Organometallics 1992, 11, 98–103

product R_3SiEt by $CpRh(C_2H_4)(SiR_3)H$ which satisfies the principal observations. If this mechanism operates, we would expect the production of a new Rh(III) complex when $CpRh(C_2H_4)(SiEt_3)H$ catalyzes the hydrosilation of R'_3SiH ($R' \neq Et$) and C_2H_4. The rate of formation of such products would depend on the rate of the back-reaction connecting 1 to the cycle. Although such new Rh(III) complexes are observed, they could also originate from a simple silane exchange process based on the reductive elimination of the initial silane. The failure to detect significant exchange when the cross-silane is more reactive than the original silane is consistent with the failure to regenerate $CpRh(C_2H_4)(SiR_3)H$ in the cycle. It is understandable if the rate of reaction of 1 within the cycle exceeds the rate of the back-reaction external to the cycle. All the steps in the proposed cycle are consistent with the need for retention of the original configuration at silicon throughout the hydrosilation process.[24] Significantly, if $(CO)_3Co$ is replaced by CpRh(Et) in Wrighton's scheme for hydrosilation (Scheme III), then the cycle obtained is identical to that presented in Scheme VI.[7a] Since the ethyl group acts as a bystander, we predict that other sources of $CpRh(SiR_3)X$ (X = alkyl, silyl, etc.) should be active hydrosilation catalysts. Experimental tests of this prediction will be undertaken.

Conclusions

Scheme VI is supported by the following evidence: (i) the lack of isotopic exchange during hydrosilation of C_2D_4 with Et_3SiH, catalyzed by **1a**; (ii) the replacement of the $SiEt_3$ group of **1a** by $SiPr^{i}_3$, when C_2H_4 is hydrosilated by $HSiPr^{i}_3$ in the presence of **1a**; (iii) the accessibility of complexes formally in the Rh(V) oxidation state; (iv) the intramolecular hydrogen-exchange reactions of 1; (v) the fact that $CpRh(C_2H_4)(SiR_3)H$ is isolable makes it implausible that it is the key intermediate in the cycle; (vi) the stoichiometric reactions of 1, especially with Me_2SO, match the steps of the cycle.

It is likely that Scheme VI is only a description of the main pathway of reaction, since our observations require additional processes that account for the unsaturated products formed in the presence of excess alkene. Quantitative kinetic analysis of this system is under consideration at the present time.

In conclusion, the Chalk–Harrod hydrosilation cycle does not operate for $CpRh(C_2H_4)(SiR_3)H$. The mechanism illustrated in Scheme VI, in which the coordinated alkene behaves as a spectator ligand, is supported by numerous observations. This reaction cycle involves the generation of a Rh(V) intermediate and fails to re-form $CpRh(C_2H_4)(SiR_3)H$ directly.

Acknowledgment. We are grateful to the support give by the SERC, The Royal Society, the EC, British Gas, and Dow Corning. We appreciated helpful discussions with Prof. P. Maitlis.

Registry No. **1a**, 102744-67-2; **1b**, 137203-36-2; **2**, 12211-95-9; **3a**, 102744-68-3; **3b**, 137259-27-9; **5a**, 118869-81-1; $CpRh(SiEt_3)(C_2H_4)D$, 137203-35-1; Et_3SiH, 617-86-7; C_2H_4, 74-85-1; Et_3SiD, 1631-33-0; C_2D_4, 683-73-8; Et_4Si, 631-36-7; $Et_3SiCH_2CH_2SiEt_3$, 2295-15-0; Me_3SiEt, 3439-38-1; $CH_2{=}CHSiMe_3$, 754-05-2; $Me_2ClSiEt$, 6917-76-6; $CH_3CH_2CH_2SiEt_3$, 994-44-5; $CH_3CH{=}CHSiEt_3$, 3931-84-8; (*E*)-$CH_3CH{=}CHSiEt_3$, 83053-45-6; (*Z*)-$CH_3CH{=}CHSiEt_3$, 83053-46-7; $EtSiPr^{i}_3$, 56568-90-2; $CH_2{=}CHSiPr^{i}_3$, 121675-48-7; Pr^{i}_3SiH, 6485-79-6; $CH_2{=}CHCH_3$, 115-07-1.

---

[24] Sommer, L. H.; Lyons, J. E.; Fujimoto, H. *J. Am. Chem. Soc.* **1969**, *91*, 7051.

Synthesis and Spectroscopic and Structural Characterization of $PhB[P(Mes)BMes_2]_2$: A Boron–Phosphorus Analogue of the Pentadienyl Cation

Doris C. Pestana and Philip P. Power*

Department of Chemistry, University of California, Davis, California 95616

Received April 17, 1991

The synthesis and spectroscopic (^1H, ^{11}B, and ^{31}P NMR) and X-ray structural characterization of the bis(borylphosphino)arylborane $PhB[P(Mes)BMes_2]_2$ are described. Its structure is composed of an array of planar coordinated boron and phosphorus atoms with a mean B–P distance of 1.864 (15) Å. These features suggest significant delocalization of the phosphorus lone pairs throughout the B_3P_2 skeleton. The dynamic behavior of $PhB[P(Mes)BMes_2]_2$ in solution was examined by variable-temperature ^1H NMR (−99 to +152 °C). These studies indicated that the ΔG^{*} rotation for B–P π-bonds is about 17–18 kcal mol^{-1}. Crystal data with Cu Kα (λ = 1.54178 Å) at 130 K: a = 22.052 (7) Å, b = 15.662 (8) Å, c = 41.107 (7) Å, orthorhombic, space group $Pna2_1$ (33), Z = 8 (2 molecules per asymmetric unit), R = 0.105.

Introduction

Much of the impetus in the study of boron–nitrogen compounds[1] comes from their isoelectronic relationship to the corresponding carbon species. Thus, borazine[2] and aminoboranes[1] of the type $R_2BNR'_2$ (where R and R′ = alkyl, aryl, halogens, etc.) have been recognized for many years as the inorganic analogues of benzene and ethylene. The chemistry of the corresponding compounds with boron bonded to P, As, Sb, or Bi has just recently begun to attract attention.[3,4] Thus, the X-ray crystal structures of

---

[1] Niedenzu, K.; Dawson, J. W. *Boron-Nitrogen Compounds*; Springer-Verlag: Berlin, 1965.

[2] Stock, A.; Pohland, E. *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 2215.

[3] Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 449.

[4] Dias, H. V. R.; Petrie, M. A.; Shoner, S. C.; Power, P. P., *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1030.

0276-7333/92/2311-0098$03.00/0

monomeric phosphinoboranes of the type R$_2$BPR$'_2$, where R and R$'$ = alkyl or aryl, have been published only within the past 5 years.[5,6] Normally, such compounds tend to associate in a head to tail manner through the intermolecular donation of the phosphorus lone pair into the empty boron p orbital.[7,8] The recent work has shown that this can be avoided by using bulky substituents.[3,6] The synthesis and structure of a number of B–P analogues of the borazines have also been reported,[9,10] and a number of additional publications have detailed other B–P systems in which there is delocalization of the phosphorus lone pair on to boron.[3] Among these are analogues of the allyl system,[11,12] for example PhP(BMes$_2$)$_2$[11] and MesB(PPh$_2$)$_2$.[11] Dynamic ^{1}H NMR studies on the former compound have shown that there exist barriers to rotation around the B–P bonds of 21.3 kcal mol^{-1}.[13] In this paper these studies are extended to include the new compound PhB[P(Mes)BMes$_2$]$_2$, which features the five-atom BPBPB skeletal array and may be regarded as an analogue of the pentadienyl cation.

Experimental Section

All experiments were performed under N$_2$ with use of either modified Schlenk techniques or a Vacuum Atmosphere HE 43-2 drybox. Solvents were freshly distilled under N$_2$ from Na/K alloy-benzophenone ketyl and degassed three times immediately before use.

The reagents MesPH$_2$,[14] Mes$_2$BF,[15] PhBCl$_2$,[16] and Mes$_2$BP(Mes)Li(Et$_2$O)$_2$[17] were prepared according to literature methods. *n*-BuLi (1.6 M in hexanes) was obtained commercially and used as received. ^{11}B, ^{31}P, and ^{1}H NMR and variable-temperature ^{1}H NMR data were recorded on a QE-300 spectrometer operating at 96.46, 121.70, and 300.66 MHz, respectively. The ^{31}P NMR spectrum was referenced to external 85% H$_3$PO$_4$ and recorded with 2W proton decoupling. The ^{11}B spectrum was referenced to external BF$_3$·OEt$_2$. Variable-temperature studies were performed in C$_7$D$_8$, from −99 °C to +120 °C and in *o*-C$_8$D$_{10}$, from room temperature to 152 °C. Energy barriers were calculated by using an approximate formula as previously described.[18]

Mes$_2$BP(Mes)Li(Et$_2$O)$_2$ (1). Compound 1 was prepared according to a procedure described in general terms in the literature.[17,19] A detailed description is provided here. A 1-equiv portion of *n*-BuLi (5.60 mL, 1.6 M, 8.96 mmol) was added dropwise by use of a syringe to a cooled solution of MesPH$_2$ (1.34 g, 8.81 mmol) in an ice bath. The resulting turbid dark yellow solution was allowed to reach room temperature and stirred for 1 h. Mes$_2$BF (2.38 g, 8.87 mmol) dissolved in Et$_2$O (35 mL) was then added, and the reaction mixture, which was maintained in an ice bath during the addition, gradually became pale orange with concomitant precipitation of a white solid. The solution was then allowed to reach room temperature and stirred for 14 h. A second 1-equiv portion of *n*-BuLi (5.60 mL, 1.6 M, 8.96 mmol) was then added, and the mixture immediately became dark orange-red. Stirring was continued for a further 2 h at room temperature. The volume was then reduced under low pressure to ~40 mL, and the mixture was filtered through Celite, after which the volume was reduced further to ~15 mL. Cooling of the solution in a freezer at −20 °C for 48 h gave the product as yellow crystals. Yield: 2.50 g, 51.2%. Mp: 118–121 °C. ^{1}H NMR (C$_6$D$_6$): δ 0.88 (t, 12 H, CH$_3$ of Et$_2$O); 2.12 (s, 6 H, *o*-Me of PMes); 2.19 (s, 3 H, *p*-Me of PMes); 2.43 (s, 6 H, *p*-Me of BMes$_2$), 2.54, 2.68 (2 s, 6 H each, *o*-Me of BMes$_2$); 3.02 (q, 8 H, CH$_2$ of Et$_2$O); 6.74, 6.77, 6.83 (3 s, 2 H each, *m*-H). ^{11}B NMR (C$_6$D$_6$): δ 63.7. ^{31}P NMR (C$_6$D$_6$): δ 55.5.

Table I. Crystallographic Data for PhB[P(Mes)BMes$_2$]$_2$ (2)

formula	C$_{88.5}$H$_{125}$B$_3$P$_2$[a]
fw	1283.35
crystal system	orthorhombic
space group	$Pna2_1$ (No. 33)
a, Å	22.052 (7)
b, Å	15.662 (8)
c, Å	41.107 (7)
V, Å^3	14197 (9)
T, K	130
Z	8 (2 molecules per asymmetric unit)
d(calcd), g cm^{-3}	1.20
radiation (λ, Å)	Cu Kα (1.541 78)
μ(Cu Kα), cm^{-1}	7.66
range of transmsn fctrs	0.88, 0.68
no. data collected	10 406
no. data used in rfmt	6480 [$I > 2\sigma(I)$]
no. parameters refined	1046
R[b]	0.105
G[b]	0.0982
R_w[b]	0.140

[a] The asymmetric unit of 2 contains two molecules of the title compound (60 carbon atoms each) and nine molecules of pentane, which adds 22.5 carbons to the formula weight. [b] $R = \sum||F_o|-|F_c||/|F_o|$, $R_w = \sum||F_o|-|F_c||w^{1/2}/\sum|F_o|w^{1/2}$, $w = 1/\sigma^2(F_o) + GF_o^2$.

PhB[P(Mes)BMes$_2$]$_2$ (2). Freshly isolated Mes$_2$BP(Mes)Li(Et$_2$O)$_2$ (2.50 g, 4.51 mmol) was dissolved in a mixture of hexane (60 mL) and ether (20 mL) and was added dropwise, by use of a double-tipped needle, to a solution of PhBCl$_2$ (0.37 g, 2.33 mmol) in hexane (35 mL) with cooling in an ice bath. The reaction mixture became greenish yellow immediately and turned orange about halfway through the addition. The resulting bright orange solution was then allowed to reach room temperature and stirred for 14 h. All the volatile materials were pumped off, and the oily, bright orange residue was taken up in 60 mL of toluene. The solution was stirred for 0.5 h at room temperature. It was then filtered through Celite, and the volume was reduced to ~5 mL. Cooling overnight in a refrigerator at 4 °C resulted in the isolation of an orange powder, which was very soluble in hexane, pentane, or ether. Orange crystals, adequate for X-ray crystal structure determination, were obtained by freezing at liquid N$_2$ temperature a 3-mL pentane solution of the product, followed by slow thawing in a freezer at −20 °C for 1 week. Yield: 0.84 g, 42%. Mp: 275–278 °C, turned red at 235 °C. ^{1}H NMR (C$_6$D$_6$) at 19 °C: δ 1.81 (s, 6 H); 1.91 (s, 12 H); 1.99 (s, 6 H); 2.23 (s, 6 H); 2.26 (s, 6 H); 2.35 (s, 6 H); 2.67 (s, 6 H); 2.88 (s, 6 H); 5.96, 6.16, 6.45 (3 s, 2 H each, *m*-H); 6.49 (m, 5 H, *p*- and *m*-H of Ph and *m*-H); 6.55, 6.59 (2 s, 4 H, m-H); 7.51 (d, 2 H, *o*-H of Ph). ^{11}B NMR (C$_6$D$_6$, 20 °C): δ 53.1 and 63.6. ^{31}P NMR (C$_6$D$_6$): δ 20.6.

X-ray Data Collection and the Solution and Refinement of the Structure. X-ray data were collected with a Siemens R3 m/V diffractometer equipped with a graphite monochromator and a locally modified Enraf-Nonius LT apparatus. Calculations

---

(5) Arif, A. M.; Cowley, A. H.; Pakulski, M.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1986**, 889.

(6) Feng, X.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1986**, *25*, 4616.

(7) Wasson, J. R. *Gmelin Handbuch der Anorganischen Chemie, Ergranzungswerk zur 8. Aufl.*; Bd. 19, Borverbindungen, Teil 3: Springer: Berlin, 1975; p 93.

(8) Köster, R. *Methoden der Organischen Chemie, Organobor-Verbindungen II: VI. Organobor-Phosphor-und-Arsen-Verbindungen*; Band XIII/3b: Georg Thieme Verlag: Stuttgart, 1983; p 386.

(9) Dias, H. V. R.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1270.

(10) Dias, H. V. R.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 144.

(11) Bartlett, R. A.; Dias, H. V. R.; Power, P. P. *Inorg. Chem.* **1988**, *27*, 3919.

(12) Karsh, H. H.; Hanika, G.; Huber, K.; Mundl, K.; König, S.; Krüger, C.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1989**, 373.

(13) Pestana, D. C.; Power, P. P. *J. Am. Chem. Soc.*, in press.

(14) Oshikawa, T.; Yamashita, M. *Chem. Ind.* (*London*) **1985**, 126.

(15) We thank Professor A. Pelter for a high-yield synthesis of Mes$_2$BF when the published procedure did not work in our hands. The method of synthesis is identical to that described for (2,6-Me$_2$C$_6$H$_3$)BF in the following reference: Chen, H.; Bartlett, R. A.; Olmstead, M. M.; Shoner, S. C. *J. Am. Chem. Soc.* **1990**, *112*, 1048.

(16) Treichel, P. M.; Benedict, J.; Haines, R. G. *Inorg. Synth.* **1972**, *13*, 32.

(17) Bartlett, R. A.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 6817.

(18) Kost, D.; Carlson, E. H., Raban, M. *J. Chem. Soc., Chem. Commun.* 1971, 656.

(19) Bartlett, R. A.; Dias, H. V. R.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 1306.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for Selected Atoms of PhB[P(Mes)BMes$_2$]$_2$ (2)

	x	y	z	U(eq)[a]
P(1)	2931 (1)	6522 (2)	−2031[b]	49 (1)
P(2)	2177 (1)	7264 (2)	−2650 (1)	46 (1)
B(1)	2692 (6)	6457 (11)	−2467 (3)	53 (5)
B(2)	3631 (6)	6041 (8)	−1867 (3)	38 (4)
B(3)	1702 (6)	7097 (11)	−3022 (3)	50 (5)
C(6)	2497[b]	5693[b]	−2678[b]	49 (4)
C(7)	2447 (3)	7146 (5)	−1765 (2)	49 (4)
C(16)	2063 (3)	8258 (4)	−2429 (2)	49 (4)
C(25)	4120 (3)	5559 (5)	−2093 (2)	42 (4)
C(34)	3751 (3)	6195 (6)	−1476 (1)	48 (4)
C(43)	1269 (3)	7847 (4)	−3153 (2)	50 (4)
C(52)	1784 (3)	6199 (4)	−3213 (2)	45 (4)
P(3)	1133 (1)	4225 (2)	432 (1)	48 (1)
P(4)	1587 (1)	5958 (2)	73 (1)	47 (1)
B(4)	997 (6)	5354 (10)	296 (6)	46 (5)
B(5)	526 (6)	3436 (10)	493 (3)	49 (5)
B(6)	1627 (6)	7164 (9)	61 (3)	45 (4)
C(66)	352[b]	5766[b]	369[b]	43 (4)
C(67)	1929 (2)	3934 (5)	520 (2)	49 (4)
C(76)	2226 (3)	5327 (5)	−87 (2)	43 (4)
C(85)	721 (3)	2482 (4)	621 (2)	51 (4)
C(94)	−163 (2)	3682 (5)	422 (2)	45 (4)
C(103)	2187 (3)	7585 (5)	−142 (2)	38 (4)
C(112)	1114 (3)	7716 (5)	222 (2)	46 (4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Coordinates fixed during refinement as described in text.

Table III. Selected Bond Distances (Å) and Angles (deg) for PhB[P(Mes)BMes$_2$]$_2$ (2)

	Molecule 1		
P(1)–B(1)	1.869 (14)	B(1)–P(1)–B(2)	124.4 (6)
P(1)–B(2)	1.847 (13)	B(1)–P(1)–C(7)	116.2 (5)
P(1)–C(7)	1.812 (7)	B(2)–P(1)–C(7)	119.4 (5)
P(2)–B(1)	1.859 (16)	B(1)–P(2)–B(3)	125.2 (7)
P(2)–B(3)	1.874 (14)	B(1)–P(2)–C(16)	117.6 (5)
P(2)–C(16)	1.820 (8)	B(3)–P(2)–C(16)	116.8 (6)
B(1)–C(6)	1.583 (17)	P(1)–B(1)–P(2)	121.5 (8)
		P(1)–B(1)–C(6)	117.9 (9)
		P(2)–B(1)–C(6)	120.6 (9)
B(2)–C(25)	1.611 (14)	P(1)–B(2)–C(25)	122.6 (8)
B(2)–C(34)	1.646 (14)	P(1)–B(2)–C(34)	115.6 (8)
		C(25)–B(2)–C(34)	121.6 (9)
B(3)–C(43)	1.605 (17)	P(2)–B(3)–C(43)	120.1 (10)
B(3)–C(52)	1.620 (18)	P(2)–B(3)–C(52)	117.1 (9)
		C(43)–B(3)–C(52)	122.7 (9)
	Molecule 2		
P(3)–B(4)	1.879 (16)	B(4)–P(3)–B(5)	123.8 (6)
P(3)–B(5)	1.839 (15)	B(4)–P(3)–C(67)	116.2 (5)
P(3)–C(67)	1.847 (6)	B(5)–P(3)–C(67)	119.9 (5)
P(4)–B(4)	1.850 (4)	B(4)–P(4)–B(6)	123.8 (6)
P(4)–B(6)	1.891 (15)	B(4)–P(4)–C(76)	116.1 (5)
P(4)–C(76)	1.843 (7)	B(6)–P(4)–C(76)	119.4 (5)
B(4)–C(66)	1.590 (15)	P(3)–B(4)–P(4)	121.1 (7)
		P(3)–B(4)–C(66)	117.9 (8)
		P(4)–B(4)–C(66)	121.0 (10)
B(5)–C(85)	1.641 (17)	P(3)–B(5)–C(85)	117.7 (8)
B(5)–C(94)	1.596 (15)	P(3)–B(5)–C(94)	120.4 (9)
		C(85)–B(5)–C(94)	121.9 (10)
B(6)–C(103)	1.629 (15)	P(4)–B(6)–C(103)	117.0 (8)
B(6)–C(112)	1.570 (15)	P(4)–B(6)–C(112)	120.4 (8)
		C(103)–B(6)–C(112)	122.5 (10)

Table IV. Important Interplanar Angles (deg) in PhB[P(Mes)BMes$_2$]$_2$ (2)

	Molecule 1		
B(2) and P(1)	3.3	C(7) and C(16)	2.3
P(1) and B(1)	22.4	C(43) and C(52)	78.4
B(1) and P(2)	18.6	C(25) and C(34)	83.0
P(2) and B(3)	1.2		
	Molecule 2		
B(5) and P(3)	0.7	C(67) and C(76)	1.7
P(3) and B(4)	27.1	C(85) and C(94)	76.6
B(4) and P(4)	19.1	C(103) and C(112)	81.8
P(4) and B(6)	2.9		

were carried out on a Micro VAX 3200 computer using the SHELXTL PLUS program system. Neutral atom scattering factors and the correction for anomalous dispersion were from ref 20. Crystals of 2 were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. A suitable crystal was selected, attached to a glass fiber by silicon grease, and immediately placed in the low-temperature N_2 stream.[21] The structure was solved by direct methods in the noncentrosymmetric group $Pna2_1$ (33). Attempted refinement in the $Pnma$ (62) centrosymmetric group did not give convergence. Some details of the data collection and refinement are given in Table I. There are two crystallographically independent molecules of 2 in the asymmetric unit, as well as nine pentane molecules with various degrees of disorder. This disorder is mainly responsible for the higher than usual R index. Due to the large number of parameters to be refined, the phenyl and mesityl rings were fitted as regular hexagons with fixed C–C bond lengths equal to 1.395 Å. The nine pentane molecules were located in the difference map and refined with fixed positional parameters. Hydrogen atoms on the C(6) and C(66) phenyl rings and on the carbon atoms C(31)–C(33), C(40)–C(42), C(49)–C(51), C(58)–C(60), C(91)–C(93), C(100)–C(102), C(109)–C(111), and C(118)–C(120) were included at calculated positions using a riding model with C–H of 0.96 Å and $U_{iso}(H) = 0.08$. All non-hydrogen atoms, except the carbon atoms of the nine pentane molecules, were refined anisotropically. An absorption correction was applied by use of the program XABS.[22] The handedness of the structure could not be determined. Important atom coordinates and isotropic thermal parameters are given in Table II. Important bond distances and angles are listed in Tables III and IV.

Results and Discussion

Compound 2 is the first of its kind to be characterized by X-ray diffraction and by ^{11}B, ^{31}P, and variable-temperature ^1H NMR spectroscopy. The only precedent for a species similar to 2 involves the compound PhB[P(Ph)B(Cl)Ph]$_2$,[23] which was cited as a side product of the thermolysis of a mixture of $PhBCl_2$ and $PhPH_2$. Its formulation was based solely on cryoscopic molecular weight determination and an elemental analysis. In contrast, PhB[P(Mes)BMes$_2$]$_2$ (2) was prepared in a moderate yield, under milder conditions, by the straightforward salt elimination reaction between the boryl phosphide 1 and $PhBCl_2$, as shown by

$$\underset{1}{2Mes_2BP(Mes)Li(Et_2O)_2} + PhBCl_2 \xrightarrow[(5:1)]{hexane/Et_2O} \underset{2}{PhB[P(Mes)BMes_2]_2} + 2LiCl$$

The product was isolated as yellow crystals in moderate yield.

X-ray Crystal Structure. The structure of one of the crystallographically independent molecules present in the asymmetric unit is illustrated in Figure 1. The core atoms of the second molecule are presented in Figure 2. The boron and phosphorus atoms in both molecules exhibit essentially planar coordination, with angles that deviate by no more than 4.4° from the regular trigonal value of 120°. The deviations of the phosphorus atoms from the plane formed by the three atoms directly bonded to each

---

(20) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(21) This method is described in: *ACS Symp. Ser.* **1987**, *357*.

(22) Hope, H.; Moezzi, B. XABS, University of California, Davis. The program obtains an absorption tensor from $F_o - F_c$ differences. Moezzi, b. Ph.D. Dissertation, University of California, Davis, 1987.

(23) Tevebaugh, A. D. *Inorg. Chem.* **1964**, *3*, 302.

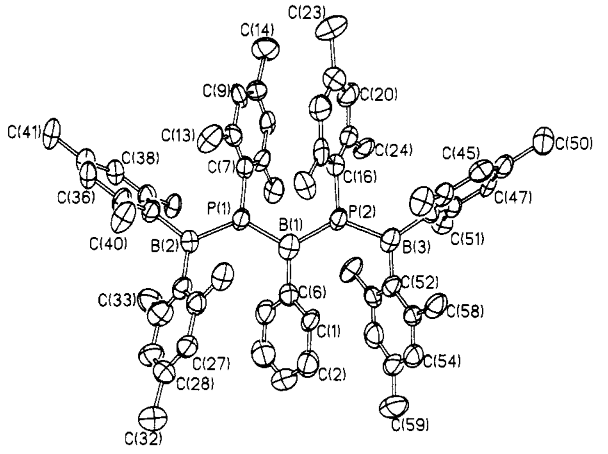


Figure 1. Thermal ellipsoid plot of one of the crystallographically independent molecules of 2. Hydrogen atoms are omitted for clarity.

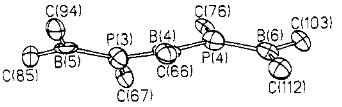


Figure 2. View of the core atoms of the other crystallographic independent molecule of 2.

of them are −0.03 Å for P(1), 0.06 Å for P(2), −0.02 Å for P(3), and −0.09 Å for P(4). The corresponding values for the bridging and terminal boron atoms do not exceed 0.03 Å. The B–P bond lengths vary from 1.839 (15) to 1.891 (15) Å. In each molecule the two terminal B–P distances are consistently different, e.g., the P(3)–B(5) and P(4)–B(6) distances are 1.839 (15) and 1.891 (15) Å, respectively. Such differences are also discernible, but less marked, in the P–B bonds of the central boron atoms (Table III). A pattern of short–long–short–long B–P bonds is thus suggested by the data. For the terminal boron centers the angles between adjacent boron and phosphorus planes are ∼3° (Table IV). Larger interplanar angles, ∼18–27°, are observed in the case of the central boron atoms. The angle between the plane containing B(1) and the plane of the C(6) phenyl ring is 42.8°; the corresponding angle between the B(4) plane and the C(60) phenyl ring is 40.0°. The B–C(phenyl) bond lengths average 1.587 (14) Å. The angles between the planes at the phosphorus atoms and the plane of their substituent mesityl rings average 64.4°. Other dihedral angles are listed in Table IV. The P–C bonds average 1.831 Å. The mean B–C(mesityl) bond distance is 1.615 (19) Å, and the average angle between the mesityl rings on the boron atoms and the boron planes is 61.1°.

The most conspicuous feature of the structure of 2 is the planar coordination of all boron and phosphorus centers and the short B–P bond lengths. The latter show some variability—from 1.839 (15) to 1.891 (15) Å—but the magnitude of the uncertainties warrant caution in the assignment of great significance to such variation. Nonetheless, the observation of differences in the terminal B–P bond lengths in both molecules is suggestive of a tendency of the B–P multiple bonds to become localized. Very small twist angles (maximum 3.3°) are observed between the planes of the terminal borons and the planes of the phosphorus atoms bonded to them, whereas much larger interplanar angles (up to 27.1°) are observed between the plane of the central boron and its substituent phosphorus centers. Similar structural features are also found in 1[17] and other, recently reported, monomeric phosphinoboranes.[3,6,13,19] The B–P bond lengths and twist angles in monomeric phosphinoboranes and related species are found to vary widely. The currently available data display a range of 1.810–1.927 Å for the B–P bond distances and twist angles of up to 23.2°. The B–P bonding in these compounds has been interpreted on the basis of sp^2 hybridization at the boron and phosphorus atoms and the existence of π-conjugation between the phosphorus lone pair and the empty boron p orbital. A similar interpretation may be applied to the B–P bonding in 2 which, clearly, has B–P bond distances and angles within the known ranges. The variable twist angles between the boron and phosphorus planes in 2 may be explained on the basis of different degrees of crowding at the various B and P centers within the molecule.

Table V. ^{31}P and ^{11}B NMR Data for 1, 2, and Related Compounds

compound	$\delta(^{31}P)$	$\delta(^{11}B)$	ref
$Mes_2BP(Mes)Li(Et_2O)_2$ (1)	55.5	63.7	this work
$PhB[P(Mes)BMes_2]_2$ (2)	20.6	53.1, 63.6	this work
$Mes_2BP(Mes)H$	−66.0		19
$[Mes_2B(Mes)P]_2$	−22.3	54.0	25
$(MesBPMes)_3$	40.4	49.6	9, 10
$(Mes_2B)_2PPh$	60.1	47.8	11
$Mes_2BP(Ph)H$	−41.5		19

The ^{11}B and ^{31}P spectra of 2 may be compared to the available data of some related compounds (Table V). The ^{11}B spectrum of 2 displays two signals, one (63.6 ppm) at essentially the same chemical shift as 1 and another at 53.1 ppm. Due to the similarity in structural features between the terminal B centers in 1[17] and 2, as well as the previously observed lack of sensitivity of the ^{11}B chemical shifts[13,19] to changes in substitution at the phosphorus center (e.g., $Mes_2BP(Ad)H$ and $Mes_2BP(Ad)Li(Et_2O)$ have essentially identical ^{11}B chemical shifts),[13] the signal at lower field (63.6 ppm) may be assigned to the terminal borons. The assignment of the higher field (53.1 ppm) signal to the central boron is consistent with the more shielded nature of this center as a result of substitution by two electropositive donor phosphorus atoms. The chemical shifts and broad nature ($\nu_{1/2}$ = 2411–4341 Hz) of these ^{11}B NMR signals are consistent with an asymmetric three-coordinate environment at the boron atoms.[24]

The ^{31}P NMR spectrum of 2 displays only one signal at δ = 20.6 which underlines the magnetic equivalence of the chemically identical phosphorus centers in 2. An estimate of the extent of the π-delocalization in 2 may be gauged from the comparison of its ^{31}P chemcial shift with those of $[Mes_2B(Mes)P]_2$,[25] $(MesBPMes)_3$,[9,10] and $(Mes_2B)_2PPh$.[11] These compounds feature planar three-coordinate phosphorus centers with environments similar to those observed in 2. $(MesBPMes)_3$ is considered to be a B–P analogue of borazine or benzene, whereas $[Mes_2B(Mes)P]_2$ and $(Mes_2B)_2PPh$ can be viewed as localized 1,3-butadiene and delocalized allyl cation analogues, respectively. The location of the ^{31}P signal of 2 between those of the latter compounds suggests that the phosphorus centers of 2 are less shielded than those of $[Mes_2B(Mes)P]_2$[25] but more so than the corresponding ones in $(MesBPMes)_3$[9,10] and $(Mes_2B)_2PPh$.[11] This is consistent with the view of 2 as the B–P analogue of a pentadienyl cation, which is expected to have more π-delocalization than a 1,3-butadiene but less than benzene or an allyl cation.

Variable-Temperature ^{1}H NMR. The ^{1}H NMR spectra of 2 in o-C_8D_{10} at selected temperatures above 18 °C are illustrated in Figure 3. The integrations of all the

---

(24) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*: Springer Verlag: Berlin, 1978.

(25) (a) Pestana, D. C.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 6887. (b) *Inorg. Chem.* **1991**, *30*, 528.

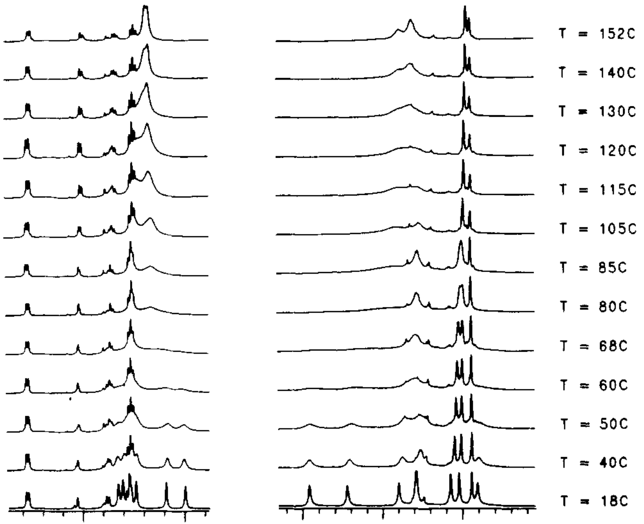


Figure 3. Stacked plot of the variable-temperature (18–152 °C) ^{1}H NMR spectra of 2 in o-C_8D_{10}.

signals in these spectra were referenced to the doublet signal at ~7.55 ppm, which corresponds to the o-hydrogens of the phenyl ring on the central boron. At 18 °C, the methyl region of the ^{1}H NMR spectrum of 2 displayed eight different peaks. The signals at 2.96, 2.72, 2.40, and 1.91 ppm were broader and lower in height than those at 2.07, 2.02, and 1.94 ppm, although they all possessed the same area integration (6 H). The remaining signal at 2.29 ppm had an intensity corresponding to 12 H, and its height was very much the same as those at 2.96, 2.72, 2.40, and 1.91 ppm. As the temperature was increased, the four broad signals, together with the one at 2.29 ppm, decreased steadily in height and broadened until all five coalesced into a wide peak centered at ~2.38 pm at 120 °C. The values for the energy barrier ($\Delta G^{\ddagger}$) of this dynamic process were calculated by using the separation of the signals at 2.96 and 2.72 ppm (18.6 kcal mol^{-1}), 2.40 and 2.29 ppm (18.8 kcal mol^{-1}), and 2.29 and 1.91 ppm (18.9 kcal mol^{-1}). The signals at 2.07 and 2.02 ppm coalesced at 85 °C; the corresponding energy barrier was calculated to be a very similar 18.6 kcal mol^{-1}. Further heating of the sample above the coalescence temperatures led to the increase in height and sharpness of the signal at 2.02 ppm in comparison to the one at 2.00 ppm, whereas the broad signal at 2.38 ppm split into two peaks of approximate intensity ratio 1:2, which were not completely separated by 152 °C. At this temperature, the combined intensities of these broad peaks were in a ratio of 2:1 with respect to the sum of the intensities of the peaks at 2.02 and 2.00 ppm. This ratio, together with the dynamic behavior described, suggest the following assignment for the methyl region at 18 °C. The signals at 2.96, 2.72, and 2.40 correspond to the o-Me groups of three of the mesityl substituents on the boron atoms, whereas the peaks at 2.29 (12 H) and 1.91 ppm correspond to the o-Me groups of the mesityl rings on the phosphorus and the remaining boron mesityl ring. The singlets at 2.07, 2.02, and 1.94 ppm correspond to the p-Me groups of the boron and phosphorus mesityls.

The phenyl region of the ^{1}H NMR spectrum of 2 at 18 °C displayed, in addition to the doublet at 7.55 ppm, five sharp singlets of equal area (2 H each) and a multiplet of 5 H centered at 6.55 ppm. As the temperature was increased, these singlets broadened and decreased in height and coalesced at 68 °C under a triplet centered at 6.55 ppm. The presence of five distinct signals, and possibly a sixth one, under the multiplet at 6.55 ppm, underlines the magnetic inequivalence of the boron and phosphorus mesityl rings. Unfortunately, the assignment of these m-H peaks to either boron- or phosphorus-bonded mesityl rings is complicated by the apparent coalescence of all six at the same temperature. The best agreement with the energy barriers calculated by using the variable-temperature ^{1}H NMR data of the methyl region was found by considering the singlets at 6.65 and 6.60 ppm to belong to the same $BMes_2$ moiety. This yielded a $\Delta G^{\ddagger}$ rotation of 17.8 kcal mol^{-1}. Similar treatment of the singlets at 6.53 and 6.47 ppm resulted in an energy barrier equal to 17.5 kcal mol^{-1}. Thus, the remaining singlets at 6.18 and 5.99 ppm may be assigned to the m-H on the mesityl groups bonded to the phosphorus atoms; the corresponding energy barrier is slightly lower (16.8 kcal mol^{-1}). Further heating of the sample above 68 °C resulted in the gradual separation of the triplet centered at 6.55 ppm from the m-H of the mesityl groups. The ^{1}H NMR spectrum of 2 at 152 °C displayed the mesityl m-H as a broad doublet upfield from the triplet of the p- and m-H on the phenyl ring bonded to the central boron. The assignments obtained by using o-C_8D_{10} as the solvent were further confirmed by performing the variable-temperature experiment in deuterated toluene (C_7D_8).

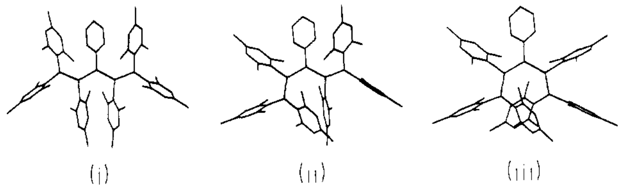


Figure 4. Schematic drawings of three possible configurations of 2 in solution.

The dynamic ^{1}H NMR data may most easily be interpreted by assuming that 2 exists in solution in the conformation shown in Figure 4 (ii). It should, however, be borne in mind that several dynamic processes are possible for molecule 2 in solution. The major ones involve the rotation around the terminal and central B–P bonds and rotation around the P–C and B–C bonds. Previous data[13] on related compounds have shown that rotational barriers around B–P bonds are in the range 12–22 kcal mol^{-1}, whereas rotational barriers around P–C[26] or B–C[27] bonds are generally less than 10 kcal mol^{-1} and display coalescence temperatures below 0 °C. Thus, it seems safe to assume that any dynamic processes occurring in 2 above room temperature arise from restricted rotation around the two types of B–P bonds. Thus, the observation of four different resonances for the o-Me groups of the boron mesityls at ambient temperature strongly suggests that conformation ii depicted in Figure 4 exists in solution at room temperature. The four different o-Me peaks also imply that rotation is restricted around the outer (or terminal) B–P bonds as well as the inner B–P bonds at this temperature. The assignments of the four signals at lower field to the o-Me groups of $BMes_2$ were based on comparisons between the ^{1}H NMR spectra of 1, 2, and other monomeric phosphinoboranes,[13] where the o-Me groups of the boron substituents were always found to be located at $\delta > 2.20$ ppm. This implies that the signals at 2.29 and 1.91 ppm probably correspond to the o-Me groups of the mesityl substituents on phosphorus. The changes in the spectrum of 2 at lower temperature are due only to the variation of chemical shift with temperature and not to

---

(26) Goldwhite, H.; Power, P. P. *Org. Magn. Reson.* **1978**, 499.

(27) (a) Blount, J. F.; Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 7019. (b) Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 7029. (c) Braun, N. M. D.; Davidson, F.; McMullen, R.; Wilson, J. W. *Organomet. Chem.* **1980**, *193*, 271.

a dynamic process. The fact that the signals at 6.12 and 5.93 ppm (*m*-H of PMes) remained separate at $T < 0$ °C further confirms that 2 exists in solution in conformation ii of Figure 4. It follows that the collapse of the spectrum to singlets that indicate just one type of boron mesityl and one type of phosphorus mesityl, at ca. 120 °C, implies that the rapid rotation around both types of B–P bond is occurring at this temperature. In effect, the variable-temperature studies do not distinguish between the rotations around the two types of B–P bonds, since this would involve the detection of rotamers i and iii of Figure 4 in the variable-temperature experiments. The observation of only three *o*-Me group resonances, one for the phosphorus mesityls and two attributable to the mesityl on boron, does not occur. Quite possibly, the two barriers are very close in energy, and this is consistent with the similar average B–P bond lengths for the inner and outer B–P bonds. The average energy value for the barriers (near 18 kcal mol^{-1}) is entirely consistent with the numbers measured recently in other B–P molecules.[13] The magnitude of this barrier demonstrates that noncyclic extended B–P arrays may exhibit extensive and moderately strong π-electron delocalization.

Acknowledgment. We thank the National Science Foundation for financial support.

Registry No. 1, 112059-41-3; 2, 136805-17-9; $2\cdot{}^{9}/_{2}$pentane, 136805-18-0; MesPH$_2$, 1732-66-7; Mes$_2$BF, 436-59-9; PhBCl$_2$, 873-51-8; Mes$_2$BPHMes·Li, 130417-23-1.

Supplementary Material Available: Description of the variable-temperature ^{1}H NMR spectra of 2, full tables of data collection parameters, atomic coordinates and isotropic displacement coordinates for non-hydrogen atoms, bond distances and angles, hydrogen coordinates, anisotropic thermal parameters, hydrogen atom coordinates and isotropic displacement coordinates, and ^{1}H NMR data assignments, and a figure of the variable-temperature ^{1}H NMR spectrum of 2 in C$_7$D$_8$ (21 pages). Ordering information is given on any current masthead page.

Carbon–Sulfur Bond Cleavage with a Loss of Stereochemistry in the Ring Opening of *trans*-2,4-Diphenylthietane by Os$_3$(CO)$_{10}$(NCMe)$_2$

Richard D. Adams* and Michael P. Pompeo

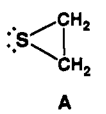
Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

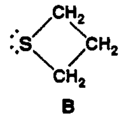
Received June 25, 1991

The reaction of Os$_3$(CO)$_{10}$(NCMe)$_2$ with *trans*-2,4-diphenylthietane (2,4-DPT) at 25 °C resulted in the formation of two isomers, *cis*- and *trans*-Os$_3$(CO)$_{10}$[μ-SC(H)PhCH$_2$C(H)Ph] (1), in a combined yield of 76%. The cis product was characterized by single-crystal X-ray diffraction analysis and was found to contain a thiametalladiphenylcyclopentane ring formed by the opening of the thietane ring. The cis and trans isomers differ in the orientation of their phenyl substituents. The isomers are formed in approximately equal amounts in the early stages of the reaction, but the trans isomer subsequently slowly isomerizes to the cis isomer. The observed loss in stereochemistry at the carbon center is attributed to a stepwise ring-opening mechanism. When compound 1 was heated to 97 °C under a CO atmosphere, five compounds were formed: Os$_3$(CO)$_{10}$[μ-SC(H)PhC(H)=C(H)Ph[(μ-H) (2) (22%), Os$_2$(CO)$_7$[μ-SC(H)(C$_6$H$_4$)CH$_2$CH$_2$Ph] (3) (11%), Os$_3$(CO)$_{11}$[μ-SC(H)PhCH$_2$C(H)Ph] (4) (39%), H$_2$Os$_6$(CO)$_{17}$(μ_3-S)(μ_4-S) (5) (a trace amount), and Os$_3$(CO)$_{12}$. Compounds 3 and 5 and the known compound Os$_3$(CO)$_9$(μ_3-CO)(μ_3-S) (6) were obtained in better yields by heating 2 to 125 °C in octane solvent. Compounds 2–4 were characterized by IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses. Compound 2 is an isomer of 1 and contains a diphenylpropenethiolate and hydride ligand formed by a "β-elimination" transformation of the ring system in 1. The mechanism of this transformation was not established. Compound 3 contains only two metal atoms and an ortho-metalated phenyl ring. Compound 4 is a CO adduct of 1 formed by the cleavage of the sulfur-bridged metal–metal bond. Crystallographic data are as follows. *cis*-1: space group $P2_1/c$, $a = 8.674$ (2) Å, $b = 35.09$ (1) Å, $c = 9.449$ (2) Å, $\beta = 106.41$ (1)°, $Z = 4$, 2053 reflections, $R = 0.033$. 2: space group $C2/c$, $a = 13.845$ (2) Å, $b = 14.545$ (4) Å, $c = 28.907$ (6) Å, $\beta = 98.88$ (1)°, $Z = 8$, 2519 reflections, $R = 0.027$. 3: space group $P2_1/c$, $a = 8.337$ (1) Å, $b = 17.311$ (4) Å, $c = 16.409$ (3) Å, $\beta = 100.82$ (1)°, $Z = 4$, 2299 reflections, $R = 0.036$. 4: space group $P\bar{1}$, $a = 14.319$ (2) Å, $b = 17.794$ (5) Å, $c = 12.257$ (4) Å, $\alpha = 106.69$ (2)°, $\beta = 90.74$ (2)°, $\gamma = 82.56$ (2)°, $Z = 4$, 4020 reflections, $R = 0.041$.

Introduction

The ring-opening cleavage of carbon–sulfur bonds in sulfur-containing heterocycles is of great interest because it is believed to be a key step in the purification of fossil fuels by the process of hydrodesulfurization.[1] Strained-ring thioethers, such as thiirane A and thietane B, have


A


B

attracted attention since the release of ring strain in these molecules makes their carbon–sulfur bond cleavage processes more facile. Thiiranes and thietanes are known to undergo facile desulfurization on some metal surfaces.[1b,2]

---

(1) (a) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387. (b) Friend, C. M.; Roberts, J. T. *Acc. Chem. Res.* **1988**, *21*, 394. (c) Markel, E. J.; Schrader, G. L.; Sauer, N. N.; Angelici, R. J. *J. Catal.* **1989**, *116*, 11. (d) Prins, R.; De Beer, V. H. H.; Somorjai, G. A. *Catal. Rev. Sci. Eng.* **1989**, *31*, 1.

0276-7333/92/2311-0103$03.00/0