $CpFe(CO)_2(DPB)$		
Fe(1)−Cp (average Fe−C)	2.097	B(1)−P(1)−Fe(1)	115.3(3)
		B(1)−P(1)−C(21)	109.0(4)
Fe(1)−P(1)	2.276(2)	B(1)−P(1)−C(31)	106.8(3)
Fe(1)−C(6)	1.741(10)	C(31)−P(1)−C(21)	104.0(3)
Fe(1)−C(7)	1.743(10)	C(31)−P(1)−Fe(1)	114.7(3)
P(1)−B(1)	1.967(9)	C(21)−P(1)−Fe(1)	106.4(2)
P(1)−C(21)	1.840(8)	P(1)−Fe(1)−C(6)	95.4(3)
P(1)−C(31)	1.838(8)	P(1)−Fe(1)−C(7)	92.3(3)
C(6)−O(2)	1.170(9)	C(6)−Fe(1)−C(7)	94.8(4)
C(7)−O(1)	1.167(9)		
	(c) $Rh(PMe_3)_3(DPB)$		
Rh−P(1)	2.299(2)	P(1)−Rh−P(2)	96.13(7)
Rh−P(2)	2.285(2)	P(1)−Rh−P(3)	146.36(8)
Rh−P(3)	2.307(2)	P(1)−Rh−P(4)	92.59(7)
Rh−P(4)	2.306(2)	P(2)−Rh−P(3)	93.60(8)
P(1)−B	1.927(8)	P(2)−Rh−P(4)	148.03(8)
P(1)−C(1)	1.856(8)	P(3)−Rh−P(4)	95.96(8)
P(1)−C(7)	1.871(7)	B−P(1)−Rh	104.2(3)
		B−P(1)−C(1)	109.3(3)
		B−P(1)−C(7)	105.4(3)
		C(1)−P(1)−Rh	123.5(3)
		C(1)−P(1)−C(7)	102.8(3)
		C(7)−P(1)−Rh	110.5(3)

$$\mathrm{CpFe(CO)_2I} + \text{K-DPB} \xrightarrow[\substack{\text{THF, -78} \rightarrow \text{20 °C} \\ 65\%}]{} \underset{\mathbf{4}}{\mathrm{CpFe(CO)_2(DPB)}} \qquad (2)$$

$[CpFe(CO)_2(PPh_3)]^+$ and $CpFe(CO)_2(PPh_2)$ are isoelectronic with complex **4**.[8,9] Comparison of the C−O stretching frequencies (Table 2) suggests that the iron atom of $[CpFe(CO)_2(PPh_3)]^+$ is the least electron-rich and that of $CpFe(CO)_2(PPh_2)$ is the most electron-rich. It is important to note that the diphenylphosphido group is unique among the three phosphorus ligands in that it bears a "lone pair" which can contribute electron density to the metal. The IR data as well as the Fe−

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[1] For a review of phosphine complexes of transition metals, see: Dias, P. B.; de Piedade, M. E. M.; Simoes, J. A. M. *Coord. Chem. Rev.* **1994**, *135*, 737−807.

[2] Qiao, S.; Hoic, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **1996**, *118*, 6329−6330.

[3] This general approach has proved to be extremely interesting in early transition metal metallocene chemistry. For examples and leading references, see: (a) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455−1457. (b) Quan, R. W.; Bazan, G. C.; Kiely, A. F.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4489−4490.

[4] Data for compound **3**: A wheat-colored plate (0.08 × 0.09 × 0.39 mm; grown from toluene/reaction-mixture at −35 °C for three weeks) was mounted with a glass fiber on a Siemens SMART/CCD three circle diffractometer (χ fixed at 54.78°). Data collection was done at −120 °C using Mo Kα radiation. The crystal was found to be monoclinic, belonging to the space group $P2_1/c$. The cell constants are a = 9.1017(6) Å, b = 17.6952(12) Å, c = 17.8481(12) Å, β = 104.2750(10)°, V = 2785.8(3) Å^3, Z = 4, ρ_{calc} = 1.334 g/cm^3. 10 886 reflections were collected, of which 3977 were unique (R_{int} = 0.0550). Solution was done by direct methods. The final refinement by full-matrix least-squares was done on F^2 (3971 data, 312 parameters) and yielded R_1 = 0.0641 and wR_2 = 0.1104 (for data with $I > 2\sigma(I)$); GOF = 1.411. All computations were handled by the Siemens software package (SMART, SAINT, SHELXTL).

[5] Kreutzer, K. A.; Fisher, R. A.; Davis, W. M.; Spaltenstein, E.; Buchwald, S. L. *Organometallics* **1991**, *10*, 4031−4035.

[6] Data for compound **4**: Orange plate (0.28 × 0.12 × 0.07 mm; from pentane/toluene/THF at −35 °C). Monoclinic, $C2/c$, a = 17.1939(14) Å, b = 15.0376(13) Å, c = 15.9249(13) Å, β = 92.5420(10), V = 4113.4(6) Å^3, Z = 8, ρ_{calc} = 1.415 g/cm^3. 5705 reflections, 1914 unique (R_{int} = 0.0713). The final refinement (1898 data, 262 parameters) yielded R_1 = 0.0649 and wR_2 = 0.1389 for data with $I > 2\sigma(I)$; GOF = 1.290.

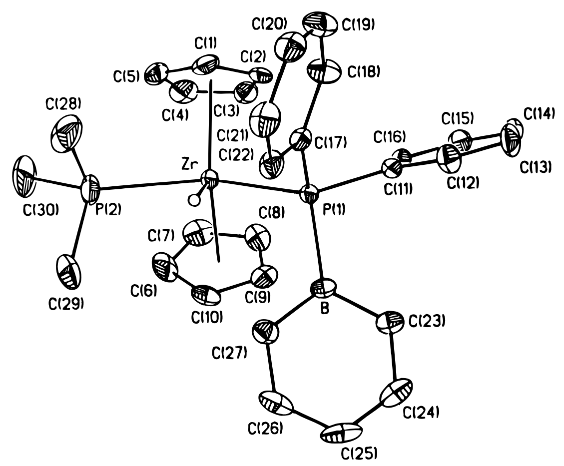
[7] For a discussion, see: Brunner, H.; Hammer, B.; Kruger, C.; Angermund, K.; Bernal, I. *Organometallics* **1985**, *4*, 1063−1068.

[8] (a) $[CpFe(CO)_2PPh_3]Cl{\cdot}3H_2O$: Riley, P. E.; Davis, R. E. *Organometallics* **1983**, *2*, 286−292. See also: Davison, A.; Green, M. L. H.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3172−3177. (b) $[CpFe(CO)_2PPh_3]^+$-$[(NC)_2CC(CN)C(CN)_2]^-$: Sim, G. A.; Woodhouse, D. I.; Knox, G. R. *J. Chem. Soc., Dalton Trans.* **1979**, 629−635. (c) $[CpFe(CO)_2PPh_3]PF_6$: Janik, T. S.; Krajkowski, L. M.; Churchill, M. R. *J. Chem. Cryst.* **1995**, *25*, 751−754. $[CpFe(CO)_2PPh_3]Cl{\cdot}3H_2O$, $[CpFe(CO)_2PPh_3]^+[(NC)_2CC(CN)C(CN)_2]^-$, and $[CpFe(CO)_2PPh_3]PF_6$ differ by less than 0.01 Å for all of the bond distances reported in Table 2.

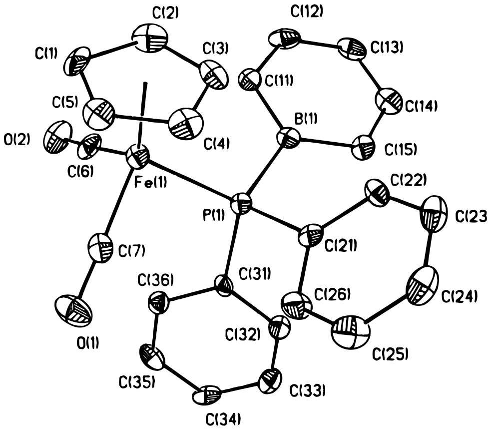
[9] $CpFe(CO)_2(PPh_2)$: Burckett-St. Laurent, J. C. T. R.; Haines, R. J.; Nolte, C. R.; Steen, N. D. C. T. *Inorg. Chem.* **1980**, *19*, 577−587.

S0002-7863(96)01574-0 CCC: $12.00

(a) $Cp_2ZrH(DPB)(PMe_3)$



(b) $CpFe(CO)_2(DPB)$



(c) $Rh(PMe_3)_3(DPB)$

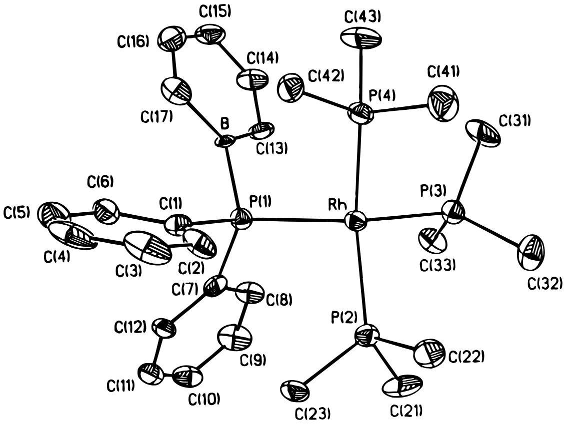


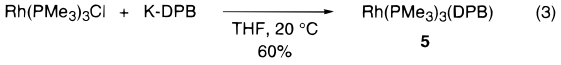
Figure 1. ORTEP illustrations, with thermal ellipsoids drawn at the 35% probability level, of transition metal complexes of DPB: (a) $Cp_2ZrH(DPB)(PMe_3)$, (b) $CpFe(CO)_2(DPB)$, and (c) $Rh(PMe_3)_3(DPB)$.

(CO) and C−O bond distances (Table 2) indicate that the DPB ligand donates significantly more electron density to iron than does the PPh_3 ligand.

Table 2. Comparison of $[CpFe(CO)_2(PPh_3)]Cl{\cdot}3H_2O$,[8] $CpFe(CO)_2(DPB)$, and $CpFe(CO)_2(PPh_2)$[9]

		av bond distances (Å)	
	ν (CO) (cm^{-1})	Fe−(CO)	C−O
$[CpFe(CO)_2(PPh_3)]Cl{\cdot}3H_2O$	2025, 2070 (Nujol)	1.771	1.139
$CpFe(CO)_2(DPB)$	1982, 2024 (KBr) 1989, 2035 (CH_2Cl_2)	1.742	1.168
$CpFe(CO)_2(PPh_2)$	1966, 2015 (cyclohexane)	not available	

Finally, we have determined that treatment of $Rh(PMe_3)_3Cl$ with K-DPB generates $Rh(PMe_3)_3(DPB)$ (**5**; eq 3). A single-crystal X-ray diffraction study of complex **5** (Figure 1c; Table 1c)[10] reveals a distorted square planar geometry, with angles between cis phosphorus ligands ranging from 92 to 96° and angles between trans phosphorus ligands of 146° and 148° (P−Rh−P).[11] The Rh−P bond distance for the PMe_3 group trans to DPB is 2.307(2) Å, and the Rh−P bond distances for the PMe_3 groups cis to DPB are 2.285(2) and 2.306(2) Å. The P−C bonds of the DPB ligand of $Rh(PMe_3)_3(DPB)$ are only ~0.06 Å shorter than the P−B bond, about half the difference found for **3** and **4**, possibly reflecting the lower Lewis acidity of the rhodium center.[12]



$$Rh(PMe_3)_3Cl + K\text{-}DPB \xrightarrow[60\%]{THF,\ 20\ °C} \underset{\mathbf{5}}{Rh(PMe_3)_3(DPB)} \qquad (3)$$

In conclusion, we have established that a range of complexes containing DPB, a new anionic ligand, can be synthesized via substitution reactions of transition metal halides. It is worth noting that the chemistry of K-DPB differs from that of its nitrogen analogue, potassium diphenylamidoboratabenzene, which does not afford an η^1 adduct in any of the reactions described above.[13,14] Given the structural similarity of PPh_3 (**1**) and DPB (**2**), we anticipate that studies comparing the reactivity of complexes which bear these ligands may prove to be particularly interesting. The development of a chiral variant of DPB is also underway.[15]

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Supporting Information Available: A listing of experimental procedures and compound characterization data (31 pages). See any current masthead page for ordering and Internet access instructions.

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[10] Data for compound **5**: Dark red prisms (0.22 × 0.22 × 0.13 mm; from pentane/THF at room temperature). Monoclinic, $P2_1/n$, $a = 9.4031(8)$ Å, $b = 17.692(2)$ Å, $c = 17.672(2)$ Å, $\beta = 95.6350(10)$, $V = 2925.8(4)$ Å^3, $Z = 4$, $\rho_{calc} = 1.344$ g/cm^3. 7705 reflections, 2710 unique ($R_{int} = 0.1446$). The final refinement (2640 data, 290 parameters) yielded $R_1 = 0.0572$ and $wR_2 = 0.1000$ for data with $I > 2\sigma(I)$; GOF = 1.166.

[11] For a closely related structure, see: Thorn, D. L.; Harlow, R. L. *Inorg. Chem.* **1990**, *29*, 2017−2019.

[12] A preliminary reactivity study indicates that treatment of complex **5** with H_2 results in the formation of two rhodium hydride species. Further investigations are underway.

[13] DPB adducts **3**−**5** are the first boratabenzene complexes in which the ligand is σ-bound, rather than π-bound, to the metal. For leading references to π-bound boratabenzene complexes, see: (a) Herberich, G. E. In *Comprehensive Organometallic Chemistry II*; Abel, E. W.; Stone, F. G. A.; Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 1, Chapter 5. (b) Herberich, G. E.; Ohst, H. *Adv. Organomet. Chem.* **1986**, *25*, 199−236. (c) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Muller, C. *J. Am. Chem. Soc.* **1996**, *118*, 2291−2292.

[14] (η^6-$C_5H_5BNPh_2$)$Rh(PMe_3)_2$ is formed cleanly upon treatment of $Rh(PMe_3)_3Cl$ with potassium diphenylamidoboratabenzene.

[15] Examples of anionic η^1 ligands in which the ligating atom is both stereogenic and configurationally stable are rare. See: Brunner, H.; Zettlmeier, W. *Handbook of Enantioselective Catalysis*; VCH: New York, 1993; Vol. 2.