Reactivity of a Phosphavinylidene. Reactions at Both Phosphorus–Carbon and Phosphorus–Molybdenum Double Bonds and a New Approach to Three-electron Donor Phosphido Complexes

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The phosphavinylidene, $[Mo(CO)_2\{\eta^1\text{-}P{=}C(SiMe_3)_2\}(\eta\text{-}C_5H_5)]$, reacts with both electrophilic and nucleophilic reagents, thus representing a new synthetic method for $3e^-$ donor phosphido complexes; MeOH will add to both the phosphorus–carbon and molybdenum–phosphorus double bonds.

The observation that the phosphorus atom of phosphavinylidenes, $L_nM{\doteq}P{=}CR_2$,[1,2] is double-bonded to both carbon and a transition metal stimulated our interest in the reactivity of this class of compound. We report (i) reactivity towards both electrophiles and nucleophiles, (ii) sequential reactions at the P=C and P≐M functionalities, (iii) a new synthetic approach to $3e^-$ donor phosphido (neutral phosphenium) complexes, and (iv) use of this approach to prepare the first thio-substituted complex of this type.

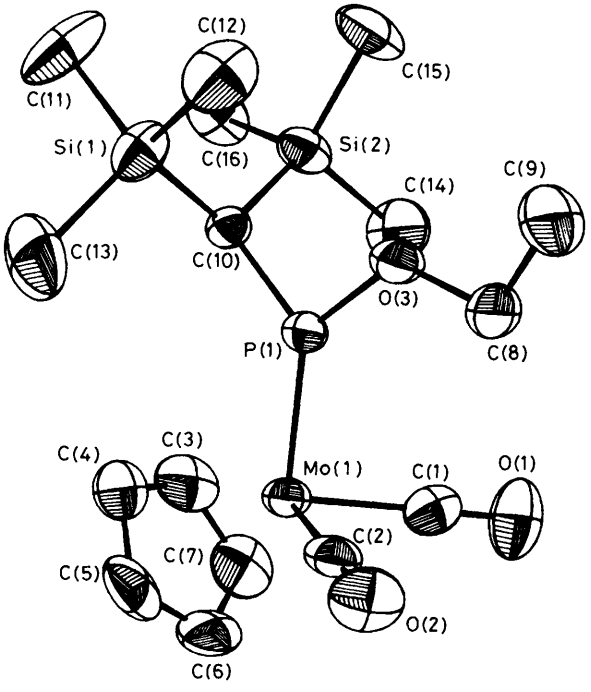
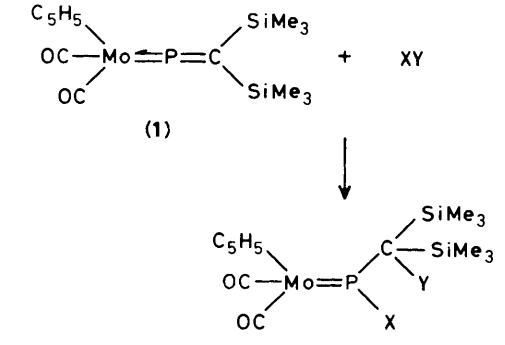


Figure 1. ORTEP view of (**2**) showing the atom numbering scheme. Important parameters: Mo(1)–P(1) 2.207(2), P(1)–C(10) 1.794(9), P(1)–O(3) 1.616(6) Å; Mo(1)–P(1)–C(10) 129.0(3), Mo(1)–P(1)–O(3) 132.9(3), C(10)–P(1)–O(3) 97.9(3)°.



	(2)	(3)	(4)	(5)
X	EtO	CD_3O	Pr^i_2N	C_6F_5S
Y	H	D	H	H
δ_P	367.9	369.1	344.2	297.7

Scheme 1

The phosphavinylidene, $[Mo(CO)_2\{\eta^1\text{-}P{=}C(SiMe_3)_2\}(\eta\text{-}C_5H_5)]$,[1] (**1**), reacted rapidly and quantitatively with one equivalent of EtOH in tetrahydrofuran (THF) at 25 °C as evidenced by the complete disappearance of the $^{31}P\{^1H\}$ (32.38 MHz) resonance of (**1**) (δ_P +497 p.p.m.)[1] and its replacement by a singlet at +367.9 p.p.m. Solvent removal, redissolution in n-hexane, filtration, chromatographic purification, concentration and storage at −20 °C resulted in high quality crystals of $[Mo(CO)_2(\eta^1\text{-}PR^1R^2)(\eta\text{-}C_5H_5)]$ [(**2**); R^1 = $(Me_3Si)_2CH$, R^2 = OEt].† The *X*-ray crystal structure of (**2**) (Figure 1)‡ confirmed that it is a $3e^-$ donor phosphido (neutral phosphenium)§ complex. Like other complexes of this type,[3] (**2**) features a trigonal planar phosphorus atom together with a relatively short metal–phosphorus distance. Note that the Mo–P bond length increases from 2.174(1) Å in (**1**) to 2.207(2) Å in (**2**), presumably due to the change in phosphorus hybridisation from ~sp to ~sp^2.

Other electrophiles react virtually quantitatively with (**1**) as summarised in Scheme 1. The foregoing reactions represent a new synthetic method for $3e^-$ donor phosphido complexes.

† All new compounds had satisfactory chemical analyses and spectroscopic characteristics.

‡ *Crystal data* for (**2**): $C_{16}H_{29}MoO_3PSi_2$, a = 11.775(3), b = 12.876(2), c = 15.107(3) Å, β = 101.48(2)°, U = 2244.7 Å^3, monoclinic, space group $P2_1/n$ (No. 14), Z = 4, D_c = 1.339 g cm^{-3}, μ(Mo-K_α) = 7.54 cm^{-1}. (**5**): $C_{20}H_{24}F_5MoO_2PSSi_2$, a = 12.446(3), b = 12.595(3), c = 8.881(1) Å, α = 102.64(2), β = 100.72(2), γ = 81.34(2)°, U = 1325.9 Å^3, triclinic, space group $P\bar{1}$ (No. 2), Z = 2, D_c = 1.520 g cm^{-3}, μ(Mo-K_α) = 7.55 cm^{-1}. (**6**): $C_{16}H_{31}MoO_4PSi_2$, a = 16.127(2), b = 9.447(2), c = 16.737(2) Å, β = 116.67(1)°, U = 2278.7 Å^3, monoclinic, space group $P2_1/c$ (No. 14), Z = 4, D_c = 1.371 g cm^{-3}, μ(Mo-K_α) = 7.48 cm^{-1}. Data were collected (293 K) on an Enraf–Nonius CAD 4-F diffractometer over the range 3.0 ≤ 2θ ≤ 48.0° for all three compounds. Corrections for Lorentz, polarisation, and absorption were applied in each case, but not for decay (<1%). Totals of 3515, 4151, and 3007 unique reflections were measured for (**2**), (**5**), and (**6**) respectively. Of these, 2103, 2870, and 2424 [$I > 3.0\sigma(I)$] were considered observed and used to solve (direct methods) and refine (difference Fourier, full-matrix least-squares) the structures of (**2**), (**5**), and (**6**), respectively. The final least-squares refinements converged smoothly to give residuals R = 0.0441 and R_w = 0.0534 for (**2**), R = 0.0497 and R_w = 0.0590 for (**5**), and R = 0.0433 and R_w = 0.0562 for (**6**). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

§ For a summary of the view that these are $[R_2P]^+$ complexes of organometallic mono-anions such as $[Mo(CO)_2(\eta\text{-}C_5H_5)]^-$, see R. T. Paine, L. D. Hutchins, D. A. Dubois, and E. N. Duesler, *Phosphorus Sulfur*, 1983, **18**, 263.

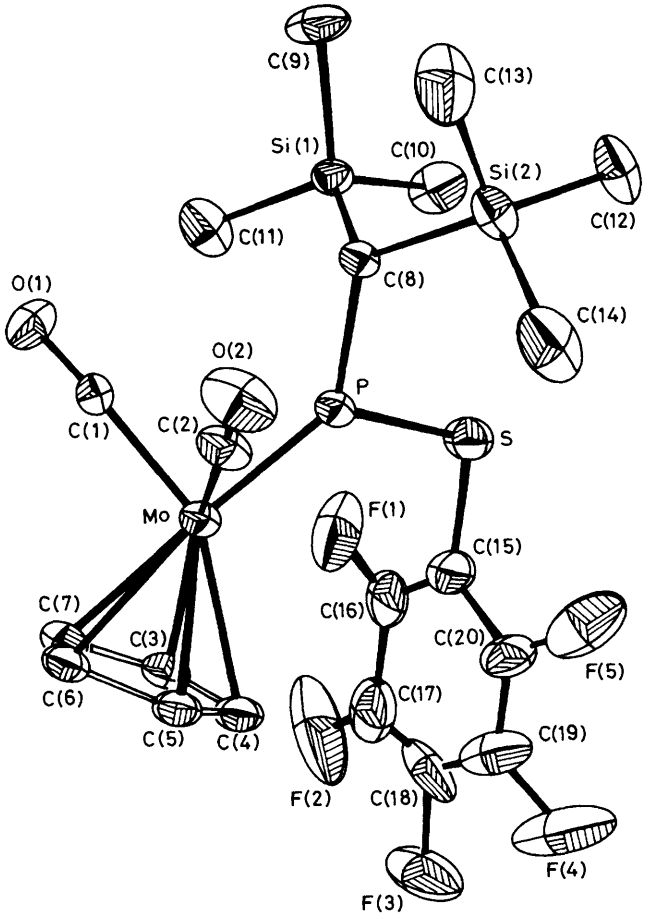
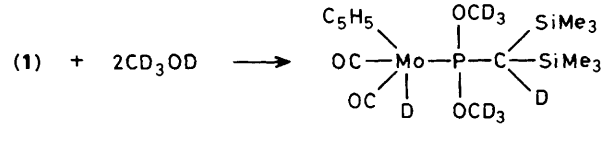


Figure 2. ORTEP view of (**5**) showing the atom numbering scheme. Important parameters: Mo–P 2.221(2), P–C(8) 1.805(7), P–S 2.147(3) Å, Mo–P–C(8) 129.9(2), Mo–P–S 132.9(1), C(8)–P–S 97.1(2)°.

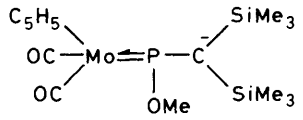
The utility of the approach is illustrated by the facile introduction of deuterium labels and by the preparation of the first thio-substituted complex of this type. The structure of (**5**)‡ (Figure 2) is similar to that of (**2**). We also note that, in contrast with phosphavinyl complexes,[2] proton attachment occurs at carbon rather than phosphorus.

Treatment of (**1**) with an excess of CD_3OD results in reaction at both the Mo=P and P=C bonds. The identity of (**6**) (δ_P 225.2) was established by *X*-ray crystallography (Figure 3).‡ As expected, the addition of two moles of CD_3OD results in considerable increases in both the phosphorus–carbon and phosphorus–molybdenum bond lengths.

Compound (**1**) is also reactive towards nucleophiles. For example, treatment with NaOMe in tetrahydrofuran results in (**7**). We have not yet succeeded in isolating a salt of (**7**) in crystalline form. However, the identity of this anion is clear from n.m.r. spectroscopy; moreover, treatment of (**7**) with MeOH–HCl affords (**3'**), the protio analogue of (**3**).



(**6**)



(**7**) (δ_P - 20.1 p.p.m.)

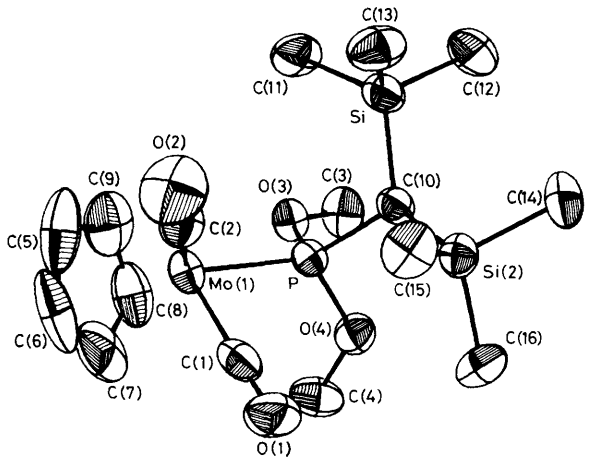


Figure 3. ORTEP view of (**6**) showing the atom numbering scheme. Important parameters: Mo(1)–P 2.387(2), P–C(10) 1.818(7), P–O(3) 1.617(5), P–O(4) 1.627(6) Å; Mo(1)–P–O(3) 106.1(2), Mo(1)–P–O(4) 119.1(2), Mo(1)–P–C(10) 125.2(3)°.

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3 See, for example, L. D. Hutchins, R. T. Paine, and C. F. Campana, *J. Am. Chem. Soc.*, 1980, **102**, 4521; E. Gross, K. Jörg, K. Fiederling, A. Göttlein, W. Malisch, and R. Boese, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 738.