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Coordination chemistry of aminoborylphosphanes. Crystal structure determinations of $(^iPr_2N)_2BP(H)SiPh_3\cdot Cr(CO)_5$ and $[(^iPr_2N)_2BP(H)]_2SiMe_2\cdot W(CO)_4$☆

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Abstract

The reactions of the aminoborylphosphanes, $(^iPr_2N)_2BP(H)SiPh_3$ (**1**), $[(^iPr_2N)_2BP(H)]_2SiMe_2$ (**2**), and $[(^iPr_2N)_2BP(H)Si(Me)_2]_2$ (**3**) with $M(CO)_5\cdot NMe_3$ or $M(CO)_4$ (norbornadiene) (M = Cr, Mo, W) gave solid, crystalline adducts, three of which have been fully characterized. The molecular structures of $(^iPr_2N)_2BP(H)SiPh_3\cdot Cr(CO)_5$ (**4**) and $[(^iPr_2N)_2BP(H)]_2SiMe_2\cdot W(CO)_4$ (**5′**) have been determined by single crystal X-ray diffraction techniques. Ligand **1** acts as a monodentate σ donor ligand while **2** coordinates as a chelating phosphane. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Aminoborylphosphanes; Metal carbonyls; Coordination complexes

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1. Introduction

Relatively few primary and secondary phosphanes or bis-phosphanes containing inorganic substituents, e.g. $(X_nE)PH_2$, $(X_nE)_2PH$, $(X_nE)(Y_mE')PH$ and $(X_nE)P(H)$-$(EY_m)P(H)(X_nE)$ (E = main group element, excluding carbon; X = alkyl, aryl, halide, alkoxy, amino substituents) have been reported [1], and examples containing boryl substituents, until recently, have been especially rare [2]. During efforts to develop synthetic routes to new main group element cage molecules containing boron and phosphorus atoms, we have found it necessary to prepare a collection of new aminoborylphosphanes [2–5]. Subsequently, it became of interest to examine the coordination ability of some of these compounds toward metal carbonyl fragments since the metal carbonyl might act as protecting groups in cage assembly reactions. In this report we describe the formation of complexes with the phosphane $(^iPr_2N)_2BP(H)SiPh_3$ **1**, and the bis-phosphanes $[(^iPr_2N)_2BP(H)]_2SiMe_2$ **2** and $[(^iPr_2N)_2BP(H)Si(Me)_2]_2$ **3**.

2. Experimental

Standard inert atmosphere techniques were employed in all syntheses and product manipulations. Solvents were dried, deoxygenated, and distilled prior to use. Mass spectra were obtained by using a Finnegan GC/MS or from the Midwest Center for Mass Spectrometry, University of Nebraska. IR spectra were obtained with a Mattson 2020 FTIR and NMR spectra were recorded from Bruker WP–250 and JEOL GSX–400 spectrometers. All samples were sealed in 5 mm NMR tubes containing a deuterated lock solvent and references were set with external samples: Me_4Si (^1H, ^{13}C),

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☆ Dedicated to Professor Alan H. Cowley, in honor of his 65th birthday.

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H_3PO_4 (^{31}P) and $F_3B·OEt_2$ (^{11}B). Elemental analyses were obtained at the UNM microanalysis facility.

2.1. Synthesis of ligands

The ligands **1**–**3** were prepared and purified in the same general fashion, and the procedure for **1** is described in detail here. The syntheses of **2** and **3** are described in a paper outlining their utility in cage building chemistry [5,6]. Equimolar amounts of $(^iPr_2N)_2BP(H)Li·DME$ (DME = 1,2-dimethoxyethane) (1.16 g, 3.4 mmol) [3] and Ph_3SiCl (1.0 g, 3.4 mmol) were combined in 40 ml of hexane at 0°C and stirred at 0°C (1 h) and then at 23°C (6 h). Insoluble LiCl was removed by filtration under nitrogen and the solvent vacuum evaporated from the filtrate. The resulting colorless oil formed colorless crystals of **1** upon standing at 23°C for several days: yield 1.7 g, 100%, m.p. 164–167°C (dec.). Anal. Found: C, 71.04; H, 8.83; N, 5.57. $C_{30}H_{44}N_2BPSi$ (502.54): C, 71.70; H, 9.21; N, 5.75. MS (*m*/*e*, relative intensity): 211 (100%, $B(N^iPr_2)_2$). IR spectrum (KBr, cm^{-1}): 3054 (m), 2967 (s), 2930 (s), 2872 (s), 2326 (w, PH), 1464 (m), 1425 (s), 1364 (s), 1310 (s), 1221 (s), 1198 (s), 1107 (s), 1071 (s), 1001 (m), 907 (w), 822 (w), 740 (m), 652 (w), 527 (s), 492 (m). ^{31}P-NMR (C_6D_6): δ -206.5 ($^1J_{PH} = 215$ Hz). ^{11}B{^{1}H}-NMR (C_6D_6): δ 40.1. ^{1}H-NMR (C_6D_6): δ 1.09 (CH_3, $^3J_{HH} =$ 6.9 Hz, 24H), 2.05 (PH, $^1J_{PH} = 220$ Hz, 1H), 3.71 (CH, $^3J_{HH} = 6.9$ Hz, 4H), 7.16–7.21 (m; Ph), 7.80–7.85 (m, Ph). ^{13}C{^{1}H}-NMR (C_6D_6): δ 24.6 (CH_3), 49.1 (CH, $^3J_{PC} = 3.1$ Hz), 128.1 (Ph), 129.5 (Ph), 136.4 (Ph), 137.2 (Ph, $^2J_{PC} = 8.6$ Hz). Characterization data for ligands **2** and **3** are available in the literature [5,6], and selected NMR data are discussed in Section 3 along with data for the complexes.

2.2. Formation of complexes

Equimolar amounts of ligand **1** (1.71 g, 3.4 mmol) and $Cr(CO)_5·NMe_3$ (0.87 g, 3.4 mmol) were combined in 50 ml of hexane at 23°C and stirred overnight. The yellow reaction mixture was filtered and the filtrate concentrated to ca. 20 ml, or until some solid deposited. The flask was then warmed to 40°C and cooled slowly overnight. Pale yellow crystals of **4** deposited and were collected. A second crop could be obtained by further solution concentration: yield 1.4 g, 60%; m.p. 78–80°C (dec.). Complex **5** was obtained by combination of **2** (1.22 g, 2.24 mmol) and $(NBD)Mo(CO)_4$ (0.68 g, 2.3 mmol) (NBD = norbornadiene) in 40 ml hexane at 23°C for 1 day. The volatiles were removed, the resulting yellow solids redissolved in diethylether, and the mixture filtered. The filtrate was reduced in volume and cooled to -20°C, whereupon yellow crystals deposited. Two crops were obtained: yield, 0.96 g, 57%. Complex **5**′ was synthesized by combination of **2** (0.40 g, 0.73 mmol) and $(NBD)W(CO)_4$ (0.28 g, 0.72 mmol) in 30 ml hexane at 23°C for 1 day. The solvent volume was reduced, and two crops of orange crystals were obtained by cooling to -20°C: yield 0.194 g, 32%. Complex **5**″ was prepared by combination of **2** (1.22 g, 2.24 mmol) and $(NBD)Cr(CO)_4$ (0.58 g, 2.26 mmol) in 40 ml of hexane at 23°C for 1 day. The resulting mixture was reduced in volume and a yellow solid deposited which was recrystallized from hexane at -20°C: yield 0.56 g, 35%. Compound **6** was obtained from an equimolar combination of **3** with $(NBD)Mo(CO)_4$ and purified as described for **4**.

2.3. Characterization data for complexes

Complex **4**. Anal. Found: C, 59.65; H, 6.46; N, 4.17. $C_{35}H_{44}N_2BO_5PSiCr$ (694.59): C, 60.52; H, 6.39; N, 4.03. Mass spectrum (FAB) (*m*/*e*, intensity): 693–690 (6%, M^+), 259 (100%). IR spectrum (KBr, cm^{-1}) (carbonyl region): 2058 (m), 1975 (m), 1935 (s). ^{31}P-NMR (C_6D_6): δ -170.9 ($^1J_{PH} = 275$ Hz). ^{11}B{^{1}H}-NMR (C_6D_6): δ 35.8. ^{1}H-NMR (C_6D_6): δ 0.89–1.20 (m, CH_3, $^3J_{HH} \cong 6$ Hz, 24H), 2.83 (PH, $^1J_{PH} = 276$ Hz), 3.43 (CH, $^3J_{HH} =$ 6.9 Hz, 2H), 3.81 (CH, $^3J_{HH} = 6.9$ Hz, 2H), 7.14–7.18 (m, Ph), 7.73–7.77 (m, Ph). ^{13}C{^{1}H}-NMR (C_6D_6): δ 24.7, 24.9, 25.5, 26.6 (CH_3), 50.23, 51.4, 51.5 (CH), 128.6, 130.7, 133.5 ($^2J_{P-C} = 7.7$ Hz), 136.5 (Ph), 218.0 (CO, *cis* $^2J_{PC} = 8.3$ Hz), 222.4 (CO, *trans* $^2J_{PC} = 6.0$ Hz). Complex **5**. IR spectrum (KBr, cm $-$ ^{1}) (carbonyl region): 2012 (w), 1892 (s), 1865 (s). ^{31}P-NMR (C_6D_6): δ -163. ^{1}H-NMR (C_6D_6): δ 0.20 (Me_2Si, 6H), 1.86 ($NCH(CH_3)_2$, 48H), 2.78 (CH, 8H). Complex **5**′. ^{31}P-NMR (C_6D_6): δ -195. Complex **5**″. ^{31}P-NMR (C_6D_6): δ -136. Complex **6**. IR spectrum (KBr, cm^{-1}) (carbonyl region only): 2002 (m), 1886 (s), 1851 (s). ^{31}P-NMR (C_6D_6): δ -190.5. ^{1}H-NMR (C_6D_6): δ 0.39 ($SiMe_2$, $^3J_{PH} = 3.2$ Hz), 0.47 ($SiMe_2$, $^3J_{PH} = 6.3$ Hz), 1.30 ($CHCH_3$, $^3J_{HH} = 6.9$ Hz), 1.31 ($CHCH_3$, $^3J_{HH} =$ 6.8 Hz), 1.96, 3.04. ^{13}C{^{1}H}-NMR (C_6D_6): δ -5.1 ($SiMe_2$), -2.0 ($SiMe_2$), 24.9 ($CH(CH_3)_2$ $J_{CP} = 70.3$ Hz), 48.6, 50.9 (*C*H), 212.9 ($J_{CP} = 55.5$ Hz), 216.0, 217.5, 217.7, 218.

2.4. Structure determinations

Suitable crystals of **4** and **5**′ were obtained from hexane solutions at -10°C. Crystals were placed in glass capillaries under nitrogen and sealed. The crystals were centered on a Siemens R3m/V four-circle diffractometer and determinations of the crystal class, orientation matrix and accurate unit cell parameters were made at 20°C. The crystal parameters and data collection details are summarized in Table 1. The intensity data were collected with Mo–K$_\alpha$ ($\lambda = 0.71073$ Å) monochromated radiation, a scintillation counter, and pulse height analyzer. Intensities for three standard reflections were monitored every 97 reflections. No crystal decay was detected. All calculations were performed on the Siemens P3 structure solution system using SHELXTL PLUS. Neutral atom scattering factors and anomalous dispersion terms were used for all non-hydrogen atoms. A small empirical adsorption correction based on psi scans was applied in each case. The structures were solved by direct methods (**4**) and Patterson techniques (**5′**). Full matrix least-squares methods were used in the refinements. Tables 2 and 3 contain listings of the atom positional parameters and bond distances, and angles are given in Table 4.

3. Results and discussion

The equimolar combination of $({}^{i}Pr_2N)_2BP(H)$-$Li{\cdot}DME$ and Ph_3SiCl in hexane gives the borylsilylphosphane **1** as described in Eq. 1. Ligand **1** is obtained in quantitative yield as a colorless oil that slowly crystallizes upon standing at 23°C. Subsequent equimolar combination of this ligand with $Cr(CO)_5{\cdot}NMe_3$ in hexane gives a yellow solution (Eq. 2) from which pale yellow crystals deposit.

Table 1
Summary of X-ray diffraction data for complexes **4** and **5′**

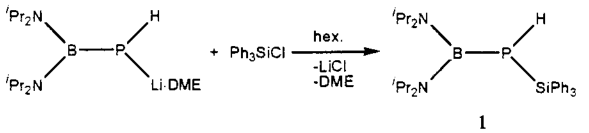
	4	**5′**
Formula	$C_{35}H_{44}N_2BO_5PSiCr$	$C_{30}H_{64}N_4B_2O_4P_2SiW$
Color	Colorless	Pale yellow
Crystal dimensions (mm)	0.18 × 0.21 × 0.46	0.56 × 0.46 × 0.20
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	$P2_1/c$
a (Å)	19.323(2)	13.533(2)
b (Å)	10.572(1)	17.620(2)
c (Å)	18.425(1)	17.908(2)
α (°)	90	90
β (°)	90	96.91(1)
γ (°)	90	90
V (Å^3)	3763.7(6)	4239.2(9)
Z	4	4
Formula weight	694.6	840.35
$D_{calc.}$ (g cm^{-3})	1.226	1.317
Absorption coefficient (mm^{-1})	0.419	2.862
$F(000)$	1464	1728
Temperature (K)	293	293
2θ limit (°)	2–50	4–45
Indices	$\pm h, \pm k, \pm l$	$-h, \pm k, \pm l$
Scan type	ω	ω
Max/min transmission	0.950/0.887	1.000/0.528
No. collected reflections	6855	11320
No. observed reflections	3278 ($F > 1.5\sigma(F)$)	3275 ($F > 4\sigma(F)$)
Parameters refined	417	388
R (%)[a]	4.88	3.45
R_w (%)[b]	5.20	6.14

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

[b] $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_{o2}]^{1/2}$.

Table 2
Atomic positional parameters ($\times 10^4$) for complex **4**

	x	y	z
Cr	1486(1)	9528(1)	8572
C(1)	1468(6)	8825(10)	9488(5)
O(1)	1459(5)	8386(9)	10054(4)
C(2)	1852(5)	7968(11)	8228(6)
O(2)	2074(4)	7022(8)	8073(6)
C(3)	1108(5)	11007(10)	8991(5)
O(3)	878(4)	11832(7)	9299(4)
C(4)	2395(5)	10132(9)	8745(5)
O(4)	2937(4)	10467(9)	8883(4)
C(5)	584(5)	8936(8)	8388(5)
O(5)	41(3)	8585(8)	8287(4)
P	1431(1)	10435(2)	7330(1)
B	1777(5)	9384(9)	6495(4)
N(1)	1242(3)	8707(6)	6121(4)
N(2)	2485(3)	9330(7)	6346(4)
C(6)	649(4)	9405(9)	5809(4)
C(7)	−66(5)	8980(11)	6055(6)
C(8)	683(5)	9511(10)	4983(5)
C(9)	1278(6)	7304(9)	6108(5)
C(10)	1181(7)	6701(10)	5372(6)
C(11)	827(7)	6672(10)	6672(6)
C(12)	3004(5)	9849(11)	6859(5)
C(13)	3469(6)	10861(11)	6547(6)
C(14)	3433(5)	8850(11)	7243(7)
C(15)	2712(6)	8720(11)	5646(5)
C(16)	3124(8)	7518(16)	5743(7)
C(17)	3009(7)	9614(15)	5098(5)
Si	1448(1)	12563(2)	7110(1)
C(18)	895(5)	14325(8)	8120(5)
C(19)	392(5)	14852(8)	8561(6)
C(20)	−233(4)	14302(9)	8628(6)
C(21)	−385(4)	13324(10)	8223(5)
C(22)	105(4)	12722(10)	7772(5)
C(23)	763(4)	13252(8)	7708(4)
C(24)	567(5)	13117(8)	5913(5)
C(25)	396(6)	13199(10)	5179(6)
C(26)	874(8)	12942(11)	4663(6)
C(27)	1543(7)	12603(10)	4862(5)
C(28)	1693(5)	12493(10)	5580(4)
C(29)	1228(4)	12763(7)	6129(4)
C(30)	2671(5)	14066(9)	6874(6)
C(31)	3260(5)	14704(11)	7101(8)
C(32)	3475(6)	14610(12)	7803(9)
C(33)	3116(6)	13898(11)	8288(7)
C(34)	2528(4)	13255(10)	8067(5)
C(35)	2292(4)	13340(8)	7353(5)



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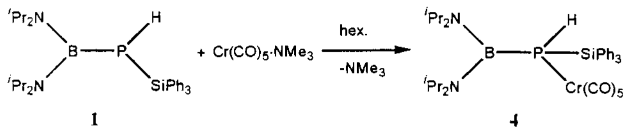
(1)



1 4

(2)

Both ligand **1** and the complex, $[(^i\mathrm{Pr}_2\mathrm{N})_2\mathrm{BP(H)}\text{-}\mathrm{SiPh}_3]\cdot\mathrm{Cr(CO)}_5$ **4**, have been fully characterized. Ligand **1** does not display a parent ion in an electron impact mass spectrum under the conditions employed; however, the parent ion is seen in a FAB MS. The IR spectrum for **1** shows a weak ν_{PH} stretching frequency at 2326 cm^{-1}. In the complex this weak band disappears and a new band for the coordinated PH group is not confidently identified. The IR spectrum does show the expected three-band pattern in the ν_{CO} region with absorptions centered at 2058, 1975 and 1935 cm^{-1}.

Table 3
Atomic positional parameters ($\times 10^4$) for complex **5′**

	x	*y*	*z*
W	3161(1)	8898(1)	2336(1)
P(1)	1440(1)	8887(1)	2821(1)
P(2)	3235(1)	7833(1)	3328(1)
Si	2039(2)	8363(1)	3939(1)
O(1)	4037(5)	10138(3)	3520(3)
O(2)	2473(6)	7663(4)	1105(4)
O(3)	5313(5)	8655(4)	1957(4)
O(4)	2755(6)	10179(4)	1124(4)
B(1)	282(7)	9592(5)	2712(5)
B(2)	4386(6)	7208(5)	3811(5)
N(1)	373(4)	10311(3)	3033(3)
N(2)	−622(5)	9323(3)	2275(4)
N(3)	5162(4)	7575(3)	4241(3)
N(4)	4318(4)	6402(3)	3647(3)
C(1)	3699(6)	9679(5)	3108(5)
C(2)	2712(7)	8126(5)	1542(5)
C(3)	4468(8)	8752(5)	2083(5)
C(4)	2900(7)	9702(5)	1571(5)
C(5)	2519(6)	9055(4)	4671(4)
C(6)	1172(5)	7689(4)	4340(4)
C(7)	−553(6)	10794(5)	3025(5)
C(8)	−468(7)	11562(4)	2726(6)
C(9)	−969(7)	10785(5)	3798(5)
C(10)	1333(6)	10604(4)	3393(5)
C(11)	1200(13)	10821(10)	4307(10)
C(11′)	1466(13)	11032(12)	4033(11)
C(12)	1887(13)	11150(12)	3116(10)
C(12′)	1761(13)	11105(10)	2666(10)
C(13)	1092(6)	8626(5)	2560(6)
C(14)	−1123(7)	8709(5)	3398(6)
C(15)	−2153(6)	8478(6)	2191(6)
C(16)	−716(8)	9357(6)	1452(6)
C(17)	−176(9)	8768(6)	1049(5)
C(18)	−384(10)	10130(7)	1198(6)
C(19)	5163(6)	8394(4)	4402(5)
C(20)	5958(12)	8818(10)	3872(9)
C(20′)	5963(14)	8845(12)	4333(10)
C(21)	5255(13)	8723(10)	5112(10)
C(21′)	4926(16)	8412(12)	5323(12)
C(22)	6020(7)	7093(5)	4566(6)
C(23)	6972(14)	7324(9)	4577(11)
C(23′)	6965(16)	7235(11)	4000(12)
C(24)	5865(15)	7028(10)	5541(11)
C(24′)	6447(17)	6992(12)	5230(13)
C(25)	4580(6)	6121(5)	2925(5)
C(26)	3733(8)	6012(6)	2342(6)
C(27)	5336(8)	6614(6)	2606(6)
C(28)	3618(8)	5947(4)	3994(5)
C(29)	3204(14)	6169(12)	4584(11)
C(29′)	3619(15)	6283(10)	4862(10)
C(30)	3892(11)	5120(6)	4054(8)

Table 4
Selected bond distances and angles for complexes **4** and **5′**

4		**5′**	
Bond distances (Å)			
Cr–C(1)	1.85(1)	W–C(1)	2.02(1)
Cr–C(2)	1.90(1)	W–C(2)	2.007(9)
Cr–C(3)	1.89(1)	W–C(3)	1.90(1)
Cr–C(4)	1.895(9)	W–C(4)	1.972(9)
Cr–C(5)	1.884(9)		
Cr–P	2.483(2)	W–P(1)	2.582(2)
		W–P(2)	2.578(2)
P–B	2.013(9)	P(1)–B(1)	1.990(8)
		P(2)–B(2)	2.016(8)
P–Si	2.286(3)	P(1)–Si	2.264(3)
		P(2)–Si	2.262(3)
B–N(1)	1.43(1)	B(1)–N(1)	1.392(9)
B–N(2)	1.40(1)	B(1)–N(2)	1.45(1)
		B(2)–N(3)	1.386(9)
		B(2)–N(4)	1.451(9)
Bond angles (°)			
C(1)–Cr–P	176.3(4)	C(4)–W–P(2)	172.0(3)
		C(3)–W–P(1)	170.0(3)
		P(1)–W–P(2)	74.03(6)
Cr–P–B	118.5(3)	W–P(1)–B(1)	133.9(3)
Cr–P–Si	122.9(1)	W–P(2)–B(2)	131.1(2)
B–P–Si	113.7(3)	W–P(1)–Si	93.37(8)
		W–P(2)–Si	93.53(8)
		B(1)–P(1)–Si	122.4(3)
		B(2)–P(2)–Si	125.4(2)

The NMR spectra for **1** and **4** provide additional definitive characterization data. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ spectra for **1** and **4** each show a single resonance: **1**, δ -206.5; **4**, δ -170.9. The downfield shift upon coordination is consistent with removal of electron density from the P atom donor center. The values of $^1J_{\mathrm{PH}}$, **1**, 215 Hz; **4**, 275 Hz, also suggest some degree of phosphorus atom rehybridization. The increase in J_{PH} with coordination suggests that more s character is directed to the P–H bond in the complex, which in turn requires that the P–Cr bond has more p orbital character. Similar trends have been observed with coordination complexes of diborylphosphanes [3,4] and some organophosphanes [7]. The ^{1}H-NMR spectra for **1** and **4** show a single resonance assigned to the P–H group, each of which is split into a doublet by one-bond P–H coupling. The resonance in **1**, δ 2.05, is slightly upfield of that in the complex **4**, δ 2.83. The ^{1}H- and $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR spectra show only one $^i\mathrm{Pr}$ CH_3 and CH environment in the free ligand, consistent with free B–N and/or C–N bond rotation. The complex, on the other hand, displays at least two distinguishable environments, suggesting that bond rotation is now hindered. The $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR spectrum of **4** in the carbonyl region shows two resonances, δ 218.0 and 224.4, which are assigned to *cis* and *trans* COs. Both display two-bond P–C coupling, $^{2}J_{PC} = 8.3$ and 6.0 Hz, respectively.

The structure of **4** was confirmed by single crystal X-ray diffraction analysis. A view of the molecule is shown in Fig. 1, and selected bond lengths and angles appear in Table 4. The Cr atom has a distorted pseudo-octahedral geometry while the P atom geometry more closely approximates a trigonal pyramid rather than a tetrahedron. This is evidenced by the fact that the three heavy-atoms in the substituents, $Cr(CO)_5$, Ph_3Si and $B(N^{i}Pr_2)_2$, are nearly coplanar with the central P atom, as indicated by the sum of bond angles about the P atom: 355.1°. The Cr–P bond distance, 2.483(2) Å, is similar to the value in $P_2(^{i}Pr_2NB)_2(tmpB){\cdot}Cr(CO)_5$, 2.486(4) Å [8], (tmp = 2,2,6,6-tetramethylpiperidino) but it is longer than the distances in $Ph_3P{\cdot}Cr(CO)_5$, 2.422(1) Å [9] and $(tmpBPH)_2{\cdot}Cr(CO)_5$, 2.458(2) Å [10]. Based upon these data and the IR CO frequencies, it can be concluded that **1** is a modest σ donor and a poor π acceptor. This is further reflected by the shortening of the *trans* Cr–C(O) bond distance, 1.85(11) Å, relative to the average *cis* Cr–C(O) bond distance, 1.89(1) Å. Within the ligand fragment, the B–P bond length, 2.012(9) Å, and the Si–P distance, 2.286(3) Å, are in the normal ranges for single bonds [11].

The syntheses for the ligands **2** and **3** follow similar procedures to that described for **1**, and full details can be found in descriptions of other aspects of their chemistry [5,6]. Each ligand was allowed to react with equimolar amounts of $M(CO)_4$ (norbornadiene), M = Cr, Mo, W, in an effort to obtain $M(CO)_4(PP)$ complexes. In particular, ligand **2** combines in a 1:1 ratio with $(CO)_4Cr(NBD)$, $(CO)_4Mo(NBD)$ or $(CO)_4W(NBD)$, forming pale yellow complexes $[(^{i}Pr_2N)_2BP(H)]_2SiMe_2{\cdot}Mo(CO)_4$ **5**, $[(^{i}Pr_2N)_2BP(H)]_2SiMe_2{\cdot}W(CO)_4$ **5′**, and $[(^{i}Pr_2N)_2BP(H)]_2SiMe_2{\cdot}Cr(CO)_4$ **5″** as summarized in Eq. (3).

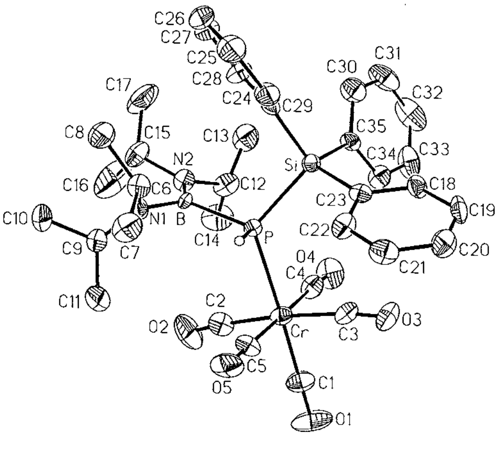


Fig. 1. Molecular structure and atom labeling scheme for $(^{i}Pr_2N)_2BP(H)SiPH_3{\cdot}Cr(CO)_5$, **4** (30% thermal ellipsoids).

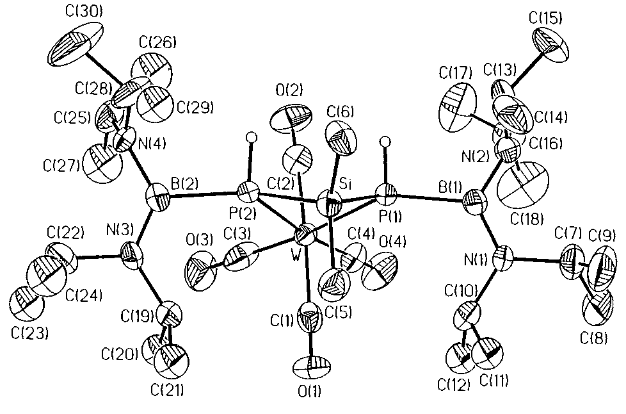
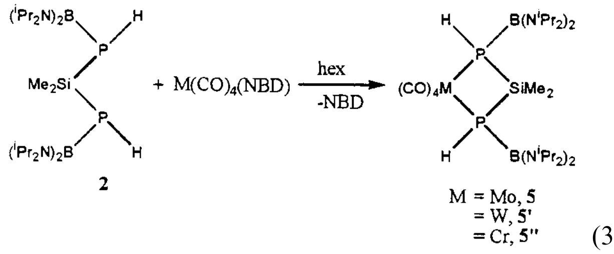


Fig. 2. Molecular sturcture and atom labeling scheme for $[(^{i}Pr_2N)_2BP(H)]_2SiMe_2{\cdot}W(CO)_4$ **5′** (30% thermal ellipsoids).

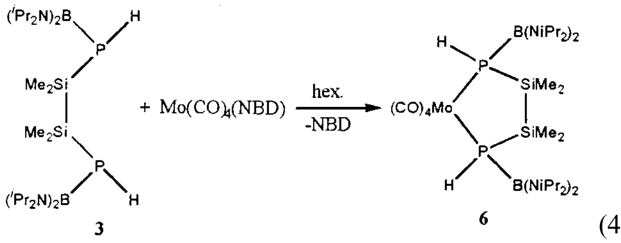


(3)

Only the M=Mo species was obtained with reasonable purity; however, the crystal quality was poor. Some single crystals of the M=W species were obtained and the X-ray crystal structure of this compound was determined. As seen in Fig. 2, the ligand bonds to the $W(CO)_4$ unit in a bidentate manner. The four-membered WPSiP chelate ring is slightly folded along the W···Si vector and the BN_2 planes are twisted so that they are roughly perpendicular to the chelate ring. The borylamine groups, $(^{i}Pr_2N)_2B$, are *cis* to each other across the ring. The W–P bond lengths, W–P(1) 2.582(2) and W–P(2) 2.578(2) Å, are identical and typical of W–P bond lengths in complexes containing chelating diphosphanes. The average W–(CO) bond length, 1.97(1) Å, is also typical of distances in $W(CO)_4$ (LL) complexes. Similar to **4**, the geometry at the phosphorus atoms generated by the heavy atom groups $W(CO)_4$, $SiMe_2$ and $B(N^{i}Pr_2)_2$ are relatively flat as indicated by the sums of angles: P(1) 349.7 and P(2) 350.0°. The average P–Si bond length, 2.263(3) Å, is typical of single bond distances in a variety of borylphosphanes [2–4]. Finally, the B–N bond lengths fall into two groups as found in many diaminoborane fragments: 1.389(9) and 1.450(9) Å. The shorter distances, B(1)–N(1) and B(2)–N(3) are positioned below the WPSiP ring and the two longer distances, B(1)–N(2) and B(2)–N(4) are above the ring.

The $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$-NMR spectrum of ligand **2** consists of a single resonance centered at δ -186.1. The proton-coupled spectrum displays a first-order doublet, $^{1}J_{\mathrm{PH}} = 213$ Hz. The $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$-NMR spectra for **5**, **5′** and **5″** contain major singlet resonances centered at δ -136, -163 and -195, respectively. In addition, each spectrum contains several weak signals that may belong to impurities, or perhaps diastereomers. The coordination shifts (δ complex—δ (free ligand)) are: $+50$, $+23$ and -9 ppm, respectively. These shifts are comparable to those reported for a series of di(tertiaryphosphine) $\mathrm{M(CO)_4}$ complexes that also contain four-membered chelate rings [12,13]. The proton-coupled $^{31}\mathrm{P}$-NMR spectra of the complexes show interesting variations. The W complex **5′** displays a doublet pattern with $^{1}J_{\mathrm{PH}} = 287$ Hz, while the Cr complex **5″** shows a 'pseudo triplet' pattern with peak spacings of ca. 280 Hz. The Mo complex produces a complex second order pattern that is not fully reproduced in all detail with an AA′XX′ spin system simulation. A complete interpretation of the P–H coupling details and the differences between the complexes will require further study of these complexes, as well as related new derivatives.

Ligand **3** produces a pale yellow crystalline solid **6** when combined with $\mathrm{Mo(CO)_4(NBD)}$, as shown in Eq. 4. The complex displays three carbonyl stretching frequencies at 2002, 1886, and 1851 $\mathrm{cm^{-1}}$. The fourth band expected for a *cis*-$\mathrm{M(CO)_4L_2}$ complex is not resolved. The NMR spectra for **6** is diagnostic of its structure. The $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$-NMR spectrum displays a single resonance centered at δ -190.5, and restoration of proton coupling reveals a doublet pattern, $^{1}J_{\mathrm{PH}} = 278$ Hz.



(4)

This resonance is downfield of the resonance for the free ligand, **3**, δ -212.3, $^{1}J_{\mathrm{PH}} = 213$ Hz, and the increased $^{1}J_{\mathrm{PH}}$ value in **6** is consistent with increased s character in the P–H bond of the coordinated ligand. The $^{1}\mathrm{H}$-NMR spectrum of the free ligand **3** shows a single $\mathrm{SiMe_2}$ methyl environment δ 0.61, $^{3}J_{\mathrm{PH}} = 4.2$ Hz, one $^{i}\mathrm{Pr_2NB}$ methyl group environment δ 1.26, $^{3}J_{\mathrm{HH}} = 7.0$ Hz, and a P–H resonance δ 1.78, $^{1}J_{\mathrm{PH}} = 213$ Hz. However, the complex shows two $\mathrm{SiMe_2}$ and $^{i}\mathrm{Pr_2NB}$ methyl environments: δ 0.39 ($^{3}J_{\mathrm{HH}} = 3.2$ Hz), 0.47 ($^{3}J_{\mathrm{HH}} = 6.3$ Hz), 1.30 ($^{3}J_{\mathrm{HH}} = 6.9$ Hz, 1.31 ($^{3}J_{\mathrm{HH}} = 6.8$ Hz). This is consistent with bidentate coordination of the ligand with the inequivalence generated by the presence of *meso* and *rac* isomers of the chelated phosphane. The $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$-NMR data are also consistent with this conclusion, and together they support the bidentate structure proposed in Eq. 4. Attempts to obtain a data set for the X-ray structure determination of **6** have been frustrated thus far by an inability to obtain adequate single crystals.

4. Conclusion

The borylphosphane ligands **1**–**3** provide a new class of σ donor phosphanes that are shown to form monodentate and bidentate complexes on $\mathrm{M(CO)_5}$ and $\mathrm{M(CO)_4}$ fragments. The coordination chemistry provides a means to protect fragile primary and secondary borylphosphane ligands that are useful in ring and cage construction chemistry. That utility will be expanded upon in future reports from our group.

5. Supplementary material available

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 108008 for Compound **4** and 108009 for Compound **5′**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax: +44-1223-336-033; e-mail: deposite@ccdc.com.ac.uk or www: http://www.ccdc.com.ac.uk).

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