

Metallophospha-alkenes: A Simple Access and some Reactivities involving the Phosphorus Atom

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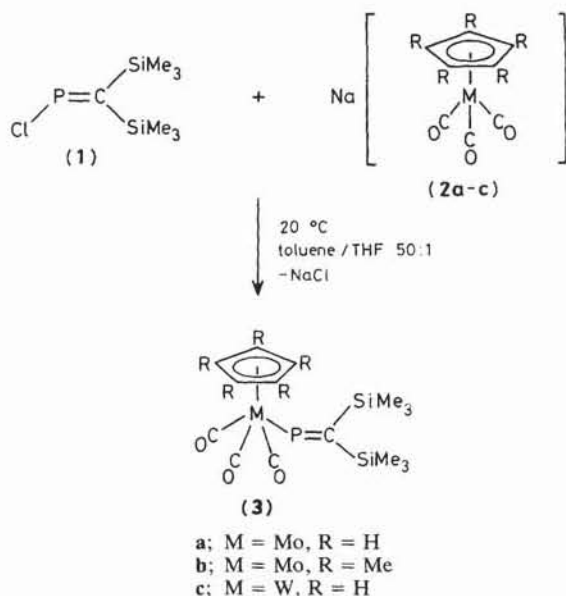
The synthesis and studies on the reactive behaviour of metallophospha-alkenes are reported.

Phospha-alkenes are potential candidates for ambident reactivity, because they possess two energetically high lying, closely spaced molecular orbitals, Π and $n(\text{P})$.¹ A change in reactivity, from 'olefinic' towards 'carbenic' character, has been verified recently for iminophosphanes.² On this basis metallophospha-alkenes are of considerable interest, owing to the electron σ -donating effect of the transition metal ligand

which may destabilize the $n(\text{P})$ orbital and bring the 'carbene' character of the phospha-alkene to the fore.

Here we report the synthesis and studies on the reactivity of metallophospha-alkenes.³ The synthesis has been performed according to the procedure of heterogeneous metallation;⁴ a simple, versatile access to metallophospha-alkenes.

Treatment of chloro-bis(trimethylsilyl)methylenephosphane⁵ (**1**) with sodium carbonylmetallates (**2a-c**) yields the molybdenum and tungsten substituted phospha-alkenes (**3a-c**) (Scheme 1), which are purified by filtration of the reaction mixture, evaporation of the solvent, and recrystallisation of the residue from hexane. Composition and constitution of (**3a-c**) are proved by satisfactory elemental analysis, spectroscopic data,[†] and X-ray structure analysis[‡] in the case of (**3a,c**).



Scheme 1. (**3a**) m.p. 72–74 °C (decomp.), yield 56%; (**3b**) m.p. 74–76 °C (decomp.), yield 76%; (**3c**) m.p. 99–101 °C (decomp.), yield 63%.

[†] (**3a**) ³¹P n.m.r. (C₆D₆): 528.5 p.p.m.; ¹³C n.m.r. (C₆D₆): 213.6 (¹J_{PC} 109.5 Hz, P=C); i.r. (hexane solution): 1996, 1930, 1915 cm⁻¹ (ν_{CO}), 1065 cm⁻¹ (ν_{P=C}). (**3b**) ³¹P n.m.r.: 588.8 p.p.m.; ¹³C n.m.r.: 218.0 (¹J_{PC} 106.9 Hz, P=C); i.r.: 1992, 1924, 1914 cm⁻¹ (ν_{CO}), 1062 cm⁻¹ (ν_{P=C}). (**3c**) ³¹P n.m.r.: 505.2 p.p.m. (¹J_{WP} 5 Hz); ¹³C n.m.r.: 209.8 (¹J_{PC} 106.4 Hz, P=C); i.r.: 1992, 1922, 1910 cm⁻¹ (ν_{CO}), 1068 cm⁻¹ (ν_{P=C}).

[‡] *Crystal Data:* C₁₅H₂₃O₃PSi₂Mo (**3a**) [C₁₅H₂₃O₃PSi₂W (**3c**)], *M* = 434.4 [522.3], monoclinic, space group *P*2₁/*n*, *a* = 8.755(4) [11.640(1)], *b* = 18.607(4) [13.199(2)], *c* = 12.351(5) [13.162(2)] Å, β = 104.89(3) [91.63(1)]°, *U* = 1944 [2021] Å³, *Z* = 4, λ(Mo-K_α) = 0.71069 Å, μ(Mo-K_α) = 8.7 [60.4] cm⁻¹, *D*_c = 1.48 [1.72] g cm⁻³. The structures were solved by direct methods and refined by full-matrix least-squares refinement to a current *R*_w = 0.029 [0.069], based on 3388 [2282] reflections with *F*_o > 2 [3] σ(*F*_o). The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

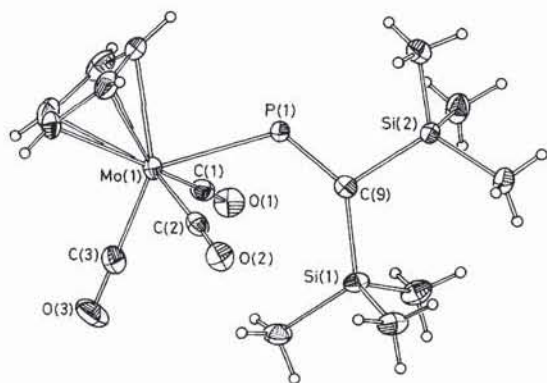


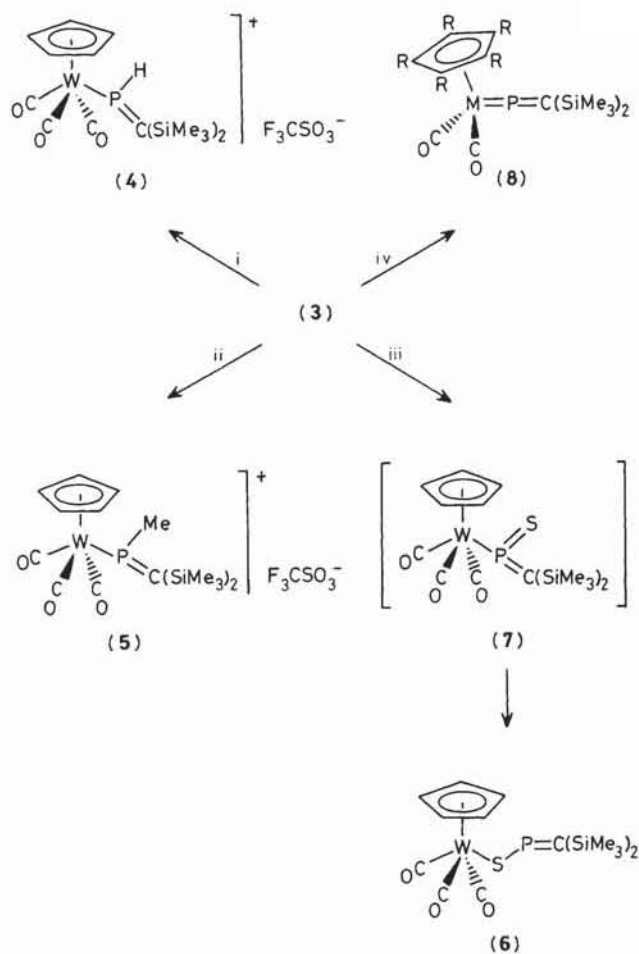
Figure 1. ORTEP view of the structure of (**3a**). Important bond lengths (Å) and angles (°) are [the corresponding values for (**3c**) are given in parentheses]: P(1)–C(9) 1.665(3) [1.66(2)], Mo(1)[W(1)]–P(1) 2.568(1) [2.569(5)], Mo(1)[W(1)]–C(1) 1.980(3) [2.03(2)], Mo(1)[W(1)]–C(2) 1.967(3) [2.02(2)], Mo(1)[W(1)]–C(3) 1.973(3) [2.03(2)]; Mo(1)[W(1)]–P(1)–C(9) 123.45(11) [125.0(6)], P(1)–C(9)–Si(1) 107.4(2) [108.3(9)], P(1)–C(9)–Si(2) 107.4(2) [108.3(9)].

The transition metal ligand causes a significant opening of the M–P–C angle [123 for (**3a**), 125° for (**3c**)] (Figure 1), as compared to metal free phospho-alkenes.⁶ The P–C bond lengths [1.67 for (**3a**), 1.66 Å for (**3c**)] are in accord with the reported values for phospho-alkenes.⁶ The molecules are planar with respect to the MPCSi₂-fragment and reveal the characteristic *E/Z* asymmetry of the P–C–Si angles.⁶ Destabilization of the *n*(P) orbital (as a consequence of the strong electron donating effect of the transition metal ligand) is evidenced by the large bathochromic shift of the *n*– π^* optical transition of the P=C chromophore and the strong deshielding of the ³¹P nucleus in the n.m.r. spectrum.

The transition metal increases the nucleophilicity of the λ^2 -phosphorus atom and enhances its reactivity towards electrophilic reagents, which is in accord with the behaviour of λ^3 -metallophosphanes.³ Reaction of (**3c**) with trifluoromethanesulphonic acid yields the complex (**4**), which exhibits the as yet unknown phospho-alkene, HP=C(SiMe₃)₂, as a ligand. The P–H bond is verified by the ³¹P and ¹H n.m.r. data ($\delta^{31}\text{P}$ 187 p.p.m., $\delta^1\text{H}$ 8.91, J_{HP} 397 Hz). The formation of (**4**) as the product in the reaction of a phospho-alkene with acid is of special interest: (**3c**) confirms the first example in which the regioselectivity (usually observed in the addition of protic substrates to P–C double bonds) is reversed. In the same way, reaction of (**3c**) with trifluoromethanesulphonic acid methyl ester produces (**5**), *via* P-alkylation.

Treatment of (**3c**) with an equivalent amount of sulphur in benzene solution yields the tungsten substituted thiophospho-alkene (**6**). Its constitution is established by the downfield shift of the ³¹P resonance signal (δ 418 p.p.m.) and the low value of the ³¹P–¹⁸³W coupling constant (J 14 Hz). Presumably (**6**) is produced by rearrangement of intermediate (**7**), corresponding to the formation of metallothioxophosphoranes from metallophosphanes under the same conditions.³

On heating (**3a–c**), intramolecular substitution of one carbonyl ligand occurs with formation of the metallophospho-alkenes (**8a–c**). Compound (**8c**) has been described previously as the product in the reaction of K[Mo(CO)₃(C₅H₅)] with (**1**) in tetrahydrofuran (THF).⁷ The conditions required for the extrusion of CO are strongly dependent on the transition metal: (**3a,b**) are transformed in non-polar solvents



Scheme 2. i, CF₃SO₃H in CH₂Cl₂ at –70 °C, then treatment with hexane and filtration; yield 45%, m.p. 94–95 °C (decomp.), ³¹P n.m.r. (CH₂Cl₂): 187 p.p.m. (J_{PW} 201, J_{PH} 397 Hz); ¹H n.m.r. (CD₂Cl₂): 8.91 (P–H); i.r. (Nujol): 2058, 1987, 1960 cm^{–1} (ν_{CO}). ii, CF₃SO₃Me in toluene, 2 h at 30 °C, then filtration; yield 80%, m.p. 89–90 °C (decomp.), ³¹P n.m.r. (CH₂Cl₂): 231 p.p.m. (J_{PW} 198 Hz); ¹H n.m.r. (CD₂Cl₂): 2.77 (J_{PH} 14.8 Hz, P–CH₃); i.r. (Nujol): 2054, 1981, 1940 cm^{–1} (ν_{CO}). iii, S₈ in benzene, 2 h at 5 °C, then evaporating the solvent and washing the residue with hexane; yield 90%, m.p. 51 °C (decomp.); ³¹P n.m.r. (C₆D₆): 417 p.p.m. (J_{PW} 14 Hz); i.r. (hexane solution): 2034, 1960, 1952 cm^{–1} (ν_{CO}). iv, (**8a**) (M = Mo, R = H) and (**8b**) (M = Mo, R = Me): 45 °C in benzene for 6 h, then evaporating the solvent and recrystallizing from hexane. (**8a**): 51%, m.p. 98–103 °C (decomp.), see ref. 7. (**8b**): 48%, m.p. 67–69 °C (decomp.), ³¹P n.m.r. (C₆D₆): 493 p.p.m.; i.r. (hexane solution): 1954, 1891 cm^{–1} (ν_{CO}). (**8c**): reflux in MeCN for 6 h, then evaporation of the solvent and recrystallizing from hexane; yield 43%, m.p. 84–88 °C (decomp.); ³¹P n.m.r. (C₆D₆): 446 p.p.m. (J_{PW} 617 Hz); i.r. (hexane solution): 1952, 1880 cm^{–1} (ν_{CO}).

and slightly above ambient temperatures completely into (**8a,b**) while the formation of (**3c**) requires several hours reflux in acetonitrile. The increase of p-character at the phosphorus atom in (**8a–c**) is in agreement with J_{PW} , 5 in (**3c**) and 617 Hz in (**8c**).⁸ The physical data as well as the studies on the reactivity indicate the 'carbene' character of these metallo-phospho-alkenes.

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References

- 1 W. W. Schoeller and E. Niecke, *J. Chem. Soc., Chem. Commun.*, 1982, 569.
 - 2 E. Niecke, D. Gudat, W. W. Schoeller, and P. Rademacher, *J. Chem. Soc., Chem. Commun.*, 1985, 1050, and cited literature.
 - 3 A. M. Arif, A. H. Cowley, and S. Quashie, *J. Chem. Soc., Chem. Commun.*, 1985, 428; L. Weber, K. Reizig, R. Boese, and M. Polk, *Angew. Chem.*, 1985, **97**, 583.
 - 4 W. Malisch, R. Maisch, I. J. Colquhoun, and W. MacFarlane, *J. Organomet. Chem.*, 1981, **220**, C1.
 - 5 R. Appel and A. Westerhaus, *Tetrahedron Lett.*, 1981, **22**, 2159.
 - 6 R. Appel, F. Kindl, and I. Ruppert, *Angew. Chem.*, 1981, **93**, 771; *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 731; A. H. Cowley, R. A. Jones, J. G. Lasch, N. C. Norman, C. A. Stewart, A. L. Stuart, J. L. Atwood, W. E. Hunter, and H.-M. Zhang, *J. Am. Chem. Soc.*, 1984, **106**, 7015.
 - 7 A. H. Cowley, N. C. Norman, and S. Quashie, *J. Am. Chem. Soc.*, 1984, **106**, 5007.
 - 8 E. Gross, K. Jörg, K. Fiederling, A. Göttlein, W. Malisch, and R. Boese, *Angew. Chem.*, 1984, **96**, 705; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 738.
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