Reactivity of CS_2 towards the anion $[Mo_2Cp_2(CO)_3(PPh_2)(\mu\text{-}\eta^2\text{-}P_2)]^-$; synthesis and characterisation of $[Mo_2Cp_2(CO)_3\{\mu\text{-}\eta^3\text{-}Ph_2P\overline{C(H)SP_2S}\}]$, a complex containing an unusual $\overline{CSP_2S}$ ring

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The complex $[Mo_2Cp_2(CO)_3(PPh_2H)(\mu\text{-}\eta^2\text{-}P_2)]$ is deprotonated at −78 °C by Bu^tLi; subsequent addition of an excess of CS_2 affords the novel complex $[Mo_2Cp_2(CO)_3\{\mu\text{-}\eta^3\text{-}Ph_2P\overline{C(H)SP_2S}\}]$ in good to moderate yield.

Although a number of dimetallic complexes containing a P_2 ligand are known, the only reported reaction of this ligand in these complexes is the donation of one or both lone pairs to metal carbonyl fragments.[1] We now report that the reaction of $[Mo_2Cp_2(CO)_3(PPh_2)(\mu\text{-}\eta^2\text{-}P_2)]^-$ (Cp = cyclopentadienyl) with carbon disulfide leads, presumably *via* the formation of a coordinated $Ph_2PCS_2^-$ ligand[2] and an unusual activation of the bridging diphosphorus unit under mild conditions, to a complex containing the novel $\mu\text{-}\eta^3\text{-}Ph_2P\overline{C(H)SP_2S}$ ligand.

Reaction of a toluene solution of $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)]$, synthesised by the method of Scherer *et al.*,[3] with an excess of diphenylphosphine at 110 °C affords the monosubstituted complex $[Mo_2Cp_2(CO)_3(PPh_2H)(\mu\text{-}\eta^2\text{-}P_2)]$ **1** in near quantitative yield.† Complex **1** is readily deprotonated in thf solution at −78 °C by the addition of 1 equiv. of Bu^tLi. Addition of an excess of carbon disulfide to the solution followed by warming to room temperature and filtration through silica then affords the air-stable complex $[Mo_2Cp_2(CO)_3\{\mu\text{-}\eta^3\text{-}Ph_2P\overline{C(H)SP_2S}\}]$ **2** in good to moderate yield, in addition to other uncharacterised trace products.

The structures of **1** and **2** have been determined by X-ray diffraction analysis.‡ The molecular structures are shown in Fig. 1 and 2 respectively, and include selected bond parameters. The P–P and Mo–Mo bonds are both very slightly longer in **1** than in the unsubstituted complex,[3] but the geometry of the Mo_2P_2 core is essentially unchanged. By contrast, in **2** the tetrahedral arrangement of the Mo_2P_2 core is altered considerably, and **2** may be regarded as containing an asymmetrically bridging phosphene unit. This unit acts as a four-electron donor, with a further two electrons being donated from the PPh_2 group. Each molybdenum achieves an eighteen-electron configuration only if an Mo–Mo bond is postulated. The SP_2S fragment is planar and the Mo–Mo bond length is increased from 3.0406(8) Å in **1** to 3.349(2) Å in **2**. The P–P bond length in **2** is similar to the value found by Kirchhoff *et al.*[4] for the analogous bond in the complex $[\{Cp^*(OC)_2FeP_2C(SiMe_3)_3\}Cr(CO)_4]$ (Cp^* = C_5Me_5), and falls between the values found for free phosphenes[5] and typical single P–P bonds. The ^{31}P NMR spectrum† of **2** shows a coupling constant of 1114 Hz between the phosphene phosphorus atoms; this is slightly smaller than the 1181 Hz interaction observed in **1** but substantially larger than the 524 Hz observed in the iron–chromium complex.[4]

The coordinated $\overline{CSP_2S}$ ring system present in **2** has not been synthesised previously or structurally characterised. The synthesis of other new diphosphorus-containing ligands *via* the incorporation of a coordinated P_2 unit is under investigation.

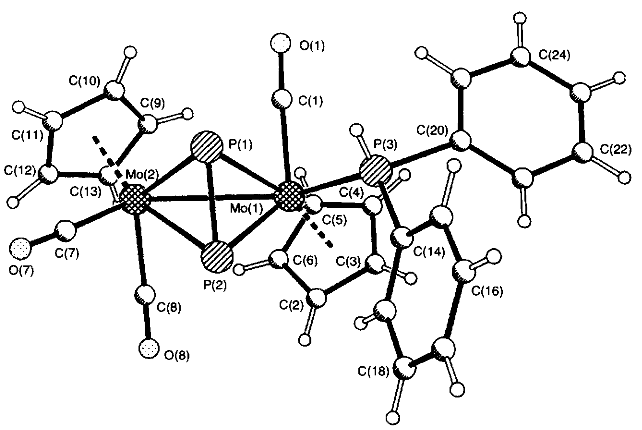

Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and angles (°): Mo(1)–Mo(2) 3.0406(8), Mo(1)–P(1) 2.541(2), Mo(1)–P(2) 2.463(2), Mo(1)–P(3) 2.434(2), Mo(2)—P(1) 2.474(2), Mo(2)–P(2) 2.574(2), P(1)–P(2) 2.085(3); P(1)–Mo(1)–P(2) 49.22(8), P(1)–Mo(2)–P(2) 48.75(8), P(1)–Mo(1)–Mo(2) 51.68(5), P(2)–Mo(1)–Mo(2) 54.55(5), P(3)–Mo(1)–P(1) 79.93(6), P(3)–Mo(1)–Mo(2) 130.43(4), P(3)–Mo(1)–P(2) 87.63(6), P(1)–Mo(2)–Mo(1) 53.69(4), Mo(2)–P(1)–Mo(1) 74.62(6), P(2)–P(1)–Mo(2) 68.12(8), P(1)–P(2)–Mo(2) 63.14(8), P(2)–Mo(2)–Mo(1) 51.21(4), P(2)–P(1)–Mo(1) 63.42(8), P(1)–P(2)–Mo(1) 67.36(7), Mo(1)–P(2)–Mo(2) 74.24(5).

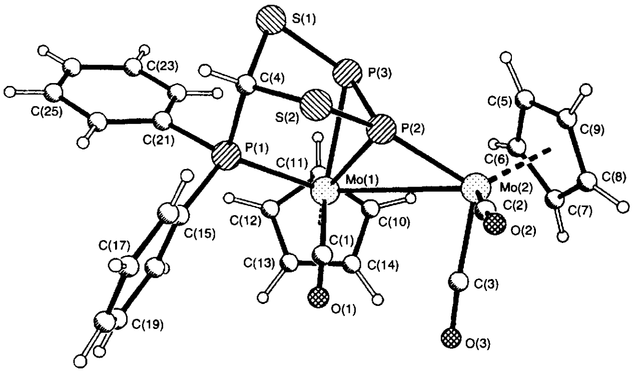

Fig. 2 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Mo(1)–Mo(2) 3.349(2), Mo(1)–P(1) 2.427(2), Mo(1)–P(2) 2.417(2), Mo(1)–P(3) 2.540(2), Mo(2)–P(2) 2.312(2), P(2)–P(3) 2.111(3), P(3)–S(1) 2.156(3), S(1)–C(4) 1.803(9), C(4)–S(2) 1.826(8), S(2)–P(2) 2.121(3), P(1)–C(4) 1.865(8); P(1)–Mo(1)–P(2) 84.31(8), P(2)–Mo(1)–P(3) 50.33(8), P(1)–Mo(1)–P(3) 80.33(8), P(1)–Mo(1)–Mo(2) 125.02, P(2)–Mo(1)–Mo(2) 43.67(6), P(3)–Mo(1)–Mo(2) 77.70(6), P(2)–Mo(2)–Mo(1) 46.21(6), C(4)–P(1)–Mo(1) 107.5(3), P(3)–P(2)–S(2) 105.65(14), P(3)–P(2)–Mo(2) 115.73(11), S(2)–P(2)–Mo(2) 138.18(13), P(3)–P(2)–Mo(1) 67.85(10), S(2)–P(2)–Mo(1) 111.60(11), Mo(2)–P(2)–Mo(1) 90.12(8), P(2)–P(3)–S(1) 97.51(13), P(2)–P(3)–Mo(1) 61.82(8), S(1)–P(3)–Mo(1) 111.32(11), C(4)–S(1)–P(3) 96.2(3), C(4)–S(2)–P(2) 93.2(3), S(1)–C(4)–S(2) 109.8(4), S(1)–C(4)–P(1) 106.8(4), S(2)–C(4)–P(1) 111.8(4).

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Footnotes

† *Selected spectroscopic data*: [IR (ν_{CO}/cm^{-1}) measured in dichloromethane solution; ^{1}H NMR and ^{31}P NMR recorded in CDCl$_3$ solution; ^{31}P chemical shifts recorded relative to P(OMe)$_3$ at δ 0 with upfield shifts negative; *J* in Hz]. For **1**: ν_{CO} 1957s, 1894vs; ^{1}H NMR δ 4.77 [d, $^3J_{HP}$ 2.3, 5 H, *Cp*Mo(CO)PPh$_2$H], 5.07 [s, 5 H, *Cp*Mo(CO)$_2$], 6.59 (d, $^1J_{HP}$ 368, 1 H, PPh$_2$*H*), 7.2–7.6 (m, 10 H, Ph); ^{31}P NMR δ −99.8 (d, $^2J_{PP}$ 113, PPh$_2$H), −170.9 (dd, $^1J_{PP}$ 1181, $^2J_{PP}$ 113, P$_2$), −217.1 (d, $^1J_{PP}$ 1181, P$_2$); ^{13}C NMR δ 83.6 (s, Cp), 85.7 (s, Cp), 128–131 (m, Ph); FAB MS 654 (M$^+$), 598 (M$^+$ − 2CO). For **2**: ν_{CO} 1958vs, 1910m, 1851m; ^{1}H NMR δ 5.16 (s, 5 H, Cp), 5.24 (s, 5 H, Cp), 5.52 (ddd, $^2J_{HP}$ 24, $^3J_{HP}$ 4, 4, HCSP$_2$S), 7.0–7.6 (m, 10 H, Ph); ^{31}P NMR δ 5.8 (s, PPh$_2$), 65.6 (d, $^1J_{PP}$ 1114, HCSP$_2$S), 140.1 (d, $^1J_{PP}$ 1114, HCSP$_2$S); ^{13}C NMR δ 63.9 [d, $^1J_{CP}$ 41, Ph$_2$P*C*(H)SP$_2$S], 86.5 (s, Cp), 89.8 (s, Cp), 127–134 (m, Ph); FAB MS 730 (M$^+$).

‡ *Crystal data*: **1**, $C_{25}H_{21}Mo_2O_3P_3$, *M* = 654.21, monoclinic, space group *Cc*, *a* = 8.801(2), *b* = 19.882(3), *c* = 16.170(2) Å, β = 104.018(14)°, *U* = 2520.6(9) Å^3 (by least-squares refinement on diffractometer angles from 25 centred reflections, 30 < 2θ < 40°), *T* = 293 K, graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, *Z* = 4, D_c = 1.724 Mg m^{-3}, *F*(000) = 1296, dark red block, 0.30 × 0.30 × 0.18 mm, μ(Mo-Kα) = 1.21 mm^{-1}, semi-empirical absorption correction based on ψ scans, relative transmission 0.874–1.000, Rigaku AFC5R diffractometer, ω–2θ scans, data collection range 4.0 < 2θ < 55°, +*h*, +*k*, ±*l*; 3 standard reflections showed no significant variation in intensity. 3713 reflections measured, 3507 unique (R_{int} = 0.064) used in all calculations. Solution by direct methods (SHELXTL PLUS)[6] and subsequent Fourier syntheses, anisotropic full-matrix least-squares refinement on F^2 (SHELXL93),[7] hydrogen atoms included using riding model. Final $wR(F^2)$ 0.213 on all data, conventional *R*(*F*) 0.032 for 3206 observed reflections [$I > 2\sigma(I)$], weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 5.19P]$ where $P = (F_o^2 + 2F_c^2)/3$, 298 parameters and 2 floating origin restraints, g.o.f. = 1.032, maximum Δ/σ = 0.001, maximum Δρ 0.57, minimum −0.82 e Å^{-3}, absolute structure parameter[8] −0.01(6).

2 $C_{26}H_{21}Mo_2O_3P_3S_2{\cdot}0.5CH_2Cl_2$, *M* = 772.80, orthorhombic, space group *Pbca*, *a* = 18.170(8), *b* = 33.064(5), *c* = 10.069(5) Å, *U* = 6049(4) Å^3 (by least-squares refinement on diffractometer angles from 25 centred reflections 30 < 2θ < 40°), *T* = 293 K, graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, *Z* = 8, D_c = 1.697 Mg m^{-3}, *F*(000) = 3064, dark yellow block, 0.20 × 0.15 × 0.10 mm, μ(Mo-Kα) = 1.24 mm^{-1}, semi-empirical absorption correction based on ψ scans, relative transmission 0.957–0.999, Rigaku AFC7R diffractometer, ω scans, data collection range 5.0 < 2θ <55°, +*h*, +*k*, +*l*; 3 standard reflections showed no significant variation in intensity. 6113 reflections measured, 5462 unique (R_{int} = 0.049) used in all calculations. Solution by direct methods (SHELXTL PLUS)[6] and subsequent Fourier syntheses, anisotropic full-matrix least-squares refinement on F^2 (SHELXL93),[7] hydrogen atoms included using riding model. Final $wR(F^2)$ 0.147 on all data, conventional *R*(*F*) 0.056 for 3249 observed reflections [$I > 2\sigma(I)$], weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0596P^2]$ where $P = (F_o^2 + 2F_c^2)/3$, 367 parameters and 20 restraints (to positional and thermal parameters of solvent), g.o.f. = 1.018, maximum Δ/σ = 0.001, maximum Δρ 0.74, minimum −0.58 e Å^{-3}.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/184.

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