Complexes of Group VI Hexacarbonyls with Group V Ligands containing an Olefinic Side-chain

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The Group VI hexacarbonyls have been treated with potentially chelating ligands of the type $CH_2{=}CHCH_2CH_2EMe_2$, where E = N, P, or As (nol, pol, and asol respectively). The amine forms solely chelate complexes with the general formula $[M(CO)_4(nol)]$ with each hexacarbonyl; however, the phosphine and arsine form not only chelate complexes with this general formula but also complexes with the general formulae $[M(CO)_4(CH_2{:}CHCH_2CH_2EMe_2)_2]$ and $[M(CO)_5(CH_2{:}CHCH_2CH_2EMe_2)]$, in each of which the ligand is co-ordinated by way of the E atom only. The factors contributing to this behavioural difference between the ligands are discussed. For the complexes $[M(CO)_4(nol)]$ and $[W(CO)_4(pol)]$ variable-temperature i.r. studies are interpreted as indicating the presence of rotational isomers in solution. The mechanism whereby the isomers interconvert is discussed. The complexes $[Mo(NO)_2Cl_2(asol)_2]$ and $[PdCl_2(asol)]$ have been isolated from the reactions of asol with $[Mo(NO)_2Cl_2]$ and $[PdCl_2(NCPh)_2]$ respectively.

THE initial studies [1,2] of the reactions of potentially chelating alkenyl ligands of the kind (I; E = P or As, R = Me or Ph) were directed towards the later transition elements. More recently, complexes of ligands of the kind (II; E = P or As, R = Me or Ph) [3-5] have been prepared, and the work has been extended to the early elements of Groups V [6] and VI.[7-10] We now report the preparations and properties of complexes of the ligands (III; E = N, P, or As; R = Me) with the Group VI hexacarbonyls. Since this work was commenced, similar complexes have been reported for ligands of the kind (III; E = P; R = Ph or Et).[11,12] For complexes

$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}ER_2$ (I)

$o\text{-}CH_2{:}CH{\cdot}C_6H_4{\cdot}ER_2$ (II)

$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}ER_2$ (III)

of type (III) ligands, involving co-ordination to the metal of atom E only, there are more conformational possibilities where the olefin is distant from the metal atom

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[1] H. W. Kouwenhoven, J. Lewis, and R. S. Nyholm, *Proc. Chem. Soc.*, 1961, 220.

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[3] M. A. Bennett, J. Chatt, G. J. Erskine, J. Lewis, R. F. Long, and R. S. Nyholm, *J. Chem. Soc.*, 1967, 501.

[4] M. A. Bennett, G. J. Erskine, and R. S. Nyholm, *J. Chem. Soc.*, 1967, 1260.

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[9] H. Luth, M. R. Truter, and A. Robson, *J. Chem. Soc.* (*A*), 1969, 28.

[10] M. A. Bennett and I. B. Tomkins, *J. Organometallic Chem.*, 1973, **51**, 289.

[11] P. E. Garrou and G. E. Hartwell, *J. Organometallic Chem.*, 1973, **55**, 331.

[12] K. Issleib and M. Haftendorn, *Z. anorg. Chem.*, 1967, **351**, 9.

than is the case for similar complexes of type (II) ligands. In this latter case the phenyl ring constrains the olefin to be near the metal atom. Hence the entropy lost on forming a chelate ring from the former is greater than that lost in forming a similar ring from the latter. As a result, factors affecting the metal–olefin bond strength are of greater consequence to the stability of the chelate ring of type (III) ligands than of type (II) ligands. In the case where E = N (type (III), the electron density on the metal atom is likely to be greater than where E = P or As, and thus π-electron back donation could lead to the possibility of more effective metal–olefin bond stabilization in the former case.

RESULTS AND DISCUSSION

Preparations and Reactivities of Complexes.—Chelate complexes of the amine (III; E = N, R = Me) (nol) have been prepared by three different routes. Under

$$\text{A } [\mathrm{M(CO)_4(nor)}] + \text{nol} \xrightarrow{\text{heat/benzene}} [\mathrm{M(CO)_4(nol)}] \quad \mathrm{M = Cr, Mo, or\ W}$$

(nor = norbornadiene)

$$\text{B } [\mathrm{Mo(CO)_6}] + \text{nol} \xrightarrow{\text{heat/toluene}} [\mathrm{Mo(CO)_4(nol)}]$$

$$\text{C } [\mathrm{Mo(CO)_6}] + \text{nol} \xrightarrow[\text{pentane}]{\text{u.v. (Hg arc)}} [\mathrm{Mo(CO)_4(nol)}] \text{ (mainly)}$$

no conditions tried could more than 1 mole of nol be made to co-ordinate to the metal atom. Even on prolonged treatment *via* routes A or B with a large excess of the ligand, the metal-containing species still only formed the complex [M(CO)$_4$(nol)] (M = Cr, Mo, or W). Moreover, when the complex [Mo(CO)$_4$(nol)] was treated with carbon monoxide at room temperature and 1 atm, only the hexacarbonyl was produced (i.r. evidence).

The reactivity of the corresponding phosphine (III; E = P, R = Me; abbreviated pol) differed from the amine. Chelate complexes were again obtained by way of route A for M = Mo or W. However, a non-chelate complex, [Mo(CO)$_5$(pol)], involving co-ordination through the phosphorus atom alone, was also obtained by reaction of [Mo(CO)$_6$] with pol (route B).

Attempts to prepare chelate complexes of the arsine (III; E = As, R = Me; abbreviated asol) by the same routes were much less successful. A chelate complex was indeed obtained by way of route A for M = W but not for M = Cr or Mo. By contrast, both the complexes [Cr(CO)$_4$(nor)] and [Mo(CO)$_4$(nor)] reacted with asol to give complexes of the type *cis*-[M(CO)$_4$(asol)$_2$] in which the ligand is co-ordinated to the metal atom by way of the E atom only (analytical, i.r., and n.m.r. evidence, see later). The reaction of hexacarbonylmolybdenum with asol (route B) gave the complex [Mo(CO)$_5$(asol)], in which again the arsenic atom but not the olefin grouping was co-ordinated to the metal atom. The reaction of hexacarbonylmolybdenum with asol (route C) gave a complicated mixture which could not be separated into its components.

The phosphine and, in particular, arsine thus appear to be much more reluctant to form chelate complexes than the amine. Consider the reaction:

$$[\mathrm{M(CO)_4(CH_2{:}CHCH_2CH_2EMe_2)}] \xrightleftharpoons[-\mathrm{CH{:}CHCH_2CH_2EMe_2}]{+\mathrm{CH_2{:}CHCH_2CH_2EMe_2}} [\mathrm{M(CO)_4(CH_2{:}CHCH_2CH_2EMe_2)_2}]$$

(co-ordination of olefin to displace an E atom)

The equilibrium for the amine case would be further to the left than for the phosphine or arsine cases, first because of the greater bond energy of the metal–phosphine or arsine bond due to π-back bonding and secondly because of the inherent instability of complexes with more than one tertiary amine, due to the small M–N–C bond angle and short M–N bond length. {For instance whereas the complex [Mo(CO)$_4$(Et$_2$PCH$_2$-CH$_2$PEt$_2$)] [13] is stable indefinitely, the complex [Mo(CO)$_4$-(Et$_2$NCH$_2$CH$_2$NEt$_2$)] [14] decomposes *in vacuo* at room temperature.} When carbon monoxide was added to a solution of [Mo(CO)$_4$(nol)] no peaks corresponding to a pentacarbonyl species [15] were seen in the i.r. spectrum, indicating that the metal–nitrogen and metal–olefin bonds do not differ much in strength.[14,16]

The difficulty in isolating chelates of the phosphine and arsine may not reflect their instability but be an artefact of the preparative method. The phosphine and arsine react very much faster with the norbornadiene complexes than does the amine.* It is possible that this much greater reactivity of the Me$_2$P and Me$_2$As groups favours the displacement of an olefin from an initially produced chelate complex rather than the displacement of a norbornadiene molecule from another reactant molecule (route A). Evidence for this was found as follows. When 40 mole percent of asol was slowly added to a solution of [Mo(CO)$_4$(nor)], a mixture of [Mo(CO)$_4$(nor)] and at least one other uncharacterised compound was isolated; moreover the n.m.r. spectrum contained the pattern of peaks expected for the chelate complex [Mo(CO)$_4$(asol)] in addition to those of [Mo(CO)$_4$(nor)]. (Attempts to obtain this asol complex pure were unsuccessful.) When more asol was added, peaks indicating the presence of *cis*-[Mo(CO)$_4$(asol)$_2$] were found in the i.r. spectrum; this complex was isolated and characterised.

When the complex [Mo(CO)$_5$(asol)] was strongly heated or irradiated with u.v. light only a slow reaction took place to produce several products including *cis*-[Mo(CO)$_4$(asol)$_2$] and [Mo(CO)$_6$]. No detectable amount of the chelate was produced.

The carbonyl stretching frequencies for the complexes

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* For a discussion of the mechanisms of the substitution reactions of [Mo(CO)$_4$(nor)] see ref. 17.

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

[14] G. R. Dobson, R. C. Taylor, and T. D. Walsh, *Inorg. Chem.*, 1967, **6**, 1929.

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[16] G. C. Faber, T. D. Walsh, and G. R. Dobson, *J. Amer. Chem. Soc.*, 1968, **90**, 4178.

[17] H. Werner, *Angew. Chem. Internat. Edn.*, 1968, **7**, 930; A. Z. Rubezhov and S. P. Gubin, *Adv. Organometallic Chem.*, 1972, **10**, 347.

of the type $[W(CO)_4(CH_2{:}CHCH_2CH_2EMe_2)]$ (E = N, P, or As) are lower for the nol complex than the others. This confirms a greater electron density on the metal in this case where nitrogen, unlike phosphorus or arsenic, cannot engage in π-back bonding. However, interpretation of the n.m.r. spectra does not suggest that this electron density in the amine complex is used in strengthening the metal–olefin bond. In the ^1H n.m.r. spectra the upfield shifts of the olefinic protons from the values for the free ligand are very similar in all three cases.

Properties of Complexes.—The complexes are yellow crystalline solids or pale liquids which are stable indefinitely at room temperature *in vacuo*, but slowly decompose in air. Some of their properties are summarised in Table 1.

TABLE 1

Some properties of the complexes prepared

				Mass spectra		
Compound	Colour	M.p. (*t*/°C) [a]	ν(C=C) (i.r. studies)	*M* Calc.	*M* Obs.	No. CO's lost
$[Cr(CO)_4(nol))]$	Yellow	130—140 (dec.)	*b*	263	263	4
$[Mo(CO)_4(nol)]$	Yellow	140—150 (dec.)	*b*	309	308	4
$[W(CO)_4(nol)]$	Yellow	160—170 (dec.)	*b*	395	395	4
$[Mo(CO)_4(pol)]$	Pale yellow	53—55	*b*	326	326	4
$[W(CO)_4(pol)]$	Pale yellow	66—68	*b*	412	412	4
$[W(CO)_4(asol)]$	Pale yellow	118—120	*b*	456	456	4
$[Cr(CO)_4(asol)_2]$	Yellow	32—33	1640	484	484	4
$[Mo(CO)_4(asol)_2]$	Yellow	36—40	1641	530	531	$\geqslant 3$
$[Mo(CO)_5(pol)]$	Colourless oil		1644	354	353	5
$[Mo(CO)_5(asol)]$	Yellow oil		1641	398	398	5
$[Mo(CO)_3(asol)_3]$	Pale yellow	30—31	1637	662	488 [c]	
$[Mo(NO)_2Cl_2(asol)_2]$	Green	30—33	*d*	548	550	
$[PdCl_2(asol)]$	Yellow	130—140 (dec.)	1522	337	*e*	

[a] Determined in sealed capillaries *in vacuo*; uncorrected. [b] This vibration is strongly coupled with the $\nu(CH_2)$ vibration and no clear assignment can be given. Many bands occur in the relevant frequency region (1250—1550 cm^{-1}). Raman studies of the first three complexes, both as solutions and as solids, failed to assist in making this assignment. [c] Highest observed ion. [d] Obscured by the 1671 cm^{-1} NO stretching band, which is very intense and broad. [e] No spectrum obtained up to 200 °C.

TABLE 2

Solution i.r. spectra of the complexes in the CO stretching region (cm^{-1}) [a]

Complex	Solvent	$a_1^{(2)}$	$a_1^{(1)}$	b_1	b_2
$[Cr(CO)_4(nol)]$	*b*	2021m	1927m	1912vs	1883s
$[Mo(CO)_4(nol)]$	*b*	2032m	1930m	1921vs 1914m	1887s
$[W(CO)_4(nol)]$	*b*	2028m	1925m	1914vs	1882s
$[Mo(CO)_4(pol)]$	*c*	2030m	1942m	1926m	1916vs
$[W(CO)_4(pol)]$	*c*	2029m	1938m	1922m	1913w, sh 1907s
$[W(CO)_4(asol)]$	*c*	2029m	1935m	1917m, sh	1907vs
$[Cr(CO)_4(asol)_2]$	*c*	2007ms	1912s	1897vs	1887s
$[Mo(CO)_4(asol)_2]$	*c*	2021m	1921s	1908vs	1894s
		a_1	b_1 [e]	e	a_1
$[Mo(CO)_5(pol)]$	*c*	2071w	(1983)	1953m, sh 1946vs	1915vw
$[Mo(CO)_5(asol)]$	*d*	2072m		1948vs	1917w [f]
				a_1	e
$[Mo(CO)_3(asol)_3]$	*b*			1941s	1847vs
		a_1		b_1	
$[Mo(NO)_2Cl_2(asol)_2]$ [g]	*h*	1781s		1671vs	

[a] Abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder. [b] Heptane. [c] Pentane. [d] Hexane. [e] Observed only in the Raman spectrum (band is depolarised). [f] The frequency difference between the 1948 and 1917 cm^{-1} bands is too great for the latter to be the ^{13}C counterpart of the former. *Cf.* F. A. Cotton, A. Musco, and G. Yagupsky, *Inorg. Chem.*, 1967, **6**, 1357. [g] NO stretching frequencies. [h] Chloroform.

The i.r. band maxima found in the hydrocarbon-solution spectra of the complexes are listed in Table 2. In all cases but two, four band maxima have been found, consistent with expectation for *cis*-octahedral complexes, and these bands have been given the usual assignments [18] according to C_{2v} nomenclature.

In two cases $[Mo(CO)_4(nol)]$ and $[W(CO)_4(pol)]$ a fifth CO stretching band has been observed, and this observation is taken to indicate the presence of isomers in solution (see following section).

In common with many previous results on substituted metal carbonyls, increase of the degree of replacement of the carbonyl groups by other ligands leads to a lowering of the stretching frequencies of the remaining CO groups, *e.g.* for the molybdenum complexes the

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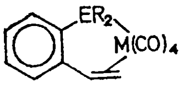
[18] L. E. Orgel, *Inorg. Chem.*, 1962, **1**, 25.

degeneracy weighted average CO stretching frequencies are $[\mathrm{Mo(CO)_5(asol)}]$ 1971, $[\mathrm{Mo(CO)_4(asol)_2}]$ 1936, and $[\mathrm{Mo(CO)_3(asol)_3}]$ 1878 $\mathrm{cm^{-1}}$. The CO stretching frequencies of the complexes lie in the order W $\sim$ Mo $>$ Cr and pol $\geqslant$ asol $>$ nol.



Rotational Isomerism.—Bennett *et al.*[10] found that certain complexes of the type show more than four bands in the carbonyl region of their i.r. spectra, and that these bands were not removed by successive recrystallisations. Noting a slight change in the intensity pattern when solutions were cooled they postulated the presence of rotational isomers which were rapidly interconverting in solution, the equilibrium constant varying with temperature. Truter *et al.*[9] had previously noted the possibility of such isomerism and found (on the basis of *X*-ray studies) that for the complex $[(\mathrm{CO})_4\mathrm{Mo}(o\text{-}\mathrm{Ph_2P{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH_3}\text{-}cis)]$ only one isomer was present in the solid state (that with the double bond almost in the equatorial plane of the molecule). For the present case, the two possible rotational isomers are illustrated in Figure 1.

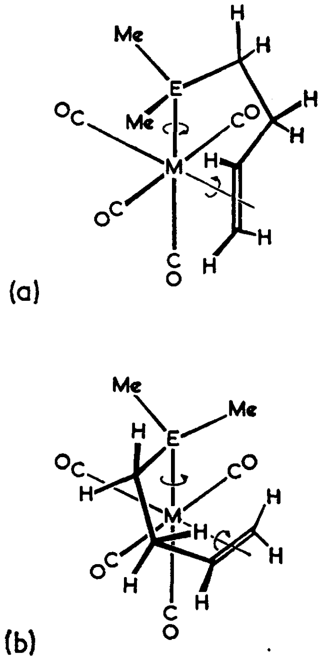


FIGURE 1 The rotational isomers of the complex $[\mathrm{M(CO)_4(CH_2{:}CHCH_2CH_2EMe_2)}]$

In the present study the solution i.r. spectra of the complexes $[\mathrm{Mo(CO)_4(nol)}]$ and $[\mathrm{W(CO)_4(pol)}]$ also show more than four bands in the carbonyl region (see Table 2) the numbers of which are not reduced by successive recrystallisations. When the solutions were cooled, slight reversible changes occurred in the intensity pattern; in the former case the band at 1914 $\mathrm{cm^{-1}}$ became progressively weaker relative to the others as the temperature was reduced (see Figure 2) while in the latter that at 1922 $\mathrm{cm^{-1}}$ became relatively weaker. These changes are not primarily caused by changes in half-band widths or slight frequency shifts of any of the bands. Taken in context with the studies of Bennett *et al.*[10] these observations indicate the presence of both rotational isomers in solution and that the equilibrium between them varies with temperature.

N.m.r. spectra of these two complexes and the others involving chelated ligands were recorded at low temperature (0 to -90 °C) in both $[^2\mathrm{H}_8]$toluene and $[^2\mathrm{H}]$chloroform. In no case did these studies indicate the presence of two isomers which were not rapidly interconverting on the n.m.r. time scale. It is not clear whether this is because the isomers rapidly interconvert even at -90 °C or because the n.m.r. spectra of the isomers are very nearly identical.

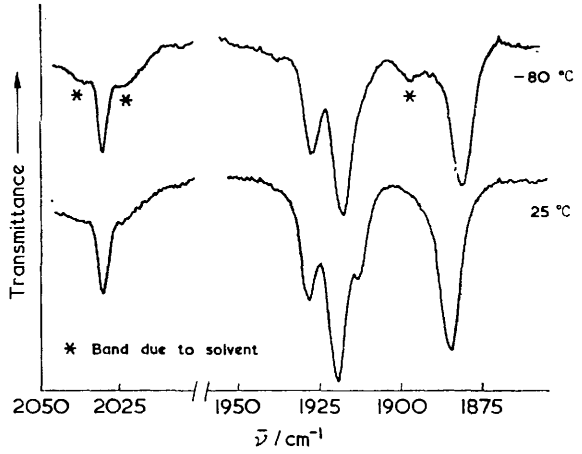


FIGURE 2 The solution i.r. spectrum of the complex $[\mathrm{M(CO)_4(nol)}]$ at 25 and -80 °C in the carbonyl stretching region. Bands due to the solvent (n-heptane) are marked with asterisks

If the differences in chemical shifts of the various protons in each isomer were large it is possible that the room temperature n.m.r. spectra chemical shifts in various solvents would differ considerably due to a solvent effect on the equilibrium. N.m.r. spectral data on some of these complexes in various solvents at 27 °C are recorded in Table 3. The differences observed are not sufficiently large to rule out the possibility that these are due to a solvent shift on the same chemical species.

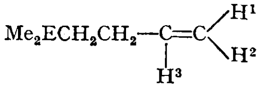
For the complexes $[\mathrm{M(CO)_4(nol)}]$ (M = Cr, Mo, or W) and $[\mathrm{Mo(CO)_4(asol)}]$ the resonance due to $\mathrm{H^1}$ appears further downfield than that due to $\mathrm{H^2}$ ($\mathrm{H^1}$ and $\mathrm{H^2}$ are assigned by their different coupling constants to $\mathrm{H^3}$). This order is the reverse of those previously reported for phosphine and arsine complexes,[10,11] although it is the same as that observed for each free ligand. The explanation for these observations is unknown.

Mechanism of Isomerisation.—The methyl resonances in the n.m.r. spectrum of $[\mathrm{Mo(CO)_4(nol)}]$ appear as two separate singlets even at room temperature. Thus the process interconverting the isomers cannot involve an intermediate or transition state where the methyl groups are equivalent. This is fully in agreement with the suggestion of Bennett *et al.*[10] that the mechanism involves a rotational isomerism and that neither end of the chelating ligand is dissociated.

Other Reactions.—The reactions of the complex $[Mo(NO)_2Cl_2]$ with both nol and asol have also been investigated (see Experimental section). Reaction took place in each case, but the product formed from the nol reaction could not be characterised. That from the asol reaction has been formulated as $[Mo(NO)_2Cl_2(asol)_2]$. On the basis of n.m.r. evidence (Table 3), the olefin grouping is considered to be unco-ordinated. On the basis of the i.r. spectrum in the NO stretching region (Table 2) as well as in the MoCl stretching region (two main bands at 307 and 286 cm^{-1}) the complex is believed to have both *cis*-NO groups as well as *cis*-chlorine atoms. However, both the NO as well as the MoCl absorption bands are structured, and the presence of smaller amounts of other isomers cannot be ruled out. On the basis of the formulations of similar complexes [19-22] (one of which is based on an *X*-ray structural investigation [22]), the arsenic atoms are probably in *trans*- rather than in *cis*-positions.

TABLE 3

N.m.r. spectral data on the complexes [a,b] at 27 °C



$Me_2ECH_2CH_2{-}\underset{H^3}{C}{=}C\begin{smallmatrix}H^1\\ H^2\end{smallmatrix}$

Compound	Solvent	δ_{H^1}	δ_{H^2}	δ_{H^3}	δ_{Me}	$J_{H^1-H^3}$	$J_{H^2-H^3}$	$J_{H^1-H^2}$
nol	$CDCl_3$	4·97m	4·93m	5·72m	2·07s	17·8	9·5	~2
$Me_2P(S)CH_2CH_2CH{:}CH_2$	CCl_4	5·08m	5·02m	5·86m	1·59d [c]	21·0	9·0	~2
asol	$CDCl_3$	5·00m	4·94m	5·82m	0·90s	19·7	8·2	2·2
$[Cr(CO)_4(nol)]$	$CDCl_3$	3·76d	3·24d	5·2m	2·31s	14·0	8·0	<1
$[Mo(CO)_4(nol)]$	$CDCl_3$	3·90d	3·29d	5·1m	2·66s	13·5	8·5	<1
$[W(CO)_4(nol)]$	$CDCl_3$	3·67d	3·38d	5·2m	2·76s	13·5	9·5	<1
$[Cr(CO)_4(nol)]$	C_6D_6	2·77d	2·34d	Too broad	1·11s	13·0	8·5	<1
$[Mo(CO)_4(nol)]$	C_6D_6	3·66d	3·13d	5·1m	1·67s 1·79s	14·0	8·5	<1
$[W(CO)_4(nol)]$	C_6D_6	3·30d	2·93d	4·6m	1·87s 1·91s	13·5	9·5	<1
$[Cr(CO)_4(nol)]$	C_7D_8	3·17d	2·75d	Too broad	1·41s 1·53s	14·0	8·5	<1
$[Mo(CO)_4(nol)]$	C_7D_8	3·75d	3·20d	5·0m	1·75s 1·86s	14·5	9·0	<1
$[W(CO)_4(nol)]$	C_7D_8	3·35d	3·00d	4·6m	1·93s 1·98s	13·5	9·5	<1
$[Cr(CO)_4(asol)_2]$	C_6D_6	4·96m	4·92m	5·6m	0·87s	17·5	11·0	~2
$[Mo(CO)_5(pol)]$	$CDCl_3$	5·12m	5·07m	5·9m	1·49d [d]	17·5	11·5	~2
$[Mo(CO)_5(asol)]$	$CDCl_3$	5·09m	5·01m	5·9m	1·40s	19·0	9·0	~2
$[Mo(CO)_4(asol)_2]$	$CDCl_3$	5·01m	4·95m	5·7m	1·30s	19·0	11·5	~2
$[Mo(CO)_3(asol)_3]$	$CDCl_3$	5·03m	4·97m	5·8m	1·27s	19·5	8·0	~2
$[Mo(CO)_4(asol)]$	C_6D_6	3·49d	3·23d	5·1m	0·82s 0·94s	12·0	7·5	<1
$[Mo(CO)_4(pol)]$	C_7D_8	3·26d	3·46	4·4m	0·83s [e] 1·00s	14·5	9·0	<1
$[W(CO)_4(pol)]$	C_7D_8	3·06d	3·38d	5·1m	1·56d [e] 1·71d	14·0	9·0	<1
$[W(CO)_4(asol)]$	C_6D_6	3·04d	3·39d	5·0m	0·98s 0·95s	13·5	9·5	<1
$[Mo(NO)_2Cl_2(asol)_2]$	$CDCl_3$	5·09m	5·04m	5·9m	1·53s	19·0	8·0	~2

[a] Chemical shifts (δ) are in p.p.m. downfield of internal Me_4Si. Coupling constants (*J*) are probably accurate to ±0·5 Hz. [b] Abbreviations: s, singlet; d, doublet; m, multiplet. [c] $J_{P-CH_3} = 11{\cdot}5$ Hz. [d] $J_{P-CH_3} = 7{\cdot}0$ Hz. [e] $J_{P-CH_3} = 8{\cdot}0$ Hz.

The ligand asol has also been treated with the benzonitrile complex $[PdCl_2(PhCN)_2]$ to give a yellow crystalline complex. The i.r. spectrum (Nujol mull) of this product shows no C=C stretching frequency at *ca.* 1640 cm^{-1} but shows bands assigned as follows: $\nu_{C=C}$ 1522w, ν_{M-Cl} 317s and 298vs. This spectrum closely resembles that of the complex $[Pd(Ph_2PCH_2CH_2CH{=}CH_2)Cl_2]$ [23] with the following reported bands: $\nu_{C=C}$ 1528w, ν_{M-Cl} 322s and 289s. The complex is thus formulated as $[PdCl_2(asol)]$ in which the ligand is chelating. No n.m.r. spectrum could be obtained in most organic solvents due to the insolubility of the complex; in $(CD_3)_2SO$, however, in which the complex was freely soluble, a spectrum was obtained which indicated the presence of a free olefin grouping. It is likely that the $(CD_3)_2SO$ has reacted with the complex in such a way as to displace the bonded olefin.

EXPERIMENTAL

Preparation of Ligands

But-3-enyldimethylamine (nol).—But-3-enyl bromide (10 g) was added slowly (½ h) with stirring to anhydrous dimethylamine (100 g) at 0 °C. The reaction evolved considerable heat and required cooling to prevent the

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dimethylamine boiling. The mixture was set aside at this temperature for 2 h and then all the volatile components distilled off and collected. This mixture was dried (Na_2SO_4) and fractionally distilled. The fraction boiling between 60 and 95 °C (760 mmHg) was collected, dried with calcium hydride, and redistilled. Pure nol distilled between 86 and 88 °C (760 mmHg). It was stored under nitrogen and freshly distilled before use (yield 75—80%).

But-3-*enyldimethylphosphine* (*pol*).—*Preparation of* $Me_2P(S)CH_2CH_2CH{=}CH_2$. A Grignard reagent was prepared from but-3-enyl bromide (13·2 g) and magnesium turnings (2·4 g) in ether (100 ml). This solution was filtered and $Me_2P(S)Br$ (17·0 g) in ether was added during 1 h to it and then set aside overnight. The mixture was then hydrolysed with an excess of 10% sulphuric acid and the ether layer washed (H_2O) and dried (Na_2SO_4). The ether was removed to give a white crystalline solid. This was recrystallised from a 1 : 1 mixture of pentane and toluene to give the sulphide as a white crystalline air-stable solid in 70% yield.

Samples of but-3-enyldimethylphosphine sulphide in toluene were heated in sealed tubes at 105 °C for 48 h with an excess of lithium aluminium hydride during which time the phosphine sulphide was reduced to the phosphine. The tubes were cooled, cracked open, and rapidly filtered free of solids under nitrogen and the solution of pol used immediately for the reactions described below.

But-3-*enyldimethylarsine* (*asol*).—To a Grignard reagent prepared from but-3-enyl bromide (8 g) and magnesium turnings (1·6 g) in ether (100 ml), iododimethylarsine (13·75 g) in ether (50 ml) was slowly added at 0 °C. The mixture was stirred for a further hour, decomposed with ammonium chloride solution, and siphoned under nitrogen into a separating funnel. The organic layer was separated, dried (Na_2SO_4), and distilled under nitrogen to yield the arsine as a colourless air-sensitive liquid in 40% yield (b.p. 130 °C, 760 mmHg). It was contaminated with small traces of ether. It was stored under nitrogen and freshly distilled before use.

Preparation of Complexes

Reaction of nol with $[M(CO)_4(nor)]$ (M = Cr, Mo, *or* W).—The appropriate $[M(CO)_4(nor)]$ complex was heated under nitrogen at reflux in benzene with nol (1·5 mol equiv.). After 3—4 h the reaction reached equilibrium with much of the starting material still remaining. It is likely that the displaced norbornadiene competes with nol for coordination to the metal atom. The benzene was removed at 30 °C, 0·1 mmHg; in the case of M = Cr, the excess of $[Cr(CO)_4(nor)]$ was sublimed out. The solid was extracted with heptane, filtered, and crystallised. The crude product was crystallised two or three more times (heptane or pentane) to yield the final product which was washed with pentane, then isopentane, and finally dried for 2 h at 10^{-2} mmHg. Infrared studies showed this product to be free of $[M(CO)_4(nor)]$ in each case. All products are formulated as $[M(CO)_4(nol)]$.

With a very large excess of nol (4—5 molar excess) less $[M(CO)_4(nor)]$ was left after 3 h but no bands were seen in the i.r. spectrum other than those produced by the complexes isolated above. On removal of benzene the solid was recrystallised as above (Found: C, 45·6; H, 4·9; N, 4·9. $C_{10}H_{13}CrNO_4$ requires C, 45·7; H, 5·0; N, 5·3%. Found: C, 39·8; H, 4·4; N, 4·5. $C_{10}H_{13}MoNO_4$ requires C, 39·2; H, 4·3; N, 4·5%. Found: C, 31·4; H, 3·4; N, 3·5. $C_{10}H_{13}WNO_4$ requires C, 30·4; H, 3·3; N, 3·5%).

Reaction of nol with $[M(CO)_6]$ (M = Mo *or* W).—$[M(CO)_6]$ Was heated under nitrogen by reflux in toluene with nol (1·5 mol equiv.). For M = Mo, much substitution had occurred after 6 h. The toluene was removed (30 °C, 10^{-1} mmHg), the excess of $[Mo(CO)_6]$ sublimed out, and the $[Mo(CO)_4(nol)]$ crystallised from heptane. For M = W, substitution was much slower and even after 10 h only a very little nol had reacted. No products were isolated in this case.

Irradiation of $[Mo(CO)_6]$ and nol (1 mol equiv.) in pentane at *ca.* 20 °C with a mercury arc in a water-cooled photolysis cell produced $[Mo(CO)_4(nol)]$ as the main product (identified by its i.r. spectrum). Two other i.r. bands (1940m, 1953vs,br) were also found in the i.r. spectrum of the product, but the compound giving rise to these bands was not identified.

Reaction of pol with $[Mo(CO)_6]$.—A solution of $[Mo(CO)_6]$ in toluene was heated with pol (mol ratio 3 : 1) in a sealed tube at 105 °C for 48 h. At the end of this time the tube was cooled, cracked open, and the solution decanted free of excess of $[Mo(CO)_6]$. The toluene was removed at 30 °C, 10^{-2} mmHg, and the colourless oil so obtained fractionally sublimed at 60 °C, 10^{-2} mmHg. The early fractions contained $[Mo(CO)_6]$ (identified by its i.r. spectrum) but later fractions were free of this impurity. The product was collected on a cooled (−78 °C) probe as a white solid which melted at *ca.* 0 °C to a colourless oil. This was formulated as $[Mo(CO)_5(pol)]$ (Found: C, 38·0; H, 3·8; P, 8·7. $C_{11}H_{13}MoO_5P$ requires C, 37·6; H, 3·7; P, 8·8%).

Reaction of pol with $[M(CO)_4(nor)]$ (M = Cr, Mo, *or* W).—M = Cr. A solution of pol in toluene (prepared as above) was rapidly filtered onto a frozen solution of $[Cr(CO)_4(nor)]$ in the same solvent (mol ratio 1 : 1). This was slowly warmed to 55—60 °C and held at this temperature for *ca.* 2 h. The solvent was removed and the yellow oil so obtained was extracted with pentane. The i.r. spectrum of this solution showed the presence of several substitution products together with $[Cr(CO)_4(nor)]$. Fractional sublimation and crystallisation failed to achieve separation of these complexes.

M = Mo *or* W. A solution of pol in toluene (prepared as above) was rapidly filtered onto a frozen solution of $[M(CO)_4(nor)]$ in the same solvent (mol ratio 1 : 1). This was slowly warmed to 55—60 °C and held at this temperature for *ca.* 2 h. At the end of this period the solvent was removed and the solid obtained was extracted with pentane, filtered, and cooled to −78 °C. Pale yellow crystals were slowly deposited. These were recrystallised first from pentane then isopentane and finally dried at 20 °C, 10^{-2} mmHg for 2 h. In both cases the product was formulated as $[M(CO)_4(pol)]$ (Found: C, 38·1; H, 4·2; P, 9·7. $C_{10}H_{13}MoO_4P$ requires C, 37·0; H, 4·1; P, 9·6%).

In the case of $[W(CO)_4(pol)]$, repeated recrystallisation failed to produce satisfactory C and H analyses (Found: P, 7·5. $C_{10}H_{13}O_4PW$ requires P, 7·5%).

Reaction of asol with $[Mo(CO)_6]$.—$[Mo(CO)_6]$ In toluene was heated under reflux with asol (1·2 mol equiv.) for 3 h. Toluene was removed to leave a dark brown oil. After pumping for some hours at 20 °C, this material was sublimed onto a cooled probe to give a yellow solid which melted to a pale yellow oil at *ca.* 0 °C. This was formulated as $[Mo(CO)_5(asol)]$ (Found: C, 33·6; H, 3·3. $C_{11}H_{13}AsMoO_5$ requires C, 33·4; H, 3·3%).

Reaction of asol with [M(CO)$_4$(nor)] (M = Cr, Mo, *or* W).—M = Mo. When a solution of [Mo(CO)$_4$(nor)] was mixed with asol in a mol ratio of 1 : 1, a mixture of several products was obtained. Unlike nol, asol required no heating for reaction to take place, and the reaction went to equilibrium at room temperature in *ca.* 1 h in both toluene and pentane. Attempts to separate this mixture by crystallisation and chromatography were unsuccessful. By use of a large excess of asol, [Mo(CO)$_4$(asol)$_2$] was isolated by holding the reagents under reflux in benzene for 4 h, and then recrystallising the product from pentane (Found: C, 37·9; H, 5·3. $C_{16}H_{26}As_2MoO_4$ requires C, 36·4; H, 5·0%).

Evidence for an olefin-co-ordinated complex was obtained as follows. A dilute solution of asol in pentane was slowly added to a solution of [Mo(CO)$_4$(nor)] in pentane. The reaction was monitored by i.r. spectroscopy; until more than 40 mol percent of asol had been added only one new group of peaks was produced. In addition to [Mo(CO)$_4$(nor)], the n.m.r. spectrum showed the pattern of peaks expected for [Mo(CO)$_4$(asol)] (see Table 3).

M = Cr. [Cr(CO)$_4$(nor)] Was held under reflux in benzene with asol (2·2 mol equiv.) under nitrogen. After 2 h, benzene was removed and the excess of [Cr(CO)$_4$(nor)] was sublimed out. Two recrystallisations from pentane yielded the product, [Cr(CO)$_4$(asol)$_2$], as yellow needles. These were washed with pentane and then dried at 20 °C, 10^{-2} mmHg for 2 h (Found: C, 41·1; H, 5·6; As, 31·7. $C_{16}H_{26}As_2CrO_4$ requires C, 39·7; H, 5·4; As, 31·0%).

M = W. A chelate olefin complex was isolated as follows. [W(CO)$_4$(nor)] Was held under nitrogen in refluxing benzene with (asol) (0·95 mol equiv.). After 1 h, the solvent was removed and the solid extracted from pentane. The yellow crystals deposited on cooling were recrystallised twice from pentane, and finally isopentane, to yield the complex [W(CO)$_4$(asol)] (Found: C, 27·0; H, 2·9. $C_{10}H_{13}AsO_4W$ requires C, 26·4; H, 2·9%).

When more asol was used in a similar procedure several substitution products were indicated in the carbonyl region of the i.r. spectrum of the products. N.m.r. studies indicated that the major species was an olefin-co-ordinated product, together with a complex containing free olefin. In the mass spectrum of the product an ion corresponding to the molecular ion of [W(CO)$_4$(asol)$_2$] was seen in low abundance. This complex could not, however, be isolated pure.

Reaction of [Mo(CO)$_3$(cht)] *with nol, pol, or asol.—nol.* The cycloheptatriene (cht) complex [Mo(CO)$_3$(cht)] in toluene was mixed with an excess (5 mol equiv.) of nol. After 1 h at 20 °C no change had occurred. After 4 h at 110 °C nearly all the [Mo(CO)$_3$(cht)] had reacted. The solvent was removed and the solid recrystallised from heptane. The golden-yellow crystals gave identical n.m.r., i.r., and mass spectra as well as analytical data to those previously obtained for the complex [Mo(CO)$_4$(nol)].

asol. [Mo(CO)$_3$(cht)] In toluene or pentane reacted very rapidly with an excess (5 mol equiv.) of asol at room temperature. Crystallisation of the product from heptane followed by recrystallisation from pentane produced pale yellow platelets. These were washed with pentane and dried at 20 °C, 10^{-2} mmHg for 2 h. The product was formulated as *fac*-[Mo(CO)$_3$(asol)$_3$] (Found: C, 38·4; H, 5·8. $C_{21}H_{39}As_3MoO_3$ requires C, 38·3; H, 5·9%).

pol. [Mo(CO)$_3$(cht)] In toluene was mixed at room temperature with a toluene solution of pol (2 mol equiv.). After 1 h at room temperature much of the starting complex had reacted. Toluene was removed and the oil so obtained was extracted with cyclohexane. The i.r. spectrum of this solution showed very many bands in the CO stretching region. However, after three recrystallisations (twice from cyclohexane and once from heptane) a small quantity of solid was obtained which contained only one species absorbing in the CO region. However this solid has not been fully characterised.

Reaction of [Mo(NO)$_2$Cl$_2$] *with nol and asol.—nol.* [Mo(NO)$_2$Cl$_2$] In acetone was filtered onto a solution of nol also in acetone (1 mol equiv.). After *ca.* ½ h the green solution had lightened in colour and the acetone was removed to leave an oil. Attempts to crystallise this from various solvents failed, but on pumping for a long time a dry solid was produced. This has not been fully characterised.

asol. [Mo(NO)$_2$Cl$_2$] Was suspended in benzene and a solution of asol was filtered onto this. The supernatant liquid slowly turned green and after having been boiled for *ca.* 20 min it was filtered. The solvent was removed and the oil so produced heated to 100—120 °C for 2 h at 10^{-2} mmHg. The oil was then recrystallised from heptane to yield dark green plates, m.p. *ca.* 30 °C. The complex was formulated as [Mo(NO)$_2$Cl$_2$(asol)$_2$] (Found: C, 26·9; H, 4·7; N, 5·3. $C_{12}H_{26}As_2Cl_2MoN_2O_2$ requires C, 26·4; H, 4·8; N, 5·1%).

Reaction of [PdCl$_2$(PhCN)$_2$] *with asol.*—To a solution of the benzonitrile complex [PdCl$_2$(PhCN)$_2$] in benzene, asol (1 mol equiv.) in benzene was slowly added with stirring. Benzene was removed, the solid washed with a little fresh benzene, and then extracted with methanol, from which yellow needles crystallised. These were washed with methanol and dried. The product was formulated as [PdCl$_2$(asol)] (Found: C, 21·4; H, 3·8; Cl, 21·2. $C_6H_{13}Cl_2Pd$ requires C, 21·4; H, 3·9; Cl, 21·0%).

Techniques.—The solvents were dried over LiAlH$_4$ and degassed and distilled prior to use. All compounds were prepared under nitrogen, and subsequently handled in a nitrogen-filled vacuum dry box or rapidly in air.

The i.r. spectra were recorded on a Perkin-Elmer 225 spectrometer from Nujol mulls or hydrocarbon solutions using NaCl plates. The low-temperature i.r. spectra were recorded by use of an RIIC VLT-2 *ca.* 0·5 mm path-length cell in conjunction with an RIIC temperature controller TEM-1. Liquid nitrogen coolant was employed. The solid-state data are listed elsewhere.[24] Raman spectra of some of the compounds were recorded on a Spex 1401 spectrometer in conjunction with a Coherent Radiation model 52 Kr$^+$ laser (647·1 nm excitation). However, studies on the solutions were hampered by low solubilities of the compounds in suitable solvents, and by sample decomposition in the laser beam, while solid-state studies were hindered by fluorescence background to the spectra.

Proton n.m.r. spectra were recorded on a Varian HA-100 or T60 spectrometer using Me$_4$Si as internal standard. Mass spectra were recorded on an AEI MS9 instrument at probe temperatures of 80—100 °C and with 70 eV exciting voltage.

The mercury arc lamp used was a Philips medium-pressure 125 W lamp.

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