

Reactivity of acryloyl chloride towards the anion $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPhH})]^-$; synthesis of an unusual phosphalkene

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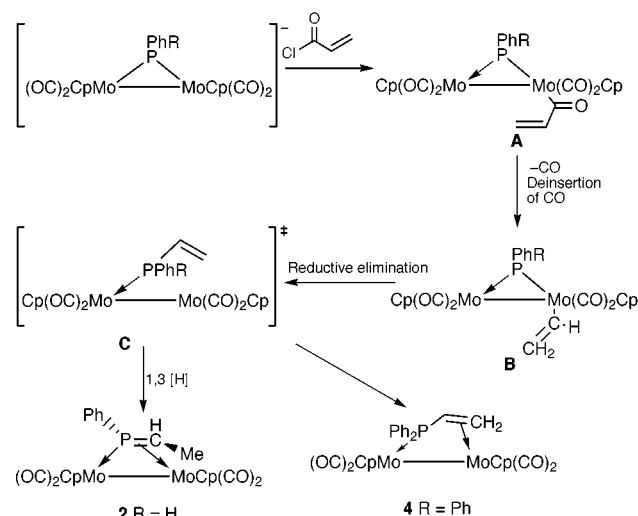
Received (in Basel, Switzerland) 25th September 1999, Accepted 1st November 1999

Deprotonation of the complex $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-H})]$ by Bu^tLi at -78°C and subsequent addition of acryloyl chloride affords the metallophosphaalkene complex $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\eta^1\text{-}\eta^2\text{-PhP=CHMe})]$ in high yield; the complex exhibits *cis/trans* isomerism, both isomers having been crystallographically characterised.

Metallophosphaalkenes have been shown to be important synthons in the preparation of phosphorus-functionalised heterocycles owing to the highly polar P=C moiety present in such complexes.^{1,2} A high yield route to the previously unknown dinuclear Group 6 metallophosphaalkenes is now described.

We have previously demonstrated that the anion obtained from deprotonation of $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-Ph}_2)(\mu\text{-H})]$ with Bu^tLi at -78°C reacts with ECl_3 to give $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-}\eta^2\text{-PE})]$ (E = P, As, Sb)³ and with organometallic halides to give $[\text{Cp}_2(\text{CO})_4\text{Mo}_2\{\mu\text{-P(R)ML}_n\}(\mu\text{-H})]$ [$\text{ML}_n = \text{W}(\text{CO})_3\text{Cp}$, $\text{Fe}(\text{CO})_2\text{Cp}$, $\text{Mn}(\text{CO})_5$].^{4,5} We now report that reaction of $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-H})]$ **1** with Bu^tLi and acryloyl chloride leads to the unusual metallophosphaalkene *trans*- $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\eta^1\text{-}\eta^2\text{-PhP=CHMe})]$ **2** in high (70–80%) yield rather than to the formation of a complex containing an acyl-substituted bridging phosphido group as would have been predicted on the basis of earlier work.⁴ Previously only mononuclear Group 6 metal complexes containing phosphalkenes have been characterised; these involve coordination of the ligand *via* the phosphorus atom only.⁶ To the authors' knowledge there exists only one other group of complexes containing a phosphalkene bonding in an $\eta^1\text{-}\eta^2$ fashion to a bimetallic fragment. These were formed in low yield by the reaction of $[\text{Cp}_2(\text{CO})_2(\mu\text{-CO})\text{Fe}_2(\mu\text{-CSMe})]^+$ with $\text{HP}(\text{SiMe}_3)_2$.⁷

A possible reaction pathway for the formation of *trans*- $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\eta^1\text{-}\eta^2\text{-PhP=CHMe})]$ **2** is shown in Scheme 1. It is proposed that electrophilic attack of the acryloyl chloride on deprotonated **1** to give intermediate **A** is followed by deinsertion



Scheme 1 Possible reaction pathway for formation of **2** and **4**.

of CO to give **B** and reductive elimination to give **C**. A 1,3 hydrogen shift within the bridging ligand then leads to **2**. This reaction sequence is supported by the isolation and structural characterisation of $[\text{Cp}_2(\text{CO})_4(\eta^1\text{-}\eta^2\text{-Ph}_2\text{PCH=CH}_2)]$ **4**, an analogue of intermediate **C**. Complex **4** is obtained by treatment of deprotonated $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPh}_2)(\mu\text{-H})]$ with acryloyl chloride. Presumably the final [1,3] sigmatropic shift which converts intermediate **C** into the metallophosphaalkene **2** is precluded in **4** by the absence in $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPh}_2)]^-$ of a hydrogen atom on the bridging phosphido group. The vinyl phosphine moiety present in **4** acts as an $\eta^1\text{-}\eta^2$ 4-electron ligand; such a mode of coordination has only previously been reported in Fe_3 and Ru_5 clusters as the result of alkyne insertion into a P–M bond.^{8,9}

Thermolysis of the *trans* isomer **2** leads to the formation of *cis*- $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\eta^1\text{-}\eta^2\text{-PhP=CHMe})]$ **3**, in which the methyl group of the phosphalkene now lies *cis* to the PPh group and points towards a cyclopentadienyl ring.† Presumably thermolysis of **2** overcomes the barrier to rotation of the P=CHMe moiety to yield **3** as the thermodynamically favoured product.

The structures of **2** and **3** have been determined by X-ray diffraction analysis, confirming the *trans* and *cis* assignments (Fig. 1). The two molecules exhibit several significant differences.‡

Thus complex **3** shows a significantly shorter Mo–Mo bond length of 3.220(1) Å as compared to 3.240(1) Å in **2** and the P–Mo separations are both significantly shorter in the former

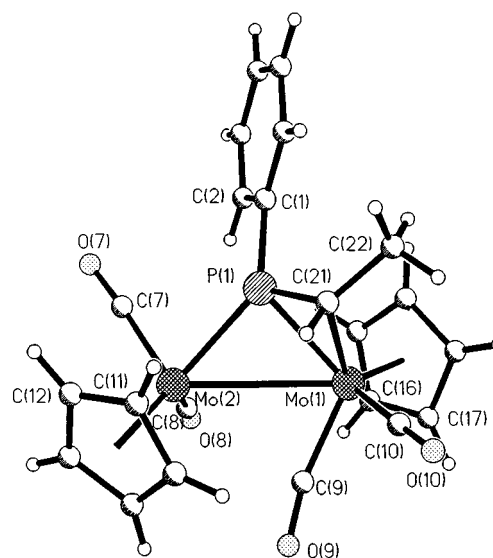


Fig. 1 Molecular structure of **2** and **3**. Selected bond lengths (Å) and angles ($^\circ$): **2**: Mo(1)–Mo(2) 3.240(1), Mo(1)–P(1) 2.435(2), Mo(1)–C(21) 2.382(7), Mo(2)–P(1) 2.346(2), P(1)–C(21) 1.754(7); C(1)–P(1)–C(21) 107.3(4), P(1)–C(21)–C(22) 121.2(6), P(1)–C(21)–Mo(1) 70.3(2), P(1)–C(21)–Mo(2) 121.0(3), P(1)–Mo(1)–Mo(2) 46.19(5), C(21)–Mo(1)–Mo(2) 77.46(5), Mo(1)–C(9)–O(9) 166.6(6). **3**: Mo(1)–Mo(2) 3.220(1), Mo(1)–C(21) 2.392(3), Mo(1)–P(1) 2.418(1), Mo(2)–P(1) 2.334(1), P(1)–C(21) 1.749(3); C(1)–P(1)–C(21) 114.6(2), P(1)–C(21)–C(22) 127.4(3), P(1)–C(21)–Mo(1) 69.5(1), P(1)–Mo(1)–Mo(2) 46.27(2), C(21)–Mo(1)–Mo(2) 74.96(8), Mo(1)–C(9)–O(9) 167.2(3).

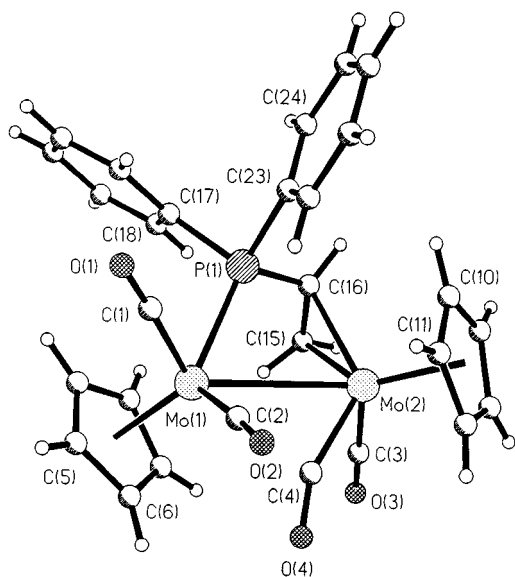


Fig. 2 Molecular structure of **4**. Selected bond lengths (Å) and angles (°): Mo(1)–Mo(2) 3.288(1), Mo(1)–P(1) 2.408(1), Mo(2)–C(16) 2.295(3), Mo(2)–C(15) 2.339(3), C(16)–C(15) 1.409(4); C(23)–P(1)–C(16) 101.9(2), P(1)–C(16)–Mo(2) 97.3(2), C(15)–C(16)–Mo(2) 74.0(2), Mo(1)–Mo(2)–C(16) 74.6(2).

complex (see Figs. 1 and 2). The P(1)–C(21)–C(22) bond angle increases from 121.2(6) to 127.4(3) on conversion of **2** to **3**.

The P=C bond lengths of 1.754(7) and 1.749(3) Å for **2** and **3**, respectively, are significantly shorter than the 1.812(9) Å recorded by Weber *et al.* for their related complex [Cp₂(CO)₂Fe₂{η¹–η²–(Cp(CO)₂Fe)P=CHSMe}].⁷ However, they do fall within the range recorded by Williams *et al.* for their series of cluster-stabilised phosphalkenes.¹⁰ Both **2** and **3** contain a semi-bridging carbonyl group linking to the second molybdenum atom.

The molecular structure of **4** shows a Mo–Mo bond length of 3.288(1) Å, which is slightly longer than that present in **2** and **3** (Fig. 2). The C(15)–C(16) bond length of 1.409(4) Å is typical of that in other complexes containing a η¹–η² vinyl phosphine.^{11,12}

The ¹H NMR spectra of **2** and **3** highlight the different environments of the vinylic proton. In **2** the proton resonates as a doublet of quartets at δ 4.14, whereas the analogous resonance in **3** occurs as a broad peak at δ 1.48; this latter value is in good agreement with that recorded by Weber *et al.* for their compound.⁷

Bimetallic Group 6 metal complexes coordinated to phosphalkenes have not been reported previously, and an η¹–η² bonding mode for a phosphalkene is extremely rare. Additionally, the described method represents the first high yield route to metallophosphalkenes that contain no other heteroatom substituents.

We thank the EPSRC for a quota award to A. D. W. and ICI for a CASE award to A. D. W. EPSRC support for the purchase of the Nonius Kappa CCD diffractometer is also gratefully acknowledged.

Notes and references

† Selected spectroscopic data: [IR (ν_{CO}/cm⁻¹) measured in hexane; ¹H NMR and ³¹P {¹H} NMR spectra were recorded in CDCl₃ solution relative to TMS and 85% H₃PO₄(aq) respectively, with upfield shifts negative; *J* in Hz].

For **2**: ν_{CO} 1955m, 1927.6vs, 1822s, 1851m; NMR: ¹H δ 7.8–7.3 (m, 5H, Ph), 5.24 (s, 5H, Cp), 4.82 (s, 5H, Cp), 4.14 (dq, ²J_{PH} 14.1, ³J_{HH} 7.1, 1H, P=CH), 1.42 (dd, ³J_{PH} 17.82, ³J_{HH} 7.1, 3H, P=CCH₃); ³¹P{¹H}, δ 158.32; ¹³C, δ 242.31 (d, ²J_{PC} 22.96, Mo–CO), 235.32 (d, ²J_{PC} 7.55, Mo–CO), 230.02 (s, Mo–CO), 141.03–128.27 (m, PPh), 92.90 (s, Cp), 91.39 (s, Cp), 42.29 (d, ¹J_{PC} 12.4, P=C), 18.62 (d, ²J_{PC} 7.23, P=CCH₃) FAB MS: *m/z* 572 (M⁺), 544 (M⁺ – CO); C₂₂H₁₉MoO₄P requires C, 46.34; H, 3.36; P 5.43. Found: C, 46.21; H, 3.38; P 5.42%.

For **3**: ν_{CO} 1951m, 1921vs, 1880s, 1847m; NMR: ¹H, δ 7.69–7.45 (m, 5H, Ph), 5.04 (s, 5H, Cp), 5.03 (s, 5H, Cp), 1.80 (dd, ³J_{PH} 13.03, ³J_{HH} 7.04, 3H, P=CCH₃), 1.48 (dq, ²J_{PH} 20.84, ³J_{HH} 7.04, 1H, P=CH); ³¹P{¹H}, δ 164.81; ¹³C, δ 229.71 (Mo–CO), 134.88–128.54 (m, phenyl region), 93.17 (s, Cp), 91.39 (s, Cp), 49.14 (d, ¹J_{PC} 22.82, P=C), 24.05 (d, ²J_{PC} 12.68, P=CCH₃); FAB MS: *m/z* 572 (M⁺), 544 (M⁺ – CO). C₂₂H₁₉MoO₄P requires C, 46.34; H, 3.36; P, 5.43. Found: C, 46.10; H, 3.29; P, 5.42%.

For **4**: ν_{CO} 1938m, 1888vs, 1868s; NMR: ¹H, δ 7.79–7.17 (m, 10H, Ph), 4.75 (s, Cp), 4.72 (s, Cp), 3.32 (ddd, ²J_{PH} 29.2, ³J_{HH} 9.1, ³J_{HH} 2.3, 1H, Ph₂PCH=CH₂), 1.96 (ddd, ³J_{PH} 21.8, ³J_{HH} 12.4, ³J_{HH} 2.3, 1H, *cis*-Ph₂PCH=CH₂), 1.61 (ddd, ³J_{HH} 12.4, ³J_{HH} 9.1, ³J_{PH} 2.1, 1H, *trans*-CH=CH₂); ³¹P{¹H}, δ 35.93; ¹³C, δ 238 (CO), 228 (CO), 137.37–128.10 (m, phenyl groups), 91.71 (s, Cp), 91.16 (s, Cp), 50.84 (d, ²J_{PC} 14.17, Ph₂PC=C), 10.64 (d, ¹J_{PC} 41.70, Ph₂PC=C); FAB MS: *m/z* 650 (M⁺). C₂₈H₂₃Mo₂O₄P requires C, 52.03; H, 3.59; P 4.79. Found: C, 52.29; H, 3.66; P, 4.68%.

‡ Crystal data: Data in common: graphite monochromated Mo-Kα radiation; λ = 0.71069; data collected at 180(2) K using an Oxford Cryostream cooling apparatus. Solution by direct methods (SIR 91)¹³ and subsequent Fourier syntheses, anisotropic full-matrix least-squares refinement on *F*² (SHELXL 93),¹⁴ hydrogen atoms included using a riding model.

2: *trans*-C₂₂H₁₉Mo₂O₄P, *M* = 570.22, red plate, 0.20 × 0.15 × 0.10 mm, monoclinic, space group *P*2₁/*n*, *a* = 8.278(3), *b* = 14.908(6), *c* = 16.694(6) Å, β = 92.97(3)°, *U* = 2057.4(13) Å³, *Z* = 4, *D*_c = 1.841 Mg m⁻³, μ(Mo-Kα) = 1.323 mm⁻¹, *F*(000) = 1128, 5467 reflections measured using ω–2θ method on a Rigaku AFC7R diffractometer, 3631 unique (*R*_{int} = 0.059) used in all calculations. Data collection range 2.69 < θ < 25.03. *R*₁ = 0.0538, *wR*₂ = 0.1540 for 2960 observed reflections [*I* > 2σ(*I*)] and 262 parameters.

3: *cis*-C₂₂H₁₉Mo₂O₄P, *M* = 570.22, red plate, 0.15 × 0.12 × 0.12 mm, orthorhombic, space group *P*2₁2₁2₁, *a* = 9.615(3), *b* = 14.568(4), *c* = 15.191(3) Å, *U* = 2127.8(1) Å³, *Z* = 4, *D*_c = 1.780 Mg m⁻³, μ(Mo-Kα) = 1.279 mm⁻¹, *F*(000) = 1128. 8608 reflections measured on a Nonius Kappa CCD diffractometer, 4896 unique (*R*_{int} = 0.0031). Data collection range 1.94 < θ < 27.48. *R*₁ = 0.025, *wR*₂ = 0.0735 for 4648 observed reflections [*I* > 2σ(*I*)] and 263 parameters.

4: C₂₈H₂₃Mo₂O₄P, *M* = 646.31, red plate, 0.10 × 0.05 × 0.03 mm, triclinic, space group *P*1, *a* = 8.304(1), *b* = 9.978(1), *c* = 16.024(1) Å, α = 94.19(1), β = 102.92(1), γ = 106.26(1)°, *U* = 1229.2(2) Å³, *Z* = 4, *D*_c = 1.746 Mg m⁻³, μ(Mo-Kα) = 1.119 mm⁻¹, *F*(000) = 644, 8421 reflections measured on a Nonius Kappa CCD diffractometer, 5589 unique (*R*_{int} = 0.037). Data collection range 1.32 < θ < 27.46. *R*₁ = 0.0398, *wR*₂ = 0.0732 for 5582 observed reflections [*I* > 2σ(*I*)] and 316 parameters.

CCDC 182/1469. See <http://www.rsc.org/suppdata/cc/1999/2455/> for crystallographic files in .cif format.

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