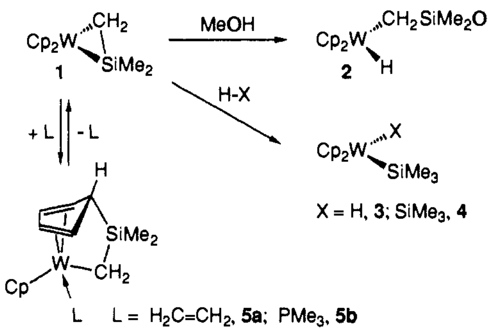
Scheme I



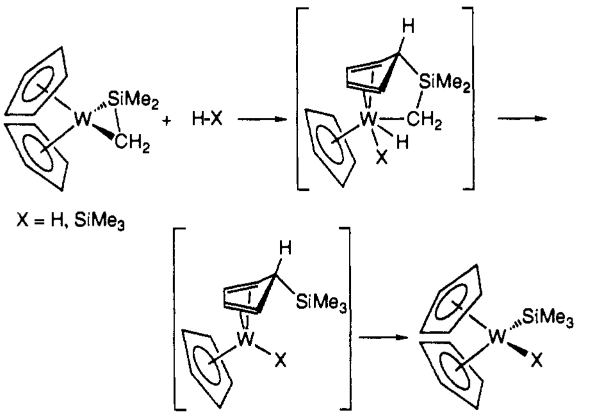
presumably be attributed to partial Si–C double bond character. The silene Si–C distance in this tungsten complex is very similar to values found in silene complexes of ruthenium (1.78 (2) Å)[2a] and iridium (1.810 (6) Å),[2b] despite the different coordination environments at the metals and substituents on silicon in the three compounds.

Preliminary studies indicate that **1** is highly reactive toward a variety of reagents under mild conditions (Scheme I). Methanolysis of **1** in benzene results in cleavage of the W–Si bond to produce $Cp_2W(H)(CH_2SiMe_2OMe)$ (**2**).[14] In contrast, **1** reacts with nonpolar reagents such as hydrogen and trimethylsilane at 25 °C to yield quantitatively $Cp_2W(H)(SiMe_3)$ (**3**)[15] and $Cp_2W(SiMe_3)_2$ (**4**),[16] the products of W–C bond cleavage.

Treatment of **1**, an $18e^-$, coordinatively saturated complex, with donor ligands such as C_2H_4 and PMe_3 at 25 °C results in the formation of η^4:η^1-$C_5H_5SiMe_2CH_2$ complexes in which the donor ligand occupies a coordination site on tungsten generated by migration of the silene silicon to the Cp ring (**5a**,**b**; L = C_2H_4, PMe_3). Surprisingly, this transformation is completely reversible. An equilibrium mixture of **5a** and **1** (ca. 4:1) is formed in benzene solution under 4 atm of ethylene, and removal of the ethylene atmosphere results in quantitative conversion back to **1**. Compound **5a** has been characterized by ^1H, ^{13}C, and 2-D (COSY) NMR.[17] Related migration of silicon ligands to Cp rings has been observed in several metal silyl complexes, generally following ring deprotonation.[18] The reverse migration of alkyl groups from endo-substituted η^4-C_5H_5R complexes has also been observed.[19] Compound **5b** is less labile than **5a**, although it also reverts to **1** in the absence of PMe_3 at 65 °C in benzene solution. Compound **5b** has been isolated in 90% yield and fully characterized.[20] The structure of **5b** has been conclusively established by a single-crystal X-ray diffraction study, the results of which will be reported in a future publication.[21]

Although reaction of **1** with H_2 or Me_3SiH could proceed via concerted addition across the W–C bond[22] or through a $16e^-$ η^3-Cp intermediate,[23] the formation of **5a**,**b** suggests an interesting alternative in which H–X oxidative addition (X = H, $SiMe_3$) occurs at the $16e^-$ center in an η^4-Cp intermediate generated by silene to ring migration (Scheme II). Reductive elimination of the C–H bond would yield an η^4-*endo*-$C_5H_5SiMe_3$ complex, and silyl-group migration back to tungsten would then yield the observed products.

Scheme II



Acknowledgment. Financial support of this work by the National Science Foundation (Grant No. CHE-8808161) is gratefully acknowledged. D.H.B. also thanks the University of Pennsylvania Natural Science Association for a Young Faculty Award.

Supplementary Material Available: Description of synthetic procedures and spectroscopic data for all new compounds, details of X-ray data collection and refinement for **1**, and tables of positional parameters, anisotropic thermal parameters, and intramolecular distances and angles for **1** (9 pages); listing of final structure factor amplitudes for **1** (7 pages). Ordering information is given on any current masthead page.

---

(12) (a) Bazant, V.; Chvalovsky, V.; Rathousky, J. In *Organosilicon Compounds*; Academic Press: New York, 1965; p 179. (b) Gordon, A. J.; Ford, R. A. In *The Chemist's Companion*; Wiley: New York, 1972; p 107 and references therein.

(13) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1.

(14) $Cp_2W(H)(CH_2SiMe_2OMe)$ (**2**): ^1H NMR δ 4.17 (Cp), 3.42 (OMe), 0.19 ($SiMe_2$), −0.74 (CH_2), −11.33 (W–H, J_{W-H} = 72 Hz); $^{13}C\{^1H\}$ NMR δ 78.80 (Cp), 49.76 (OMe), 0.20 ($SiMe_2$), −42.15 (CH_2, J_{W-C} = 58 Hz).

(15) Jiang, Q.; Koloski, T. S.; Berry, D. H., manuscript in preparation.

(16) $Cp_2W(SiMe_3)_2$ (**4**): ^1H NMR δ 3.87 (Cp), 0.40 ($SiMe_3$). Anal. Calcd for $C_{16}H_{28}Si_2W$: C, 41.74; H, 6.13. Found: C, 41.87; H, 5.95.

(17) Spectroscopic data are included in the supplementary material.

(18) See, for example: (a) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Vinceti, S. *Organometallics* **1986**, *5*, 1056. (b) Berryhill, S. R.; Clevenger, G. L.; Burdurlui, P. Y. *Organometallics* **1985**, *4*, 1509. (c) Crocco, G. L.; Young, C. S.; Lee, K. E.; Gladysz, J. A. *Organometallics* **1988**, *7*, 2158. (d) Schubert, U.; Schenkel, A. *Chem. Ber.* **1988**, *121*, 939.

(19) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324.

(20) (η^4:η^1-$C_5H_5SiMe_2CH_2$)W(Cp)(PMe_3) (**5b**): ^1H NMR δ 5.43 (m, 1 H, C_5H_5Si), 4.74 (m, 1 H, C_5H_5Si), 3.95 (Cp, d, J_{P-H} = 3.1 Hz), 3.89 (m, 1 H, C_5H_5Si), 2.22 (m, 1 H, C_5H_5Si), 1.06 (m, 1 H, C_5H_5Si), 0.86 (d, J_{P-H} = 7.9 Hz, 9 H, PMe_3), 0.55 (dd, J_{P-H} = 4.4 Hz, J_{H-H} = 11.6 Hz, 1 H, $SiCH_2$), 0.47 (s, 3 H, SiMe), 0.36 (s, 3 H, SiMe), 0.10 (t, J_{P-H} = J_{H-H} = 11.6 Hz, 1 H, $SiCH_2$); ^{29}Si NMR (DEPT) δ 27.91 (d, J_{Si-P} = 4.0 Hz). Anal. Calcd for $C_{16}H_{27}PSiW$: C, 41.57; H, 5.89. Found: C, 40.74; H, 5.74.

(21) Koloski, T. S.; Carroll, P. J.; Berry, D. H., manuscript in preparation.

(22) See, for example: (a) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51–56. (b) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425–437. (c) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 204–219. (d) Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043.

(23) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

Synthesis and Structure of an *in*-Phosphaphane: Enforced Interaction of a Phosphine and an Aromatic Ring

Robert A. Pascal, Jr.,* Anthony P. West, Jr., and
Donna Van Engen

Department of Chemistry, Princeton University
Princeton, New Jersey 08544

Received May 10, 1990

A major theme of cyclophane chemistry is the study of functional-group interactions resulting from enforced mutual proximity. Lone-pair electrons are frequently brought into contact with benzene rings in the heterophanes,[1] and the pyridinophane **1** is perhaps the most extreme example of this sort.[2] Its crystal structure shows the pyridine to be perpendicular to the benzene ring,[2b] and the basicity of the pyridine is substantially reduced;[2c]

---

(1) Paudler, W. W.; Bezoari, M. D. *Synthesis and Properties of Heterophanes.* In *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic: New York, 1983; Vol. 2, pp 359–441 and references cited therein.

(2) (a) Boekelheide, V.; Galuszko, K.; Szeto, K. S. *J. Am. Chem. Soc.* **1974**, *96*, 1578–1581. (b) Weaver, L. H.; Matthews, B. W. *J. Am. Chem. Soc.* **1974**, *96*, 1581–1584. (c) Reingold, I. D.; Schmidt, W.; Boekelheide, V. *J. Am. Chem. Soc.* **1979**, *101*, 2121–2128.

0002-7863/90/1512-6406$02.50/0 © 1990 American Chemical Society

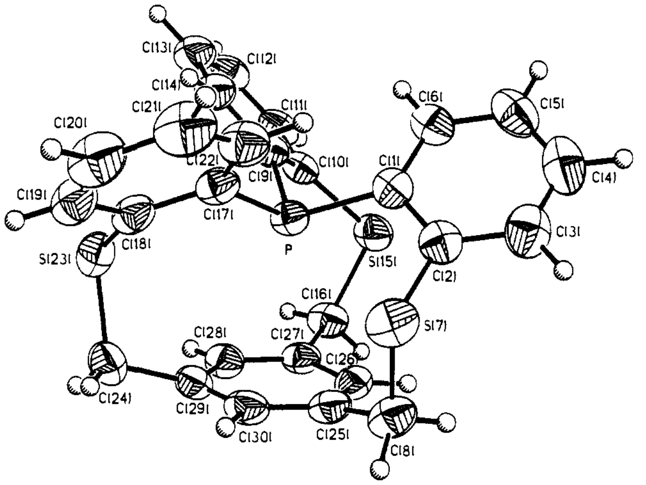
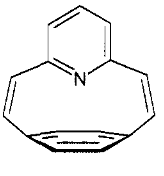
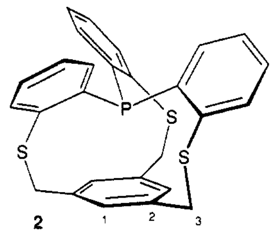


Figure 1. X-ray structure of compound **2**.

however, even in this particularly favorable case, unambiguous evidence of an electronic interaction between the nitrogen lone pair and the benzene ring is absent.[3] We have begun to examine the properties of cyclophanes containing second-row heteroatoms poised above aromatic rings, and we now report the synthesis and crystallographic characterization of cyclophane **2** and the spectroscopic and chemical consequences of the enforced interaction of a phosphine and a benzene ring.



1



2

Compound **2** was prepared in 12% yield by addition of KOH to a refluxing solution of tris(2-mercaptophenyl)phosphine[4] and 1,3,5-tris(bromomethyl)benzene[5] (2.8 mM each) in 2:1 benzene–ethanol. The product **2** was purified by silica gel column chromatography (2:1 hexane–benzene), and it crystallized readily from chloroform and methanol.[6] An X-ray crystallographic analysis[7] yielded the structure illustrated in Figure 1. The phosphine is strongly pyramidalized toward the basal aromatic ring, which is nearly planar. The average C–P–C bond angle (104.9°) in **2** is only slightly larger than that observed in triphenylphosphine (103.0°[8]), and the distance from the phosphorus to the ring center is 2.90 Å.

Interestingly, the proton-decoupled ^{13}C NMR spectrum of **2** shows spin–spin coupling between the phosphorus and *all* of the aromatic carbons. In particular, the C-1 and C-2 resonances are doublets with J_{CP}'s of 7.5 and 3.5 Hz, respectively,[9] so the coupling to the basal ring is substantial. This is unlikely to result from normal through-bond interactions (six and five bonds) for the reason that no coupling is observed between the phosphorus and the bridging methylene carbons (C-3). The ^{31}P NMR spectrum of compound **2** shows a single resonance at δ 5.0,[10] quite a bit downfield from the δ −26.7 resonance (lit.[4] δ −26.4) of the starting tris(2-mercaptophenyl)phosphine. This shift, which is in the opposite direction from that which would result from simple ring current effects, suggests a more phosphonium-like character for the phosphorus of **2**. In addition to its unusual spectroscopic characteristics, the phosphorus of **2** is remarkably unreactive. Heating compound **2** for 24 h in refluxing 2:1 acetic acid and 30% hydrogen peroxide yields only the corresponding trisulfone;[11] the phosphorus is not attacked![12]

Is there a special interaction between the phosphorus and the basal ring? Obviously, yes! The observed strong ^{31}P–^{13}C spin–spin coupling can only result from mixing of orbitals on the phosphorus and the benzene ring. Such "through-space" coupling appears to be unprecedented for phosphorus, but well documented for fluorines in close contact,[13] and in a recent and particularly relevant example, spin–spin coupling between remote fluorines was found to be enhanced by nonbonded contacts to an intervening aromatic ring.[14] However, there is no compelling evidence of an attractive interaction (i.e., a bond) between the phosphorus and the aromatic ring. The crystallographically observed phosphorus-to-ring distance is only 0.2 Å less than the 3.1-Å gap calculated for **2** by both MMPI[15] (which treats the interaction as purely repulsive) and MNDO,[16] and it is much longer than the corresponding distance in typical η^6-arene metal complexes. Furthermore, the low reactivity of the phosphorus may reasonably be attributed to steric encumbrance and a preference for an *in* geometry due to bond-angle constraints. It remains to be seen, however, whether the phosphorus imparts any special reactivity to the basal aromatic ring.

Acknowledgment. This work was supported in part by National Science Foundation Grant CHE-88121390.

Supplementary Material Available: Single-crystal structure report for $C_{27}H_{21}PS_3$ including experimental details, a labeled drawing of the final crystallographic model, a unit cell packing diagram, and tables of atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates and isotropic thermal parameters (10 pages). Ordering information is given on any current masthead page.

---

(3) It must be noted that the photoelectron spectrum of a related doubly capped pyridinophane exhibited a very low first ionization potential, but the authors declined to speculate about its origin.[2c]

(4) Block, E.; Ofori-Okai, G.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 2327–2329.

(5) Vogtle, F.; Zuber, M.; Lichtenthaler, R. G. *Chem. Ber.* **1973**, *106*, 717–718.

(6) For **2**: mp 315–320 °C dec; ^1H NMR (270 MHz, $CDCl_3$) δ 3.78 (d, J = 13 Hz, 3 H), 3.84 (d, J = 13 Hz, 3 H), 6.81 (d, J = 8 Hz, 3 H), 6.84 (s, 3 H), 7.20 (t, J = 8 Hz, 3 H), 7.29 (t, J = 8 Hz, 3 H, collapses to doublet upon irradiation at δ 7.71), 7.71 (dd, J = 8 Hz, J_{PH} = 4 Hz, 3 H); $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$) δ 44.5 (s), 129.0 (d, J_{PC} = 1 Hz), 129.6 (d, J_{PC} = 1.5 Hz), 130.0 (d, J_{PC} = 7.5 Hz), 134.7 (d, J_{PC} = 2 Hz), 138.6 (d, J_{PC} = 40 Hz), 139.5 (d, J_{PC} = 4.5 Hz), 144.66 (d, J_{PC} = 3.5 Hz), 144.69 (d, J_{PC} = 22 Hz); MS, m/z 472 (M^+, 100), 439 (M − SH, 33), 406 (M − 2SH, 15), 323 (35), 215 (42), 162 (43), 131 (79); exact mass 472.0556, calcd for $C_{27}H_{21}PS_3$ 472.0543.

(7) Crystal data: $C_{27}H_{21}PS_3$; monoclinic, space group $P2_1/c$; $a = 16.635$ (2) Å, $b = 9.2834$ (14) Å, $c = 16.593$ (2) Å, $\beta = 118.308$ (8)°, $V = 2256.1$ (4) Å^3, $Z = 4$, $D_{calcd} = 1.39$ g/cm^3. A single crystal measuring 0.13 × 0.15 × 0.48 mm was used for intensity measurements, which were made with $3° \leq 2\theta \leq 114°$ by using graphite-monochromated Cu Kα radiation (λ = 1.541 78 Å) at room temperature on a Nicolet R3m diffractometer. A total of 3401 unique reflections were measured, of which 3041 were considered to be observed $[|F_0| > 3\sigma(F_0)]$. The structure was solved by direct methods using the SHELXTL software. Refinement converged at $R = 0.033$, $R_w = 0.037$. Full details are given in the supplementary material.

(8) Daly, J. J. *J. Chem. Soc.* **1964**, 3799–3810.

(9) The methine carbon resonances were unambiguously assigned by means of a ^1H–^{13}C heteroscalar correlated 2D NMR experiment, and the basal-ring quaternary carbon (C-2) was identified by selective irradiation of the adjacent methylene (C-3) proton resonance in the proton-coupled ^{13}C NMR spectrum.

(10) Chemical shifts were referenced to an external standard of $(MeO)_3P$ at δ 140.

(11) Trisulfone of **2**: mp >350 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 4.66 (d, J = 14 Hz, 3 H), 4.89 (d, J = 14 Hz, 3 H), 6.91 (d, J = 8 Hz, 3 H), 7.50 (t, J = 8 Hz, 3 H), 7.51 (s, 3 H), 7.57 (t, J = 8 Hz, 3 H), 8.07 (dd, J = 8 Hz, J_{PH} = 4 Hz, 3 H); MS, m/z 568 (M^+, 33), 440 (M − $2SO_2$, 48), 439 (M − $2SO_2$ − H, 58), 376 (M − $3SO_2$, 100); exact mass 568.0224, calcd for $C_{27}H_{21}O_6PS_3$ 568.0238. Due to the trisulfone's insolubility, its ^{13}C NMR spectrum was not recorded.

(12) This stands in contrast to the behavior of [2.2](2,6)pyridinoparacyclophane (an analogue of **1** with saturated bridges), which is converted to the *N*-oxide upon treatment with peracid.[2a]

(13) See: Mallory, F. B.; Mallory, C. W. *J. Am. Chem. Soc.* **1985**, *107*, 4816–4819 and references cited therein.

(14) Mallory, F. B.; Mallory, C. W.; Baker, M. B. *J. Am. Chem. Soc.* **1990**, *112*, 2577–2581.

(15) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893–3907. Some ad hoc parameters were included for phosphorus and sulfur.

(16) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4907, 4907–4917.