Synthesis, *X*-Ray Crystal Structure,† and Reactions of Dihydridopentakis(trimethylphosphine)molybdenum(II): Crystal Structure of the Carbon Dioxide Insertion Product, (Formato-*O*,*O*′)hydridotetrakis-(trimethylphosphine)molybdenum(II)

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The reduction of $MoCl_4(thf)_2$ (thf = tetrahydrofuran) by magnesium, in the presence of trimethylphosphine, in thf produces the dihydride $MoH_2(PMe_3)_5$. This compound reacts with CO_2 to give the formate $MoH(O_2CH)(PMe_3)_4$, with acetic and trifluoroacetic acids to give $MoH(O_2CR)(PMe_3)_4$ (R = Me or CF_3), respectively, and with phenyl isocyanate to give $MoH[PhNC(H)O](PMe_3)_4$. The structures of the dihydride and the formate have been determined by *X*-ray crystallography. Crystals of the dihydride contain two independent molecules, the structures of which are identical within the limits of experimental error and have a pentagonal bipyramidal co-ordination geometry with the hydrides in the equatorial girdle along with three phosphines. In this equatorial group two phosphines are almost '*trans*' to the hydrides and show the longest Mo–P distances 2.460(3)—2.478(3) Å. The unique equatorial Mo–P bond length is 2.403(3), 2.407(3) Å, whilst the axial Mo–P lengths are in the range 2.424(3)—2.428(3) Å. The Mo–H distances lie in the range 1.67(3)—1.76(4) Å. Molecules of the formate are also pentagonal bipyramidal with *mm* (C_{2v}) molecular symmetry. The hydride and symmetrically bidentate formate groups are mutually *trans*. The Mo–P bond lengths show similar differences to those found in the hydride [$Mo-P_{ax}$ 2.426(3), $Mo-P_{eq}$ 2.369(3) Å]. The Mo–H and Mo–O distances are 1.68(3) and 2.318(4) Å, respectively.

We report herein details of the synthesis, reactions, and *X*-ray crystal structure of dihydridopentakis(trimethylphosphine)-molybdenum(II). A preliminary communication of some of this work has already appeared.[1] Compounds of similar stoicheiometry are the phosphite complexes $MH_2[P(OMe)_3]_5$ (M = Cr,[2] Mo,[3] or W [3]), while the tungsten analogue, $WH_2(PMe_3)_5$,[4] is known. The geometries of these compounds, although indicated by n.m.r. spectra, were not determined with certainty.

Results and Discussion

Nuclear magnetic resonance data for new compounds are given in Tables 1 and 2.

Dihydridopentakis(trimethylphosphine)molybdenum(II).—The interaction of $MoCl_4(thf)_2$ in tetrahydrofuran (thf) in the presence of excess trimethylphosphine and magnesium under hydrogen (3 atm) leads to a high yield of the yellow, air-sensitive compound, $MoH_2(PMe_3)_5$, which is very soluble in hydrocarbon solvents, from which it can be precipitated by the addition of acetonitrile.

The ^1H and ^{31}P n.m.r. spectra of $MoH_2(PMe_3)_5$ indicate that the molecule is non-rigid in solution and at temperatures down to 190 K the spin system is A_5X_2, giving rise to a binomial sextet in the hydride region of the ^1H n.m.r. and a binomial triplet in the proton coupled ^{31}P n.m.r.

In the i.r. spectrum of $MoH_2(PMe_3)_5$ bands at 1 945, 1 920, 1 670, and 1 605 cm^{-1} can be assigned to Mo–H; all other bands can be assigned to trimethylphosphine.

The crystal structure of $MoH_2(PMe_3)_5$ contains two crystallographically independent molecules. A diagram of one of these is shown in Figure 1 whilst selected bond lengths and angles of both molecules are given in Table 3. The structures of the two molecules, which have pentagonal bipyramidal geometry, are equal within the limits of experimental error. Angular distortions in the equatorial girdle can be rationalised in terms of steric interactions. The four equatorial $H-Mo-P_{eq}$ angles in each molecule all lie in the range 59(1)—70(1)° whilst the unique $P_{eq}-Mo-P_{eq}$ angles are 98.8(1) and 99.2(1)°. Adoption of this particular angle may be correlated with the orientations of the methyl groups on the two phosphines, which place two methyls approximately in the equatorial plane and facing each other.

It is worth noting that, given suitable PMe_3 orientations, much smaller P–Mo–P angles are possible. Thus, angles between axial and equatorial PMe_3 groups are as low as 88°. Nevertheless, in all PMe_3 groups, the Mo–P–C angles are larger than tetrahedral (117—124°) and the C–P–C angles smaller (94.4—98.9°), indicative of the strong steric crowding in the molecule.

The Mo–P bond lengths show a considerable variation in length. The four axial Mo–P distances are all very similar in the range 2.424(3)—2.428(3) Å. In the equator, the one unique Mo–P bond in each molecule, which lies between the two hydrogens, is much shorter than the other $Mo-P_{eq}$ bonds 2.403(3), 2.407(3) *vs.* 2.460(3)—2.478(3) Å. These differences may be ascribed to a hydrogen *trans* influence, since the long bonds are almost *trans* to the hydrides (H–Mo–P = 157—165°). It is also possible, but perhaps less likely, that this lengthening is due to steric effects.

An n.m.r. study on the phosphite analogue, $CrH_2[P(OMe)_3]_5$,[2] predicted a pentagonal bipyramidal co-ordination geometry, but with the hydrides *cis*.

Reactions of $MoH_2(PMe_3)_5$.—(*a*) *Carbon dioxide*. The interaction of $MoH_2(PMe_3)_5$ in toluene at −78 °C with carbon dioxide (1 atm) gives a high yield of the red formate complex,

† *Supplementary data available* (No. SUP 23840, 47 pp.): structure factors, anisotropic thermal parameters, H-atom co-ordinates, full bond distance and angle data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. unit employed: atm = 101 325 N m^{-2}.

Table 1. Proton and ^{13}C nuclear magnetic resonance data

Compound	Chemical Shift [a] ^{1}H δ/p.p.m.	Multiplicity and coupling constants [b]	Assignment [c]	Chemical Shift [a] ^{13}C δ/p.p.m.	Multiplicity and coupling constants [b]: ^{1}H decoupled	^{1}H coupled	Assignment
$MoH_2(PMe_3)_5$	1.40	s	P–CH_3	25.30	s		P–CH_3
	−5.23	sextet, $J(PH) = 40.41$	Mo–*H*				
$MoH(O_2CH)(PMe_3)_4$	8.05	ttd, $J(PH) = 1.9$	*H*–CO_2	166.6	s	d, $J(CH) = 196.27$	H–CO_2
	1.39	't,' $\lvert{}^2J(PH) + {}^4J(PH)\rvert = 7.62$	P_{eq}–CH_3	27.67	'quintet' [d]		P_{eq}–CH_3
	1.13	s	P_{ax}–CH_3	21.04	't,' $\lvert{}^1J(PC) + {}^3J(PC)\rvert = 12.61$		P_{ax}–CH_3
	−8.66	tt{ $J(P_{ax}H) = 11.08$, $J(P_{eq}H) = 86.27$ }	Mo–*H*				
$MoH(O_2CMe)(PMe_3)_4$	1.86	s	H_3CCO_2	27.88	'quintet' [d]		P_{eq}–CH_3
	1.42	't,' $\lvert{}^2J(PH) + {}^4J(PH)\rvert = 6.46$	P_{eq}–CH_3	21.47	't,' $\lvert{}^1J(PC) + {}^3J(PC)\rvert = 13.75$		P_{ax}–CH_3
	1.16	s	P_{ax}–CH_3	26.67	s		H_3CCO_2
	−8.51	tt{ $J(P_{eq}H) = 87.03$, $J(P_{ax}H) = 11.38$ }	Mo–*H*				
$MoH(O_2CCF_3)(PMe_3)_4$	1.32	't,' $\lvert{}^2J(PH) + {}^4J(PH)\rvert = 7.58$	P_{eq}–CH_3	27.27	'quintet'		P_{eq}–CH_3
	1.03	s	P_{ax}–CH_3	20.98	't,' $\lvert{}^1J(PC) + {}^3J(PC)\rvert = 15.13$		P_{ax}–CH_3
	−8.75	tt{ $J(P_{eq}H) = 85.20$, $J(P_{ax}H) = 10.72$ }	Mo–*H*				
$MoH[PhNC(H)O](PMe_3)_4$				162.53	s	d, $J(CH) = 180.07$	*H*CONPh
	8.21	s	*H*CONPh	150	s	s	Ph, *ipso*
	7.20	t	Ph	128.95		dd{ $^{1}J(CH) = 155.25$, $^{2}J(CH) = 2.3$ }	Ph, *ortho*
	6.94	d	Ph				
	1.43	d, $J(P_{eq}H) = 7.48$	P_{eq}–CH_3	128.80		dt [e]	Ph, *para*
	1.36	d, $J(P_{ax}H) = 6.52$	P_{eq}–CH_3	122.00		dt{ $^{1}J(CH) = 157$, $^{2}J(CH) = 3.21$ }	Ph, *meta*
	1.16	s	P_{ax}–CH_3	31.21	d, $J(PC) = 23.88$		P_{eq}–CH_3
	−8.42	ddt{ $J(P_{eq}H) = 85.04, 89.46$, $J(P_{ax}H) = 19.32$ }	Mo–*H*	27.76	d, $J(PC) = 22.00$		P_{eq}–CH_3
				27.14	't,' $\lvert{}^1J(PC) + {}^3J(PC)\rvert = 13.75$		P_{ax}–CH_3

[a] Referenced to $SiMe_4$ at δ 0.00 p.p.m., in C_6D_6; positive shifts downfield of $SiMe_4$. [b] Coupling constants in Hz. [c] See text for assignment arguments. [d] The quintet pattern observed (intensity ratio 1 : 4 : 6 : 4 : 1) is due to virtual coupling between the two equatorial phosphines and can be simulated with $J(PP) = 24$, $^{1}J(PC) = 22$, and $^{3}J(PC) = 0$ Hz. [e] Partially obscured by C_6D_6.

Table 2. Phosphorus-31 nuclear magnetic resonance data

Compound	Chemical shift [a] ^{31}P δ/p.p.m.	Multiplicity and coupling constants [b,c] ^{1}H decoupled	Assignment
$MoH_2(PMe_3)_5$	3.07	s [d]	Mo–*P*
$MoH(O_2CH)(PMe_3)_4$	40.00	t, $J(P_{ax}P_{eq})$ = 20.47	Mo–P_{eq}
	5.03	t, $J(P_{ax}P_{eq})$ = 20.47	Mo–P_{ax}
$MoH(O_2CMe)(PMe_3)_4$	38.63	t, $J(P_{ax}P_{eq})$ = 20.69	Mo–P_{eq}
	6.15	t, $J(P_{ax}P_{eq})$ = 20.69	Mo–P_{ax}
$MoH(O_2CCF_3)(PMe_3)_4$	41.82	t, $J(P_{ax}P_{eq})$ = 19.94	Mo–P_{eq}
	4.41	t, $J(P_{ax}P_{eq})$ = 19.94	Mo–P_{ax}
MoH[PhNC(H)O]$(PMe_3)_4$	37.60	dt {$J(P_{ax}P_{eq})$ = 23.78; $J(P_{eq}P_{eq})$ = 23.94}	*P*–Mo–O
	26.04	dt {$J(P_{ax}P_{eq})$ = 21.30; $J(P_{eq}P_{eq})$ = 23.94}	*P*–Mo–N
	4.26	t, $J(P_{ax}P_{eq})$ = 23.2	*P*–Mo–P

[a] Referenced to external 85% H_3PO_4 (δ 0.00); measured in C_6D_6, positive chemical shifts downfield of reference. [b] Coupling constants in Hz. [c] P_{ax} = axial phosphines; P_{eq} = equatorial phosphines. [d] ^{1}H coupled spectrum: t, J(PH) = 40.16 Hz.

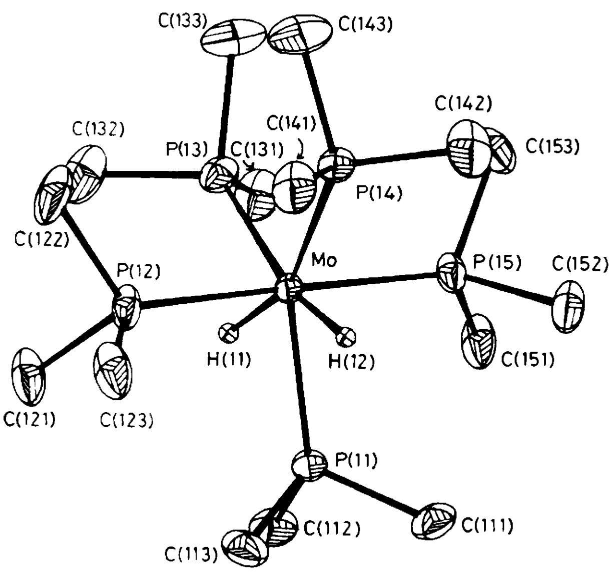


Figure 1. The molecular structure of $MoH_2(PMe_3)_5$

$MoH(O_2CH)(PMe_3)_4$, in what is formally an 'insertion' of the CO_2 molecule into the molybdenum–hydride bond.[5]

The i.r. spectrum of $MoH(O_2CH)(PMe_3)_4$ has a sharp band at 2 800 cm^{-1} that can be assigned to the formate hydrogen, a band at 1 750 cm^{-1} (Mo–H stretch), and carboxylate [6] bands at 1 570 and 1 360 cm^{-1}.

The ^{1}H and ^{31}P n.m.r. spectra (see Tables 1 and 2) indicate an A_2B_2X spin system; this is consistent with the structure determined by *X*-ray diffraction. A diagram of the molecule is shown in Figure 2 and selected bond lengths and angles are given in Table 4. The pentagonal bipyramidal co-ordination geometry is similar to that of $MoH(O_2CCF_3)[P(OMe)_3]_4$ [7] [*cf.* also $MoH(BH_4)(PMe_3)_4$ [8]], with the hydride and bidentate carboxylate group in a mutually *trans* arrangement. In fact, the H–C ··· Mo–H chain is accurately linear and coincides with the two-fold axis at the intersection of the two mirror planes present in the molecule.

In the equatorial girdle the P_{eq}–Mo–H angles of 59° are similar to those in the dihydride pentaphosphine. The O–Mo–O chelate angle is 55.8° whilst the O–Mo–P angle is 93.1°. The main steric interaction appears to be the contacts between the carboxyl oxygens and one methyl group [C(22)] of the equatorial phosphine, which also lies in the equatorial plane (see Figure 2). In this molecule the axial phosphines do not give a closely linear P–Mo–P unit, but are bent towards the carboxylate so that O–Mo–P_{ax} = 84.5° and P_{ax}–Mo–P_{ax} = 167.6°.

Table 3. Selected bond lengths (Å) and angles (°) for $MoH_2(PMe_3)_5$

Mo(1)–H(11)	1.69(4)	Mo(2)–H(21)	1.76(4)
Mo(1)–H(12)	1.67(3)	Mo(2)–H(22)	1.69(4)
Mo(1)–P(11)	2.403(3)	Mo(2)–P(21)	2.407(3)
Mo(1)–P(13)	2.469(3)	Mo(2)–P(23)	2.477(3)
Mo(1)–P(14)	2.478(3)	Mo(2)–P(24)	2.460(3)
Mo(1)–P(12)	2.426(3)	Mo(2)–P(22)	2.428(3)
Mo(1)–P(15)	2.424(3)	Mo(2)–P(25)	2.427(3)
P–C	1.820—1.860(8) (av. 1.841)		

P(11)–Mo(1)–H(11)	70(1)	P(21)–Mo(2)–H(21)	68(1)
P(11)–Mo(1)–H(12)	66(2)	P(21)–Mo(2)–H(22)	70(1)
H(11)–Mo(1)–P(13)	59(1)	H(22)–Mo(2)–P(23)	60(1)
H(12)–Mo(1)–P(14)	66(2)	H(21)–Mo(2)–P(24)	63(1)
P(13)–Mo(1)–P(14)	99.2(1)	P(23)–Mo(2)–P(24)	98.8(1)
P(13)–Mo(1)–H(12)	165(1)	P(23)–Mo(2)–H(21)	162(1)
P(14)–Mo(1)–H(11)	157(1)	P(24)–Mo(2)–H(22)	158(1)
P(12)–Mo(1)–H(11)	84(1)	P(22)–Mo(2)–H(22)	94(1)
P(12)–Mo(1)–H(12)	91(1)	P(22)–Mo(2)–H(21)	89(1)
P(12)–Mo(1)–P(11)	90.9(1)	P(22)–Mo(2)–P(21)	88.2(1)
P(12)–Mo(1)–P(13)	91.8(1)	P(22)–Mo(2)–P(23)	88.1(1)
P(12)–Mo(1)–P(14)	89.8(1)	P(22)–Mo(2)–P(24)	91.4(1)
P(12)–Mo(1)–P(15)	178.9(1)	P(22)–Mo(2)–P(25)	179.1(1)
P(15)–Mo(1)–H(11)	96(1)	P(25)–Mo(2)–H(21)	91(1)
P(15)–Mo(1)–H(12)	89(1)	P(25)–Mo(2)–H(22)	86(1)
P(15)–Mo(1)–P(11)	87.9(1)	P(25)–Mo(2)–P(21)	91.1(1)
P(15)–Mo(1)–P(13)	88.8(1)	P(25)–Mo(2)–P(23)	91.9(1)
P(15)–Mo(1)–P(14)	91.0(1)	P(25)–Mo(2)–P(24)	89.5(1)

The axial and equatorial Mo–P bond lengths are different with Mo–P_{ax} = 2.426(3) Å (very similar to the analogous bond in the dihydride), but with the unique Mo–P_{eq} distance quite short at 2.369(3) Å. Similar distances (and differences) were found for the phosphite complex, $MoH(O_2CCF_3)[P(OMe)_3]_4$.[7]

(*b*) *Acetic and trifluoroacetic acids.* The interaction of acetic or trifluoroacetic acid in diethyl ether with $MoH_2(PMe_3)_5$ gives high yields of the corresponding carboxylate $MoH(O_2CR)(PMe_3)_4$ (R = Me or CF_3).

The ^{1}H and ^{31}P n.m.r. spectra of both compounds indicate an A_2B_2X spin system as in the formate complex.

The i.r. spectra show Mo–H stretching frequencies at 1 725 cm^{-1}, for the acetate, and 1 750 cm^{-1} for the trifluoroacetate,

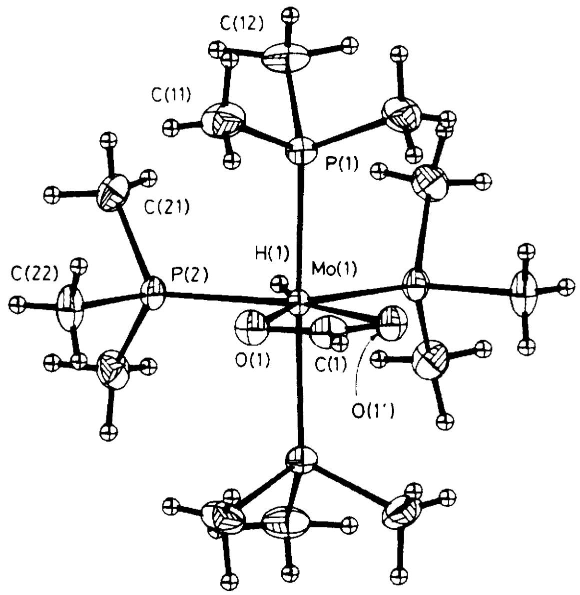


Figure 2. The molecular structure of $MoH(O_2CH)(PMe_3)_4$

Table 4. Selected bond lengths (Å) and angles (°) for $MoH(O_2CH)(PMe_3)_4$

Mo–H(1)	1.68(3)	Mo–O(1)	2.318(4)
Mo–P(1)	2.426(3)	Mo–P(2)	2.369(3)
C(1)–O(1)	1.240(5)	C(1)–H(11)	1.00(3)
P(1)–Mo–H(1)	96.2(1)	P(1)–Mo–O(1)	84.5(1)
H(1)–Mo–P(2)	59.0(1)	P(2)–Mo–O(1)	93.1(1)
O(1)–Mo–O(1')	55.8(2)		

while bands at 1 550 and 1 440 cm^{-1} of the acetate, and 1 620 and 1 420 cm^{-1} of the trifluoroacetate can be assigned to the chelate carboxylate groups.

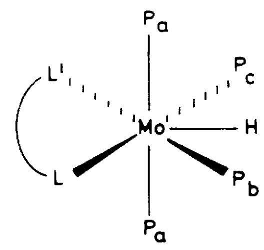
The hydridoacetate is thermally very stable and is unchanged on refluxing in toluene for 24 h. Attempts to alkylate the acetate with $MgMe_2$, LiMe, $LiCH_2SiMe_3$, *etc.*, were unsuccessful.

(*c*) *Phenyl isocyanate.* The interaction of $MoH_2(PMe_3)_5$ in toluene with phenyl isocyanate gives a moderate yield of the red crystalline complex $MoH[PhNC(H)O](PMe_3)_4$ in formally an insertion of the isocyanate into the Mo–H bond. Insertions of RNCO into M–C bonds are established [9] but, to our knowledge, this is the first example of isocyanate insertion into a metal–hydride bond.

The ^1H and ^{31}P n.m.r. spectra (Tables 1 and 2) indicate an A_2BCX spin system which is consistent with the compound having a structure similar to that of the formate complex.

The i.r. spectrum of $MoH[PhNC(H)O](PMe_3)_4$ has a band at 2 790 cm^{-1} that can be assigned to the formamide hydrogen, and a band at 1 755 cm^{-1} that is probably due to Mo–H, although this assignment is made difficult by the bands due to the chelate phenylformamide ligand in the same area.

Nuclear Magnetic Resonance Spectra of Seven-co-ordinate Tetraphosphine Species.—The four seven-co-ordinate tetraphosphine compounds discussed above have essentially the same pentagonal bipyramidal co-ordination geometry as shown in Figure 2 and structure (1). The compounds are stereochemically rigid at room temperature, thus allowing a



(1)

For L–L' = RCO_2 (R = H, Me, or CF_3), $P_c \equiv P_b$ and spin system is A_2B_2X; for L–L' = PhNC(H)O, $P_c \not\equiv P_b$ and spin system is A_2BCX

detailed study of the n.m.r. parameters with respect to co-ordination geometry (Tables 1 and 2).

Heteronuclear double resonance and nuclear Overhauser enhancement (n.O.e.) experiments have been carried out on the formate complex and the results, along with a consideration of the spectra of the PhNC(H)O species have allowed unambiguous assignments of all the resonances in the ^1H and ^{31}P spectra of these compounds.

Selective irradiation of the methyl proton resonance at δ 1.13 p.p.m. gives a measurably greater n.O.e. to the ^{31}P resonance at δ 5.03 p.p.m., thus indicating that the nuclei responsible for these resonances are physically adjacent. If the methyl protons at δ 1.13 p.p.m. are selectively decoupled the ^{31}P resonance at δ 5.03 p.p.m. is split into a well resolved doublet of triplets [$J(P_{ax}P_{eq})$ = 20.53, $J(P_{ax}H)$ = 11.10 Hz], whereas the resonance at δ 40.00 p.p.m. appears as a very broad doublet [$J(P_{eq}H)$ = 85 Hz]. If both the methyl proton resonances are selectively decoupled (leaving only the hydride coupled), both ^{31}P resonances appear as doublets of triplets [the one at δ 40.00 p.p.m. having $J(P_{ax}P_{eq})$ = 20.45 and $J(P_{ax}H)$ = 86.3 Hz].

In the ^{31}P n.m.r. spectrum of the phenylformamide compound, there are two low-field resonances at δ 37.60 and 26.04 p.p.m. and one at higher field, δ 4.26 p.p.m., the former two being doublets of triplets [$J(P_{ax}P_{eq})$ = 23.78 and 21.30 Hz, respectively and $J(P_{eq}P_{eq})$ = 23.94 Hz] and the latter being a triplet [$J(P_{ax}P_{eq})$ = 23.2 Hz]. In the hydride region of the ^1H spectrum a doublet of doublets of triplets is observed. The two doublet coupling constants, due to the equatorial phosphines being the larger (*ca.* 87 Hz), the triplet coupling constant due to the axial phosphines is smaller (19.32 Hz).

As all of the four compounds are isostructural these results lead to the following conclusions. The higher field ^{31}P resonances, due to the axial phosphines, are associated with the higher field phosphine methyl ^1H resonances, and the lower field ^{31}P resonances, due to the equatorial phosphines, are associated with the lower field phosphine methyl ^1H resonances.

It should also be noted that the larger phosphine–hydride coupling constant is due to interaction between the equatorial phosphines and the hydride.

Although these molecules are not octahedral the ^{31}P chemical shifts can be rationalised in terms of the *trans* influence [10] of the ligands most nearly *trans* to the phosphine.

For example, in the carboxylates the phosphines '*trans*' to the oxygen atoms (which have a smaller *trans* influence than phosphine) have a larger co-ordination chemical shift [defined as $\delta(P_{co\text{-}ord}) - \delta(P_{free})$; for PMe_3 $\delta(P_{free}) = -63$ p.p.m.] than the axial phosphines which are '*trans*' to each other. In the case of the phenylformamide compound, the resonance at δ 37.60 is probably due to the equatorial phosphine '*trans*' to the oxygen and the resonance at δ 26.04 p.p.m. due to the equatorial phosphine '*trans*' to the nitrogen atom as nitrogen has a greater *trans* influence than oxygen. The differing '*trans*' influences are also evident in the crystal structure of the formate compound where the axial Mo–P distances are greater than the equatorial Mo–P distances.

Experimental

Microanalyses were by Pascher, Bonn. Spectrometers were as follows: i.r., Perkin-Elmer 683 (spectra in Nujol mulls in cm^{-1}); n.m.r., Bruker WM-250 and JEOL FX 90 Q (data given in p.p.m. relative to $SiMe_4$ and 85% H_3PO_4).

The light petroleum used had the boiling point range 40—60 °C. All operations were carried out under oxygen-free argon using conventional Schlenk-tube techniques. Carbon dioxide was purified by passage first through concentrated sulphuric acid then through a P_2O_5 tube; it was condensed at −100 °C, and thoroughly evacuated to remove oxygen.

1. *Dihydropentakis(trimethylphosphine)molybdenum*(II).—To a suspension of tetrachlorobis(tetrahydrofuran)molybdenum-(IV) [11] (11.5 g, 30 mmol) in tetrahydrofuran (70 cm^3) at −78 °C was added trimethylphosphine (19 cm^3, 190 mmol) and the mixture transferred cold to a pressure bottle containing magnesium turnings (2 g). The bottle was pressurised with hydrogen (3 atm) and the mixture allowed to warm to room temperature. After stirring for *ca.* 18 h, the pressure was released and the yellow-brown reaction mixture transferred to a flask and evaporated. The residue was extracted with light petroleum (3 × 200 cm^3), the solution filtered, and evaporated to give a bright yellow powder, yield 12 g (84%), m.p. 120 °C (decomp.). The compound so obtained is sufficiently pure for use in the subsequent preparations but it can be further purified by recrystallisation from light petroleum from which crystals of *X*-ray quality can be obtained (Found: C, 37.8; H, 9.7; P, 32.4. $C_{15}H_{47}MoP_5$ requires C, 37.7; H, 9.9; P, 32.3%). I.r.: 1 945w, 1 920w, 1 670w, 1 605s, 1 430s, 1 295s, 1 270s, 1 115w, 930s, 850s, 680s, 645s, and 560m cm^{-1}.

2. (*Formato*-O,O′)*hydridotetrakis(trimethylphosphine)molybdenum*(II).—The dihydride (0.5 g, *ca.* 1 mmol) was dissolved in toluene (20 cm^3), cooled to −78 °C, and partially evacuated. Carbon dioxide (1 atm) was introduced to the reaction mixture; the yellow solution darkened slowly to deep red. The red solution was allowed to warm to room temperature under carbon dioxide (1 atm) and then stirred for 30 min, filtered, concentrated, and cooled to −20 °C overnight to afford red crystals; two more crops were obtained from the supernatant. Yield 0.36 g (77.2%), m.p. 120—160 °C (decomp.) (Found: C, 35.2; H, 8.6; P, 27.6. $C_{13}H_{38}MoO_2P_4$ requires C, 35.0; H, 8.6; P, 27.7%). I.r.: 2 800s, 1 750br, 1 570s, 1 420m, 1 360s, 1 315s, 1 290m, 1 275s, 930s, 840m, 790m, 700s, and 650s cm^{-1}.

3. (*Acetato*-O,O′)*hydridotetrakis(trimethylphosphine)molybdenum*(II).—To a solution of the dihydride (0.5 g, *ca.* 1 mmol) in diethyl ether (30 cm^3) at −78 °C was added acetic acid (0.6 cm^3 of a 1.73 mol dm^{-3} solution in diethyl ether). A white precipitate forms immediately, but on warming the mixture to room temperature the solid dissolves with gas evolution to form an orange solution, which after stirring for *ca.* 6 h at room temperature darkens to deep red. This solution was evaporated and the residue extracted into light petroleum. The solution was filtered, concentrated, and cooled to −20 °C to give red crystals. Yield 0.34 g (70.7%), m.p. >350 °C (Found: C, 36.3; H, 8.7; P, 26.4. $C_{14}H_{40}MoO_2P_4$ requires C, 36.5; H, 8.8; P, 26.8%). I.r.: 1 725w, 1 630w, 1 550s, 1 440s, 1 290s, 1 270s, 930s, 845m, 800w, 695s, 660m, and 650s cm^{-1}.

Table 5. Fractional atomic co-ordinates (× 10^4) for $MoH_2(PMe_3)_5$

Atom	*x*	*y*	*z*
Mo(1)	3 125	2 918	7 407
P(11)	4 114(1)	2 986(1)	9 261(1)
C(111)	5 178(3)	3 366(4)	9 074(6)
C(112)	4 002(3)	1 948(3)	9 666(6)
C(113)	4 280(4)	3 711(4)	11 146(4)
P(12)	2 362(1)	3 372(1)	9 231(1)
C(121)	1 991(4)	2 670(4)	10 427(7)
C(122)	1 409(3)	3 460(5)	8 638(9)
C(123)	2 801(5)	4 470(4)	10 684(7)
P(13)	1 916(1)	1 614(1)	5 968(1)
C(131)	2 030(4)	544(3)	5 264(7)
C(132)	1 042(4)	1 162(5)	6 835(9)
C(133)	1 330(4)	1 582(4)	4 291(8)
P(14)	3 025(1)	4 047(1)	6 271(1)
C(141)	3 099(4)	5 122(3)	7 490(6)
C(142)	3 811(4)	4 529(4)	5 261(8)
C(143)	2 139(4)	3 838(4)	4 989(9)
P(15)	3 905(1)	2 463(1)	5 623(1)
C(151)	4 212(3)	1 519(3)	5 627(6)
C(152)	4 905(3)	3 269(4)	5 493(7)
C(153)	3 490(4)	2 066(5)	3 663(5)
Mo(2)	7 922	2 074	1 581
P(21)	6 826(1)	1 800(1)	2 939(1)
C(211)	5 887(3)	1 883(4)	2 287(6)
C(212)	6 397(4)	710(4)	3 241(7)
C(213)	6 934(3)	2 497(4)	4 820(5)
P(22)	6 932(1)	1 284(1)	−638(1)
C(221)	6 174(3)	147(3)	−885(6)
C(222)	6 225(4)	1 767(5)	−1 190(7)
C(223)	7 270(3)	1 035(4)	−2 402(5)
P(23)	8 668(1)	1 122(1)	599(1)
C(231)	8 076(3)	−73(3)	−258(7)
C(232)	9 367(5)	951(5)	1 826(9)
C(233)	9 323(4)	1 311(5)	−792(9)
P(24)	8 590(1)	3 332(1)	637(1)
C(241)	8 998(4)	4 471(3)	1 945(7)
C(242)	8 001(5)	3 579(4)	−686(7)
C(243)	9 479(5)	3 419(5)	−253(13)
P(25)	8 897(1)	2 845(1)	3 817(1)
C(251)	9 988(3)	3 313(5)	3 753(10)
C(252)	8 881(4)	3 869(4)	5 158(8)
C(253)	8 930(5)	2 213(5)	5 106(7)

4. *Hydrido(trifluoroacetato*-O,O′)*tetrakis(trimethylphosphine)molybdenum*(II).—To a solution of the dihydride (0.5 g, *ca.* 1 mmol) in diethyl ether (30 cm^3) at −78 °C was added trifluoroacetic acid (0.9 cm^3 of 1.16 mol dm^{-3} solution in diethyl ether). As for the acetate, a white precipitate forms immediately and on warming this slowly redissolves with evolution of gas to give a deep red solution after stirring overnight. Work-up as for the acetate gives red crystals. Yield 0.38 g (73.9%), m.p. 174—178 °C (decomp.) (Found: C, 32.7; H, 7.2; P, 23.2. $C_{14}H_{37}F_3MoO_2P_4$ requires C, 32.7; H, 7.2; P, 24.1%). I.r.: 1 750m, 1 700m, 1 620s, 1 420s, 1 290s, 1 275s, 1 200s, 1 145s, 930s, 850s, 800w, 780m, 730s, 700s, 690s, and 650s cm^{-1}.

5. *Hydrido(phenylformamido*-O,N)*tetrakis(trimethylphosphine)molybdenum*(II).—The dihydride (0.5 g, *ca.* 1 mmol) in toluene (20 cm^3) was cooled to −78 °C, and phenyl isocyanate (0.25 cm^3, *ca.* 2.3 mmol) added; the reaction mixture slowly turned deep red. The solution was allowed to warm to room temperature and then stirred for a further 30 min. Removal of solvent left a red oil which was evacuated overnight. The re-

Table 6. Fractional atomic co-ordinates for $MoH(O_2CH)(PMe_3)_4$

Atom	*x*	*y*	*z*
Mo(1)	0	2 462	2 500
P(1)	0	2 672(1)	4 242(1)
C(11)	1 065(3)	3 448(4)	4 736(3)
C(12)	0	1 590(4)	5 138(4)
P(2)	1 550(1)	1 481(1)	2 500
C(21)	1 874(3)	571(3)	1 507(3)
C(22)	2 686(3)	2 342(4)	2 500
C(1)	0	4 589(4)	2 500
O(1)	828(2)	4 107(2)	2 500

sulting dark red powder was extracted with diethyl ether (3 × 50 cm^3), the solution filtered, concentrated, and cooled to give red crystals. Yield 0.32 g (61.4%), m.p. 110—120 °C (decomp.) (Found: C, 44.0; H, 8.0; N, 3.0; P, 22.2. $C_{12}H_{43}MoNOP_4$ requires C, 43.8; H, 8.3; N, 2.7; P, 23.8%). I.r.: 2 790w, 1 850w, 1 820w, 1 780w, 1 755m, 1 600w, 1 580w, 1 535w, 1 490s, 1 430w, 1 420w, 1 320w, 1 290s, 1 275s, 1 270s, 1 260s, 1 215s, 1 170s, 1 070w, 1 020w, 1 000w, 970m, 960m, 930s, 890m, 845s, 760s, 695s, 680m, 645s, 530w, and 510w cm^{-1}.

X-Ray Crystallographic Studies.—Crystals of both compounds were sealed under argon in Lindemann capillaries. After preliminary photographic examination, unit-cell parameters were determined and intensity data recorded at 295 K using a Nonius CAD4 diffractometer and graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) in a manner previously described in detail.[12] For the intensity recording, the $\omega/2\theta$ scan mode was used with the ω scan width set by the expression $\omega = 0.8 + 0.35 \tan\theta$, and a variable scan speed of 1.35—6.77° min^{-1}.

The structures were solved and refined *via* routine procedures using previously noted programs, computers, and scattering factor data. Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms (which were experimentally located and freely refined in both structures) with individual isotropic parameters. Both sets of data were corrected for absorption.

Crystal data. $MoH_2(PMe_3)_5$. $C_{15}H_{47}MoP_5$, M = 478.32, triclinic, a = 18.020(3), b = 16.767(7), c = 9.650(2) Å, α = 105.29(2), β = 93.25(1), γ = 110.97(2)°, U = 2 589 Å^3, space group $P\bar{1}$, Z = 4, D_c = 1.23 g cm^{-3}, μ(Mo-K_α) = 7.30 cm^{-1}. Data recorded over $1.5 \leqslant \theta \leqslant 25°$, giving 6 318 unique and 5 268 observed [$I > 7.5\sigma(I)$] reflections; R = 0.0247, R' = 0.0242; 378 parameters and least-squares weights = $1/[\sigma^2(F_0) + 0.0005(F_0)^2]$.

$MoH(O_2CH)(PMe_3)_4$. $C_{13}H_{38}MoO_2P_4$, M = 414.25, orthorhombic, a = 13.096(4), b = 12.455(3), c = 13.845(3) Å, U = 2 258 Å^3, space group *Cmcm*, Z = 4 (molecule has *mm* symmetry), D_c = 1.21 g cm^{-3}, μ(Mo-K_α) = 7.77 cm^{-1}. Data recorded over $1.5 \leqslant \theta \leqslant 25$, giving 1 090 unique and 922 observed [$I > 1.5\sigma(I)$] reflections; R = 0.0275, R' = 0.0255; 99 parameters, $w = 1/[\sigma^2(F_0) + 0.0002(F_0)^2]$.

Final atomic fractional co-ordinates are given in Table 5 for the dihydride and Table 6 for the formate.

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