lengths in **2** are abnormally long. Addition of the 0.176 Å difference in radii between Ce(III) and Yb(III) to the Yb–C(ring) and Yb–Cl distances in **3** gives values similar to those found in **1**, not in **2**. Eight-coordinate $(C_5Me_5)CeI_2(THF)_3$[27] also has a Ce–C(ring) average [2.80 (3) Å] closer to that of **1** than **2**.

The five-coordinate geometry around potassium is not regular and displays major distortions from either square-pyramidal or trigonal-bipyramidal idealized geometries. In Figure 1, the geometry around potassium can be viewed as a distorted trigonal bipyramid in which Cl(2) and Cl(2)″ are the axial ligands and Cl(1), Cl(1)′, and THF are at the equatorial positions. The angles in the plane, Cl(1)–K–Cl(1)′, 128.7 (1)°, Cl(1)–K–O, 104.3 (3)°, and O–K–Cl(1)′, 124.6 (2)°, are reasonably close to the 120° angles of a trigonal bipyramid. However, the Cl(2)–K–Cl(2)″ angle of 156.1 (1)° is not near the theoretical 180° angle for this geometry. The orientation of the ligands around potassium is such that the THF ligand is pointing away from the $(C_5Me_5)_2Ce$ unit. This is sterically optimal.

The K–Cl distances in **1** fall into two ranges. The distances within the $(C_5Me_5)_2CeCl_2K(THF)$ unit, K–Cl(1), 3.081 (3) Å, and K–Cl(2), 3.077 (3) Å, are in the range expected in comparison to Li–Cl distances in **2** and **3** after the difference in alkali-metal radii is taken into account.[51,52] The K–Cl bonds that connect the $(C_5Me_5)_2CeCl_2K(THF)$ units, K–Cl(1)′, 3.157 (3) Å, and K–Cl(2)″, 3.152 (3) Å, are longer. The K–O(THF) distance of 2.70 (1) Å is in the range of K–O(THF) values in the literature: Co(*n*-Pr-Salen)K(CO_2)(THF),[53] six-coordinate potassium, 2.70 (2) Å, K$[(C_6H_5)_2PCHP(C_6H_5)_2CH(NC_5H_4)](THF)_2$,[54] five- to seven-coordinate potassium, 2.620 (7) and 2.745 (9) Å; $[C_5Me_5Rh(CO)]_2K_2(THF)_2$,[55] three-coordinate potassium, 2.74 (6)–2.840 (7) Å; $Cr(C_2Ph_2)(C_4Ph_4)(CO)_2K$(dibenzo-18-crown-6)(THF),[56] eight-coordinate potassium, 2.680 (7) Å; $[K(pinacolonenolate)(THF)]_6$,[57] four-coordinate potassium, 2.731 (9) and 2.747 (4) Å.

Conclusion

The particular product obtained from the synthesis of a "$(C_5Me_5)_2CeCl$" material is a sensitive function of the alkali metal used and the method in which the sample is handled and recrystallized. Alkali-metal halide adducts as well as the "$(C_5Me_5)_2CeCl$" unit alone can be obtained, and both systems can exist in various levels of solvation. Clearly, the development of the chemistry of the $(C_5Me_5)_2Ce$ unit will require careful attention to experimental details.

The structure of $[(C_5Me_5)_2CeCl_2K(THF)]_n$ provides one fully characterized example of how desolvation can lead to oligomerization in these systems. This result helps to explain why molecules of this type sometimes become insoluble upon loss of solvent. Complete desolvation could lead to oligomerization in three dimensions giving an insoluble material.

Acknowledgment. For support of this research, we thank the Division of Chemical Sciences of the Office of Basic Energy Sciences of the Department of Energy (W.J.E.) and the National Science Foundation (J.L.A.). We also thank Dr. Joseph W. Ziller for experimental assistance.

Registry No. **1**, 111559-68-3; **2**, 111559-69-4; KC_5Me_5, 94348-92-2; $CeCl_3$, 7790-86-5.

Supplementary Material Available: A table of thermal parameters (1 page); a listing of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

(51) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th Ed.; Wiley: New York, 1980.
(52) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr. Theor. Gen. Crystallogr.* **1976**, *A32*, 751–767.
(53) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082–5092.
(54) Schmidbauer, H.; Deschler, U.; Milewski-Mahria, D. *Chem. Ber.* **1982**, *115*, 3290–3299.
(55) Krause, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2972–2973.
(56) Wink, D. J.; Fox, J. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 5012–5014.
(57) Willard, P. G.; Carpenter, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 462–468.

Preliminary Chemical Study of (2-Oxo-1,2-dihydrophosphete(*P*–*W*))pentacarbonyltungsten Complexes

Angela Marinetti and François Mathey*

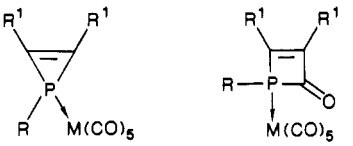
Laboratoire de Chimie du Phosphore et des Métaux de Transition DCPH—Ecole Polytechnique, 91128 Palaiseau Cedex, France

Received June 18, 1987

The chemistry of the new four-membered 2-oxo-1,2-dihydrophosphete ring has been investigated in two P–$W(CO)_5$ complexes. All reactions which have been observed take place at the P–C(O) bond. Hydrolysis gives the corresponding open-chain carboxylic acids. Reduction by $(AlH_3)_n$ at −60 °C in ether gives the corresponding cyclic alcohols as mixtures of two isomers. The 3,4-diphenyl-substituted ring reacts with $NaBH_4$ at room temperature to yield two isomeric 1,2-oxaphospholenes. The more strained 3,4-diethyl-substituted ring gives the open-chain primary alcohol. It appears that the reactivity of the P–C(O) bond is controlled by the substitution scheme.

In a preliminary note,[1] we recently have described the insertion of carbon monoxide into one of the internal P–C bonds of phosphirene *P* complexes (**1**). This led to the previously unknown 2-oxo-1,2-dihydrophosphete ring (**2**).

0276-7333/88/2307-0633$01.50/0



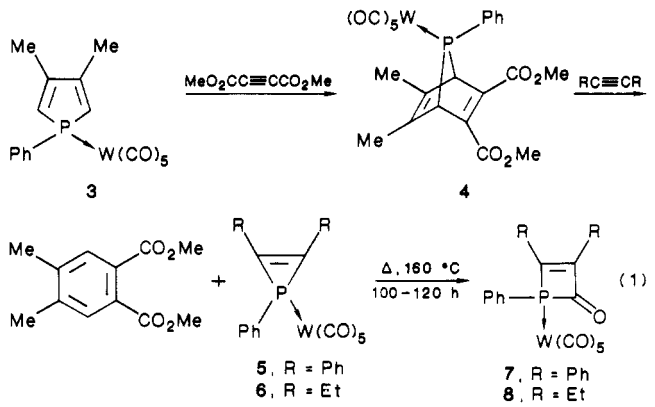
1 2

M = Cr, Mo, W

From the standpoint of phosphorus heterocyclic chemistry, this discovery is significant since the chemistry of the unsaturated PC_3 rings is, still today, practically a virgin territory. Indeed, only two accounts dealing with this topic can be found in the literature. In the first report, Russian authors[2] have described the synthesis of some 1,2-dihydrophosphete *P*-oxides but their claimed structure was not backed up with an X-ray diffraction study. In another preliminary report,[3] Neilson et al. stated that a hindered 1-phosphabutadiene cyclizes upon sulfurization to give a 1,2-dihydrophosphete *P*-sulfide. These observations prompted us to perform a preliminary chemical study of the easily obtained (2-oxo-1,2-dihydrophosphete(*P*–*W*))-pentacarbonyltungsten complexes.

Results and Discussion

For practical reasons, all our experimental work has been performed with the two dihydrophosphete complexes **7** and **8**. These complexes are normally obtained in three steps from (1-phenyl-3,4-dimethylphosphole)pentacarbonyltungsten (**3**) via the sequence outlined in eq 1. In previous



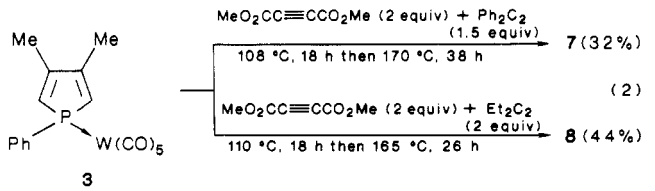
3 4

5, R = Ph
6, R = Et

7, R = Ph
8, R = Et

(1)

work,[4] we had already demonstrated that it is possible to obtain **5** directly from **3** by combining the first two steps. Encouraged by this result, we tried to obtain **7** and **8** directly from **3** in a one-pot reaction in order to simplify access to our two starting products. This proved to be possible (eq 2). In doing so, we also sharply improved the

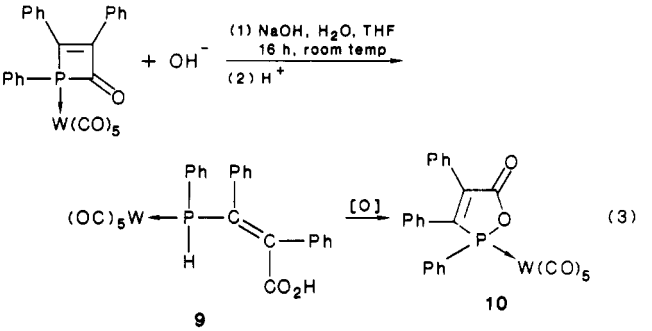


3

(2)

overall yields of **7** and **8** from **3** (32% and 44% versus ca. 11%). The rationale behind the successful combination of the first two steps has already been discussed.[4]

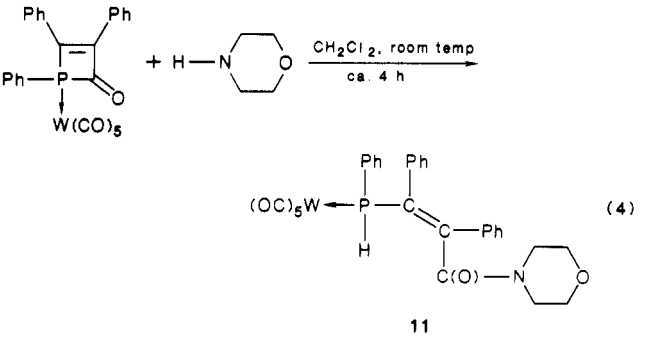
Having in hand substantial quantities of **7** and **8**, we investigated their chemistry, first studying the hydrolysis of the P–acyl bond in basic medium (eq 3). The reaction



9 10

(3)

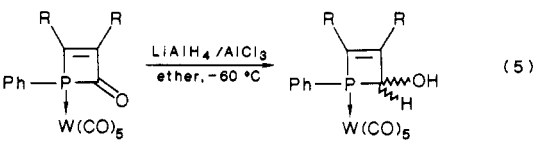
proceeds easily and gives the expected carboxylic acid **9**, which is unambiguously characterized by ^{31}P NMR [δ ^{31}P (**9**) −15.7 in CH_2Cl_2, $^1J(^{31}P-^{183}W)$ = 230 Hz, ^1J(P–H) = 371 Hz], ^1H NMR [δ(P*H*) 7.30 in C_6D_6], and ^{13}C NMR spectroscopy [δ(*C*OOH) 174.6 in C_6D_6]. However, **9** appears to be unstable upon standing or heating in solution and is readily oxidized to give the cyclic product **10**. This oxidation is easily monitored by ^{31}P NMR spectroscopy [$\delta^{31}P$ (**10**) +117.6 in toluene, $^1J(^{31}P-^{183}W)$ = 298 Hz, no ^1J(P–H) coupling]. The oxaphospholene complex (**10**) is stable and has been fully characterized. The aminolysis of **7** also follows the normal path but, in that case, the product thus obtained is stable (eq 4). Here again, ^{31}P



11

(4)

and ^1H NMR spectroscopy unambiguously demonstrate the presence of the P–H bond (**11**: δ ^{31}P −14.5 in CH_2Cl_2, $^1J(^{31}P-^{183}W)$ = 232 Hz, ^1J(P–H) = 351 Hz; δ (P*H*) 7.12 in C_6D_6] thus proving the attack of the amine at the carbonyl carbon. Contrary to the hydrolysis and aminolysis, which are clear-cut reactions, the reduction of **7** and **8** is rather complex. Indeed, it can yield three types of products according to the experimental conditions and to the substitution patterns. Under mild conditions at low temperature and with a neutral reagent such a $(AlH_3)_n$, the reduction gives the expected alcohols as mixtures of two isomers (eq 5). When R = Ph, one isomer (**12a**) is pref-



7, R = Ph
8, R = Et

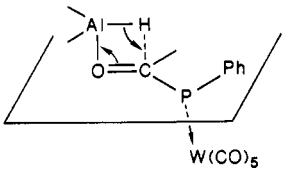
12a,b, R = Ph
13a,b, R = Et

(5)

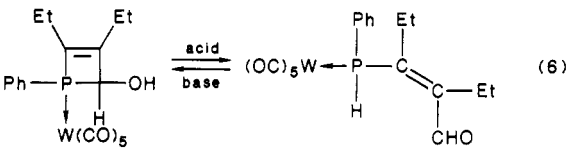
erentially obtained, but the minor one (**12b**) is observable in the ^{31}P NMR spectrum of the crude reaction mixture [$\delta^{31}P$ (**12a**) 42.8, $\delta^{31}P$ (**12b**) 48.6 in CH_2Cl_2]. That the four-membered ring is preserved in **12a** is immediately obvious from the huge *P*–*C*(OH) coupling [δ(*C*H(OH))

(1) Marinetti, A.; Fischer, J.; Mathey, F. *J. Am. Chem. Soc.* **1985**, *107*, 5001.
(2) Nurtdinov, S. Kh.; Ismagilova, N. M.; Fakhrutdinova, R. A.; Zykova, J. V. *Zh. Obshch. Khim.* **1983**, *53*, 1045; *Chem. Abstr.* **1983**, *99*, 122548z.
(3) Neilson, R. H.; Boyd, B. A.; Dubois, D. A.; Hani, R.; Scheide, G. M.; Shore, J. T.; Wettermark, U. G. *Phosphorus Sulfur* **1987**, *30*, 463.
(4) Marinetti, A.; Mathey, F. *J. Am. Chem. Soc.* **1985**, *107*, 4700.

75.43 in CD_2Cl_2, ^1J(C–P) = 40.3 Hz]. The ^{1}H NMR spectrum of **12a** provides a clue for establishing the stereochemistry at the sp^3 carbon: no ^2J(*P*–C*H*) coupling is observed. According to several previous reports,[5] this means that H is trans to $W(CO)_5$ contrary to what was intuitively expected. As a logical consequence, the hydroxy group is very hindered and exchanging the OH proton becomes difficult, thus allowing one to observe ^3J(H–P) and ^3J(H–H) couplings [δ(O*H*) 1.80 in C_6D_6, ^3J(H–P) = 2.44 Hz, ^3J(H–H) = 6.84 Hz]. This stereochemistry is easily explained if we accept that $(AlH_3)_n$ selectively attacks the less hindered side of the carbonyl group (**7**).



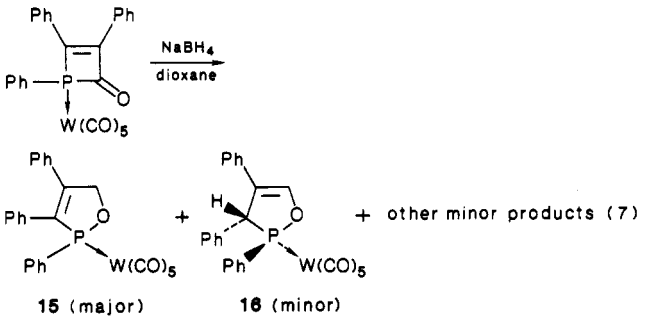
Before leaving **12a**, it is of interest to note that the ^{31}P NMR spectrum of the crude reaction mixture shows, besides the resonance of the minor isomer **12b**, two other minor resonances at δ +156 and −17.4 in CH_2Cl_2 which very likely correspond, respectively, to a five-membered oxaphospholene ring and to an open-chain aldehyde (see later). When R = Et, the two isomeric alcohols **13a,b** are obtained in approximately similar quantities. We have been able to obtain **13a** in the pure state and thus to establish the stereochemistry of both isomers by ^{1}H NMR spectroscopy of their mixture. **13a**: δ ^{31}P +44.2, δ (C*H*) 3.93, ^2J(*P*–C*H*) $\simeq$ 0 Hz in C_6D_6, OH cis to W. **13b**: δ ^{31}P +48.5, δ (C*H*) 4.72, ^2J(*P*–C*H*) = 7.57 Hz in C_6D_6, OH trans to W. Apparently, the four-membered ring is less stable in **13** than in **12**. An equilibrium seems to exist between **13** and the open-chain aldehyde **14** (eq 6). While we have



(6)

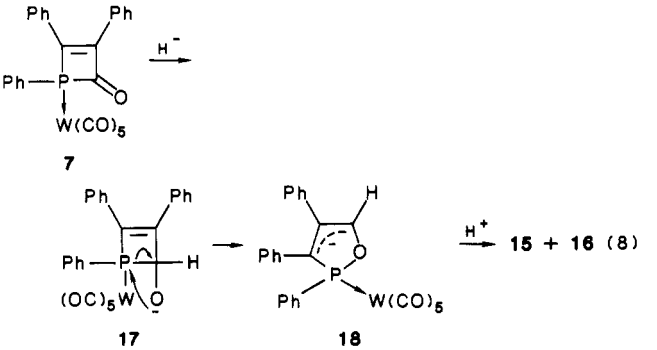
13a,b **14**

been unable to obtain **14** in the pure state, its formula has been reasonably well established on the basis of the ^{1}H and ^{31}P NMR spectra of its mixture with **13a,b**:**14**: δ ^{31}P −24.8 ^1J(P–H) = 356.4 Hz, δ (C*H*O) 9.64, ^4J(H–P) = 1.46 Hz in C_6D_6. Water and triethylamine appear to favor the closure of **14** back to **13a,b** while HCl seems to catalyze the opening of **13a,b** to give **14** and to simultaneously induce an equilibration between **13a** and **13b**. An additional minor product has been sometimes observed in these experiments with a ^{31}P resonance at δ +149.8. This is very likely an oxaphospholene complex (see later). Indeed, when the reduction of **7** is now carried out with sodium borohydride in dioxane at room temperature or above, it does not yield the expected alcohols but two oxaphospholene complexes **15** and **16** (eq 7) are produced instead. The mass spectra of **15** and **16** are identical to the mass spectrum of **12a** thus establishing the identity of their empirical formulas but the ^{31}P NMR spectra clearly indicate that **15** and **16** contain a P–O–C bond: δ^{31}P (**15**) +153 in CH_2Cl_2, δ^{31}P(**16**) +143.6 in C_6D_6. In the ^{13}C spectrum of **15** in CD_2Cl_2, the P–O–CH_2 resonance appears at δ 81.95 with the weak expected ^2J(*P*–O–*C*) coupling of 8.5 Hz. In the ^{1}H spectrum, the same CH_2 unit appears

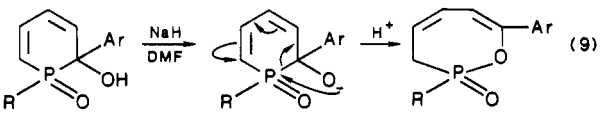


15 (major) **16** (minor)

as an ABX system: δ (A) 5.28, δ (B) 5.02, ^2J(A–B) = 14.9 Hz, ^3J(A–X) = 9.0 Hz, ^3J(B–X) $\simeq$ 0 Hz. On the other hand, the P–C*H*Ph proton signal of **16** appears at δ 5.53 in C_6D_6 with weak ^2J(H–P) coupling of 4.39 Hz (typical ^2J(*H*–C–*P*–W) couplings in such oxaphospholene complexes are ca. 17 Hz[6]) which suggests that **16** has the hindered structure with H trans to W. In the ^{13}C spectrum in C_6D_6, the *C*HPh appears at δ 61.58 (^1J(C–P) = 13.6 Hz) and the ethylenic *C*H at δ 144.11 (^2J(C–P) = 6.0 Hz). The oxaphospholenes **15** and **16** probably result from the spontaneous isomerization of the oxanion **17** into the allylic carbanion **18** after the initial attack of H^- on the carbonyl group of **7** (eq 8). α-Protonation yielding **16** would take



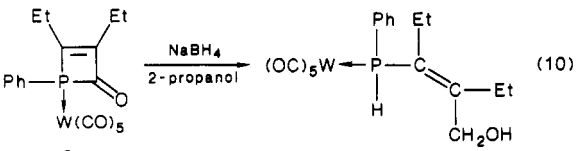
place at the less hindered side of **18**. Similar rearrangements have been described in the literature such as the six- to seven-membered ring conversion depicted in eq 9.[7]



(9)

In the case of **7**, of course, the strain of the four-membered ring provides a strong driving force for the rearrangement.

Under the same experimental conditions as for **7**, the reduction of **8** by $NaBH_4$ gives a different result. Only a minor amount of oxaaphospholene complex similar to **15** or **16** is thus produced (giving a ^{31}P resonance at δ +149.8 as already stated) and by far the major product is now the open-chain alcohol **19** (eq 10). The ^{1}H and ^{31}P NMR



(10)

8 **19**

spectra establish the presence of the P–H bond in **19**: δ^{31}P −31.06 in CH_2Cl_2, ^1J(P–H) = 349 Hz, δ (P*H*) 6.16 in C_6D_6. The CH_2 group appears as an AB system: δ (A) 3.77, δ (B)

(5) See for example ref 6.

(6) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.
(7) Mathey, F. *Tetrahedron* **1973**, *29*, 707.

3.96, ^2J(A–B) 12.5 Hz. The OH group absorption is seen in the IR spectrum. Since under the mild experimental conditions which are used for the reduction, the oxaphospholene ring is very likely stable, we believe **19** to be produced by reduction of the open-chain aldehyde **14**. Thus, from all these data, it is clear that the chemistry of the 2-oxa-1,2-dihydrophosphete ring is controlled by the substitution pattern. The 3,4-diphenyl substitution favors the rearrangement of the alcohols **12** into the corresponding oxaphospholenes **15** and **16** whereas the 3,4-diethyl substitution favors the opening of the ring of **13** to give **14**.

All the chemistry thus far described takes place at the P–acyl bond, which is, according to the X-ray crystal structure analysis of **7**,[1] by far the weakest bond of the ring. We have tried without success to perform a [2 + 4] cycloaddition involving the C=C double bond of **7** and 2,3-dimethylbutadiene. No reaction was observed at 160 °C for 100–120 h. The double bond of **7** is thus far less reactive than the corresponding double bond of a (2-ethoxycarbonyl)phosphirene complex, which reacts with the same diene at 75 °C.[4] Less strain and more steric hindrance perhaps explain the lower reactivity of the double bond of **7**.

Experimental Section

NMR spectra were recorded on a Bruker WP80 instrument at 80.13 MHz for ^{1}H, 32.435 MHz for ^{31}P, and 20.15 mHz for ^{13}C. Chemical shifts are reported in parts per million from internal Me_4Si for ^{1}H and ^{13}C and from external H_3PO_4 for ^{31}P. IR spectra were recorded on a Perkin-Elmer Model 297 spectrometer. Mass spectra were recorded on VG 30F spectrometers by Service Central d'Analyse du CNRS (Lyon). All reactions were carried out under argon. Chromatographic separations were performed on silica gel columns (70–230 mesh Riedel de Haën).

One-Step Synthesis of Complex 7. **3** (20 g, 39 mmol), dimethyl acetylenedicarboxylate (9.6 mL, 78 mmol), and diphenylacetylene (10 g, 56 mmol) in xylene (30 mL) were heated at 108 °C for 18 h. The reaction mixture then was heated at 170 °C in a sealed tube for 38 h. After evaporation of the solvent, the residue was chromatographed with hexane/ether mixtures of increasing polarity. **7** was eluted with hexane/ether (97:3): orange solid;[1] yield 6.6 g (32%).

One-Step Synthesis of Complex 8. **3** (25 g, 48.8 mmol), dimethyl acetylenedicarboxylate (12 mL, 97 mmol), and 3-hexyne (11 mL, 97 mmol) in xylene (35 mL) were heated at 110 °C for 18 h. The reaction mixture then was heated at 165 °C for 26 h in a sealed glass tube. After evaporation, complex **8** was purified by chromatography with hexane/ether (98:2): yellow oil;[1] yield 9.7 g (44%).

Hydrolysis of Complex 7. Complex **7** (1 g, 1.6 mmol) was stirred overnight in THF with 2 mL of aqueous NaOH at room temperature. After evaporation of the THF, the residue was extracted with ether. Drying with Na_2SO_4 and crystallization from an ether/pentane mixture afforded 720 mg (70%) of complex **9**: colorless crystals; ^{31}P NMR CH_2Cl_2) δ –15.7 ($^1J(^{183}W-^{31}P)$ = 229.5 Hz; ^{1}H NMR (C_6D_6) δ 2.5 (1 H, OH), 7.30 (d, ^1J(H–P) = 374.8 Hz, 1 H, PH), 6.7–7.7 (m, 15 H, Ph); ^{13}C NMR (C_6D_6) δ 174.59 (s, CO_2H), 198.37 (d, ^2J(C–P) = 6.0 Hz, cis CO), 199.49 (d, ^2J(C–P) = 22.1 Hz, trans CO); IR (CH_2Cl_2) ν(CO) 2065 (m), 1940 (vs) cm^{-1}; mass spectrum (^{184}W) m/e (relative intensity) 654 (M – 2H, 19), 628 (M – CO, 34), 572 (M – 3CO, 62), 544 (M – 4CO, 36), 516 (M – 5CO, 75), 488 (M – 6CO, 51), 409 (100).

Oxidation of 9 into 10. When heated at 50 °C, complex **9** was oxidized to **10**. Mixtures of **9** + **10** were also obtained when chromatographic purification of **9** was attempted, or by leaving **9** in solution for extended periods of time. Complex **10**: colorless solid; mp 133 °C; ^{31}P NMR (hexane) δ 117.6 ($^1J(^{183}W-^{31}P)$ = 298 Hz); ^{1}H NMR (C_6D_6) δ 6.7–7.8 (m, Ph); ^{13}C NMR (CD_2Cl_2) δ 161.83 (d, ^2J(C–P) = 20.7 Hz, *C*O), 195.33 (d, ^2J(C–P) = 8.5 Hz, cis CO), 197.9 (d, ^2J(C–P) = 30.5 Hz, trans CO); IR (decalin) ν(CO) 2075 (m), 1967 (s), 1950 (vs) cm^{-1}; IR (KBr) ν(CO ester) 1745 cm^{-1}; mass spectrum (^{184}W) m/e (relative intensity) 654 (M, 25), 598 (M – 2CO, 37), 570 (M – 3CO, 86), 542 (M – 4CO, 95), 514 (M – 5CO, 100). Anal. Calcd for $C_{26}H_{15}O_7PW$: C, 47.73; H, 2.31. Found: C, 48.16; H, 2.02.

Aminolysis of Complex 7. Complex **7** (1 g, 1.6 mmol) and morholine (0.2 mL, 2.3 mmol) were stirred in CH_2Cl_2 at room temperature for 4 h. After evaporation, the residue was chromatographed with toluene/ethyl acetate (95:5). **11**: yield 1.0 g (95%) of colorless solid; mp 157 °C (CH_2Cl_2–pentane); ^{31}P NMR (CH_2Cl_2) δ –14.5 ($^1J(^{183}W-^{31}P)$ = 232 Hz); ^{1}H NMR (C_6D_6) δ 2.8–3.5 (m, 8 H, CH_2), 7.12 (d, ^1J(H–P) = 351.1 H, P–H), 6.7–7.8 (m, 15 H, Ph); ^{13}C NMR (C_6D_6) δ 42.04 (s, NCH_2), 47.04 (s, NCH_2), 66.18 (s, OCH_2), 66.34 (s, OCH_2), 167.21 (d, ^3J(C–P) = 5.0 Hz, CO), 196.85 (d, ^2J(C–P) = 6.5 Hz, cis CO), 199.05 (d, ^2J(C–P) = 22.6 Hz, trans CO); IR (decalin) ν(CO) 2070 (m), 1935 (vs) cm^{-1}; IR (KBr) ν(PH) 2310 cm^{-1}, ν (CO–amide) 1615 cm^{-1}; mass spectrum (^{184}W) m/e (relative intensity) 697 (M – CO, 14), 669 (M – 2CO, 21), 641 (M – 3CO, 42), 613 (M – 4CO, 9), 585 (M – 5CO, 100). Anal. Calcd for $C_{30}H_{24}O_7PNW$: C, 49.68; H, 3.34; P, 4.27; W, 25.35. Found: C, 49.84; H, 3.47; P, 4.32; W, 25.35.

Reduction of 7 with $(AlH_3)_n$. Complex **7** (2 g, 3.1 mmol) was added at –70 °C to a $LiAlH_4$ (125 mg, 3.3 mmol)/$AlCl_3$ (439 mg, 3.3 mmol) mixture in ether. The reaction mixture was stirred between –70 °C and –55 °C for 2 h and then hydrolyzed with water. The ether solution was dried, the solvent removed, and the residue chromatographed (elution with toluene). Complex **12** was obtained as a mixture of two isomers in 1:12 ratio, yield 1.3 g (65%). Only the major isomer was completely characterized. **12a**: colorless solid; mp 133 °C (ether–hexane); ^{31}P NMR (CH_2Cl_2) δ 42.85 ($^1J(^{183}W-^{31}P)$ = 244 Hz); ^{1}H NMR (C_6D_6) δ 1.81 (dd, ^3J(H–P) = 2.4 H, ^3J(H–H) = 6.8 Hz, 1 H, OH), 4.45 (d, ^3J(H–H) = 6.8 Hz, 1 H, C*H*OH), 6.8–7.7 (m, 15 H, Ph); ^{13}C NMR (CD_2Cl_2) δ 75.43 (d, ^1J(C–P) = 40.3 Hz, P-*C*HOH), 197.3 (d, ^2J(C–P) = 7.3 Hz, cis CO), 199.4 (d, ^2J(C–P) = 24.4 Hz, trans CO); IR (decalin) ν(CO) 2070 (m), 1945 (vs) cm^{-1}; IR (KBr) ν(OH) 3520 cm^{-1}; mass spectrum (^{184}W) m/e (relative intensity) 640 (M, 33), 612 (M – CO, 15), 556 (M – 3CO, 67), 500 (M– 5CO, 100). Anal. Calcd for $C_{26}H_{17}O_6PW$: C, 48.78; H, 2.68; P, 4.84. Found: C, 48.75; H, 2.80; P, 4.84. **12b**: ^{31}P NMR (CH_2Cl_2) δ 47.59.

Reduction of 8 with $(AlH_3)_n$. A solution of $LiAlH_4$ (0.15 g, 3.9 mmol) and $AlCl_3$ (0.52 g, 3.9 mmol) in ether was cooled at –70 °C. Complex **8** (2 g, 3.7 mmol) (solution in ether) was then added. After 15 min, the reaction mixture was hydrolyzed with water and allowed to warm to room temperature. The ether layer was dried with Na_2SO_4. A mixture of two isomers **13a+b** thus was obtained and characterized by ^{1}H NMR, ^{31}P NMR and mass spectroscopy. A very small amount of **13a** could be obtained by crystallization from pentane. **13a**: colorless solid; ^{31}P NMR (C_6D_6) δ 40.67 ($^1J(^{183}W-^{31}P)$ = 239 Hz); ^{1}H NMR (C_6D_6) δ 0.84 (t, ^3J(H–H) = 7.8 Hz, 3 H, CH_3), 0.87 (t, ^3J(H–H) = 7.8 Hz, 3 H, CH_3), 1.5 (m, 1 H, OH), 1.7–2.4 (m, 4 H, CH_2), 3.88 (s broad, 1 H, PCH), 7.0–7.7 (m, 5 H, Ph); IR (decalin) ν(CO) 2065 (m), 1945 (s) cm^{-1}; IR (KBr) ν(OH) 3320 cm^{-1}. Mass spectrum (^{184}W) m/e (relative intensity) 544 (M, 23), 516 (M – CO, 15), 488 (M – 2CO, 14), 432 (M – 4CO, 23), 404 (M – 5CO, 100). **13b** (mixture with **13a**): ^{31}P NMR (ether) δ 48.3 ($^1J(^{183}W-^{31}P)$ = 220 Hz); ^{1}H NMR (C_6D_6) δ 4.71 (d, ^2J(H–P) = 7.6 Hz, P–C*H*OH). After chromatography with toluene, only the equilibrium mixture of **13a,b** with the open-chain aldehyde **14** was obtained.

Reduction of 7 with $NaBH_4$. A solution of **7** (2 g, 3.1 mmol) in dioxane was added to $NaBH_4$ (0.14 g, 3.8 mmol) in dioxane at room temperature. The mixture was stirred for 3 h, cooled at 0 °C, and hydrolyzed with water. After evaporation, the residue was extracted with CH_2Cl_2 and chromatographed with hexane–ether (99:1). Yield was 1.1 g (55%) of the mixture **15** + **16** (3:1 ratio). Both isomers were obtained in the pure state by chromatography with hexane (silica gel 40–60 mesh Riedel de Haën). Complex **16** was eluted first: colorless oil; ^{31}P NMR (C_6D_6) δ 143.59 ($^1J(^{183}W-^{31}P)$ = 286 Hz); ^{1}H NMR (C_6D_6) δ 5.53 (dd, ^2J(H–P) = 4.4 Hz, ^4J(H–H) = 2.2 Hz, ^{1} H, PC*H*Ph), 6.5–7.0 (m, 16 H, Ph + OCH=); ^{13}C NMR (C_6D_6) δ 61.59 (d, ^1J(C–P) = 13.6 Hz, P*C*HPh), 196.08 (d, ^2J(C–P) = 8.1 Hz, cis CO), 198.87 (d, ^2J(C–P) = 28.7 Hz, trans CO); IR (decalin) ν(CO) 2075 (m), 1965 (s), 1950 (vs) cm^{-1}; mass spectrum (^{184}W) m/e (relative intensity) 640 (M, 74), 556 (M – 3CO), 89), 500 (M – 5CO, 100). Complex **15**: colorless solid; mp 102 °C (pentane); ^{31}P NMR (hexane) 152.9 ($^1J(^{183}W-^{31}P)$ = 290 Hz); ^{1}H NMR (C_6D_6) δ 4.98 (*A*BX, $^2J(H_A-H_B)$

= 14.9 Hz, ^3J(H–P) ≃ 0 Hz, 1 H, CH_2), 5.19 (ABX, $^2J(H_A–H_B)$ = 14.9 Hz, ^3J(H–P) = 10.3 Hz, 1 H, CH_2), 6.8–7.8 (m, 15 H, Ph); ^{13}C NMR (CD_2Cl_2) δ 81.92 (d, ^2J(C–P) = 8.5 Hz, OCH_2), 196.78 (d, ^2J(C–P) = 8.5 Hz, cis CO); IR (decalin) ν(CO) 2075 (m), 1960 (vs), 1950 (sh) cm^{-1}; mass spectrum (^{184}W) m/e (relative intensity) 640 (M, 40), 612 (M – CO, 23), 556 (M – 3CO, 91), 500 (M – 5CO, 100). Anal. Calcd for $C_{26}H_{17}O_6PW$: C, 48.78; H, 2.68; P, 4.84; W, 28.72. Found: C, 48.98; H, 2.58; P, 4,82; W, 28,92.

Reduction of 8 with $NaBH_4$. Complex 8 (1.2 g, 2.2 mmol) was added to $NaBH_4$ (0.1 g, 2.6 mmol) in *i*-PrOH at room temperature. After being stirred for 30 min the reaction mixture was hydrolyzed. The solvent was removed and the residue extracted with methylene chloride and chromatographed with toluene to yield 0.54 g (45%) of colorless oil. **19**: ^{31}P NMR (CH_2Cl_2) δ –31.06 ($^1J(^{183}W–^{31}P)$ = 225 Hz); ^{1}H NMR (C_6D_6) δ 0.72 (t, ^3J(H–H) = 7.3 Hz, 3 H, Me), 0.88 (t, ^3J(H–H) = 7.4 Hz, 3 H, Me), 1.9–2.2 (m, 4 H, CH_2), 3.82 (AB, $^2J_{AB}$ = 12.6 Hz, 1 H, CH_2), 3.94 (AB, J_{AB} = 12.6 Hz, 1 H, CH_2), 6.16 (d, ^1J(H–P) = 349 Hz, 1 H, PH), 6.8–7.8 (m, 5 H, Ph); ^{13}C NMR (C_6D_6) 13.22 (s, Me), 13.86 (s, Me), 24.06 (d, ^3J(C–P) = 8.6 Hz, CH_2); 25.60 (d, ^2J(C–P) = 13.1 Hz, CH_2), 62.71 (d, ^3J(C–P) = 12.6 Hz, CH_2OH), 197.07 (d, ^2J(C–P) = 6.5 Hz, cis CO), 199.30 (d, ^2J(C–P) = 20.6 Hz, trans CO); IR (decalin) ν(CO) 2070 (m), 1940 (vs) cm^{-1}; IR (KBr) ν(OH) 3400 cm^{-1}; mass spectrum (^{184}W) m/e (relative intensity) 544 (M – 2H, 10), 528 (M – H_2O, 11), 544 (M – CO, 8), 460 (M – 2H – 3CO, 20), 404 (M – 2H – 5CO, 26), 388 (M – H_2O – 5CO, 31), 236 ($C_{13}H_{17}PO$, 100).

Registry No. **3**, 74363-95-4; **7**, 97704-77-3; **8**, 97704-78-4; **9**, 111958-68-0; **10**, 111958-69-1; **11**, 111958-70-4; **12a**, 111958-71-5; **12b**, 112065-79-9; **13a**, 111958-72-6; **13b**, 112019-13-3; **15**, 111958-73-7; **16**, 111958-74-8; **19**, 111958-75-9; dimethyl acetylenedicarboxylate, 762-42-5; diphenylacetylene, 501-65-5; 3-hexyne, 928-49-4; morpholine, 110-91-8.

Gas-Phase Acidities of Methylsilanes: C–H versus Si–H

Robert Damrauer,*† Steven R. Kass, and Charles H. DePuy*‡

Department of Chemistry, University of Colorado, Denver, Colorado 80202, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215

Received June 23, 1987

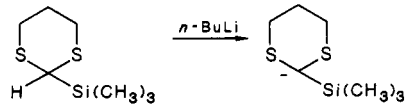
The gas-phase acidities of silane, methylsilane, dimethylsilane, trimethylsilane, tetramethylsilane, and phenylsilane have been measured in the flowing afterglow by using standard techniques. In those methylsilanes having both C–H and Si–H bonds, abstraction occurs from both positions and, correspondingly, both C–H and Si–H acidities are reported. Quite unusually, the thermodynamically more stable products resulting from Si–H abstraction by base are not the first formed products. Thus, C–H abstraction occurs readily by a kinetically more accessible path. The measured gas-phase acidities are used to calculate electron affinities for the corresponding anions. The electron binding energies and basicity of the methyl-substituted silyl anions do not vary with methyl substitution. Furthermore, phenyl-substituted silyl anion has the same electron binding energy and basicity as the silyl anion itself.

α-Silyl carbanions ($R_3SiCH_2^-$) and silyl anions (R_3Si^-) play important roles in synthetic chemistry, the α-silyl species in the Peterson olefination and a wide variety of condensation reactions and the silyl anion in its 1,4-addition to α,β-unsaturated ketones.[1] These anions are prepared in solution as organometallic species in a number of ways using metalation, halogen–metal exchange, addition, and exchange reactions. However, they have been less often prepared by proton abstraction despite the direct nature of such an approach. Thus, demonstrations that KH reacts with trisubstituted silanes to give the corresponding silyl anion (eq 1) and that silyl-substituted

$$R_3SiH + KH \xrightarrow[HMPA]{DME\ or} R_3SiK \qquad (1)$$

$$R = CH_3CH_2,\ C_6H_5$$

thioketals react with BuLi to form α-silyl carbanions (eq 2) are among the relatively few direct deprotonations re-



(2)

ported in solution.[1] In the gas phase the trimethylsilyl anion results from reaction of hexamethyldisilane and fluoride ion (eq 3) and proton abstraction from tetra-

$$(CH_3)_3SiSi(CH_3)_3 \xrightarrow{F^-} (CH_3)_3Si^- + (CH_3)_3SiF \qquad (3)$$

methylsilane with amide ion forms the α-silyl carbanion, $(CH_3)_3SiCH_2^-$ (eq 4).[2] Bowie and co-workers reported, and

$$(CH_3)_4Si \xrightarrow{NH_2^-} (CH_3)_3SiCH_2^- \qquad (4)$$

we confirmed, that when strong bases react with trimethylsilane to give its M – 1 ion (eq 5), the α-silyl car-

$$(CH_3)_3SiH \xrightarrow{NH_2^-} (CH_3)_2SiHCH_2^- \qquad (5)$$

banion is formed.[3] Bowie's group used a deuterium label to demonstrate that proton abstraction occurs from a methyl group rather than from silicon, while we were led to the same conclusion through the development of a reaction scheme using N_2O in which α-silyl carbanions and silyl anions can be distinguished (eq 6 and 7).[4] We now

$$\underset{m/z\ 73}{(CH_3)_2Si\ HCH_2^-} \xrightarrow{N_2O} \underset{m/z\ 75}{(CH_3)_2SiHO^-} \qquad (6)$$

$$\underset{m/z\ 73}{(CH_3)_3Si^-} \xrightarrow{N_2O} \underset{m/z\ 89}{(CH_3)_3SiO^-} \qquad (7)$$

† University of Colorado at Denver.

‡ University of Colorado, Boulder.

(1) (a) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983. (b) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981.

(2) DePuy, C. H.; Damrauer, R.; Bowie, J. H.; Shelton, J. C. *Acc. Chem. Res.* **1987**, *20*, 127.

(3) Klass, G.; Trenerry, V. C.; Shelton, J. C.; Bowie, J. H. *Aust. J. Chem.* **1981**, *34*, 519.

(4) Damrauer, R.; DePuy, C. H. *Organometallics* **1984**, *3*, 362.

0276-7333/88/2307-0637$01.50/0