A Nucleophilically Promoted Cyclisation of a Phosphavinylidene

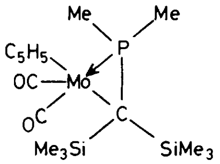
Carl J. Carrano, Alan H. Cowley,* Christine M. Nunn, Marek Pakulski, and Sapé Quashie

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, U.S.A.

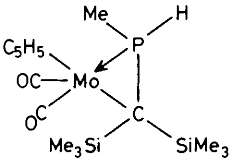
The reaction of the phosphavinylidene $[Mo(CO)_2\{\sigma\text{-}P{=}C(SiMe_3)_2\}(\eta\text{-}C_5H_5)]$ with Me^- or H^-, followed by treatment with MeOH or MeI, affords $[(\eta\text{-}C_5H_5)(CO)_2\overline{MoC(SiMe_3)_2P}R^1R^2]$ (R^1, R^2 = H, Me); the corresponding reaction with MeO^- is more complex.

To date, phosphavinylidenes, $L_nM{\leftharpoondown}P{=}CR_2$,[1,2] constitute the sole examples of stable compounds which feature both a two-co-ordinate phosphorus centre and a double bond to a transition metal.† As such, they are potentially valuable synthetic reagents. With the objective of developing a general synthetic route to terminal phosphido complexes with P–H bonds, the phosphavinylidene $[Mo(CO)_2\{\sigma\text{-}P{=}C(SiMe_3)_2\}(\eta\text{-}C_5H_5)]$ (**1**) was treated with 1 equivalent of $Li[BEt_3H]$ followed by an excess of MeI. However, the expected product, $[Mo(CO)_2\sigma\text{-}P(H)(Me)C(SiMe_3)_2\}(\eta\text{-}C_5H_5)]$, was not formed. A single crystal *X*-ray diffraction study‡ revealed that, somewhat surprisingly, the product was the cyclic derivative (**2**).

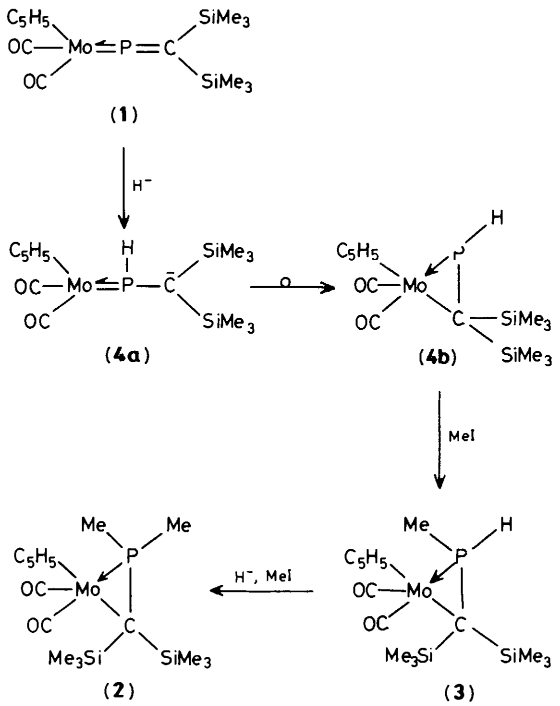
An n.m.r. spectroscopic assay revealed the presence of (**2**) and (**3**) in solution.§ We account for the production of (**2**) and (**3**) by the sequence of reactions summarised in Scheme 1. A key feature of this sequence is the isomerisation of the acyclic anion (**4a**) to the corresponding cyclic species (**4b**). Note also that the initially formed product (**3**) is partially converted into (**2**) owing to the excess of $Li[BEt_3H]$ and MeI in the reaction mixture. The attack on (**1**) by other nucleophiles has also been investigated. In the case of MeO^- attack on (**1**) we postulate that the cyclic (**5a**), and acyclic (**5b**), forms of the resulting anion are in equilibrium (Scheme 2).



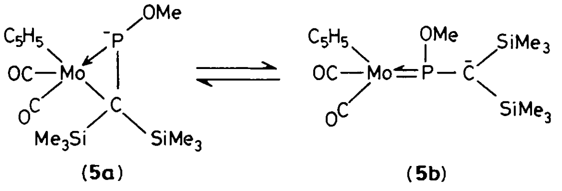
(**2**)



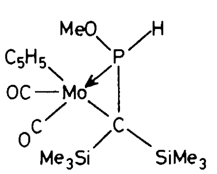
(**3**)



Scheme 1



Scheme 2



(**6**)

Thus treatment of (**5a,b**) with excess of MeOH affords (**6**) as the major product, along with smaller quantities of the known compounds $[Mo(CO)_2(\sigma\text{-}P(OMe)\{CH(SiMe_3)_2\}(\eta\text{-}C_5H_5\}]$ (**7**) and $[Mo(CO)_2(H)(\sigma\text{-}P(OMe)_2\{CH(SiMe_3)_2\}(\eta\text{-}C_5H_5)]$ (**8**).[3] Compounds (**6**) and (**7**) arise from the protonation of (**5a**) and (**5b**) respectively and, as demonstrated

---

† The compound $\overline{Os(P{=}C[O}]CF_3(CO)_2(PPh_3)_2)$ involves a two-co-ordinate phosphorus centre; however, there is also a weak Os–O interaction: D. S. Bohle, C. E. F. Rickard, and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 1985, 1594; For the very recent synthesis of aryl- and alkyl-phosphinylidene metal complexes, see P. B. Hitchcock, M. F. Lappert, and W.-P. Leung, *ibid.*, 1987, 1282.

‡ *Crystal data* for (**2**): $C_{16}H_{29}MoO_2PSi_2$, M = 436.49, monoclinic, $P2_1/c$ (No. 14), a = 14.295(3), b = 9.144(2), c = 15.751(3) Å, β = 92.60(2)°, U = 2056.7 Å^3, Z = 4, D_c = 1.410 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 8.2 cm^{-1}. A total of 3599 unique reflections was measured over the range $3.0 \leqslant 2\theta \leqslant 50.0°$ on an Enraf-Nonius CAD-4 diffractometer at 25 °C. The data were corrected for Lorentz, polarisation, and decay effects. An empirical absorption correction was also applied. The structure was solved (direct methods) and refined (difference Fourier, full-matrix, least-squares) using 2486 reflections with $I > 3.0\sigma(I)$. The final residuals were R = 0.0403 and R_w = 0.0509. 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.

§ ^{31}P n.m.r. (25 °C), chemical shifts in p.p.m. relative to 85% H_3PO_4 (ext.): (**2**)(C_6D_6), 14; (**3**)(C_6D_6), −23; (**6**)(CD_2Cl_2), 42.

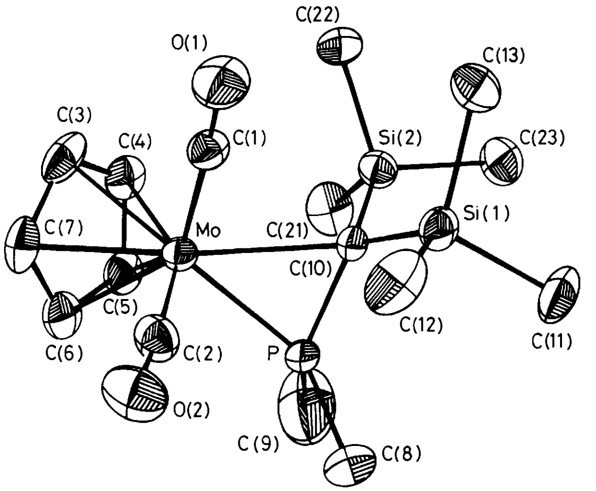


Figure 1. View (ORTEP) of $[(\eta\text{-}C_5H_5)(CO)_2\overline{MoC(SiMe_3)_2P}Me_2]$ (**2**), showing the atom numbering scheme. Important bond lengths (Å) and angles (°) are as follows: Mo–P 2.348(2), Mo–C(10) 2.471(6), P–C(10) 1.740(7), P–Mo–C(10) 42.2(2), Mo–C(10)–P 65.1(2), C(10)–P–Mo 72.7(2).

previously,[3] (**7**) is converted to (**8**) in the presence of excess of MeOH.

Finally we note the structure of (**2**) is similar to that of $[(\eta\text{-}C_5H_5)(CO)_2MoCH_2PPh_2]$.[4]

We thank the U.S. Army Research Office for financial support.

Received, 6th July 1987; Com. 951

References

1 A. H. Cowley, N. C. Norman, and S. Quashie, *J. Am. Chem. Soc.*, 1984, **106**, 5007.

2 D. Gudat, E. Niecke, W. Malisch, U. Hofmockel, S. Quashie, A. H. Cowley, A. M. Arif, B. Krebs, and M. Dartmann, *J. Chem. Soc., Chem. Commun.*, 1985, 1687.

3 A. M. Arif, A. H. Cowley, and S. Quashie, *J. Chem. Soc., Chem. Commun.*, 1986, 1437.

4 E. Lindner, E. V. Küster, W. Hiller, and R. Fawzi, *Chem. Ber.*, 1984, **117**, 127.