Co-condensation of Molybdenum Atoms with the Bulky Tertiary Diphosphine 1,2-Bis(di-isopropylphosphino)ethane: the Molecular Structure of $[MoH_4(Pr^i{}_2PCH_2CH_2PPr^i{}_2)_2]$‡

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Co-condensation of molybdenum atoms with the tertiary diphosphine 1,2-bis(di-isopropylphosphino)ethane affords the stereochemically non-rigid, eight-co-ordinate tetrahydride complex $[MoH_4(Pr^i{}_2PCH_2CH_2PPr^i{}_2)_2]$. The crystal structure has been determined in the orthorhombic space group *Ccca* (no. 68), with cell parameters $a = 18.351(2)$, $b = 20.164(2)$, $c = 9.150(6)$ Å, and $Z = 4$.

Co-ordinatively unsaturated transition-metal compounds are often highly reactive and are important as intermediates in the activation of normally inert systems such as carbon–hydrogen bonds and dinitrogen. Although unsaturated species are readily generated by photochemical and/or thermal activation of 18-electron precursors, their intrinsic reactivity often precludes a direct study of their properties under normal conditions. One strategy which has been employed to lend kinetic stability to such intermediates is the use of sterically demanding pentamethylcyclopentadienyl[1,2] and tertiary phosphine ligands.[3,4] We were interested to see to what extent it would be possible to stabilise a 14-electron compound of the general type $[Mo(R_2PCH_2CH_2PR_2)_2]$ by employing an appropriately bulky diphosphine ligand. The reasons behind the choice of this general class of ligand were two-fold: first, the availability of the precursor $Cl_2PCH_2CH_2PCl_2$ *via* the reaction of ethylene, white phosphorus, and phosphorus trichloride;[5] secondly, metal-vapour synthesis has been shown to be a suitable technique for the preparation of homoleptic tertiary phosphine complexes such as $[Mo(PMe_3)_6]$[6] and $[M(dmpe)_3]$ (M = V, Nb, Ta, Cr, Mo, or W; dmpe = $Me_2PCH_2CH_2PMe_2$).[7] Moreover, examination of models of the ligand $Pr^i{}_2PCH_2CH_2PPr^i{}_2$ suggested that formation of the corresponding compound $[Mo(Pr^i{}_2PCH_2CH_2PPr^i{}_2)_3]$ would be unfavourable due to steric interaction between the bulky alkyl substituents, and that a sterically saturated system would arise with two diphosphine molecules bound to the metal centre. On the basis of these observations it was decided to examine the co-condensation of molybdenum atoms with $Pr^i{}_2PCH_2CH_2PPr^i{}_2$ in the hope that a highly reactive, electronically unsaturated compound of the type $[Mo(Pr^i{}_2PCH_2CH_2PPr^i{}_2)_2]$ or a derivative thereof would be formed.

Results and Discussion

The tertiary diphosphine $Pr^i{}_2PCH_2CH_2PPr^i{}_2$ was prepared as a colourless, pyrophoric liquid by treatment of 1,2-bis(dichlorophosphino)ethane with an excess of isopropylmagnesium chloride in diethyl ether [equation (1)]. It has been

$$Cl_2PCH_2CH_2PCl_2 + 4MgPr^iCl \longrightarrow Pr^i{}_2PCH_2CH_2PPr^i{}_2 + 4MgCl_2 \quad (1)$$

characterised spectroscopically as the free diphosphine and as a ligand in metal complexes.[8,9] Notably, the prochiral nature of the phosphorus centres results in inequivalent isopropyl methyl environments (giving rise to overlapping CH_3 signals centred at δ 0.98 and 1.02 in the ^1H n.m.r. spectrum for the free ligand).

Co-condensation of the ligand with molybdenum vapour at 77 K gave, on work-up, a white crystalline, light petroleum-soluble compound which has been characterised by spectroscopic and crystallographic methods. We were surprised to find strong evidence for metal-bound hydrogens, both in the i.r.

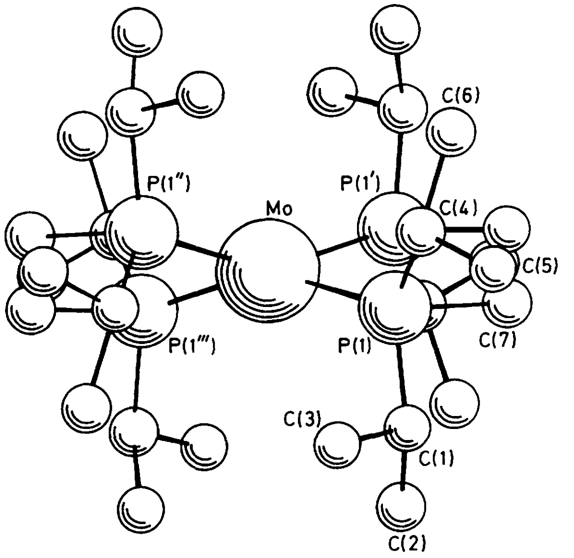

Figure 1. Molecular structure of $[MoH_4(Pr^i{}_2PCH_2CH_2PPr^i{}_2)_2]$. The four hydride hydrogens were not located. The ligand hydrogens are omitted to improve clarity

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‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Bond lengths (Å) and interbond angles (°) with estimated standard deviations (e.s.d.s) in parentheses for $[MoH_4(Pr^i_2PCH_2CH_2PPr^i_2)_2]$

Mo–P(1)	2.441(1)	C(1)–C(3)	1.51(1)
P(1)–C(1)	1.871(6)	C(4)–C(5)	1.54(1)
P(1)–C(4)	1.882(6)	C(4)–C(6)	1.54(1)
P(1)–C(7)	1.864(6)	C(7)–C(7′)	1.54(1)
C(1)–C(2)	1.52(1)		
P(1)–Mo–P(1′)	82.04(7)	P(1)–C(4)–C(5)	115.8(6)
P(1)–Mo–P(1″)	104.18(7)	P(1)–C(4)–C(6)	111.5(5)
Mo–P(1)–C(1)	121.3(3)	C(5)–C(4)–C(6)	108.7(8)
Mo–P(1)–C(4)	120.7(2)	P(1)–C(7)–C(7′)	112.7(3)
Mo–P(1)–C(7)	109.9(2)	C(4)–P(1)–C(1)	100.6(6)
P(1)–C(1)–C(2)	112.6(5)	C(4)–P(1)–C(7)	101.6(6)
P(1)–C(1)–C(3)	112.8(6)	C(1)–P(1)–C(7)	99.4(6)
C(2)–C(1)–C(3)	109.6(8)		

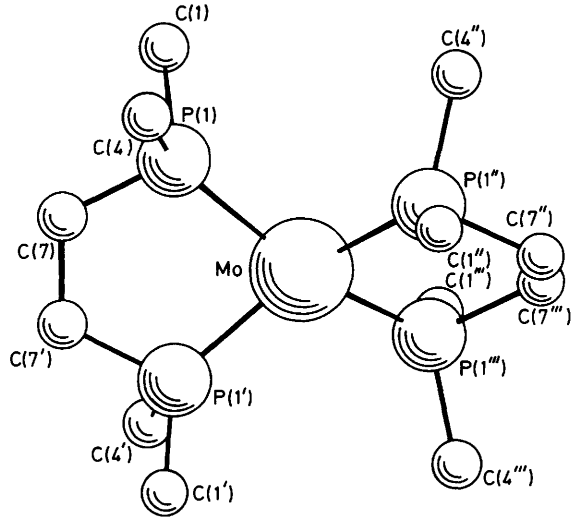

Figure 2. A view of $[MoH_4(Pr^i_2PCH_2CH_2PPr^i_2)_2]$ excluding the isopropyl methyl groups and ligand hydrogen atoms

spectrum [ν(Mo–H) at 1 775 and 1 790 cm^{-1}] and in the high-field region of the ^{1}H n.m.r. spectrum at room temperature. A complex symmetrical signal possessing two sharp outer lines and a broadened central region is observed at δ −6.19. The band shape is consistent with that observed for the family of stereochemically non-rigid eight-co-ordinate molybdenum and tungsten tetrahydride compounds, $[MH_4(PR_3)_4]$ (M = Mo or W).[10–12] Indeed, an analogous temperature dependence of the high-field hydride signal is observed resulting in a high-temperature-limiting binomial quintet at +90 °C thus confirming the presence of four metal-bound phosphorus nuclei. Therefore, these data are consistent with a formulation corresponding to the tetrahydrido complex, $[MoH_4(Pr^i_2PCH_2CH_2PPr^i_2)_2]$. In order to corroborate this assignment a single crystal was grown from light petroleum at −20 °C, and its structure determined by *X*-ray diffraction methods. The molecular structure is shown in Figure 1, and a view omitting the isopropyl methyl substituents is shown in Figure 2. Atomic numbering is included in the Figures, and bond lengths and angles are listed in Table 1.

The molecule possesses a distorted square-planar arrangement of phosphorus atoms around the molybdenum centre with all the Mo–P distances being equal [2.441(1) Å] as required by the crystallographic symmetry. This bond length and the P–Mo–P bite angle of 82.1° lie within the observed range for other diphosphine chelate complexes.[13–18] The exact conformation adopted by the $Pr^i_2PCH_2CH_2PPr^i_2$ ligands and the overall geometry of the molecule appear to be determined by the interaction between the isopropyl substituents. Although the hydride ligands were not located, the co-ordination geometry is presumed to be distorted dodecahedral with the phosphorus atoms occupying pseudo-equatorial **B** sites at displacements of 0.563 Å from a calculated 'best plane' through the MoP_4 substructure. The diphosphine ligands effectively form a protective cage at a distance from the metal centre, while at the same time creating a 'hole.' This can be seen quite well in Figure 1 in which the methyl carbons of the isopropyl substituents are included. Thus, the metal centre is still quite accessible and highly reactive, as shown by the abstraction of four hydrogens from the reaction medium. It is presumed that the hydrogen arises by intermolecular activation of ligand or solvent C–H bonds as the propensity for metal-atom reactions to give products resulting from hydrogen-abstraction reactions is well precedented.[19,20] Attempts to utilise the compound as a precursor to unsaturated species, *e.g.* by thermal or photochemical elimination of dihydrogen, have so far been thwarted due to its quite remarkable stability.

In conclusion, the co-condensation of molybdenum atoms with the sterically demanding diphosphine $Pr^i_2PCH_2CH_2PPr^i_2$ does not afford the homoleptic diphosphine complex $[Mo(Pr^i_2PCH_2CH_2PPr^i_2)_2]$ but rather the tetrahydrido derivative $[MoH_4(Pr^i_2PCH_2CH_2PPr^i_2)_2]$. The latter is believed to arise by multiple hydrogen abstractions from ligand or solvent molecules mediated by a highly reactive intermediate formed in the co-condensation experiment. It is a distinct possibility that the 14-electron fragment $Mo(Pr^i_2PCH_2CH_2PPr^i_2)_2$ may play an important role in these C–H activation processes.

Experimental

All manipulations were carried out on a conventional vacuum line using standard Schlenk techniques or in a dry-box under an atmosphere of dinitrogen. The metal-vapour synthesis apparatus has been described previously.[21] Solvents were dried and purified by prolonged reflux over a suitable drying agent followed by distillation under an atmosphere of dinitrogen. Proton and ^{31}P n.m.r. spectra were recorded on a Bruker WH-300 instrument, i.r. spectra on a Pye-Unicam SP2000 spectrophotometer. Relative intensities are abbreviated as follows: s (strong), m (medium), and w (weak).

Preparation of 1,2-Bis(di-isopropylphosphino)ethane.—A solution of $Cl_2PCH_2CH_2PCl_2$ (40 g, 0.17 mol) in tetrahydrofuran (thf) (200 cm^3) was added dropwise with stirring to isopropylmagnesium chloride (760 cm^3, 1 mol dm^{-3} solution in thf) at room temperature over 2 h. When the addition was complete, the mixture was refluxed for 90 min. The excess of isopropylmagnesium chloride was then destroyed with saturated aqueous ammonium chloride and the product was extracted with light petroleum (b.p. 60—80 °C, 4 × 200 cm^3). The petroleum extracts were combined, dried over anhydrous sodium sulphate, and reduced in volume (to *ca.* 70 cm^3). Distillation gave a major colourless fraction at an oil-bath temperature of 105—107 °C (*ca.* 6.65 × 10^{-2} Pa). Yield 30.4 g, 68%. N.m.r. (C_6D_6): ^{1}H, δ 0.98 [dd, ^2J(P–H) 10.2, ^3J(H–H) 6.9, *6*, 2CH$_3$], 1.02 [dd, ^2J(P–H) 7.2, ^3J(H–H) 6.9, *6*, 2CH$_3$], 1.50 (c, *4*, 2CH$_2$), and 1.57 [dspt, ^2J(P–H) 1.5, ^3J(H–H) 6.9, *4*, 4CH]; ^{31}P-{^{1}H}, δ 6.05 (s).

Co-condensation of Ligand and Molybdenum Atoms.—In a typical experiment, molybdenum (1.22 g, 13 mmol) was evaporated from a molten ingot at a power of 970 W (4.4 kV × 220 mA) and co-condensed (at −197 °C) with an excess

Table 2. Fractional atomic co-ordinates with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Mo	0.0000	0.2500	0.2500
P(1)	0.100 4(1)	0.324 4(1)	0.311 5(2)
C(1)	0.108 2(4)	0.362 4(3)	0.497 4(9)
C(2)	0.103 0(6)	0.311 3(4)	0.619 1(8)
C(3)	0.052 9(5)	0.416 8(4)	0.523 2(11)
C(4)	0.121 8(4)	0.398 2(3)	0.193 1(8)
C(5)	0.178 4(5)	0.446 9(4)	0.254 5(18)
C(6)	0.145 8(6)	0.376 9(5)	0.039 1(10)
C(7)	0.188 4(3)	0.278 2(3)	0.306 5(8)
H(11)	0.152 0(52)	0.378 8(37)	0.504 6(85)
H(21)	0.104 2(33)	0.335 7(32)	0.713 6(77)
H(22)	0.130 9(40)	0.274 2(33)	0.606 2(72)
H(23)	0.056 6(42)	0.289 2(33)	0.615 2(78)
H(31)	0.058 2(39)	0.435 3(32)	0.633 0(82)
H(32)	0.047 0(40)	0.450 3(34)	0.449 7(80)
H(33)	0.012 6(41)	0.401 8(35)	0.533 5(70)
H(41)	0.078 2(41)	0.421 3(32)	0.189 4(66)
H(51)	0.183 8(41)	0.478 7(36)	0.196 9(75)
H(52)	0.159 9(41)	0.477 7(37)	0.360 3(85)
H(53)	0.219 5(38)	0.423 1(30)	0.282 0(74)
H(61)	0.145 3(40)	0.419 2(36)	−0.034 9(71)
H(62)	0.190 4(42)	0.361 4(34)	0.049 1(82)
H(63)	0.115 2(42)	0.341 9(37)	−0.006 4(81)
H(71)	0.226 2(36)	0.301 6(31)	0.290 4(68)
H(72)	0.191 1(32)	0.250 7(46)	0.416 6(71)

of pure ligand (30 cm^3) over a period of 3 h. A red matrix formed. After evaporation was complete, the product was washed from the machine with toluene and immediately filtered through a bed of Celite to remove unreacted metal. The more volatile components were removed under reduced pressure to afford a dark oil which was distilled to allow recovery of the excess of diphosphine. Last traces of $Pr^i_2PCH_2CH_2PPr^i_2$ were removed by sublimation onto a liquid nitrogen-cooled probe leaving a solid residue which was extracted with light petroleum (100 cm^3). Concentration and cooling (at −20 °C) afforded colourless crystals along with a small quantity of brown amorphous material. The product was further purified by sublimation followed by recrystallisation from light petroleum to give an analytically pure sample. Yield 0.45 g {Found: C, 53.5; H, 11.5%; *M/e* 624 [P^+]. $[MoH_4(Pr^i_2PCH_2CH_2PPr^i_2)_2]$ requires C, 53.8; H, 10.9%}. ^1H N.m.r. (C_6D_6): δ 2.03 [c, *4*, 4$(CH_3)_2CH$], 1.77 [c, *4*, 4$(CH_3)_2CH$] [overlapping complex multiplets occur at δ 1.25, 1.17, and 1.14, *56*, CH_3, CH'_3, $-CH_2-$], and −6.19 (c, *4*, 4Mo–H). I.r. (Nujol mull): 1 775m and 1 790m cm^{-1}.

Crystal Structure Determination.—Crystals of $[MoH_4(Pr^i_2PCH_2CH_2PPr^i_2)_2]$ were grown as colourless prisms from light petroleum (b.p. 40—60 °C) at −20 °C. The crystal chosen for study had dimensions 0.3 × 0.25 × 0.1 mm and was sealed in a Lindemann glass capillary under nitrogen. Intensities of 4 273 reflections were measured on an Enraf-Nonius CAD-4F diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). After correction for Lorentz and polarisation effects, 853 independent reflections with $I > 3\sigma(I)$ were used in the structure analysis.

Crystal data. $C_{28}H_{68}MoP_4$, M = 624.68, orthorhombic, space group *Ccca* (no. 68), a = 18.351(2), b = 20.164(2), c = 9.150(6) Å, U = 3 385.83 $Å^3$, Z = 4, D_c = 1.23 g cm^{-3}, μ(Mo-K_α) = 5.84 cm^{-1}.

Structure solution and refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares. All hydrogen atoms were located with the exception of the four metal-bound hydrogens, and their positions refined subject to 'soft' constraints. A 3-term Chebyshev polynomial weighting scheme with coefficients 2.75, 3.39, and 1.91 was adopted for each reflection. The final cycle of refinement gave a R value of 0.037 (R' = 0.039). All calculations were performed on the Oxford University ICL 2980 computer with the CRYSTALS package. Atomic co-ordinates are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

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