Consecutive Substitution in, and Reduction of, η-Allyl Molybdenum(II) Complexes, and a Study of Ligand Exchange in a Molybdenum(0) Product

By **Deborah A. Clark, David L. Jones, and Roger J. Mawby,*** Department of Chemistry, The University of York, York YO1 5DD

Reactions of the allyl and 2-methylallyl complexes [$Mo(CO)_2Cl(\eta-C_3H_4R)(NCMe)_2$] (R = H or Me) with ligands L = PMe_2Ph or $PMePh_2$ involve initial substitution to give [$Mo(CO)_2Cl(\eta-C_3H_4R)L_2$] followed by reduction to *cis*-[$Mo(CO)_2L_4$] or [$Mo(CO)_2(NCMe)(PMePh_2)_3$]. The reduction, which is first order in the concentrations of both molybdenum complex and L, is thought to involve initial nucleophilic attack on the allyl ligand. Two of the PMe_2Ph ligands in *cis*-[$Mo(CO)_2(PMe_2Ph)_4$], believed to be the mutually *cis* pair, undergo rapid dissociative exchange with free PMe_2Ph in solution at high temperatures: the exchange occurs without scrambling the *cis* pair of ligands with the *trans* pair. In the absence of free PMe_2Ph, slow decomposition at 353 K yields specifically the *mer* isomer of [$Mo(CO)_3(PMe_2Ph)_3$]. It is shown that this is the expected result if the labile Mo–P bonds are those to the *cis* pair of PMe_2Ph ligands.

SOME time ago, tom Dieck and co-workers reported [1,2] on the reactions of a variety of nucleophiles with the η-allyl complex [$Mo(CO)_2Cl(\eta-C_3H_5)(NCMe)_2$]. Among the nucleophiles used were three ligands containing phosphorus-donor atoms, $Ph_2PCH_2CH_2PPh_2$, PPh_3, and PBu_3. Rather surprisingly, these ligands did not all react with the η-allyl complex in the same way: the bidentate ligand replaced the two acetonitrile molecules to yield the substitution product [$Mo(CO)_2Cl(\eta-C_3H_5)(Ph_2PCH_2CH_2PPh_2)$], while the two unidentate ligands caused elimination of the η-allyl ligand as $[C_3H_5PR_3]^+$ (R = Ph or Bu) and reduction of the molybdenum to [$Mo(CO)_2(NCMe)_2(PR_3)_2$].

In an attempt to discover why different phosphorus ligands reacted with [$Mo(CO)_2Cl(\eta-C_3H_5)(NCMe)_2$] in different ways, and to obtain information about the mechanism of the reaction involving elimination of the allyl ligand, we have studied reactions of [$Mo(CO)_2Cl(\eta-C_3H_5)(NCMe)_2$] and its 2-methylallyl analogue [$Mo(CO)_2Cl(\eta-C_4H_7)(NCMe)_2$] with several phosphorus ligands. The most useful information was obtained with the ligands PMe_2Ph and $PMePh_2$, and the studies carried out with these ligands are the subject of this paper.

RESULTS AND DISCUSSION

(*a*) *Initial Substitution Reaction.*—When solutions of the complexes [$Mo(CO)_2Cl(\eta-C_3H_4R)(NCMe)_2$] (R = H or Me) in the solvents MeCN, EtOH, or Me_2CO were treated with an excess of either of the ligands L = PMe_2Ph or $PMePh_2$ at room temperature there were immediate changes in the visible and near-u.v. spectra of the solutions. The i.r. spectra of the solutions contained two C–O stretching bands, somewhat shifted from the positions of the corresponding bands in the spectra of the starting materials, but not in the same region as those reported by Friedel *et al.*[2] for the molybdenum(0) complex [$Mo(CO)_2(NCMe)_2(PPh_3)_2$]. Suspecting that the reactions involved ligand substitution rather than reduction of the molybdenum, we repeated them using rather lower mol ratios of phosphorus ligand to molybdenum complex. The same changes in spectra were observed, and from the reactions of [$Mo(CO)_2Cl(\eta-C_4H_7)(NCMe)_2$] crystalline products were obtained and shown by elemental analysis to be [$Mo(CO)_2Cl(\eta-C_4H_7)L_2$], where L = PMe_2Ph or $PMePh_2$. Details of the i.r. and ^1H n.m.r. spectra of these and other complexes described in the paper are collected in Table 1. The products of the reactions of [$Mo(CO)_2Cl(\eta-C_3H_5)(NCMe)_2$] could not be isolated in a pure state [because of their more rapid reduction to molybdenum(0)], but their solution spectra were sufficiently similar to those of the isolated 2-methylallyl complexes to indicate that they were the compounds [$Mo(CO)_2Cl(\eta-C_3H_5)L_2$].

(*b*) *Subsequent Reduction Reaction.*—When the phosphorus ligand L = PMe_2Ph or $PMePh_2$ was allowed to react for longer periods, either with the starting materials [$Mo(CO)_2Cl(\eta-C_3H_4R)(NCMe)_2$] (R = H or Me) or with the substitution products [$Mo(CO)_2Cl(\eta-C_4H_7)L_2$], molybdenum(0) complexes were obtained. The final product from the reactions of both starting materials and the intermediate [$Mo(CO)_2Cl(\eta-C_4H_7)(PMe_2Ph)_2$] with PMe_2Ph proved to be the complex [$Mo(CO)_2(PMe_2Ph)_4$]. In the case of the reaction of [$Mo(CO)_2Cl(\eta-C_3H_5)(NCMe)_2$] with PMe_2Ph, the other product of the reaction, [$C_3H_5PMe_2Ph$]Cl, was also isolated and identified. The preparation of [$Mo(CO)_2(PMe_2Ph)_4$] by treatment of [$Mo(CO)_2Cl(\eta-C_3H_5)(NCMe)_2$] with PMe_2Ph was reported some years ago by Aresta and Sacco,[3] but these authors did not mention the observation of any intermediate during the reaction, nor did they suggest a mechanism for the reaction. The complex [$Mo(CO)_2(PMe_2Ph)_4$] is an analogue of [$Mo(CO)_2(PMe_3)_4$] [4] and presumably of the species claimed [5] to be [$Mo(CO)_2(PPh_3)_4$], although the latter has C–O stretching bands in positions (1 940 and 1 840 cm^{-1}) so different from those for [$Mo(CO)_2(PMe_2Ph)_4$] (at 1 835 and 1 772 cm^{-1}) and for other dicarbonylmolybdenum(0) complexes [4,6] as to raise doubts whether it really contains molybdenum in the zero oxidation state.

The final molybdenum-containing product of the reactions with $PMePh_2$ proved less easy to characterize. Again, however, it appeared that in a given solvent the same complex was obtained whether the molybdenum(II) complex used was [$Mo(CO)_2Cl(\eta-C_3H_4R)(NCMe)_2$] (R = H or Me) or [$Mo(CO)_2Cl(\eta-C_4H_7)(PMePh_2)_2$]. Analytical data for samples prepared in ethanol were rather variable, and never exactly correct for $[Mo(CO)_2(PMePh_2)_4]$, although in every case the i.r. spectrum of the product contained two C–O stretching bands (at 1 835 and 1 757 cm^{-1}) close to those for $[Mo(CO)_2(PMe_2Ph)_4]$. When acetonitrile was used as the solvent, reproducible analytical data *were* obtained for the product, which was found in this instance to be $[Mo(CO)_2(NCMe)(PMePh_2)_3]$.

In summary, then, the reactions between the complexes $[Mo(CO)_2Cl(\eta\text{-}C_3H_4R)(NCMe)_2]$ and the phosphorus ligands L = PMe_2Ph or $PMePh_2$ occur in two steps, an initial substitution reaction to give $[Mo(CO)_2Cl(\eta\text{-}C_3H_4R)L_2]$ being followed by reduction to form $[Mo(CO)_2L_4]$ or $[Mo(CO)_2(NCMe)(PMePh_2)_3]$. Brisdon and Paddick [7] have recently reported that the reaction of $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NCMe)_2]$ with $Ph_2PCH_2CH_2PPh_2$ follows the same path, yielding first $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(Ph_2PCH_2CH_2PPh_2)]$ and finally $[Mo(CO)_2(Ph_2PCH_2CH_2PPh_2)_2]$. We have also found this to be the case, and have shown that the reaction of the 2-methylallyl complex $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NCMe)_2]$ with $Ph_2PCH_2CH_2PPh_2$ proceeds in the same way.

TABLE 1

Infrared [a] and ^1H n.m.r.[b] spectra of complexes

Complex	ν(C–O)/ cm^{-1}	δ/p.p.m.	Assignment	Coupling constant/ Hz	Assignment
$[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(PMe_2Ph)_2]$	1 936,	1.84(d, 6)	P*Me*$_2$Ph [c]	8.5	$\lvert ^2J(P\text{–}H)\rvert$
	1 808	1.95(d, 6)	P*Me*$_2$Ph [c]	8.5	$\lvert ^2J(P\text{–}H)\rvert$
		2.04(s, 3)	Me in C_4H_7		
		2.72(d, 2)	H_a in C_4H_7 [d]	4.5	$\lvert ^3J(P\text{–}H)\rvert$
		3.54(d, 2)	H_s in C_4H_7 [d]	10.0	$\lvert ^3J(P\text{–}H)\rvert$
$[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(PMePh_2)_2]$	1 922,	1.78(s, 3)	Me in C_4H_7		
	1 808	2.30(d, 6)	P*Me*Ph_2	9.0	$\lvert ^2J(P\text{–}H)\rvert$
		2.72(d, 2)	H_a in C_4H_7 [d]	5.0	$\lvert ^3J(P\text{–}H)\rvert$
		3.44(d, 2)	H_s in C_4H_7 [d]	10.0	$\lvert ^3J(P\text{–}H)\rvert$
$[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(Ph_2PCH_2CH_2PPh_2)]$	1 948,	1.98(s, 3)	Me in C_4H_7		
	1 810	2.60(c, 2)	$Ph_2PC\mathit{H}_2CH_2PPh_2$		
		2.77(s, 2)	H_a in C_4H_7 [d]		
		3.00(c, 2)	$Ph_2PCH_2C\mathit{H}_2PPh_2$		
		4.14(c, 2)	H_s in C_4H_7 [d]		
$[Mo(CO)_2(PMe_2Ph)_4]$	1 835,	1.23(i, 12)	P*Me*$_2$Ph	4.0	$\lvert ^2J(P\text{–}H) + {}^4J(P\text{–}H)\rvert$
	1 772	1.48(i, 12)	P*Me*$_2$Ph	5.0	$\lvert ^2J(P\text{–}H) + {}^4J(P\text{–}H)\rvert$
$[Mo(CO)_2(NCMe)(PMePh_2)_3]$ [e]	1 838,				
	1 758				

[a] In the C–O stretching region only. Spectra were recorded on Nujol mulls of the complexes. [b] In $CDCl_3$ solution, except for *cis*-$[Mo(CO)_2(PMe_2Ph)_4]$ where the solvent was PhCl. Resonances due to phenyl protons are not included. Multiplicities and relative areas are given in parentheses after the chemical-shift values: s = singlet, d = doublet, c = complex, i = intermediate coupling. [c] Each PMe_2Ph ligand contains two inequivalent methyl groups. [d] H_a and H_s are the *anti* and *syn* protons, respectively, in the allyl ligand. [e] Satisfactory n.m.r. spectra could not be obtained for this complex.

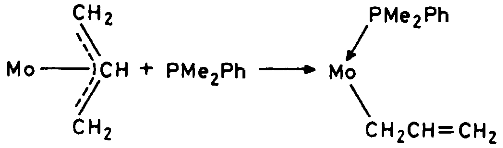
(*c*) *Kinetic Study of the Reduction Reaction.*—We wished to obtain information about the mechanism of the step in which molybdenum(II) in the complexes $[Mo(CO)_2Cl(\eta\text{-}C_3H_4R)L_2]$ (L = PMe_2Ph or $PMePh_2$) is reduced to molybdenum(0) and the allyl ligand is eliminated. Kinetic studies were hampered by solvent difficulties, it being necessary to find a solvent in which reactants and products were both stable and sufficiently soluble. No completely satisfactory solvent was found for any reaction except that between $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$ and PMe_2Ph, which could be carried out in propanone. Rough indications were also obtained of relative rates for the other reactions in propanone, and of variations in reaction rate with solvent polarity.

The study of reaction (1) was carried out by treating a propanone solution of $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NCMe)_2]$ with PMe_2Ph. The i.r. spectrum of the solution indicated

$$[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2] + 3PMe_2Ph \longrightarrow [Mo(CO)_2(PMe_2Ph)_4] + [C_3H_5PMe_2Ph]^+ + Cl^- \quad (1)$$

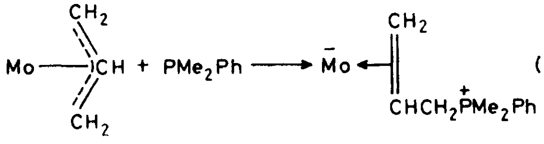
that conversion into the species $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$ was immediate and complete, and the subsequent reaction of this complex with PMe_2Ph could be followed by monitoring the disappearance of the C–O stretching band at 1 935 cm^{-1}. In order to confirm that the molybdenum-containing product under the conditions of the kinetic runs was still $[Mo(CO)_2(PMe_2Ph)_4]$, it was isolated from the solution used for one of the runs and characterized. The reaction was found to be first order in the concentration of molybdenum complex. First-order rate constants for various concentrations of PMe_2Ph {corrected to allow for the consumption of PMe_2Ph in the formation of $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$} are given in Table 2: the three values given for each concentration represent three independent kinetic runs. It can be seen that the reaction is also first order in $[PMe_2Ph]$.

The initial attack by PMe_2Ph could be either on the metal or on the allyl ligand. Attack on the metal [probably accompanied by conversion of the η-allyl ligand into the σ-allyl arrangement to provide a co-ordination site for the phosphorus ligand, see equation (2)] would appear to involve little change in polarity



(2)

between ground and activated state. By contrast, one would expect considerable charge separation as a result of attack on the allyl ligand [equation (3)]. Rough



(3)

studies of variation in reaction rate with solvent revealed a marked decrease in rate with decreasing dielectric constant of the solvent (ethanol > propanone > cyclohexanone > tetrahydrofuran > benzene), with about a hundred-fold drop in rate between ethanol and benzene. Thus it seems probable that the initial attack is on the allyl ligand.

TABLE 2

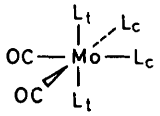
Observed rate constants for the reaction of $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$ with PMe_2Ph [a]

$[PMe_2Ph]/mol\ dm^{-3}$ [b]	$10^4k_{obs.}/s^{-1}$
0.378	31.6
	31.3
	32.0
0.288	21.1
	21.2
	21.0
0.188	13.4
	13.8
	14.0
0.093	7.33
	7.38
	7.29

[a] In propanone solution at 293.1 K. Initial concentration of molybdenum complex *ca.* 10^{-2} mol dm^{-3}. Rate constant values accurate to (at worst) ±5%. [b] After correction for consumption of PMe_2Ph in the conversion of $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NCMe)_2]$ into $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$.

Reduction of the complex $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(PMePh_2)_2]$ by $PMePh_2$ was significantly slower than that of $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$ by PMe_2Ph. This is probably due partly to the presence of the bulkier $PMePh_2$ ligands in the complex, which must inhibit attack, and partly to the fact that $PMePh_2$ is, for both steric and electronic reasons, a poorer nucleophile than PMe_2Ph. Reduction was also much slower for the 2-methylallyl complexes than for the corresponding allyl complexes. This could be due in part to the inductive effect of the methyl group, but it seems more likely that the effect is predominantly a steric one, with the methyl group hindering attack by the phosphorus ligand.

(*d*) *Dissociative Ligand Exchange in* $[Mo(CO)_2(PMe_2Ph)_4]$.—The ^1H n.m.r. spectrum of $[Mo(CO)_2(PMe_2Ph)_4]$ in chlorobenzene solution contained two resonances, centred at δ 1.23 and 1.48, attributable to the methyl protons in the PMe_2Ph ligands. This, coupled with the observation of two C–O stretching bands of similar intensity in the i.r. spectrum of the complex, showed that it is *cis*-$[Mo(CO)_2(PMe_2Ph)_4]$ [structure (I) where L = PMe_2Ph], with one methyl-proton resonance for the mutually *trans* pair of PMe_2Ph ligands L_t, and the other for the mutually *cis* pair L_c. Both resonances exhibited intermediate coupling:[8] here, as in other molybdenum(0) complexes,[9] the simple rule [10] that methyl protons in a pair of mutually ***trans*** phosphorus ligands give triplet resonances while those in a pair of equivalent mutually *cis* ligands give doublet resonances breaks down. Comparing chemical-shift and coupling-constant values with those for related complexes,[9] one would tentatively assign the resonance at δ 1.23 [$|^2J(P\text{–}H) + {}^4J(P\text{–}H)| = 4.0$ Hz] to the mutually *cis* pair of PMe_2Ph ligands, and that at δ 1.48 [$|^2J(P\text{–}H) + {}^4J(P\text{–}H)| = 5.0$ Hz] to the ***trans*** pair. The ^{13}C n.m.r. spectrum of the complex in C_6D_5Cl included a triplet of triplets resonance [both coupling constants $|^2J(P\text{–}C)|$ *ca.* 10 Hz] centred at δ 225.2 for the carbonyl-carbon atoms and resonances at δ 21.2 [$|^1J(P\text{–}C) + {}^3J(P\text{–}C)| = 8.8$ Hz] and 21.9 [$|^1J(P\text{–}C) + {}^3J(P\text{–}C)| = 9.8$ Hz] for the methyl carbon atoms in the two pairs of PMe_2Ph ligands.

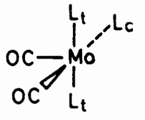


(I)

A study of the variation of the ^1H and ^{13}C n.m.r. spectra of *cis*-$[Mo(CO)_2(PMe_2Ph)_4]$ with temperature revealed that the presence of four fairly bulky phosphorus ligands in the complex makes some of the metal–ligand bonds relatively weak. At 313 K, the ^1H spectrum of a C_6D_5Cl solution of the complex containing added PMe_2Ph exhibited a sharp doublet for the methyl protons of the free PMe_2Ph in addition to the resonances for the complex. At 353 K, however, the resonance at δ 1.23 due to one pair of PMe_2Ph ligands in the complex and that for the free phosphine started to broaden, while that at 1.48 due to the other pair of ligands remained sharp. As the temperature was raised still further, the broadened resonances coalesced, while that at δ 1.48 was still relatively sharp even at 398 K. The original spectrum was regenerated on cooling. The temperature at which broadening occurred appeared to be independent of the concentration of free PMe_2Ph, indicating that the mechanism of exchange is dissociative. The ^{13}C spectrum of the solution changed with temperature in a similar manner: of the two resonances for the methyl carbon atoms in the PMe_2Ph ligands, that at δ 21.2 broadened simultaneously with the resonance for the methyl-carbon atoms in the free PMe_2Ph as the temperature was raised, whereas the resonance at δ 21.9 was still sharp at 398 K.

Thus it is clear that exchange of one pair of PMe_2Ph ligands in *cis*-$[Mo(CO)_2(PMe_2Ph)_4]$ with free PMe_2Ph occurs without scrambling of the two pairs of PMe_2Ph ligands in the complex. On the basis of the assignment of the ^1H spectrum suggested above, the labile bonds would be those to the mutually *cis* PMe_2Ph ligands. This could be taken to indicate that in this complex CO has a greater *trans*-labilizing effect than does PMe_2Ph, but it should be noted that Atwood and Brown [11] have argued in favour of a *cis* effect in low-valent octahedral transition-metal complexes: noting that the labile PMe_2Ph ligands are *cis* to three PMe_2Ph ligands and one carbonyl ligand (whereas the non-labile ligands are *cis* to two PMe_2Ph ligands and two carbonyl ligands) one could equally suggest that PMe_2Ph has a greater *cis*-labilizing influence than does CO.

The simplest explanation for the absence of scrambling in the exchange process is that the five-co-ordinate intermediate $[Mo(CO)_2(PMe_2Ph)_3]$ has square-pyramidal geometry {as has been proposed [12,13] for $[Mo(CO)_5]$ and for complexes $[Mo(CO)_4L]$ where L is a phosphorus ligand} as shown in (II) (where L = PMe_2Ph), and that (II) is stereochemically rigid and does not interconvert with the equivalent but scrambled species (III). It should, however, be noted that exchange by way of a trigonal-bipyramidal intermediate would also occur without scrambling, *provided* that it is indeed the mutually *cis* pair of PMe_2Ph ligands which exchange with free PMe_2Ph. As shown in the Scheme (where L = PMe_2Ph) loss of one of these ligands (L_c) would leave either of two such intermediates. On the basis of the principle of microscopic reversibility, L_c will re-enter *trans* to a carbonyl ligand in the equatorial plane of the trigonal bipyramid, yielding unscrambled *cis*-$[Mo(CO)_2(PMe_2Ph)_4]$. A similar mechanism for preferential exchange of the mutually *trans* pair of PMe_2Ph ligands, L_t, can, in contrast, be shown to lead to scrambling of L_c and L_t.



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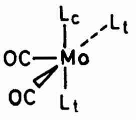

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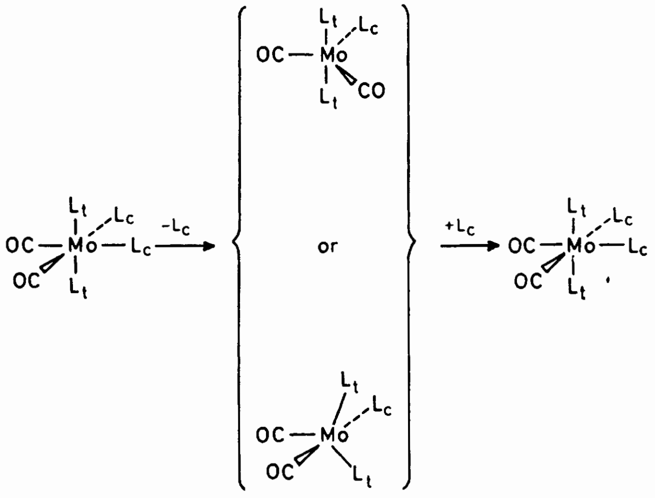

SCHEME

The contention that the labile bonds in the complex are those to the mutually *cis* PMe_2Ph ligands receives support from the manner in which the complex *cis*-$[Mo(CO)_2(PMe_2Ph)_4]$ decomposes in solution. When the complex was heated in chlorobenzene solution at 353 K in the absence of free PMe_2Ph, it was slowly converted into a single isomer, the *mer* isomer, of $[Mo(CO)_3(PMe_2Ph)_3]$ (the decomposition was shown to be inhibited by free PMe_2Ph). Both *mer* and *fac* isomers of $[Mo(CO)_3(PMe_2Ph)_3]$ are known,[9] and by subjecting a sample of the *fac* isomer to the conditions used for the decomposition of *cis*-$[Mo(CO)_2(PMe_2Ph)_4]$ we were able to rule out the possibility that the initial product of decomposition of *cis*-$[Mo(CO)_2(PMe_2Ph)_4]$ was the *fac* isomer and that this subsequently rearranged to the *mer* isomer. Thus the mechanism of decomposition must lead specifically to the *mer* isomer. This is exactly what one would expect on the basis of the results for the ligand-exchange process for *cis*-$[Mo(CO)_2(PMe_2Ph)_4]$. Since the decomposition is inhibited by free PMe_2Ph, it seems likely that the first step involves loss of PMe_2Ph to yield $[Mo(CO)_2(PMe_2Ph)_3]$. Some of this decomposes to liberate CO, which reacts with more $[Mo(CO)_2(PMe_2Ph)_3]$ to generate *mer*-$[Mo(CO)_3(PMe_2Ph)_3]$. On the assumption that it is the bonds to the mutually *cis* PMe_2Ph ligands which are labile, the *mer* isomer is the expected product regardless of whether the intermediate is assumed to be square-pyramidal or trigonal-bipyramidal. If, however, the mutually *trans* PMe_2Ph ligands were labile, the expected product would be *fac*-$[Mo(CO)_3(PMe_2Ph)_3]$.

If the difference in lability between the bonds to the two pairs of PMe_2Ph ligands in *cis*-$[Mo(CO)_2(PMe_2Ph)_4]$ *is* attributed to a *trans*- rather than a *cis*-labilizing effect, it is interesting to note that the order of *trans* effects ($CO > PMe_2Ph$) is the reverse of that observed [14,15] for octahedral complexes of ruthenium(II), which is isoelectronic with molybdenum(0). This would presumably reflect the alteration in the relative importance of σ and π contributions to metal–ligand bonding with change in oxidation state.

EXPERIMENTAL

Instrumentation.—Infrared spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer, ^1H n.m.r. spectra either on a Varian A-60A spectrometer with V-6057 variable-temperature accessory or on a JEOL N-MH-100 spectrometer using the JEOL NM-VT-3B variable-temperature attachment, ^{13}C n.m.r. spectra on a JEOL FX-60 instrument with the JEOL NM-5471 variable-temperature attachment, and visible and near-u.v. spectra on a Unicam SP 800 spectrophotometer. Kinetic data for the reaction of $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$ with PMe_2Ph were obtained by monitoring the change in absorbance of the reaction solution at 1 935 cm^{-1}. The solvent, propanone, was saturated with dry nitrogen, and the reaction was carried out under an atmosphere of dry nitrogen. The values given for the observed first-order rate constant in Table 2 were obtained from a least-mean-squares treatment of absorbance and time data.

Preparation of Complexes.—All preparative work was carried out under an atmosphere of dry nitrogen. The boiling range of the light petroleum used was 353—373 K.

$[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NCMe)_2]$. The method used was a modification of that described by tom Dieck and Friedel.[1]

A solution of $[\mathrm{Mo(CO)_6}]$ (2.64 g) and 3-chloropropene (1.21 g) in MeCN (50 $\mathrm{cm^3}$) was heated under reflux for 6 h. The solution was then allowed to cool and stand under a stream of nitrogen. Orange crystals of the product were formed. These were filtered off and washed with cold MeCN (m.p. 391—393 K, yield 77%) (Found: C, 34.7; H, 3.55; N, 9.05. Calc. for $\mathrm{C_9H_{11}ClMoN_2O_2}$: C, 34.8; H, 3.55; N, 9.00%).

$[\mathrm{Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NCMe)_2}]$. This was prepared by the same method, using 3-chloro-2-methylpropene (1.43 g) in place of 3-chloropropene (m.p. 388—390 K, yield 80%) (Found: C, 36.55; H, 3.95; N, 8.35. Calc. for $\mathrm{C_{10}H_{13}ClMoN_2O_2}$: C, 37.0; H, 4.05; N, 8.65%).

$[\mathrm{Mo(CO)_2Cl(\eta\text{-}C_4H_7)(PMe_2Ph)_2}]$. To $[\mathrm{Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NCMe)_2}]$ (0.23 g) dissolved in the minimum quantity of MeCN was added $\mathrm{PMe_2Ph}$ (0.20 g). Solvent was removed under reduced pressure until crystallization started. The mother liquor was removed from the red crystals obtained, which were washed with ethanol and then with light petroleum (m.p. 386—389 K, yield 74%) (Found: C, 50.45; H, 5.55. Calc. for $\mathrm{C_{22}H_{29}ClMoO_2P_2}$: C, 50.9; H, 5.60%).

$[\mathrm{Mo(CO)_2Cl(\eta\text{-}C_4H_7)(PMePh_2)_2}]$. To a solution of $[\mathrm{Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NCMe)_2}]$ (0.64 g) in MeCN (50 $\mathrm{cm^3}$) was added $\mathrm{PMePh_2}$ (1.20 $\mathrm{cm^3}$). After a few minutes' stirring, the solution was reduced in volume under a stream of $\mathrm{N_2}$. Golden crystals were obtained. After removal of the mother liquor, the crystals were washed with MeCN and then with pentane (m.p. 390—392 K, yield 75%) (Found: C, 59.45; H, 5.10; Cl, 5.65. Calc. for $\mathrm{C_{32}H_{33}ClMoO_2P_2}$: C, 59.8; H, 5.15; Cl, 5.50%).

$[\mathrm{Mo(CO)_2Cl(\eta\text{-}C_4H_7)(Ph_2PCH_2CH_2PPh_2)}]$. Solutions of $[\mathrm{Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NCMe)_2}]$ (0.20 g) and $\mathrm{Ph_2PCH_2CH_2PPh_2}$ (0.26 g) in minimum volumes of MeCN were mixed. Orange crystals of the product formed fairly quickly. These were filtered off, washed with ethanol and then with light petroleum (m.p. 469—472 K, yield 83%) (Found: C, 59.85; H, 4.90. Calc. for $\mathrm{C_{32}H_{31}ClMoO_2P_2}$: C, 59.95; H, 4.90%).

$[\mathrm{Mo(CO)_2(PMe_2Ph)_4}]$. A solution of $[\mathrm{Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NCMe)_2}]$ (0.62 g) in ethanol (50 $\mathrm{cm^3}$) was treated with $\mathrm{PMe_2Ph}$ (1.40 $\mathrm{cm^3}$) and then stirred to ensure complete mixing. Yellow crystals were slowly deposited in the reaction flask. These were filtered off, washed with ethanol and then with methanol (m.p. 400—402 K, yield 97%) (Found: C, 57.6; H, 6.25. Calc. for $\mathrm{C_{34}H_{44}MoO_2P_4}$: C, 57.95; H, 6.30%).

Removal of the solvent from the mother liquor under reduced pressure left a residue identified as $[\mathrm{C_3H_5PMe_2Ph}]\mathrm{Cl}$ by comparison of its ^{1}H n.m.r. spectrum with that of an authentic sample prepared from 3-chloropropene and $\mathrm{PMe_2Ph}$.

A similar reaction procedure using $[\mathrm{Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NCMe)_2}]$ yielded the same product rather more slowly, and $[\mathrm{Mo(CO)_2(PMe_2Ph)_4}]$ could also be prepared from $[\mathrm{Mo(CO)_2Cl(\eta\text{-}C_4H_7)(PMe_2Ph)_2}]$ and $\mathrm{PMe_2Ph}$ in MeCN.

$[\mathrm{Mo(CO)_2(NCMe)(PMePh_2)_3}]$. To a solution of $[\mathrm{Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NCMe)_2}]$ (0.66 g) in MeCN (50 $\mathrm{cm^3}$) was added $\mathrm{PMePh_2}$ (0.80 $\mathrm{cm^3}$). The solution was left under a slow stream of nitrogen, and orange crystals were slowly formed. These were filtered off, washed with MeCN and then with light petroleum (m.p. 407—409 K, yield 68%) (Found: C, 64.9; H, 5.45; N, 1.75. Calc. for $\mathrm{C_{43}H_{42}MoNO_2P_3}$: C, 65.05; H, 5.35; N, 1.75%).

A similar reaction procedure using $[\mathrm{Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NCMe)_2}]$ yielded the same product rather more slowly.

$[\mathrm{Mo(CO)_2(Ph_2PCH_2CH_2PPh_2)_2}]$. The complex $[\mathrm{Mo(CO)_2Cl(\eta\text{-}C_4H_7)(Ph_2PCH_2CH_2PPh_2)}]$ (0.67 g) and $\mathrm{Ph_2PCH_2CH_2PPh_2}$ (0.80 g) were placed in the thimble of a Soxhlet apparatus. In the flask was placed MeCN (50 $\mathrm{cm^3}$). When the solvent was heated under reflux, the reactants were slowly extracted into solution, and yellow crystals of the product were formed (m.p. 541—543 K, yield 77%) (Found: C, 68.15; H, 5.05. Calc. for $\mathrm{C_{54}H_{48}MoO_2P_4}$: C, 68.35; H, 5.10%).

The same complex could also be obtained by reaction of $[\mathrm{Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NCMe)_2}]$ and $\mathrm{Ph_2PCH_2CH_2PPh_2}$ in MeCN, with only the diphosphine in the Soxhlet thimble.

fac- *and* mer-$[\mathrm{Mo(CO)_3(PMe_2Ph)_3}]$. These were prepared by the methods described by Jenkins *et al.*[9]

Thermal Decomposition of cis-$[\mathrm{Mo(CO)_2(PMe_2Ph)_4}]$.—A chlorobenzene solution of *cis*-$[\mathrm{Mo(CO)_2(PMe_2Ph)_4}]$ was heated at 353 K in an n.m.r. tube. The ^{1}H n.m.r. spectrum of the solution was recorded at intervals. As the resonances due to the methyl protons in *cis*-$[\mathrm{Mo(CO)_2(PMe_2Ph)_4}]$ slowly decreased in area, new resonances characteristic of free $\mathrm{PMe_2Ph}$ and of *mer*-$[\mathrm{Mo(CO)_3(PMe_2Ph)_3}]$ (identified by comparison with the spectrum of the authentic sample of the material recorded under the same conditions) increased in area. The characteristic methyl proton resonance of *fac*-$[\mathrm{Mo(CO)_3(PMe_2Ph)_3}]$ was not observed.

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REFERENCES

[1] H. tom Dieck and H. Friedel, *J. Organometallic Chem.*, 1968, **14**, 375.

[2] H. Friedel, I. W. Renk, and H. tom Dieck, *J. Organometallic Chem.*, 1971, **26**, 247.

[3] M. Aresta and A. Sacco, *Gazzetta*, 1972, **102**, 755.

[4] R. Mattieu, M. Lenzi, and R. Poilblanc, *Inorg. Chem.*, 1970, **9**, 2030.

[5] M. Hidai, K. Tominari, and Y. Uchida, *J. Amer. Chem. Soc.*, 1972, **94**, 110.

[6] J. Chatt and H. R. Watson, *J. Chem. Soc.*, 1961, 4980.

[7] B. J. Brisdon and K. E. Paddick, *J. Organometallic Chem.*, 1978, **149**, 113.

[8] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

[9] J. M. Jenkins, J. R. Moss, and B. L. Shaw, *J. Chem. Soc. (A)*, 1969, 2796.

[10] J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 1963, 279; and many subsequent papers by Shaw and his co-workers.

[11] J. D. Atwood and T. L. Brown, *J. Amer. Chem. Soc.*, 1976, **98**, 3160.

[12] J. D. Black and P. S. Braterman, *J. Amer. Chem. Soc.*, 1975, **97**, 2908.

[13] R. N. Perutz and J. J. Turner, *J. Amer. Chem. Soc.*, 1975, **97**, 4791.

[14] J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem. Soc. (A)*, 1966, 1787.

[15] C. F. J. Barnard, J. A. Daniels, J. Jeffery, and R. J. Mawby, *J.C.S. Dalton*, 1976, 953.