Synthesis and Molecular Structure of Tris(η^4-2,4-di-*tert*-butyl-1,3-diphosphacyclobutadiene)molybdenum(0)

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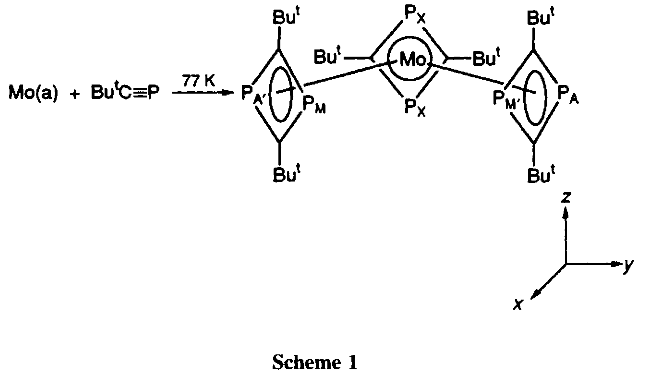
Cocondensation of molybdenum vapour with the phosphaalkyne Bu^{t}CP affords the title compound, whose molecular structure has been determined by single crystal X-ray diffraction.

The first examples of complexes containing η^4-bound 2,4-di-*tert*-butyl-1,3-diphosphacyclobutadiene, *viz.* [M(η-C_5H_5)(η-$P_2C_2Bu^t{}_2$)] (M = Co, Rh), formed *via* the formally forbidden [2 + 2] cyclodimerisation of Bu^{t}CP, were reported almost simultaneously by Nixon *et al.* and Binger, Regitz and coworkers.[1,2] Since these initial reports, ligation of $P_2C_2Bu^t{}_2$ has been observed at other metal centres,[3] and recently Regitz, Binger *et al.* reported the synthesis of the homoleptic complex [Ni(η-$P_2C_2Bu^t{}_2$)$_2$],[4] an analogue of the known compound [Ni(η-C_4Ph_4)$_2$].[5]

The labile, metal vapour synthesis (MVS) generated precursor [Fe(η-C_7H_8)(C_2H_4)$_2$] has been reacted with Bu^{t}CP *in situ* to afford mainly [Fe(η-C_7H_8)(η-$P_2C_2Bu^t{}_2$)], together with other minor products.[6] Herein we report the first direct MVS reaction between metal atoms and Bu^{t}CP, which results in cyclodimerisation of the latter.

Cocondensation of electron-beam generated molybdenum atoms with an excess of Bu^{t}CP at 77 K afforded a product of stoichiometry $MoP_6C_6Bu^t{}_6$ in low (<5%) yield, which mass spectral,† ^{1}H, ^{13}C and ^{31}P NMR‡ data show to be the homoleptic tris(1,3-diphosphacyclobutadiene) complex [Mo(η-$P_2C_2Bu^t{}_2$)$_3$], **1**, see Scheme 1. Complex **1** was obtained as red crystals from toluene at room temperature, after chromatographic work-up on deactivated alumina (4% m/m H_2O) with hexane as eluant.

The single crystal X-ray structure§ of **1** (see Fig. 1) shows the molybdenum atom surrounded by three η^4-ligated $P_2C_2Bu^t{}_2$ rings, one of which is uniquely oriented relative to the molybdenum centre, with each ring exhibiting the usual rhomboid distortions. The average ∠CPC angle of 84° and the average ∠PCP angle of 94° deviate by 2.5 and 4° respectively from previously reported average angles of 81.5 and 98° found in [M(η-C_5H_5)(η-$P_2C_2Bu^t{}_2$)] (M = Co, Rh).[1,2] The C_2P_2 ring defined by P(1)P(2)C(1)C(6) is bound in a unique orientation such that the two phosphorus atoms lie on the *z* axis, whereas the other two C_2P_2 rings have their pairs of phosphorus atoms in the *xy* plane (see Scheme 1 for definition of axes). The Mo–C bond lengths in the unique ring [2.518(4) and 2.535(4) Å] are unusually long, but the other Mo-ring atom bond lengths lie within the expected ranges. The ring P–C bond lengths, with the exception of P(1)–C(1) and P(2)–C(1) which are 0.06 Å longer than expected, fall within the range of previously reported C_2P_2 ring bond lengths. The three diphosphacyclobutadiene rings all deviate from planarity, as shown by the dihedral angles defined by the two ring PCP planes, by 10.66 (for the unique ring), 25.34 and 19.91°. There are also three inter-ring close contacts of note, namely P(3)–C(6) 2.148(4), P(4)–P(5) 2.817(2) and P(6)–C(1) 2.519(5) Å.



Scheme 1

In the ^{13}C and ^{31}P NMR spectra of **1** effects of virtual coupling between P(4) and P(5) are evident, indicating that the close approach of these atoms observed in the solid state structure is retained in solution. The experimental ^{13}C and ^{31}P NMR spectra have been satisfactorily simulated as AMXY and AA'MM'X_2 spin systems, respectively.

All of the above data suggest that the metal coordination sphere is highly congested, and it is this feature which is responsible for the observed deviations from previously reported structural parameters of bound C_2P_2 rings.

[Mo(η-$P_2C_2Bu^t{}_2$)$_3$], **1**, is the first metal complex to contain three η^4-1,3-diphosphacyclobutadiene ligands. To the best of our knowledge **1** is also unique in being a homoleptic cyclobutadiene molybdenum complex, although the somewhat related, homoleptic trisbuta-1,3-diene) molybdenum compound [Mo(η-C_4H_6)$_3$] is known.[7] The direct use of MVS in the development of organometallic compounds derived from phosphaalkynes may have significant potential, and we are currently actively pursuing this approach.

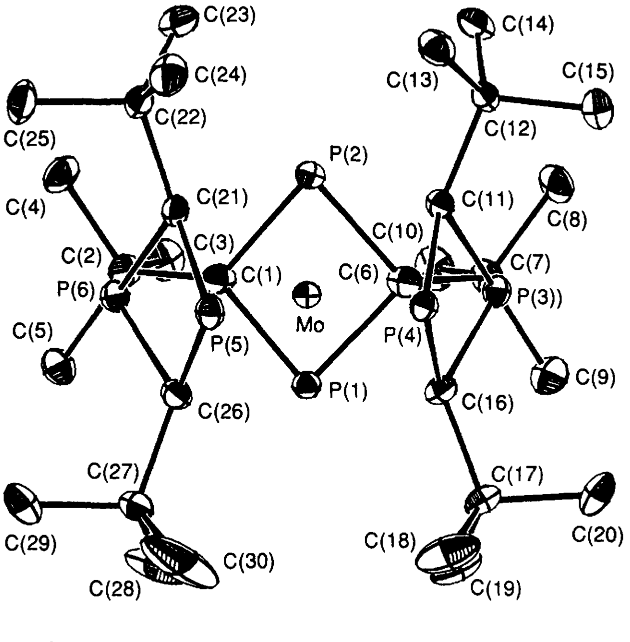


Fig. 1 ORTEP drawing of [Mo(η-$P_2C_2Bu^t{}_2$)$_3$], **1** (thermal ellipsoids at 20%). Selected bond lengths (Å) and angles (°): Mo–P(1) 2.496(1), M–P(2) 2.503(1), Mo–C(1) 2.518(4), Mo–C(6) 2.535(4), Mo–P(3) 2.529(1), Mo–(P) 2.552(1), Mo–C(11) 2.256(4), Mo–C(16) 2.255(4), P(1)–C(1) 1.811(4), P(1)–C(6) 1.860(5), P(4)–C(11) 1.810(4), P(4)–C(16) 1.802(4); C(1)–P(1)–C(6) 83.7(2), P(1)–C(1)–P(2) 97.7(2), C(11)–P(3)–C(16) 83.9(2), P(3)–C(11)–P(4) 93.2(2).

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Footnotes

† $C_{30}H_{54}MoP_6$: MS (EI, 70 eV), *m/z* 698 (M^+, 11%), with the expected isotope pattern.

‡ NMR data: spectra were recorded at probe temperature on a Bruker AMX 500 instrument. Coupling constants are in Hz. For ^1H and ^{13}C δ is relative to internal solvent ([$^2H_8$]toluene), and for ^{31}P is relative to external trimethylphosphite. ^1H: δ 0.94 [36 H, s, $C(CH_3)$], 1.49 [18 H, s, $C(CH_3)$]. $^{13}C\{^1H\}$: δ 76.04 [dt, $^2J_{CP}$ 55.08, 30.15, PCP], 64.79 [m(AMXY), J_{AM} 51.6, J_{AX} 41.4, J_{AY} 0, J_{XY} 8.0, PCP], 41.05 [dt, $^2J_{CP}$ 20.69, 6.73, $C(CH_3)$], 35.49 [m(AMXY), J_{AM} 9.2, J_{AX} 9.2, J_{AY} 0, J_{XY} 8.0, $C(CH_3)$], 35.31 [br s, $C(CH_3)$], 31.44 [dt, $^2J_{CP}$ 13.4, 3.72, $C(CH_3)$]. $^{31}P\{^1H\}$ ($AA'MM'X_2$): δ −163.44 [m, $^2J_{AM}$ 6.09, $^2J_{AMM'}$ 8, $^2J_{AX}$ 17.73, P_A], −79.06 [d, $^2J_{MA}$ 6.09, P_M], −13.18 [t, $^2J_{XA}$ 17.73, P_X].

§ *Crystal data*: $C_{30}H_{54}MoP_6$, M = 696.5, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.759(9)$, $b = 11.012(4)$, $c = 15.329(7)$ Å, $\alpha = 78.32(3)$, $\beta = 74.94(6)$, $\gamma = 87.85(5)°$, $U = 1717.2$ Å^3, $Z = 2$, $D_c = 1.35$ g cm^{-3}, $F(000) = 732$. Monochromated Mo-Kα radiation, $\lambda = 0.71069$ Å, $\mu = 6.7$ cm^{-1}, $T = 293$ K.

Data were collected on an Enraf-Nonius CAD4 diffractometer in the θ–2θ mode with $\Delta\theta = (0.8 + 0.35\tan\theta)°$ and a maximum scan time of 1 min, using a crystal *ca.* 0.4 × 0.3 × 0.3 mm sealed in a capillary under argon. A total of 8265 unique reflections were measured for $2 < \theta < 28°$ and $+h + k \pm l$, and 5808 reflections with $|F^2| > 2\sigma(F^2)$ were used in the refinement where $\sigma(F^2) = [\sigma^2(I + 0.04I)^2]^{1/2}/Lp$ (Lp = Lorentz polarisation). A correction (max 1.18, min 0.82) was applied for absorption using DIFABS[8] after isotropic refinement.

The structure was solved by routine heavy atom methods and non-hydrogen atoms refined anisotropically by full-matrix least-squares. Hydrogen atoms were held fixed at calculated positions with $U_{iso} = 1.3\,U_{eq}$ for the parent carbon atom. With a weighting scheme of $\omega = 1/\sigma^2(F)$ the final residuals were $R = 0.050$ and $R_w = 0.052$ with a ratio of observations to variables of 17.4:1, and S = 1.2. Programs from Enraf-Nonius SDP-Plus package were run on a Micro Vax II computer. 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.

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