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THE INFLUENCE OF THE STERIC PROPERTIES OF THE LIGANDS PR_2Ph AND L ON THE FORMATION AND PROPERTIES OF THE COMPLEXES $Mo(\eta^6\text{-}PhPR_2)(L)(PPh_2CH_2CH_2PPh_2)$, R = Et, L = $PPhEt_2$ and R = Ph, L = PPh_3, PR'_3, CO, CNR, N_2, H_2

JAMES J. FRIZZELL, RUDY L. LUCK, ROBERT H. MORRIS * and SHANE H. PENG

Department of Chemistry and the Scarborough Campus, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 1A1 (Canada)

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Summary

The reduction of $MoCl_4(DPPE)$ ($DPPE = PPh_2CH_2CH_2PPh_2$) with Mg or Na/Hg in the presence of 2 $PPhR_2$ under Ar results in the formation of the new complexes $Mo(\eta^6\text{-}PhPR_2)(PPhR_2)(DPPE)$ when R is Ph (Ia) or Et (II). No $\eta^6\text{-}PhPR_2$ complex is obtained when R is Me because this small ligand forms strong Mo–P σ-bonds; nor is one obtained for R = Cy because of too much steric crowding. The limits for η^6-complexation can be quantified in terms of cone angle sums.

Complex Ia is very similar to $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ (IIIa) in that both react at similar rates with a variety of small ligands L = $PMePh_2$, PMe_2Ph, PMe_3, $P(OMe)_3$, N_2, CO, $CNBu^t$ and H_2 via dissociation of a labile σ-bonded ligand. Several other less crowded η^6-arylphosphinemolybdenum complexes including II do not have labile ligands at 25°C. The new complexes $Mo(\eta^6\text{-}PhPPh_2)(L)(DPPE)$ have been characterized by ^{31}P and ^1H NMR, IR and gas uptake measurements. Ia has a higher affinity for H_2 than IIIa possibly because $Mo(\eta^6\text{-}PhPPh_2)(H)_2(DPPE)$ adopts a non-fluxional *trans*-configuration. The ^{31}P chemical shift of the η^6-bonded ligand in 8 derivatives of Ia and 12 of IIIa correlate with the sum of the cone angles of the three σ-bonded ligands in each complex.

Introduction

We have reported convenient syntheses of electron-rich complexes of molybdenum containing the $\eta^6\text{-}PhPMePh$ ligand [1,2]. Scheme 1 summarizes the preparative routes to the complex $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)(DPPE)$ (DPPE = $PPh_2CH_2CH_2PPh_2$). The magnesium reduction of $MoCl_4(DPPE)$ (reaction i) is a high

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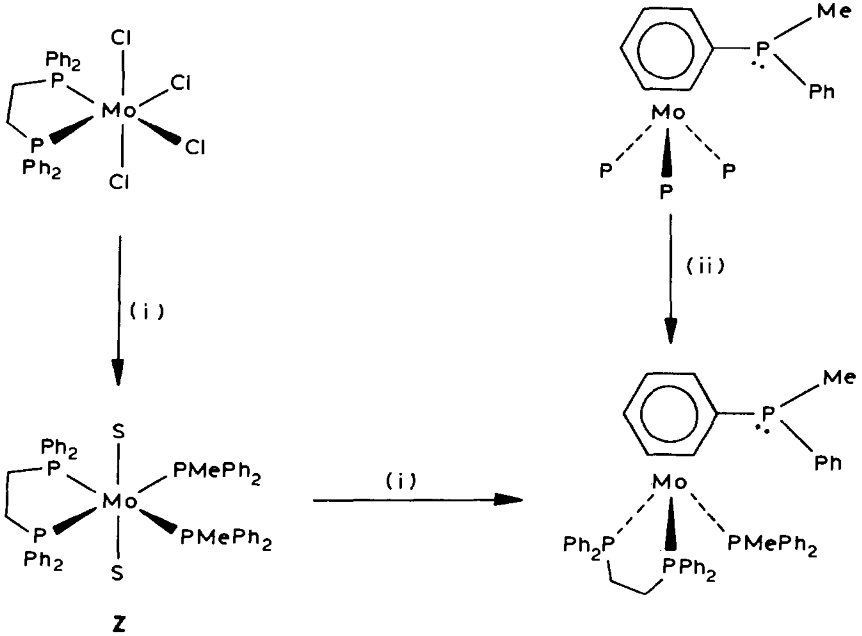
* Author to whom correspondence should be addressed.

yield route which is thought to proceed via a σ to π rearrangement of a methyldiphenylphosphine ligand in an as yet undetected intermediate, "**Z**", in order to



SCHEME 1. (i) 2 $PMePh_2$, excess Mg, THF, 22°C, 2.5 h, 75%; via a rapid rearrangement of postulated intermediate **Z**, S = solvent or η^2-Ph [1,2]; (ii) $PPh_2CH_2CH_2PPh_2$, 22°C, 30 min, 75% [1].

relieve large steric repulsions between bulky ligands σ-bonded in **Z** [2,3,4]. σ-Bonded ligands in the complex $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ are labile because of steric crowding and can be easily substituted by dinitrogen [5] or by DPPE (Scheme 1, reaction ii) whereas the σ-$PMePh_2$ ligand in $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)(DPPE)$ only becomes substitutionally labile at temperatures greater than 60°C [1]. In order to better understand these interesting steric effects we have studied the scope of the reaction (i) involving the reduction of $MoCl_4(DPPE)$ in the presence of arylphosphine ligands, PR_2Ph, of varying steric bulk and we report our findings here. In the course of this work an interesting correlation was found between the size of the σ-bonded ligands and the ^{31}P NMR chemical shift of the phosphorus atom coordinated to the η^6-bonded ring.

Discussion

The scope of the reaction

The generality of the reaction (eq. 1), used previously to prepare $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)(DPPE)$, was tested by using sodium/mercury amalgam or Grignard magnesium as the reductant and arylphosphines PR_2Ph, R = Cy (cyclohexyl), Ph, Et and Me as added ligands. Only triphenylphosphine and diethyl-

$$MoCl_4(DPPE) + 2\ PR_2Ph \xrightarrow[\text{Ar, THF}]{\substack{\text{excess}\\ \text{Na or Mg}}} \begin{array}{l} Mo(\eta^6\text{-}PhPR_2)(PR_2Ph)(DPPE) \\ \quad (\text{I, R} = \text{Ph}; \\ \quad \text{II, R} = \text{Et}) \end{array} \qquad (1)$$

TABLE 1

^{31}P NMR DATA (81 MHz) FOR THE COMPLEXES Mo(η^6-PhPR$_2$)(L)(DPPE) IN C_6H_6 AND TOLMAN'S STERIC (θ) AND ELECTRONIC (ν) PARAMETERS FOR THE LIGANDS L

Compound	L	DPPE (ppm)	L (ppm)	J(P,P) (Hz)	P-η^6-Ph, (P_x) (ppm)	θ_L [a] (deg.)	θ_T [b] (deg.)	ν_L [a] (cm^{-1})
R = Ph								
Ia	PPh_3	83.9,d	57.2,t	27	−8.29,s	145	395±10	2068.9
Ib	$PMePh_2$	83.0,d	30.3,t	28	−7.22,s	136	386±10	2067.0
Ic	PMe_2Ph	82.5,d	10.0,t	28	−6.92,s	122	372±10	2065.3
Id	PMe_3	82.7,d	−4.6,t	28	−5.97,s	118	368±10	2064.1
Ie	$P(OMe)_3$	84.3,d	174.2,t	49	−6.16,s	107	357±10	2079.5
If	N_2	81.6,s			−6.14,s	~95	345±15	2100.6 [c]
Ig	CO	83.9,s			−4.81,s	~95	345±15	
Ih	CNBu^t	84.4,s			−4.23,s	~95	345±15	2073 [d]
Ii	$(H)_2$	85.8,s			−5.00,s			
R = Et								
II	PEt_2Ph	88.3,d	32.8,t	29	−15.29,s			

[a] Tolman's parameters [7]. [b] $\theta_T = \theta_{DPPE} + \theta_L = 250 + \theta_L$. [c] ν(CO) A_1 of Ni(N_2)(CO)$_3$ [15]. [d] ν(CO) A_1 of Ni(CNMe)(CO)$_3$ [16].

TABLE 2

^{1}H NMR DATA AT 200 MHz FOR COMPLEXES Mo(η^6-PhPR$_2$)(L)(DPPE) IN C_6D_6

Compound	L	DPPE [a]	η^6-C_6H_5		C_6H_5-P			L
		H_A or H_B	*ortho* or *meta*	*para*	*ortho*(DPPE) [b]	*ortho*(L) [b]	*meta* and *para*	
R = Ph								
Ia	PPh_3	1.5–2.5, X	3.60, 4.30	4.30	7.8(8H)		6.8–7.7	
Ib	$PMePh_2$	1.9,2.9, Y	3.54, 4.42	4.37	7.7(8H)		6.8–7.4	1.54 d J 5 Hz
Ic	PMe_2Ph	1.8,2.0, Y	3.59, 4.34	4.34	7.7(8H)	6.3(2H)	6.8–7.5	0.97 d J 6 Hz
Id	PMe_3	1.8,2.0, Y	3.98, 4.26	4.26	7.8(8H)		6.8–8.0	0.56 d J 6 Hz
Ie	$P(OMe)_3$	1.5,2.5, X	4.20, 4.54	4.41	7.8(8H)		6.8–7.5	2.81 d J 10 Hz
If	N_2	2.0,2.1, Y	3.87, 4.34	3.66	7.6(8H)		6.8–7.5	
Ig	CO	2.0,2.1, Y	4.13, 4.69	4.00	7.5(4H) 7.9(4H)		7.0–7.5	
Ih	CNBu^t	2.0,2.2, X	4.06, 4.37	3.97	7.7(4H)		6.9–7.5	0.77 s
Ii	$(H)_2$	1.9,2.1, Y	4.46, 4.72	4.21			6.7–7.5 (30H)	−5.53 t J 53 Hz
R = Et								
II [d]	PEt_2Ph	1.6,2.1, Y	3.53, 4.17	4.70	7.3(4H) 8.0(4H)	6.1(2H)	6.7–7.2	1.08 dt [c,d] 1.47 q

[a] DPPE resonances appear in the region 1.5 to 2.5 ppm as pattern X (Fig. 2X) or pattern Y (Fig. 2Y). [b] Pseudotriplets. [c] J(PH) 14.7 Hz, J(HH) 7.4 Hz. [d] The Et peaks of the η^6-PhPEt$_2$ ligand are at δ 0.79 dt, J(PH) 12.7 Hz, J(HH) 7.3 Hz and δ 1.47 quartet, J(HH) 7.3 Hz.

phenylphosphine gave η^6-bonded products. The new orange-brown complex Mo(η^6-PhPPh$_2$)(PPh$_3$)(DPPE), I, can be prepared in 51% yield using 1% Na/Hg amalgam but it is not obtained using magnesium.

Magnesium is a more convenient reductant for the preparation of the new orange-red compound Mo(η^6-PhPEt$_2$)(PEt$_2$Ph)(DPPE) (II). The ^{31}P NMR and ^{1}H NMR data for the complexes, including several derivatives of I, are listed in Tables 1 and 2, respectively. Both complexes are oxygen sensitive in solution but can be handled as powders in the air for several minutes without decomposition.

The only identifiable product from reaction 1 using dicyclohexylphenylphosphine and sodium or magnesium was Mo(N$_2$)$_2$(DPPE)$_2$ (ν(N$_2$) 1980 cm^{-1}, δ(^{31}P) 65.1), obtained when the brown reaction solution was exposed to dinitrogen. The orange-brown solution obtained by reducing MoCl$_4$(DPPE) with magnesium or Na/Hg amalgam in the presence of 2 equiv. of dimethylphenylphosphine under argon reacts with dinitrogen gas to give a mixture which contains *trans*-Mo(N$_2$)$_2$-(DPPE)(PMe$_2$Ph)$_2$ [6]. The reaction solution under argon reacts with methanol. The nature of the species present which may resemble intermediate **Z** in Scheme 1 is under study. Neither the PCy$_2$Ph nor the PMe$_2$Ph reaction solution had peaks in the ^{1}H NMR spectra in the region δ 5–3 characteristic of protons on η^6-arene ligands.

Consideration of the steric requirements of the intermediate "**Z**" in Scheme 1 might explain why η^6-bonded ligands are obtained only under certain conditions. Table 3 lists the combination of ligands known to give monomeric complexes using standard reduction methods and the sum of Tolman's cone angles [7] of the four phosphorus donors σ-bonded in intermediate "**Z**". Included in Table 3 is the known complex Mo(η^6-PhPMe$_2$)(PMe$_2$Ph)$_3$ prepared with difficulty and in poor yield by the Na/Hg amalgam reduction of MoCl$_3$(THF)$_3$ and excess PMe$_2$Ph [8]. Also included is Mo(η^6-4-MeOC$_6$H$_4$)P(C$_6$H$_4$OMe-4)$_2$(triphos) made by the Na/Hg amalgam reduction of MoCl$_3$(triphos) [9]. There appears to be an optimum combination of ligand sizes totalling between 500 and 550° for complex formation. Below a total of 500° such complexes are obtained with difficulty if they form at all; this could be explained because the metal phosphorus bonds in intermediate "**Z**" are not

TABLE 3

COMBINATIONS OF FOUR ARYLPHOSPHORUS DONORS USED IN REDUCTION REACTIONS; η^6-PhPR$_2$ COMPLEXES ARE FORMED WHEN THE SUM OF CONE ANGLES OF THE FOUR DONORS FALLS IN THE RANGE ~ 500 TO ~ 550°

Ligands	Sum of θ	η^6-PhPR$_2$ complex formed?	
4 PMe$_2$Ph	4×122 = 488	Poor yield	[8]
2 PMe$_2$Ph + DPPE	2×122 + 250 = 494	no	
2 PMePh$_2$ + DPPM [a]	2×136 + 242 = 514	yes	[17]
2 PEt$_2$Ph + DPPE	2×136 + 250 = 522	yes	II
P(C$_6$H$_4$OMe-4)$_3$ + TRIPHOS	145 + 375 = 520	yes	[9]
2 PMePh$_2$ + DPPE	2×136 + 250 = 522	yes	IIIh
4 PMePh$_2$	4×136 = 544	yes	IIIa
2 PPh$_3$ + DPPE	2×145 + 250 = 540	yes	Ia
2 PPh$_2$Bu^t + DPPE	2×157 + 250 = 564	no	
2 PCy$_2$Ph + DPPE	2×160 + 250 = 570	no	

[a] DPPM = PPh$_2$CH$_2$PPh$_2$.

weakened by the ligand crowding and hence will not break to allow η^6-bonding of the ring to occur. Above 550° intermediate "**Z**" may not form so that ligand redistribution reactions occur instead; for example $Mo(N_2)_2(DPPE)_2$ is observed in the reaction involving PCy_2Ph.

Ligand lability in Mo(η^6-PhPPh$_2$)(PPh$_3$)(DPPE) (Ia)

Complex Ia contains a labile σ-bonded triphenylphosphine ligand which can be readily substituted at 22°C by a wide range of smaller ligands, that is ligands with cone angles of less than 145°. Thus PCy_2Ph (cone angle 160°) does not react with Ia whereas $PMePh_2$ (136°) and all the other small ligands in Table 1 give monosubstituted products Ib to Ii, according to reaction 2.

$$Mo(\eta^6\text{-}PhPPh_2)(PPh_3)(DPPE) + L \rightarrow Mo(\eta^6\text{-}PhPPh_2)(L)(DPPE) + PPh_3 \qquad (2)$$

The substitution chemistry of Ia resembles in many ways that of Mo(η^6-PhPMePh)($PMePh_2$)$_3$ (IIIa), which forms similar adducts Mo(η^6-PhPMePh)(L)($PMePh_2$)$_2$ (IIIa–IIIg), listed in Table 4 and whose ^{31}P NMR properties are discussed below.

One difference between complex Ia and IIIa is the size of ligand L that their respective binding sites can accommodate. Complex Ia coordinates PPh_3 with a cone angle of 145° whereas IIIa accommodates $PMePh_2$ with a cone angle of 136° but does not react with excess PPh_3. The binding site of IIIa is sterically more restricted than Ia. This is consistent with the fact that the two σ-bonded $PMePh_2$ ligands (2 × 136°) in complex III occupy more space than the DPPE ligand (250°) in complexes I and that the substituents on the "dangling" phosphorus do not contribute much to the congestion of the binding site.

The kinetics of carbon monoxide uptake by Ia in toluene indicate that reaction 2

TABLE 4

THE ^{31}P NMR CHEMICAL SHIFTS (referenced to 85% H_3PO_4, C_6H_6 solvent) OF THE PHOSPHORUS ATOM ATTACHED TO THE η^6-ring ($\delta(P_y)$) AND THE SUMS OF TOLMAN'S CONE ANGLES $\theta_T = \theta_{L(1)} + \theta_{L(2)} + \theta_{L(3)}$ AND ELECTRONIC PARAMETERS $\nu_T = \nu_{L(1)} + \nu_{L(2)} + \nu_{L(3)}$ [7] FOR THE THREE σ-BONDED LIGANDS L(1), L(2), L(3) IN COMPLEXES Mo(η^6-PhP$_y$MePh)(L1)(L2)(L3) (IIIa–IIIl)

Complex	L(1), L(2)	L(3)	$\delta(P_y)$ (ppm)	θ_T (deg)	ν_T (cm^{-1})	References
IIIa	2 $PMePh_2$	$PMePh_2$	−31.0	408	6201.0	[2]
IIIb	2 $PMePh_2$	PMe_2Ph	−30.0	394	6199.3	[2]
IIIc	2 $PMePh_2$	PMe_3	−30.2	390	6198.1	[2]
IIId	2 $PMePh_2$	$P(OMe)_3$	−27.9	379	6213.5	[2]
IIIe	2 $PMePh_2$	N_2	−24.8	367 [a]	6235 [b]	[2]
IIIf	2 $PMePh_2$	$CNBu^t$	−24.1	367 [a]	6207 [b]	[2]
IIIg	2 $PMePh_2$	CO	−23.2	367 [a]	–	[2]
IIIh	DPPE	$PMePh_2$	−28.0	386	6203 [c]	[1]
IIIi	DPPE	$P(OMe)_3$	−27.4	357	6216 [c]	[d]
IIIj	DPPE	CO	−23.7	345 [a]	–	[1]
IIIk	DPPE	$CNBu^t$	−24.3	345 [a]	6209 [b,c]	[d]
IIIl	2 PMe_2Ph	$PMePh_2$	−29.4	380	6197.6	[d]
IIIm	2 $PMePh_2$	$(H)_2$	−25.2	–	–	[5]

[a] Estimates (±15°) [7]. [b] See Table 1. [c] ν for DPPE ~ 4136 cm^{-1}. [d] This work.

proceeds via a first order process involving the rate determining dissociation of the σ-bonded PPh_3 ligand from Ia:

$$\text{Ia} \xrightarrow[k_1]{-\text{PPh}_3} \text{“Mo}(\eta^6\text{-PhPPh}_2)(\text{DPPE})\text{”} \overset{\text{CO}}{\rightarrow} \text{Ig} \tag{3}$$

$$\text{rate} = k_1[\text{Ia}] \quad k_1(303\ \text{K}) = (2.2 \pm 0.5) \times 10^{-3}\ \text{s}^{-1}$$
$$k_1(298\ \text{K}) = (0.7 \pm 0.1) \times 10^{-3}\ \text{s}^{-1}$$

The corresponding rates for the first order substitution reactions of $Mo(\eta^6$-$PhPMePh)(PMePh_2)_3$ (IIIa) are $k_1(303\ K) = (1.5 \pm 0.1) \times 10^{-3}\ s^{-1}$ and $k_1(298\ K) = (6.7 \pm 0.4) \times 10^{-4}\ s^{-1}$. Thus the two compounds display very similar reactivity. The product of reaction 3 is the monocarbonyl complex, Ig, $\nu(CO)$ 1817 cm^{-1}, which is not oxygen sensitive and is readily isolated.

Both complex Ia and IIIa react at 22°C with dinitrogen or hydrogen gas to give terminally bonded dinitrogen complexes (If, $\nu(N_2)$ 2010 cm^{-1}; IIIe, $\nu(N_2)$ 1980 cm^{-1} [2]) and the dihydride complexes $Mo(\eta^6$-$PhPPh_2)(H)_2(DPPE)$ (Ii) and $Mo(\eta^6$-$PhPMePh)(H)_2(PMePh_2)$ (IIIm) [2]. Like complex IIIa complex Ia is not completely converted by reaction with one atmosphere of N_2; instead an equilibrium free of side products is attained at 35°C at a rate approximately two times slower than that predicted by reaction 3:

$$\text{Ia} + \text{N}_2 \overset{K_2}{\rightleftarrows} \text{If} + \text{PPh}_3 \tag{4}$$

$$K_2(308\ \text{K}) = 0.8 \pm 0.1$$

The equilibrium constant for the dinitrogen reaction compares with the value $K_1 = 0.76$ (308 K) obtained using complex IIIa [5]. Surprisingly complex Ia has a much higher affinity for dihydrogen than IIIa. Whereas IIIa reversibly binds hydrogen to give the fluxional dihydride IIIm with an equilibrium constant of 0.71 (303 K) [5], complex Ia is completely converted to the dihydride Ii. Perhaps Ii adopts a non-fluxional *trans* structure like the one proposed for $W(C_6H_5Me)$-$(PMe_2CH_2CH_2PMe_2)(H)_2$ [10].

Of the known η^6-arylphosphine complexes containing σ-bonded phosphine ligands (Table 3) only complex Ia and IIIa react readily with dinitrogen or carbon monoxide at 22°C. The complex $Mo(\eta^6$-$PhPMePh)(PMePh_2)(DPPE)$ (IIIh) reacts with carbon monoxide only at temperatures above ca. 60°C [1]. Thus a sum of cone angles of the three P-donors plus the η^6-bonded ligand (to account for the steric bulk of the dangling substituents) must total about 540° (Table 3) in order to obtain a π-complex with a labile σ-bonded ligand.

^{31}P NMR spectra: chemical shift and ligand size correlation

The chemical shift $\delta(P_x)$ of the phosphorus "dangling" from the η^6-arene ring in complexes $Mo(\eta^6$-$PhP_xPh_2)(L)(DPPE)$ (Ia–Ii) (Table 1) has a roughly linear dependence on the size of the ligand L σ-bonded in the complex. The function $(0.50$–$0.0592\ \theta_L)$ where θ_L is Tolman's cone angle for the ligand [7] gives $\delta(P_x)$ with a correlation coefficient of 0.89.

It has been reported that the ^{31}P NMR chemical shift, $\delta(P_y)$, of the phosphorus "dangling" from the η^6-arene ring in the series of complexes $Mo(\eta^6$-$PhPMe$-

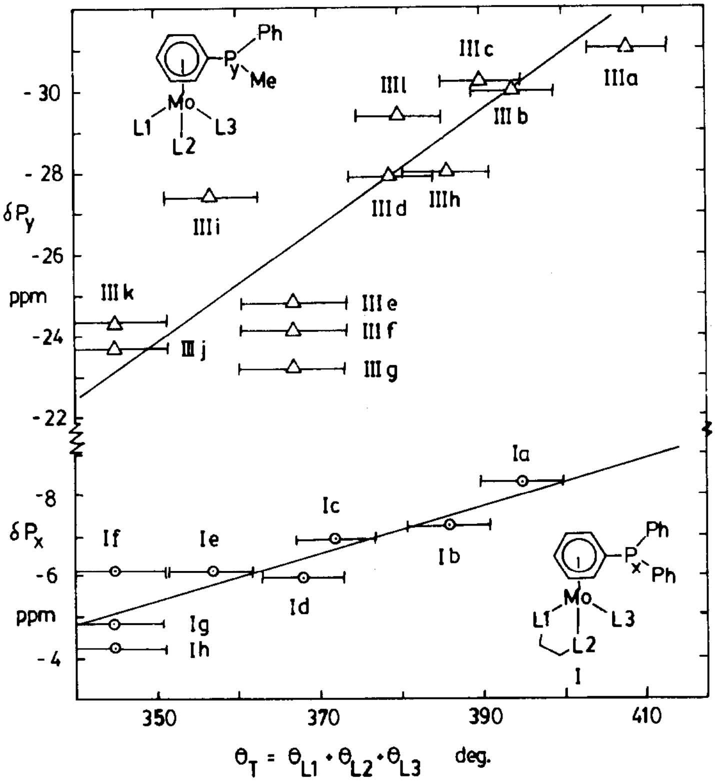


Fig. 1. Plots of the ^{31}P NMR chemical shifts, δ(P), (referenced to 85% H_3PO_4) of the phosphorus atom attached to the η^6-ring versus the sum of Tolman's angles θ_T for the three ligands L(1), L(2), and L(3) σ-bonded in complexes Ia–Ih and IIIa–IIIl (see Tables 1 and 4).

Ph)(L)(PMePh$_2$)$_2$ (III), is sensitive to the nature of the ligand L although steric and electronic influences on the chemical shift could not be distinguished [2]. A study of a wider range of ligands L(1), L(2) and L(3) σ-bonded to the Mo(η^6-PhPMePh) moiety (Table 4) reveals that a rough correlation exists (see Fig. 1) between $\delta(P_y)$ and a total cone angle parameter θ_T defined for the three σ-donors as:

$$\theta_T = \theta_{L(1)} + \theta_{L(2)} + \theta_{L(3)} \tag{5}$$

For complexes IIIa–IIIl the least squares equation with a correlation coefficient of 0.86 is:

$$\delta(P_y) = 26.2 - 0.143\ \theta_T \tag{6}$$

For complexes Ia–Ii:

$$\theta_T = \theta_L + \theta_{DPPE} = \theta_L + 250 \tag{7}$$

$$\delta(P_x) = 15.3 - 0.0592\ \theta_T \tag{8}$$

Such correlations might be expected because the shifts of the ^{31}P nuclei in phosphines are known to be sensitive to the size of the substituents attached to them [7]. In addition the η^6-ring in the complexes is assumed to be rapidly rotating at 22°

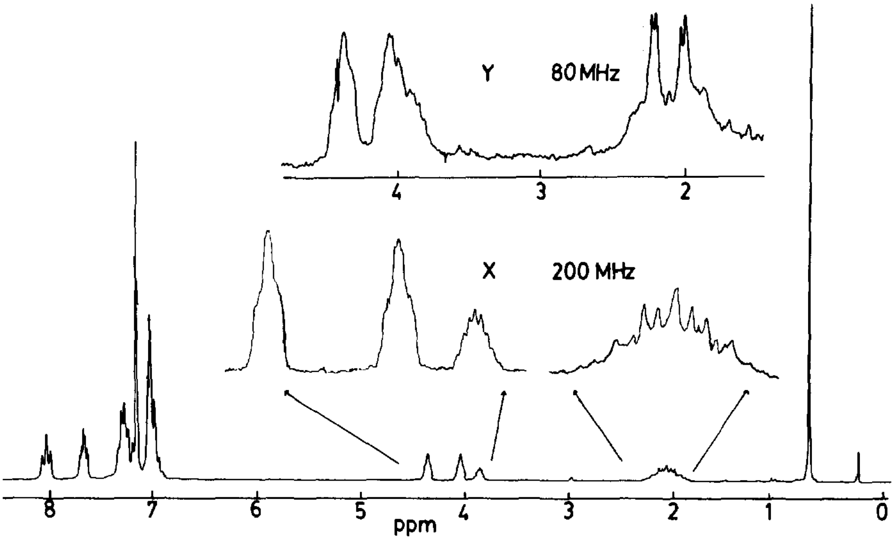


Fig. 2. The ^1H NMR spectrum at 200 MHz of $Mo(\eta^6\text{-}PhPPh_2)(CNBu^t)(DPPE)$ (Ih) in C_6D_6 with amplification of the region δ 1.5–4.5 (inset X). Inset Y shows the pattern obtained at 80 MHz (see Table 2).

and so the dangling phosphorus group experiences steric repulsions with all the σ-bonded ligands on the molybdenum; θ_T crudely expresses these interactions.

The error in θ_T is estimated at ±10° for the phosphine ligands and ±15° for the small unsaturated ligands. The deviations in $\delta(^{31}P)$ (±10%) from the linear relationships of Fig. 1 are explained by local magnetic fields caused by ligand unsaturation (C≡O, N≡N, C≡N, C=C), errors in cone angle estimation, interpenetration and asymmetric orientations of phosphine substituents and inductive effects of the σ-bonded ligands.

There is no good correlation between the ^{31}P chemical shifts and Tolman's electronic parameters for the ligands ν_L [7] (Table 1) or a sum of electronic parameters $\nu_T = \nu_{L(1)} + \nu_{L(2)} + \nu_{L(3)}$.

To verify that steric effects predominate, a few other adducts of Ia were studied only by ^{31}P NMR; here adducts were prepared with phosphines L with similar cone angles but with quite different electronic parameters ($P(n\text{-}Bu)_3$ versus $P(CH_2CH_2CN)_3$ and $P(i\text{-}Bu)_3$ versus PPh_3); see Table 5. The fact that phosphines with different ν_L values give chemical shifts that are similar (within the ±10%

TABLE 5

^{31}P NMR DATA FOR SOME DERIVATIVES OF Ia CONTAINING PHOSPHINES L OF SIMILAR θ_L BUT DIFFERENT ν_L. $\delta(P_{calc})$ ARE FROM EQ. 7 and 8

L	θ_L	ν_L	$\delta(P_x)$	$\delta(P_{calc})$
$P(n\text{-}Bu)_3$	132	2060.3	−6.7	−7.3
$P(CH_2CH_2CN)_3$	132	2077.9	−7.2	−7.3
$P(CH_2CH(Me)_2)_3$	143	2061	−7.8	−8.0
PPh_3	145	2068.9	−8.3	−8.1

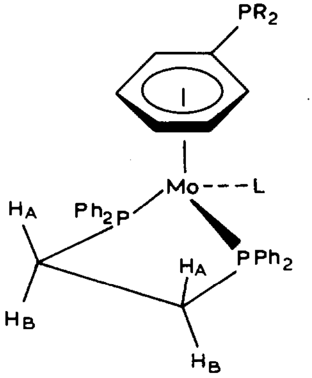
deviations) and that are predicted by eq. 7 and 8 also argues for a steric effect.

However the usual effect of increasing the bulk of substituents on phosphorus is to make the ^{31}P chemical shift more positive or move more downfield; hence the order PBu^tPh_2 (37.2 ppm) > PPh_3(−5.9 ppm) > $PMePh_2$(−27.7 ppm). It is not clear why our correlation is opposite to this. However these correlations are proving to be of use in the characterization of other new derivatives of these η^6-arylphosphine complexes.

^{1}H NMR spectra

The spectra for the complexes (Table 2) all have peaks in the region δ 3.5 and 4.7 for the protons attached to the η^6-bonded ring. The upfield displacement ($\Delta\delta \cong 3.1$ on average) of these arene resonances from their unperturbed values at ~ 7.1 ppm is slightly less than the value 3.3 observed for the more electron-rich η^6-PhPMePh complexes III [2].

All the complexes give AA'BB'XX' patterns in the region δ 1.5 to 2.5 attributed to two sets (H_A,H_B) of inequivalent methylene protons on the DPPE ligand. Figure 2 shows the field dependence of the spectrum for Mo(η^6-$PhPPh_2$)($CNBu^t$)(DPPE). The pattern for the other complexes resemble either the 200 MHz pattern (X) or the 80 MHz pattern (Y) depending on the chemical shift difference of H_A and H_B (Table 2). Other studies of the five-membered ring system of complexed DPPE conclude that the ring is undergoing a $\lambda \rightleftarrows \delta$ conformational interconversion that is very rapid on the NMR time scale so that averaged values of $\delta(H_A)$ and $\delta(H_B)$ are observed [11,12]. Approximate values for $\delta(H_A)$ and $\delta(H_B)$ are listed in Table 2.



The phenyl ring currents cause a deshielding of *ortho* protons on the DPPE rings so that they are typically observed in the region δ 7.5 to 8.0 [13]. The *ortho*-phenyl protons in the PMe_2Ph and PEt_2Ph ligands in complexes Ic and II are diamagnetically shielded so that peaks are found at δ 6.1 and 6.3, respectively.

Conclusions

Three steric effects are noted here in the chemistry of σ-bonded arylphosphine complexes. First there appears to be an optimum range of ligand sizes for the formation of these η^6-bonded complexes in reduction reactions. The range was defined as 500–550°, the sum of the Tolman cone angles for the four phosphine donors involved. Second, the two complexes with large cone angle sums, Mo(η^6-$PhPPh_2$)(PPh_3)(DPPE) (Ia, 540°) and Mo(η^6-PhPMePh) $(PMePh_2)_3$ (IIIa, 544°) have labile σ-bonded ligands that can be substituted by a wide range of small ligands with cone angles less than ~ 145° for Ia and ~ 136° for IIIa. The substitutions proceed via a dissociative mechanism in each case with very similar rates of reaction. Both react reversibly with dinitrogen. However, Ia has a much higher affinity for dihydrogen than IIIa possibly because the dihydride Mo(η^6-$PhPPh_2$)$(H)_2$(DPPE) adopts a non-fluxional *trans* geometry.

Finally the ^{31}P chemical shifts $\delta(P)$ of the "dangling" phosphorus correlates with the sum of Tolman angles θ_T of the three σ-bonded ligands in complexes Ia–Ih and IIIa–IIIm. Such correlations might be useful in estimating from $\delta(P)$ the size of other ligands σ-bonded in the complexes.

The sums of cone angles presented in this paper are used only as indicators of steric congestion. No physical significance should be associated with the absolute values. We believe that this new use of cone angles may have many applications in rationalizing steric effects.

Experimental

Oxygen and water were excluded during all operations by use of vacuum lines supplied with purified nitrogen or argon as appropriate and a glove box filled with nitrogen. Solvents other than methanol were dried over sodium benzophenone ketyl and were degassed before use. Tetrahydrofuran (THF) was further dried over and vacuum distilled from lithium aluminum hydride. Methanol was dried over magnesium methoxide. Details for the preparation of $MoCl_4DPPE$ are found in ref. 1 and 14. The phosphine ligands were used as obtained from the Strem Chemical Company.

The ^{31}P NMR spectra were recorded at 81 MHz by use of a Varian XL200 spectrometer. Chemical shifts were measured relative to $P(OMe)_3$ in an insert tube but are reported relative to 85% H_3PO_4 with the use of $\delta(P(OMe)_3) = +140.4$ in C_6D_6. The ^1H NMR spectra were obtained at 80 MHz by use of a Bruker WP80 or at 200 MHz using the XL200 spectrometer. The gas uptake measurements were conducted as reported [5].

Microanalyses were performed on samples handled under an inert atmosphere by the Canadian Microanalytical Service, Vancouver, and the results of several are listed in Table 6.

Preparation of Mo(η^6-$PhPPh_2$)(PPh_3)(DPPE) (Ia)

The tetrachloride complex $MoCl_4$(DPPE) (4.0 g, 6.28 mmol) was dissolved under argon in a solution of triphenylphosphine (3.29 g, 12.5 mmol) in 100 ml of degassed THF that was freshly vacuum distilled from $LiAlH_4$. A 50% excess of 1% sodium/mercury amalgam (0.87 g Na, 87 g Hg) was added. The solution colour turned from orange to green-brown to red-brown over a 10 minute period as the amalgam was stirred. After 2 h the residual Na/Hg amalgam was removed by filtration through a column of Celite under argon. The filtrate was concentrated to 10 ml and the orange, oxygen and nitrogen-sensitive product was precipitated with degassed methanol. Several recrystallizations from benzene/methanol and drying under vacuum gave the product as a brown powder (3.2 g, 51% yield). Although the product appears to

TABLE 6

ANALYTICAL DATA FOR SOME OF THE COMPLEXES

Complex	Analysis (Found (calcd.) (%))		
	C	H	N
Ia	73.73	4.61	< 0.6
	(73.08)	(5.35)	(0)
$Ib \cdot CH_3OH$ [a]	70.08	5.67	-
	(70.44)	(5.71)	
Ic	69.51	5.83	-
	(69.79)	(5.63)	
Id	67.53	5.81	-
	(67.78)	(5.82)	
$Ig \cdot CH_3OH$ [a]	67.74	5.10	
	(67.65)	(5.31)	-
Ih	69.30	5.87	1.56
	(70.07)	(5.77)	(1.67)
II	66.79	6.92	-
	(66.83)	(6.58)	

[a] Solvate observed by NMR.

be pure spectroscopically (^1H, ^{31}P NMR), its fails to give correct elemental analyses despite many attempts (Table 6). In this way also it is similar to compound IIIa [2]. However several derivatives of Ia have been obtained in an analytically pure form.

Preparation of Mo(η^6-PhPPh$_2$)(L)(DPPE), (Ib–Ie, Ih)

The preparation of Mo(η^6-PhPPh$_2$)(PMe$_3$)(DPPE) (L = PMe$_3$, Id) is representative: complex Ia (0.6 g, 0.61 mmol) was added to a solution of trimethylphosphine (47 mg, 0.61 mmol) in 50 ml of benzene. The solution was stirred for 2 h and then concentrated to dryness. The residue was washed with methanol and recrystallized from benzene/methanol to give the product, Id, as an orange powder (0.36 g, 64%).

Complex Ib, L = PMePh$_2$, was obtained as orange-red crystals (60%). Complex Ic, L = PMe$_2$Ph, as an orange powder (65%). Complex Ie, L = P(OMe)$_3$, as a yellow powder (70%). Complex Ih, L = $CNBu^t$, as an orange-red powder (80%).

Formation of Mo(η^6-PhPPh$_2$)(N$_2$)(DPPE) (If)

Complex Ia (54 mg, 0.053 mmol) when dropped into 15 ml toluene at 35°C saturated with nitrogen at 630 torr took up 0.030 mmol of nitrogen in 500 s to give an equilibrium mixture: $[Ia] = 1.5 \times 10^{-3}$ *M*, $[If] = [PPh_3] = 2.0 \times 10^{-3}$ *M*, $[N_2] = 3.5 \times 10^{-3}$ *M* [5], $K = 0.8 \pm 1$. Complex If can be obtained in greater than 90% purity and in good yield (70%) by stirring compound Ia (1.0 g) as a suspension in 50 ml hexanes for 48 h under nitrogen and then filtering off the yellow powder enriched in If. This process is repeated to wash away more dissociating PPh$_3$. The yellow product was recrystallized from benzene/methanol. IR (Nujol) 2010 cm^{-1}, $\nu(N_2)$.

Preparation of Mo(η^6-PhPPh$_2$)(CO)(DPPE) (Ig)

A solution of complex Ia (0.50 g, 0.51 mmol) in 50 ml of benzene was stirred under one atm carbon monoxide for 2 h. The colour changed from orange to yellow-orange. The solution was concentrated to 5 ml and the yellow product was precipitated with methanol, recrystallized from benzene/methanol and dried under vacuum (0.35 g, 90%). IR (Nujol) 1817 cm^{-1}.

The rate of the reaction of Ia (4 – 8 mM) in toluene with carbon monoxide (370–650 torr) was monitored at 25 and 30°C by use of a constant pressure, gas-uptake apparatus [2]. Rates were first order in Ia and zero-order in carbon monoxide; rate constants were $(2.2 \pm 0.5) \times 10^{-3}$ s^{-1} at 303 K and $(7 \pm 1) \times 10^{-4}$ s^{-1} at 298 K.

Formation of Mo(η^6-PhPPh$_2$)(H)$_2$(DPPE) (Ii)

Complex Ia took up 0.9 ± 0.1 mol H_2 per Mo at 35°C in toluene.

Observation by ^{31}P NMR of other phosphine adducts of Ia

Triisobutylphosphine reacts with Ia in benzene under N_2 to give a mixture containing If, Ia, free PPh_3 and Mo(η^6-PhPPh$_2$)(P(i-Bu)$_3$)(DPPE): δ –7.8 (s, P_x), –7.5(t, J 29 Hz, P(i-Bu)$_3$), 85.1 (d, J 29 Hz, DPPE). The following phosphines L react with Ia to give the expected adducts Mo(η^6-PhPPh$_2$)(L)(DPPE) and free PPh_3: L = P(CH_2CH_2CN)$_3$: –7.2 (s, P_x), 26.4 (t, J 25 Hz, L) 59.2 (d, J 25 Hz, DPPE). L = P(n-Bu)$_3$: –6.7 (s, P_x), 14.0 (t, J 27 Hz, L), 83.8 (d, J 27 Hz, DPPE).

Preparation of Mo(η^6-PhPEt$_2$)(PEt$_2$Ph)(DPPE), II

The procedure for the preparation of Mo(η^6-PhPMePh)(PMePh$_2$)(DPPE) involving the magnesium reduction of $MoCl_4$(DPPE) was followed using PEt_2Ph instead of $PMePh_2$ [1]. Orange-red crystals of II were obtained in 40% yield.

Attempted reductions

The procedures for the preparation of Ia and II were followed using the phosphines PMe_2Ph, PCy_2Ph and PPh_2Bu^t. The reaction solutions were evaporated to dryness and the ^1H NMR spectra of the residue in C_6D_6 under argon were recorded. There was no evidence of η^6-PhPR$_2$ products.

Observation of new complexes containing η^6-PhPMePh by ^{31}P NMR (Table 4)

Complexes IIIi and IIIk were observed by treating Mo(η^6-PhPMePh)(PMePh$_2$)(DPPE) with excess P(OMe)$_3$ or CNBu^t, respectively, at 60°C to give free $PMePh_2$ and the monosubstituted products. Mo(η^6-PhPMePh)(P(OMe)$_3$)(DPPE) δ –27.4 (s, P-η^6-Ph), 84.1 A, 85.6 B (ABX system at 32.3 MHz, $J_{AX} = J_{BX}$ = 50.0 Hz, J_{AB} 9.8 Hz), 172.6 X (ABX system, P(OMe)$_3$). Mo(η^6-PhPMePh)(CNBu^t)(DPPE): δ –24.3 (s, P-η^6-Ph), 83.7 A, 83.0 B (AB system at 81 MHz, J_{AB} 9.3 Hz, DPPE).

Complex IIIl was observed by treating IIIa with 2 equiv. PMe_2Ph in benzene at 20°C for 2 h. Mo(η^6-PhPMePh)(PMe$_2$Ph)$_2$(PMePh$_2$): δ –29.4 (s, P-η^6-Ph), 14.5 A, 14.1 B (ABX system, J_{AB} 30 Hz, J_{AX} 30 Hz, J_{BX} 30 Hz, PMe_2Ph), 38.9 X (ABX system, $PMePh_2$).

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Note added in proof. A recent cyclic voltammetry study of the series of complexes I and III indicates that there is a linear correlation $\delta(P_x)$ and $E_{1/2}(Mo^0/Mo^I)$ for series III but not for series I (R.L. Luck, R.H. Morris, and A. Sella, unpublished work). Thus the chemical shift of the phosphorus on the η^6-bonded ring in complexes III is influenced by both steric and electronic factors whereas that of I is dominated by steric factors.