

A 2,5-Di-(*tert*-butyl)phospholyl Complex containing a Molybdenum–Molybdenum Triple Bond: Synthesis, Molecular Structure and Coordination Chemistry of $[\text{Mo}_2(\text{PC}_4\text{H}_2\text{Bu}^t)_2(\text{CO})_4]$

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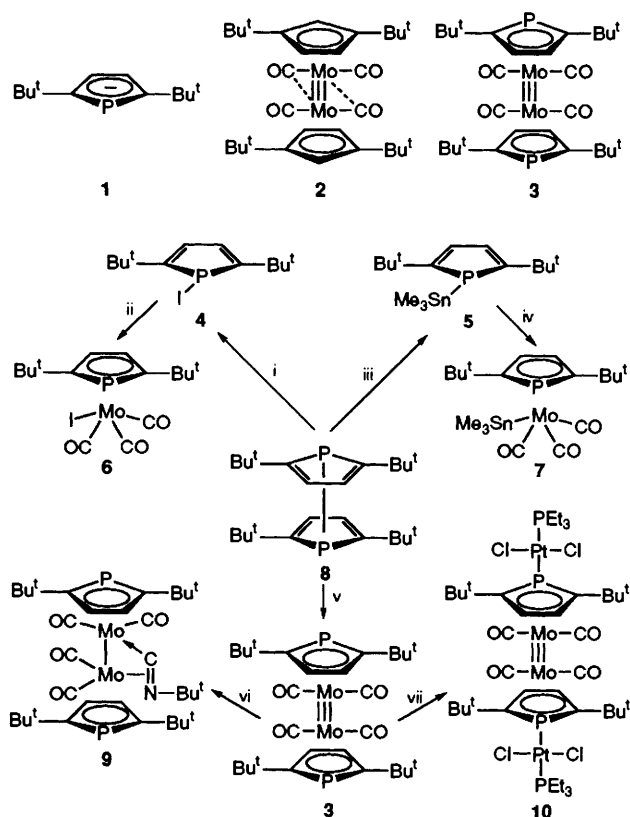
The 2,5-di-(*tert*-butyl)phospholyl ligand may be used to prepare a molybdenum–molybdenum triply bonded tetracarbonyl dimer, whose behaviour resembles that of its cyclopentadienyl analogue.

We recently described the 2,5-di(*tert*-butyl)phospholide anion **1**, which has the electronic properties of a typical phospholide, but steric characteristics which severely limit the ligating properties of the phosphorus lone pair.¹ Therefore, we hoped that it would be useful for the construction of phospholyl complexes which are coordinatively unsaturated. The synthetic² and theoretical³ importance of molybdenum–molybdenum triply bonded dimers, and the existence of the crystallographically characterised complex $[\text{Mo}_2(\text{C}_5\text{H}_3\text{Bu}^t)_2(\text{CO})_4]$ **2**,⁴ meant that the preparation of $[\text{Mo}_2(\text{PC}_4\text{H}_2\text{Bu}^t)_2(\text{CO})_4]$ **3** would be a useful test of this hypothesis.

Molybdenum cyclopentadienyl complexes may be prepared by oxidative addition reactions,⁵ and we first generalised such an approach to the synthesis of phospholyls **6** and **7**, by incorporation of $[\text{Mo}(\text{MeCN})_3(\text{CO})_3]$ into the iodo- and stannyl-phospholes **4** and **5**. No coordination at the phosphorus lone pair was observed⁶ and, therefore, the related oxidative addition of biphosphole **8**¹ to $[\text{Mo}(\text{CO})_3(\text{L})_3]$ ($\text{L}_3 = 3\text{MeCN}$, 1,3,5-cycloheptatriene) was attempted. This led directly to the cherry-red, air stable $[\text{Mo}_2(\text{PC}_4\text{H}_2\text{Bu}^t)_2(\text{CO})_4]$

3,[†] whose molecular structure shows four terminal carbonyl ligands: these may be compared with the two semibridging and two terminal carbonyls found⁴ in **2**. The semibridging carbonyl interaction involves a donation of electron density from the metal to the carbonyl π^* orbitals.³ Thus, the observed configurations are consistent with the lower electron release from the phospholyl ligand than its cyclopentadienyl analogue. However, soft potential surfaces mean that sterical considerations may influence these structures.³

Compound **3** is a very rare example of a heterocyclopentadienyl complex which contains a metal–metal multiple bond, and so its reactivity was studied. The phospholyl lone pairs



Scheme 1 Reagents and conditions: i, 1.0 equiv. I_2 , 10 min, 0 °C, CHCl_3 , 95%; ii, $[\text{Mo}(\text{MeCN})_3(\text{CO})_3]$, 20 °C, 30 min, THF, 65%; iii, Li (excess), THF, 20 °C, 30 min then TMSnCl (2.0 equiv.), THF, 75%; iv, 1.3 equiv. $[\text{Mo}(\text{MeCN})_3(\text{CO})_3]$, 60 °C, 2 h, THF, 50%; v, 1.3 equiv. $[\text{Mo}(\text{MeCN})_3(\text{CO})_3]$, 90 °C, 1 d, THF, 50%; vi, 0.5 equiv. Bu^tNC , 20 °C, 5 min, CHCl_3 , 65%; vii, $[\text{PtCl}_2(\text{PEt}_3)_2]$, 20 °C, 5 min, CHCl_3 , 95%

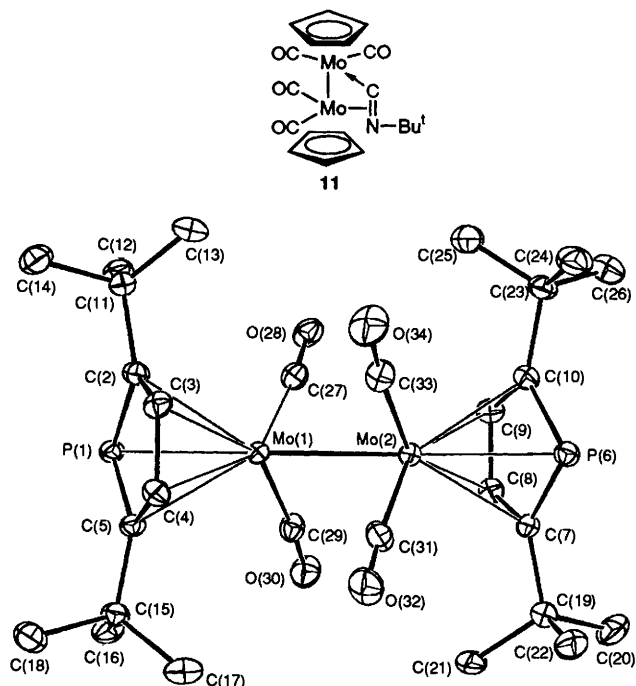


Fig. 1 Molecular structure of $[\text{Mo}_2(\text{PC}_4\text{H}_2\text{Bu}^t)_2(\text{CO})_4]$ **3**, as determined by a single crystal X-ray diffraction study. Selected bond lengths (Å) and angles (°): Mo(1)–Mo(2), 2.5057(4); Mo(1)–P(1), 2.5725(9); Mo(2)–P(6), 2.5741(9); Mo(1)–C(2), 2.394(3); Mo(1)–C(3), 2.354(3); Mo(1)–C(4), 2.346(4); Mo(1)–C(5), 2.399(4); Mo(1)–C(27), 1.963(4); Mo(1)–C(29), 1.945(4); Mo(2)–C(7), 2.403(3); Mo(2)–C(8), 2.357(3); Mo(2)–C(9), 2.347(4); Mo(2)–C(10), 2.391(4); Mo(2)–C(31), 1.967(4); Mo(2)–C(33), 1.954(4); P(1)–C(2), 1.799(4); P(1)–C(5), 1.795(4); P(6)–C(7), 1.793(4); P(6)–C(10), 1.790(4); C(2)–C(3), 1.408(5); C(3)–C(4), 1.425(5); C(4)–C(5), 1.404(5); C(7)–C(8), 1.408(5); C(8)–C(9), 1.425(5); C(9)–C(10), 1.407(5); C(27)–O(28), 1.154(5); C(29)–O(30), 1.166(5); C(31)–O(32), 1.147(5); C(33)–O(34), 1.161(5); Centroid–Mo(1)–Mo(2), 157.99; Centroid–Mo(2)–Mo(1), 155.68; Mo(1)–Mo(2)–C(31), 76.2(1); Mo(1)–Mo(2)–C(33), 75.5(1); Mo(2)–Mo(1)–C(27), 74.6(1); Mo(2)–Mo(1)–C(29), 74.6(1); Mo(1)–C(27)–O(28), 173.6(3); Mo(1)–C(29)–O(30), 174.3(3); Mo(2)–C(31)–O(32), 175.2(3); Mo(1)–C(33)–O(34), 174.0(3); C(2)–P(1)–C(5), 90.3(2); C(7)–P(6)–C(10), 90.4(2); C(27)–Mo(1)–C(29), 85.8(2); C(31)–Mo(2)–C(33), 83.3(2). Nonbonding separations: Mo(1)–C(33), 2.793; Mo(1)–C(35), 2.765; Mo(2)–C(29), 2.734; Mo(2)–C(31), 2.741.

were predictably inert towards iodomethane (80 °C, 4 h, C₇H₈) and the triple bond was equally unreactive towards hex-3-yne, *tert*-butylacetylene and oct-1-yne, presumably for steric reasons. However, *tert*-butylisocyanide gives a deep red bridging isonitrile complex **9**, and [PtCl₂(PEt₃)₂] forms the tetrametallic coordination complex **10**. A comparison of spectroscopic data for these compounds is noteworthy.‡ The ¹³C NMR chemical shifts of **9** strongly resemble their cyclopentadienyl analogue **11**:⁷ additionally, the infrared stretching frequencies in **3** (ν CO 1898, 1868 cm⁻¹) and **10** (ν CO 1910, 1884 cm⁻¹) suggest that the coordination of the phosphorus lone pairs to the platinum fragment has a relatively small effect upon the carbonyl geometries.

Clearly, the chemistry of coordinatively unsaturated phospholyl complexes can be developed by careful choice of the ring substituents. Furthermore, the relatively mild conditions employed for the synthesis of **3** suggest that the applications of phospholyl ligands as promoters of metal-metal multiple bond formation may constitute an area worthy of attention.

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Footnote

† Crystal data for **3**: cherry-red crystals from THF-octane: C₂₈H₄₀Mo₂O₄P₂, M_r = 694.46, monoclinic, P2_{1/n} (no. 14), a = 11.683(1), b = 13.369(1), c = 19.434(2) Å, β = 104.49(1)°, U = 2938.9(9) Å³, Z = 4, D_c = 1.57 g cm⁻³, λ(Mo-Kα) = 0.71073 Å, μ = 9.7 cm⁻¹, F(000) = 1416, T = 123.3(5) K. Final R = 0.036 for 5731 observed reflections, using a CAD-4 and MOLEN programs. Crystal dimensions 0.32 × 0.26 × 0.20 mm, S = 1.06 for 325 variables. (Δ/σ)_{max} = 0.01, (Δρ)_{max} = 0.9(1) Å⁻³ on a final difference map. Atomic coordinates, bond lengths and angles, and thermal parameters

have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ Selected spectroscopic data for: **3** ³¹P NMR (81.0 MHz, CDCl₃) δ -30.3, ¹³C NMR (50.3 MHz, CDCl₃) δ 235.6, 150.4, (¹J_(PC) = 68.4 Hz), 110.1, (²J_(PC) = 5.4 Hz), ¹H NMR (200.1 MHz, CDCl₃) δ 6.06, (³J_(PH) = 3.0 Hz). **4** ³¹P NMR (81.0 MHz, CDCl₃) δ -17.7. **5** ³¹P NMR (81.0 MHz, CDCl₃) δ -62.6, (¹J_(PSn) = 613, 586 Hz). **6** ³¹P NMR (81.0 MHz, CDCl₃) δ 7.2. **7** ³¹P NMR (81.0 MHz, CDCl₃) δ 0.2. **9** ³¹P NMR (81.0 MHz, CDCl₃) δ -8.0, -10.6, ¹³C NMR (50.3 MHz, CDCl₃) δ 246.1, 245.5, 235.5, 234.4, 214.2, 157.3, (¹J_(PC) = 70.3 Hz), 148.1, (¹J_(PC) = 66.6 Hz), 145.4, (¹J_(PC) = 74.0 Hz), 140.7, (¹J_(PC) = 64.9 Hz). **10** ³¹P NMR (81.0 MHz, CDCl₃) δ 18.6, (¹J_(PtP) = 2416 Hz), 18.0, (¹J_(PtP) = 3107, ²J_(PP) = 567 Hz), ¹³C NMR (50.3 MHz, CDCl₃) δ 231.8, 134.7 (¹J_(PC) = 3.4 Hz), 107.1 (²J_(PC) = 6.5 Hz).

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