

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

John E. Davies, Martin J. Mays,\* Paul R. Raithby and Anthony D. Woods

Department of Chemistry, Lensfield Road, Cambridge, UK CB2 1EW. E-mail: mjm14@cus.cam.ac.uk

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Deprotonation of the complex  $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-H})]$  by  $\text{Bu}^t\text{Li}$  at  $-78^\circ\text{C}$  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  $\text{P}=\text{C}$  moiety present in such complexes.<sup>1,2</sup> 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  $\text{Bu}^t\text{Li}$  at  $-78^\circ\text{C}$  reacts with  $\text{ECl}_3$  to give  $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-}\eta^2\text{-PE})]$  ( $\text{E} = \text{P, As, Sb}$ )<sup>3</sup> and with organometallic halides to give  $[\text{Cp}_2(\text{CO})_4\text{Mo}_2\{\mu\text{-P(R)ML}_n\}(\mu\text{-H})]$  [ $\text{ML}_n = \text{W(CO)}_3\text{Cp, Fe(CO)}_2\text{Cp, Mn(CO)}_5$ ].<sup>4,5</sup> We now report that reaction of  $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-H})]$  **1** with  $\text{Bu}^t\text{Li}$  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.<sup>4</sup> Previously only mononuclear Group 6 metal complexes containing phosphaaalkenes have been characterised; these involve coordination of the ligand *via* the phosphorus atom only.<sup>6</sup> To the authors' knowledge there exists only one other group of complexes containing a phosphaaalkene 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  $\text{HP}(\text{SiMe}_3)_2$ .<sup>7</sup>

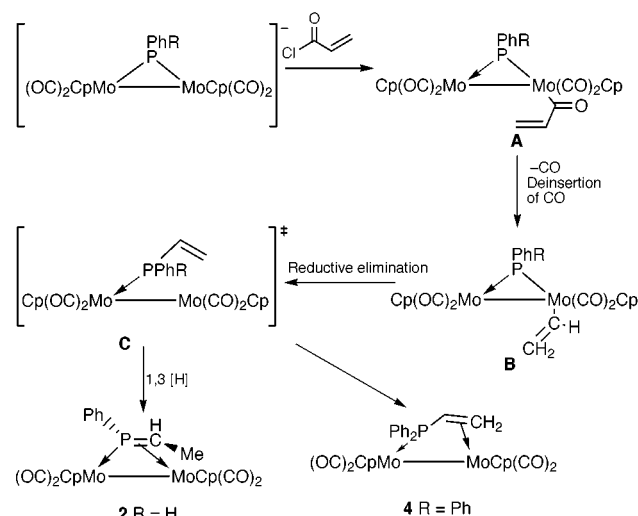
A possible reaction pathway for the formation of *trans*- $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\eta^1\text{-}\eta^2\text{-PhP=CHMe})]$  **2** is shown in Scheme 1. It is proposed that electrophilic attack of the acryloyl chloride on deprotonated **1** to give intermediate **A** is followed by deinsertion

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  $\text{Fe}_3$  and  $\text{Ru}_5$  clusters as the result of alkyne insertion into a  $\text{P-M}$  bond.<sup>8,9</sup>

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 phosphaaalkene now lies *cis* to the PPh group and points towards a cyclopentadienyl ring.<sup>†</sup> Presumably thermolysis of **2** overcomes the barrier to rotation of the  $\text{P}=\text{CHMe}$  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.<sup>‡</sup>

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



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

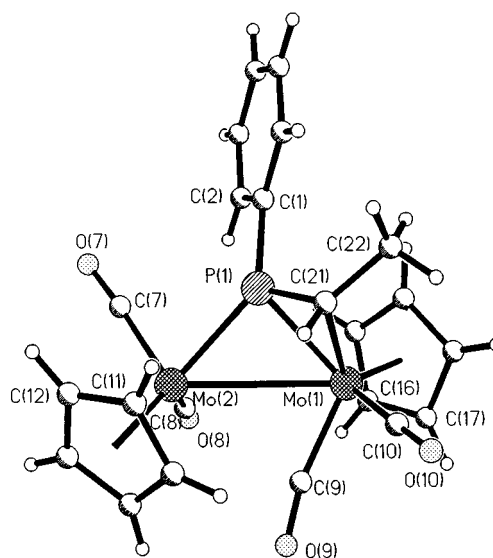
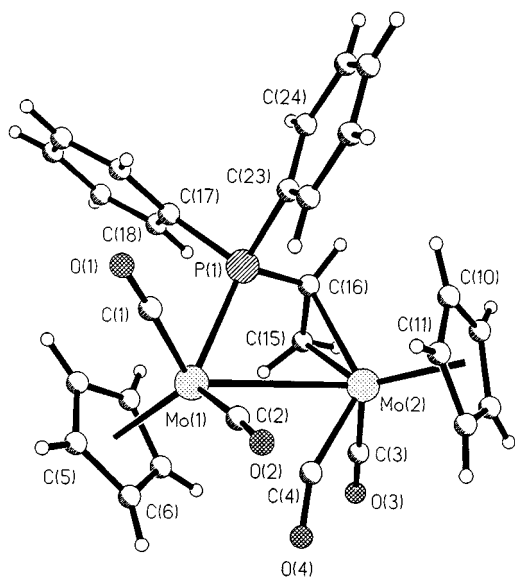


Fig. 1 Molecular structure of **2** and **3**. Selected bond lengths (Å) and angles ( $^\circ$ ): **2**: Mo(1)–Mo(2) 3.240(1), Mo(1)–P(1) 2.435(2), Mo(1)–C(21) 2.382(7), Mo(2)–P(1) 2.346(2), P(1)–C(21) 1.754(7); C(1)–P(1)–C(21) 107.3(4), P(1)–C(21)–C(22) 121.2(6), P(1)–C(21)–Mo(2) 121.0(3), P(1)–Mo(1)–Mo(2) 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 [Cp<sub>2</sub>(CO)<sub>2</sub>Fe<sub>2</sub>{η<sup>1</sup>–η<sup>2</sup>–(Cp(CO)<sub>2</sub>Fe)P=CHSMe}].<sup>7</sup> However, they do fall within the range recorded by Williams *et al.* for their series of cluster-stabilised phosphaaalkenes.<sup>10</sup> 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 η<sup>1</sup>–η<sup>2</sup> vinyl phosphine.<sup>11,12</sup>

The <sup>1</sup>H 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.<sup>7</sup>

Bimetallic Group 6 metal complexes coordinated to phosphaaalkenes have not been reported previously, and an η<sup>1</sup>–η<sup>2</sup> bonding mode for a phosphaaalkene is extremely rare. Additionally, the described method represents the first high yield route to metallophosphaaalkenes that contain no other heteroatom substituents.

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## Notes and references

† Selected spectroscopic data: [IR (ν<sub>CO</sub>/cm<sup>−1</sup>) measured in hexane; <sup>1</sup>H NMR and <sup>31</sup>P {<sup>1</sup>H} NMR spectra were recorded in CDCl<sub>3</sub> solution relative to TMS and 85% H<sub>3</sub>PO<sub>4</sub>(aq) respectively, with upfield shifts negative; *J* in Hz].

For **2**: ν<sub>CO</sub> 1955m, 1927.6vs, 1822s, 1851m; NMR: <sup>1</sup>H δ 7.8–7.3 (m, 5H, Ph), 5.24 (s, 5H, Cp), 4.82 (s, 5H, Cp), 4.14 (dq, <sup>2</sup>J<sub>PH</sub> 14.1, <sup>3</sup>J<sub>HH</sub> 7.1, 1H, P=CH), 1.42 (dd, <sup>3</sup>J<sub>PH</sub> 17.82, <sup>3</sup>J<sub>HH</sub> 7.1, 3H, P=CCH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H}, δ 158.32; <sup>13</sup>C, δ 242.31 (d, <sup>2</sup>J<sub>PC</sub> 22.96, Mo–CO), 235.32 (d, <sup>2</sup>J<sub>PC</sub> 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, <sup>1</sup>J<sub>PC</sub> 12.4, P=C), 18.62 (d, <sup>2</sup>J<sub>PC</sub> 7.23, P=CCH<sub>3</sub>) FAB MS: *m/z* 572 (M<sup>+</sup>), 544 (M<sup>+</sup> – CO); C<sub>22</sub>H<sub>19</sub>MoO<sub>4</sub>P requires C, 46.34; H, 3.36; P 5.43. Found: C, 46.21; H, 3.38; P 5.42%.

For **3**: ν<sub>CO</sub> 1951m, 1921vs, 1880s, 1847m; NMR: <sup>1</sup>H, δ 7.69–7.45 (m, 5H, Ph), 5.04 (s, 5H, Cp), 5.03 (s, 5H, Cp), 1.80 (dd, <sup>3</sup>J<sub>PH</sub> 13.03, <sup>3</sup>J<sub>HH</sub> 7.04, 3H, P=CCH<sub>3</sub>), 1.48 (dq, <sup>2</sup>J<sub>PH</sub> 20.84, <sup>3</sup>J<sub>HH</sub> 7.04, 1H, P=CH); <sup>31</sup>P{<sup>1</sup>H}, δ 164.81; <sup>13</sup>C, δ 229.71 (Mo–CO), 134.88–128.54 (m, phenyl region), 93.17 (s, Cp), 91.39 (s, Cp), 49.14 (d, <sup>1</sup>J<sub>PC</sub> 22.82, P=C), 24.05 (d, <sup>2</sup>J<sub>PC</sub> 12.68, P=CCH<sub>3</sub>); FAB MS: *m/z* 572 (M<sup>+</sup>), 544 (M<sup>+</sup> – CO). C<sub>22</sub>H<sub>19</sub>MoO<sub>4</sub>P requires C, 46.34; H, 3.36; P, 5.43. Found: C, 46.10; H, 3.29; P, 5.42%.

For **4**: ν<sub>CO</sub> 1938m, 1888vs, 1868s; NMR: <sup>1</sup>H, δ 7.79–7.17 (m, 10H, Ph), 4.75 (s, Cp), 4.72 (s, Cp), 3.32 (ddd, <sup>2</sup>J<sub>PH</sub> 29.2, <sup>3</sup>J<sub>HH</sub> 9.1, <sup>3</sup>J<sub>HH</sub> 2.3, 1H, Ph<sub>2</sub>PCH=CH<sub>2</sub>), 1.96 (ddd, <sup>3</sup>J<sub>PH</sub> 21.8, <sup>3</sup>J<sub>HH</sub> 12.4, <sup>3</sup>J<sub>HH</sub> 2.3, 1H, *cis*-Ph<sub>2</sub>PCH=CH<sub>2</sub>), 1.61 (ddd, <sup>3</sup>J<sub>PH</sub> 12.4, <sup>3</sup>J<sub>HH</sub> 9.1, <sup>3</sup>J<sub>PH</sub> 2.1, 1H, *trans*-CH=CH<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H}, δ 35.93; <sup>13</sup>C, δ 238 (CO), 228 (CO), 137.37–128.10 (m, phenyl groups), 91.71 (s, Cp), 91.16 (s, Cp), 50.84 (d, <sup>2</sup>J<sub>PC</sub> 14.17, Ph<sub>2</sub>PC=C), 10.64 (d, <sup>1</sup>J<sub>PC</sub> 41.70, Ph<sub>2</sub>PC=C); FAB MS: *m/z* 650 (M<sup>+</sup>). C<sub>28</sub>H<sub>23</sub>Mo<sub>2</sub>O<sub>4</sub>P 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)<sup>13</sup> and subsequent Fourier syntheses, anisotropic full-matrix least-squares refinement on *F*<sup>2</sup> (SHELXL 93),<sup>14</sup> hydrogen atoms included using a riding model.

**2**: *trans*-C<sub>22</sub>H<sub>19</sub>Mo<sub>2</sub>O<sub>4</sub>P, *M* = 570.22, red plate, 0.20 × 0.15 × 0.10 mm, monoclinic, space group *P*<sub>2</sub><sub>1</sub>/*n*, *a* = 8.278(3), *b* = 14.908(6), *c* = 16.694(6) Å, β = 92.97(3)°, *U* = 2057.4(13) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.841 Mg m<sup>−3</sup>, μ(Mo-Kα) = 1.323 mm<sup>−1</sup>, *F*(000) = 1128, 5467 reflections measured using ω–2θ method on a Rigaku AFC7R diffractometer, 3631 unique (*R*<sub>int</sub> = 0.059) used in all calculations. Data collection range 2.69 < θ < 25.03. *R*<sub>1</sub> = 0.0538, *wR*<sub>2</sub> = 0.1540 for 2960 observed reflections [*I* > 2σ(*I*)] and 262 parameters.

**3**: *cis*-C<sub>22</sub>H<sub>19</sub>Mo<sub>2</sub>O<sub>4</sub>P, *M* = 570.22, red plate, 0.15 × 0.12 × 0.12 mm, orthorhombic, space group *P*<sub>2</sub><sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 9.615(3), *b* = 14.568(4), *c* = 15.191(3) Å, *U* = 2127.8(1) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.780 Mg m<sup>−3</sup>, μ(Mo-Kα) = 1.279 mm<sup>−1</sup>, *F*(000) = 1128. 8608 reflections measured on a Nonius Kappa CCD diffractometer, 4896 unique (*R*<sub>int</sub> = 0.0031). Data collection range 1.94 < θ < 27.48. *R*<sub>1</sub> = 0.025, *wR*<sub>2</sub> = 0.0735 for 4648 observed reflections [*I* > 2σ(*I*)] and 263 parameters.

**4**: C<sub>28</sub>H<sub>23</sub>Mo<sub>2</sub>O<sub>4</sub>P, *M* = 646.31, red plate, 0.10 × 0.05 × 0.03 mm, triclinic, space group *P*<sub>1</sub>, *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) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.746 Mg m<sup>−3</sup>, μ(Mo-Kα) = 1.119 mm<sup>−1</sup>, *F*(000) = 644, 8421 reflections measured on a Nonius Kappa CCD diffractometer, 5589 unique (*R*<sub>int</sub> = 0.037). Data collection range 1.32 < θ < 27.46. *R*<sub>1</sub> = 0.0398, *wR*<sub>2</sub> = 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.

- 1 R. Appel, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, M. Regitz and O. J. Scherer, Thieme, Stuttgart, 1990 and references therein; J. F. Nixon, *Chem. Rev.*, 1988, **88**, 1327.
- 2 L. Weber, O. Kaminski, H.-G. Stammer, B. Neumann and V. D. Romanenko, *Z. Naturforsch., Teil B*, 1993, **48**, 1784.
- 3 J. E. Davies, L. C. Kerr, M. J. Mays, P. R. Raithby, P. K. Tompkin and A. D. Woods, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1428.
- 4 J. E. Davies, M. J. Mays, E. J. Pook, P. R. Raithby and P. K. Tompkin, *J. Chem. Soc., Dalton Trans.*, 1997, 3283.
- 5 P. K. Tompkin, PhD Dissertation, University of Cambridge, 1997.
- 6 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; S. Holand, C. Charrier, F. Mathey, J. Fischer and A. Mitschler, *J. Am. Chem. Soc.*, 1984, **106**, 826; D. Gudat, E. Niecke, B. Krebs and M. Dartmann, *Chimia*, 1985, **39**, 277; L. Weber, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 271.
- 7 L. Weber, I. Schumann, H.-G. Stammer and B. Neumann, *Organometallics*, 1995, **14**, 1626.
- 8 K. Knoll, G. Huttner, L. Zsolani and O. Orami, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1119.
- 9 C. J. Adams, M. I. Bruce, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1996, **506**, 191.
- 10 G. D. Williams, G. L. Geoffrey, R. R. Whittle and A. L. Rheingold, *J. Am. Chem. Soc.*, 1985, **107**, 729.
- 11 J. Luniss, S. A. MacLaughlin, N. J. Taylor, A. J. Carty and E. Sappa, *Organometallics*, 1985, **4**, 2066.
- 12 D. Buchholz, G. Huttner and L. Zsolani, *J. Organomet. Chem.*, 1990, **381**, 97.
- 13 A. Altomare, G. Cascarano, C. Giacavazzo, A. Guagliardi, M. C. Byrle, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.
- 14 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.