Electrophilic Additions to Diphosphenes (RP═PR)

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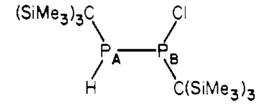
Received March 11, 1983

The deployment of ligands with large steric bulk has permitted the recent isolation of compounds with Si═Si,[1] Ge═Ge,[2] Sn═Sn,[3] and P═P[4] double bonds. However, despite the considerable progress made in the synthesis of these novel species, relatively little is known about their reactivities.[5] We report (i) that diphosphenes undergo facile electrophilic attack, (ii) differences in the reactivities of alkyl- and aryl-substituted diphosphenes $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (**1**) and (2,4,6-(*t*-Bu)$_3$C$_6$H$_2$)P═P-(2,4,6-(*t*-Bu)$_3$C$_6$H$_2$) (**2**), and (iii) an X-ray crystal structure determination of **1**.

Treatment of a solution of **1** in Et$_2$O at −20 °C with an equimolar quantity of dry, gaseous HCl led to fading of the yellow-orange color and the formation of the white solid $[(SiMe_3)_3CP(H)P(Cl)C(SiMe_3)_3]$ (**3**). The high-resolution mass spectrum (HRMS) for **3** showed the following (M$^+$): calcd 560.2081, found 560.2095. The 32.38-MHz $^{31}P\{^1H\}$ NMR spectrum of **3** exhibited two AX patterns of unequal intensity. For the more intense spectrum, (**3A**): δ_{P_A} −36.7 (d, $^1J_{PP}$ = 224.7 Hz), δ_{P_B} 173.6 (d, $^1J_{PP}$ = 224.7 Hz). For the less intense spectrum, (**3B**): δ_{P_A} −29.4 (d, $^1J_{PP}$ = 380.8 Hz), δ_{P_B} 154.1 (d, $^1J_{PP}$ = 380.8 Hz). The following ^{1}H couplings were obtained from the ^{1}H-coupled ^{31}P spectrum, **3A** $^1J_{P_AH}$ = 201.6 Hz, $^2J_{P_BH}$ = 26.7 Hz; **3B**, $^1J_{P_AH}$ = 213.9 Hz, $^2J_{P_BH}$ = 25.3 Hz. Treatment of **1** with an excess of gaseous HCl in Et$_2$O resulted in cleavage of the phosphorus–phosphorus bond and formation of $[(Me_3Si)_3CP(H)Cl]$ (**4**). The HRMS for **4** showed the following (M$^+$): calcd 298.0924, found 298.0933. ^{31}P NMR δ 70.5 (d, $^1J_{PH}$ = 160.6 Hz). It was not possible to isolate a product analogous to **3** when **2** was treated with an equimolar quantity of HCl at −78 °C. Instead, complete P═P bond cleavage was observed resulting in [(2,4,6-(*t*-Bu)$_3$C$_6$H$_2$)P(H)Cl] (**5**). The HRMS for the M − 1 peak of **5** showed the following: calcd 311.1695, found 311.1691. ^{31}P NMR δ 26.4 (d, $^1J_{PH}$ = 215.0 Hz). Phosphines of the type RP(H)(halogen) are remarkable because they are normally unstable.[6]



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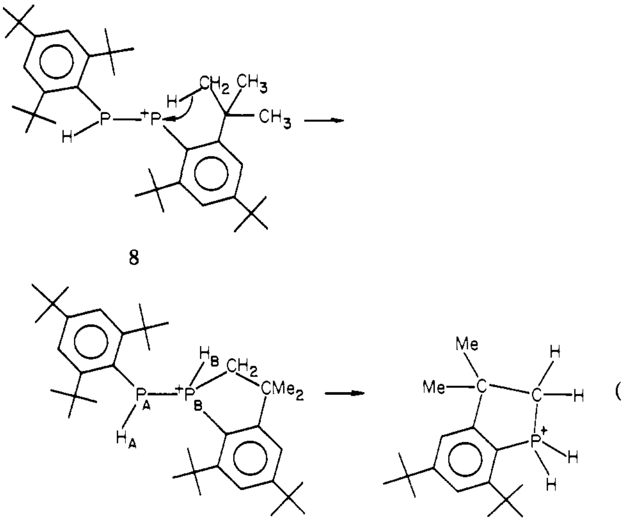
Differences in the reactivity of **1** and **2** were also apparent from protonation studies using HBF$_4$·Et$_2$O. Treatment of **1** with excess HBF$_4$·Et$_2$O in CH$_2$Cl$_2$ at −78 °C for 2 h produced $[(Me_3Si)_3CPH_3][BF_4]$ (**6**). ^{31}P NMR data for **6**: δ −56.3 (q, $^1J_{PH}$ = 502.2 Hz). Protonation of **2** with excess HBF$_4$·Et$_2$O in CH$_2$Cl$_2$ solution at −78 °C resulted initially in a compound (**7**) with an AX $^{31}P\{^1H\}$ NMR spectrum (36.43 MHz). The corresponding ^{1}H-coupled ^{31}P spectrum (−50 °C) showed additional coupling, thus indicating the attachment of one hydrogen to each phosphorus plus additional fine structure relating to P$_B$: δ_{P_A} −86.1 (ddd, $^1J_{PP}$ = 290 Hz, $^1J_{P_AH_A}$ = 229.0 Hz, $^2J_{P_AH_B}$ = 6.6 Hz), δ_{P_B} 10.6 (ddd, $^1J_{PP}$ = 290 Hz, $^1J_{P_BH_B}$ = 481 Hz, $^2J_{P_BH_A}$ = 9.8 Hz). On the basis of these data we propose the structure shown in eq 1 for **7**. We propose further that **7** arises via intramolecular C–H oxidative addition of an initially formed two-coordinate phosphorus cation, **8**.[7] Warming of a solution of **2** in HBF$_4$·Et$_2$O resulted in P–P bond cleavage and the formation of **9**: $^{31}P\{^1H\}$NMR δ 17.7 (t, $^1J_{PH}$ = 528 Hz).



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7 9 (1)

An X-ray crystallographic study of **1** was undertaken[8] because of the differences in reactivity of **1** and **2**.[9] There are two crystallographically independent molecules (A and B) in the asymmetric unit, and each contains a crystallographic center of inversion at the midpoint of the P═P bond (Figure 1). The phosphorus–phosphorus bond length in molecule A is 2.014 (6) Å while that in molecule B is 2.004 (6) Å; cf. 2.034 (2) Å in **2**.[4a] The P–P–C angles in **1** are approximately 6° wider than those

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[1] (a) West, R.; Fink, M. J.; Michl, J. *Science* (Washington, D.C.) **1981**, *214*, 1343. (b) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150. (c) Boudjouk, P.; Han, B.-H.; Anderson, K. R. *Ibid.* **1982**, *104*, 4992.

[2] Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6136.

[3] For a discussion of the bonding in the $[(Me_3Si)_2CH]_2$ Sn, see: Fjeldberg, T.; Haaland, A.; Lappert, M. F.; Schilling, B. E. R.; Seip, R.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 1407, and references therein.

[4] (a) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587. (b) Cowley, A. H.; Kilduff, J. E.; Newman, T. H.; Pakulski, M. *Ibid.* **1982**, *104*, 5820. (c) Bertrand, G.; Couret, C.; Escudie, J.; Majid, S.; Majoral, J.-P. *Tetrahedron Lett.* **1982**, *23*, 3567. (d) Cetinkaya, B.; Hudson, A.; Lappert, M. F.; Goldwhite, H. J. *J. Chem. Soc., Chem. Commun.* **1982**, 609. (e) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Thorne, A. J.; Goldwhite, H. *Ibid.* **1982**, 691. (f) Couret, C.; Escudie, J.; Satge, J. *Tetrahedron* Lett. **1982**, *23*, 4941.

[5] For a preliminary account of the reactivity of (mes)$_2$Si═Si(mes)$_2$(mes = mesityl) see: Fink, M. J.; De Young, D. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 1070.

[6] the only exception is when R═CF$_3$ (Dobbie, R. C.; Goshij, P. D.; Straughan, B. P. *J. Chem. Soc., Dalton Trans.* **1975**, 2368) or when RP-(H)(halogen) is coordinated to a transition metal: Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488 and references therein.

[7] Previously we have demonstrated that two-coordinate phosphenium cations undergo C–H oxidative addition reactions. See: (a) Cowley, A. H.; Kemp, R. A.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 3239. (b) Cowley, A. H.; Mehrotra, S. K. *Ibid.* **1983**, *105*, 2074. For ring closures of 2,4,6-(*t*-Bu)$_3$C$_6$H$_2$–phosphorus compounds, see: (c) Baceiredo, A.; Bertrand, G.; Mazerolles, P.; Majoral, J.-P. *J. Chem. Soc., Chem. Commun.* **1981**, 1197. (d) Yoshifuji M.; Shima, I.; Ando, K.; Inamoto, N. *Tetrahedron Lett.* **1983**, *24*, 933.

[8] A crystal of dimensions 1.0 × 0.6 × 0.3 mm was sealed under dry nitrogen in a Lindemann capillary and mounted on an Enraf-Nonius CAD-4 automated diffractometer. A total of 2275 reflections were measured to 2θ max of 36° by using Mo Kα radiation (λ 0.710 69 Å) and a graphite monochromator. Of these 2046 reflections were considered observed. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 4$. The unit-cell dimensions are a = 16.629 (7) Å, b = 9.155 (5) Å, c = 12.482 (6) Å, α = 91.58 (4)°, β = 111.42 (5)°, γ = 90.02 (4)°. No absorption or extinction corrections were applied. The structure was solved by direct methods using the SHELX program system. The final R and R_w values were 0.086 and 0.086. Tables of atomic coordinates, thermal parameters, bond lengths and bond angles are available as supplementary material.

[9] After the submission of this paper two reports on the reactivity of diphosphenes have appeared: (a) Niecke, E.; Rüger, R. *Angew Chem., Int. Ed. Engl.* **1983**, *22*, 155. (b) Yoshifuji, M.; Ando, K.; Toyota, K.; Shima, I.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1983**, 419.

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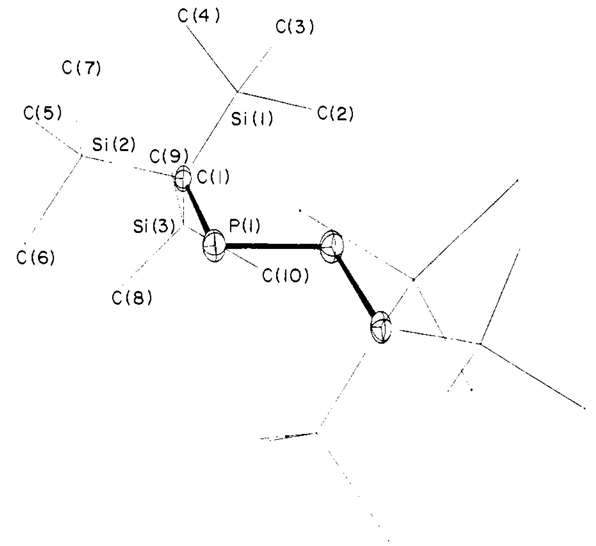

Figure 1. View of $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (**1**) showing the atom numbering scheme. Pertinent metric parameters for molecule A: P(1)-P(1)′ 2.014 (6), P(1)-C(1) 1.85 (1) Å; ∠P(1)′-P(1)-C(1) 108.2 (4)°. For molecule B: P(1)-P(1)′ 2.004 (6), P(1)-C(1) 1.87 (1) Å; ∠P(1)′-P(1)-C(1) 108.9 (4)°.

in **2**, presumably as a result of the larger size of $(Me_3Si)_3C$ over $(2,4,6\text{-}(t\text{-Bu})_3C_6H_2)$. We suggest that this difference in ligand size is responsible for the stability of the HCl addition product **3** and the absence of a corresponding product from the reaction of **2** with HCl.

Acknowledgment. Generous financial support from the National Science Foundation (Grant CHE-8205871) and the Robert A. Welch Foundation is gratefully acknowledged.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles (4 pages). Ordering information is given on any current masthead page.

Vinyl Hydrogen Activation in Mono- and Dinuclear (η^5-Cyclopentadienyl)(hexatriene)cobalt Complexes. Thermal and Photochemical Hydrogen Shifts of Complementary Stereochemistry

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Received January 31, 1983

The activation of C-H bonds in hydrocarbons by soluble transition-metal complexes has been the focus of intensive recent research.[1] Its vinyl variant has been relatively unexplored,[2] having frequently been restricted to low-yielding complex cluster reactions.[3] It also suffers from little mechanistic understanding. This is surprising, considering the ready availability of alkenes such

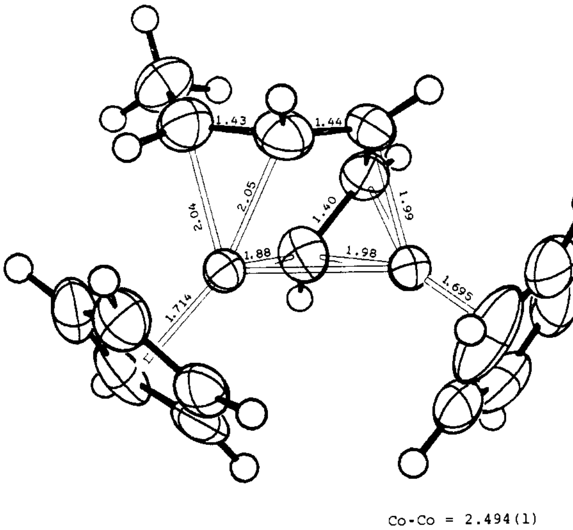
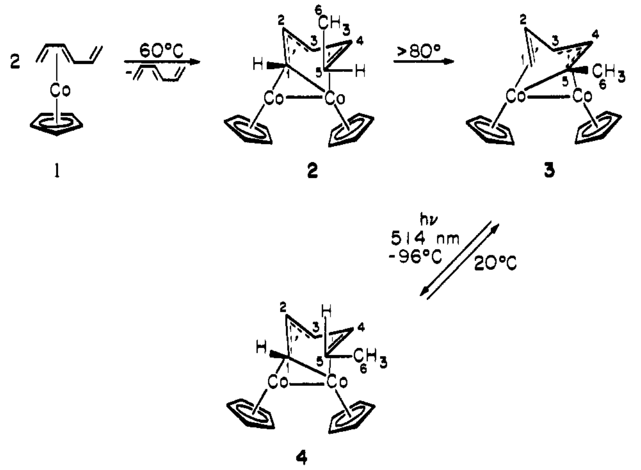


Figure 1. ORTEP drawing of **2** including selected bond lengths (angstroms). Ellipsoids are scaled to represent 50% probability surface. The hydrogen positions shown are those calculated on the basis of idealized geometry following their locations on the difference Fourier electron density map.

Scheme I



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(1) See, for example: (a) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980. (b) Parshall, G. W. *Acc. Chem. Res.* **1975**, *4*, 113-117. (c) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97-143. (d) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240-4242. (e) Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *Ibid.* **1982**, *104*, 6994-7001. (f) Janowicz, A. H.; Bergman, R. G. *Ibid.* **1982**, *104*, 352-354. (g) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1243-1244 and the references therein.

(2) See, for example: (a) Brown, T. L.; Nubel, P. O. *J. Am. Chem. Soc.* **1982**, *104*, 4955-4957. (b) Franzreb, K. H.; Kreiter, C. G. *Z. Naturforsch., B* **1982**, *37B*, 1058-1069. (c) Aumann, R.; Henkel, G.; Krebs, B. *Angew. Chem.* **1982**, *94*, 218; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 204; *Angew. Chem. Supp.* **1982**, 506-512. (d) Herrmann, W. A.; Weichmann, J.; Balbach, B.; Ziegler, M. L. *J. Organomet. Chem.* **1982**, *231*, C69-C72. (e) Eisenstadt, A.; Efraty, A. *Organometallics* **1982**, *1*, 1100-1101. (f) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4955-4957. (g) Dyke, A. F.; Guerchais, J. E.; Knox, S. A. R.; Roue, J.; Short, R. L.; Taylor, G. E.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 537-538. (h) Caddy, P.; Green, M.; Smart, L. E.; White, N. *Ibid.* **1978**, 839-841. (i) Goddard, R.; Knox, S. A. R.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *Ibid.* **1976**, 559-560. (j) Volger, H. C. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 677-686.

(3) See, for example: (a) Evans, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* **1981**, 2017-2020. (b) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Will, G. J.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Chem. Commun.* **1980**, 1190-1191. (c) Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Mann, A. L.; Raithby, P. R. *Ibid.* **1980**, 547-549. (d) Bhaduri, S.; Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Raithby, P. R.; Rehani, S.; Sheldrick, G. M.; Wong, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1979**, 562-568. (e) Ferrari, R. P., Vaglio, G. A. *J. Organomet. Chem.* **1979**, *182*, 245-249. (f) Pierpont, C. G.; Stuntz, G. F.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 616-618. (g) Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Rehani, S. K. *J. Organomet. Chem.* **1976**, *113*, C42-C44. (h) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614-1620. (i) Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *85*, C29-C31. (j) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1415-1419.

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