Reaction of *cis*-Bis[1,2-bis(dimethylphosphino)ethane]dicarbonylmetal Complexes of Chromium and Molybdenum with Alkyl Halides. Studies of a Mechanism for Oxidative Addition to d^6 Metal Complexes †

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The complexes *cis*-$[M(CO)_2(dmpe)_2]$ (M = Cr or Mo; dmpe is $Me_2PCH_2CH_2PMe_2$) react with alkyl halides RX [RX is CX_4 (X = Cl or Br), C_2Cl_6, 4-$YC_6H_4CH_2X$ (Y = H, X = Cl, Br, or I; Y = NO_2, X = Br), Ph_2CHBr, R_3CX (R = Ph, X = Cl; R = Me, X = I), or $CH_2{=}C(R)CH_2X$ (R = Me, X = Cl; R = H, X = Br)] to form *trans*-$[M(CO)_2(dmpe)_2]X$ (M = Cr or Mo) and subsequently either *cis*-$[M(CO)_2(dmpe)_2X]X$ or *trans*-$[MH(CO)_2(dmpe)_2]X$ (M = Mo only). The reaction has been studied by i.r., e.s.r., and electronic spectroscopy and the rate of the reaction has been measured as a function of the concentration of RX in certain cases. Evidence for the intervention of paramagnetic (free-radical) species is provided by e.s.r. measurements and the observation of the effect of a spin trap (nitrosodurene). The results indicate that electron transfer by an outer-sphere process from the metal(0) complex to RX produces the metal(I) cation (M = Cr or Mo), which (when M = Mo) is then converted, by a second electron transfer to the RX substrate (which involves an inner-sphere process), into the molybdenum(II) final product. Comparisons are made with reactions of *cis*-$[Mo(CO)_2(dppe)_2]$ (dppe is $Ph_2PCH_2CH_2PPh_2$) and with oxidative-addition reactions of other metal complexes.

REACTIONS between alkyl halides and transition-metal complexes have attracted interest for many years. More recently, this interest has focused upon the oxidative addition of alkyl halides to compounds of metals in low oxidation states because of the role that these reactions may play in the catalytic activation of organic molecules. The metal increases its oxidation state and will usually increase its co-ordination number as a result of such an oxidative-addition process. Studies of the oxidative addition of optically active alkyl halides to complexes of d^8 and d^{10} metals have shown that the chiral centre may undergo inversion or retention of configuration; racemization has also been observed. Three types of mechanism have been proposed on the basis of such observations, namely bimolecular nucleophilic substitution (inversion), a concerted three-centre reaction (retention), and a free-radical process (racemization). Generalizations are difficult because the mechanism of an oxidative-addition reaction can be changed as a consequence of a simple alteration in the ligand environment at the metal centre.[1]

We report the results of an investigation of the reactions between certain alkyl halides and the compounds *cis*-$[M(CO)_2(R_2PCH_2CH_2PR_2)_2]$ (M = Cr or Mo; R = Me or Ph) which has provided some clarification of the mechanism of the reaction. We shall show that it is possible to identify two successive one-electron transfer processes in the reaction and to characterize both of the paramagnetic intermediate species. We shall provide evidence to show that, in these particular oxidative-addition reactions, an outer-sphere electron transfer is followed by an inner-sphere electron transfer. A few of our findings were reported in preliminary form.[2]

RESULTS AND DISCUSSION

Earlier work has shown [3] that in solution the ditertiary alkylphosphine complex *cis*-$[Mo(CO)_2(dmpe)_2]$ (dmpe = $Me_2PCH_2CH_2PMe_2$) is more easily oxidized than its analogue *cis*-$[Mo(CO)_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$). In particular, *cis*-$[Mo(CO)_2(dmpe)_2]$ reacts [4] at low temperature with CF_3I to produce hexafluoroethane and *cis*-$[Mo(CO)_2(dmpe)_2I]I$ ‡ which can also be prepared [5] by oxidation of *cis*-$[Mo(CO)_2(dmpe)_2]$ with iodine.

(a) *Reactions with Chloroalkanes.*—The addition of pure CCl_4 to *cis*-$[Mo(CO)_2(dmpe)_2]$ at *ca.* 240 K resulted in a rapid reaction to give *cis*-$[Mo(CO)_2(dmpe)_2Cl]Cl$ together with two chlorocarbons which were shown to be C_2Cl_4 (>90%) and C_2Cl_6 (<10%) by g.c. analysis. In separate experiments it was shown that C_2Cl_6 reacts with *cis*-$[Mo(CO)_2(dmpe)_2]$ to give C_2Cl_4 at room temperature in acetonitrile solution; under these conditions C_2Cl_4 is unreactive. The reaction between *cis*-$[Mo(CO)_2(dmpe)_2]$ and CCl_4 was moderated when an inert solvent (acetonitrile) was used; under pseudo-first-order conditions {>10-fold excess of CCl_4 over *cis*-$[Mo(CO)_2(dmpe)_2]$ in solution} the progress of the reaction could be monitored by i.r., e.s.r., and electronic spectroscopy.

The i.r. spectrum of the reaction mixture in the 1 700—2 050 cm^{-1} range (Figure 1) shows the presence of an intermediate (1 858 cm^{-1}) the rate of formation and decay of which coincided both with that of an absorption in the visible spectrum ($\lambda_{max.}$ 447 nm) and with that of a signal in the e.s.r. spectrum (g 2.053, a_P 2.5×10^{-3} T). These three pieces of evidence permit the unambiguous identification of the intermediate as the cation *trans*-$[Mo(CO)_2(dmpe)_2]^+$, which has been prepared [2] from the reaction between equimolar amounts of *cis*-$[Mo(CO)_2(dmpe)_2]$ and $Ag[BF_4]$ in acetonitrile solution. The final molybdenum-containing product of the reaction, *cis*-$[Mo(CO)_2(dmpe)_2Cl]Cl$, is identified by the absorptions at 1 952 and 1 890 cm^{-1}.

The addition of chlorotriphenylmethane (2 mol) in acetonitrile solution to a solution of *cis*-$[Mo(CO)_2(dmpe)_2]$ in the same solvent at room temperature proceeded in a similar manner. Once again it was possible to monitor the production and decay of *trans*-$[Mo(CO)_2(dmpe)_2]^+$ ion; in addition, the formation of the triphenylmethyl

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† No reprints available.

‡ The designation *cis* or *trans* in seven-co-ordinate dicarbonyl complexes refers to the relative stereochemistry of the carbonyl groups.

radical was observed (Figure 2). There was no observable reaction between *cis*-[Mo(CO)$_2$(dmpe)$_2$] and either 3-chloro-2-methylprop-1-ene or benzyl chloride in acetonitrile solution at ambient temperature. In the absence of a solvent, reaction between *cis*-[Mo(CO)$_2$(dmpe)$_2$] and 3-chloro-2-methylprop-1-ene at 383 K in a sealed tube gave *cis*-[Mo(CO)$_2$(dmpe)$_2$Cl]Cl and a mixture of olefinic products which was not characterized precisely. There was no evidence for the formation of either [Mo-(η^3-C$_4$H$_7$)(CO)(dmpe)$_2$]Cl or *trans*-[MoH(CO)$_2$(dmpe)$_2$]Cl. The reaction between benzyl chloride and *cis*-[Mo(CO)$_2$-(dmpe)$_2$] in propionitrile solution (370 K) gave *cis*-[Mo(CO)$_2$(dmpe)$_2$Cl]Cl and 1,2-diphenylethane (18 h); the formation of *trans*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ ion was detected by i.r. spectroscopy. The addition of CCl$_4$ to an acetonitrile solution of the salt *trans*-[Mo(CO)$_2$(dmpe)$_2$][BF$_4$], prepared in the manner just described, produced the molybdenum(II) salt *cis*-[Mo(CO)$_2$(dmpe)$_2$Cl][BF$_4$] quantitatively at room temperature.

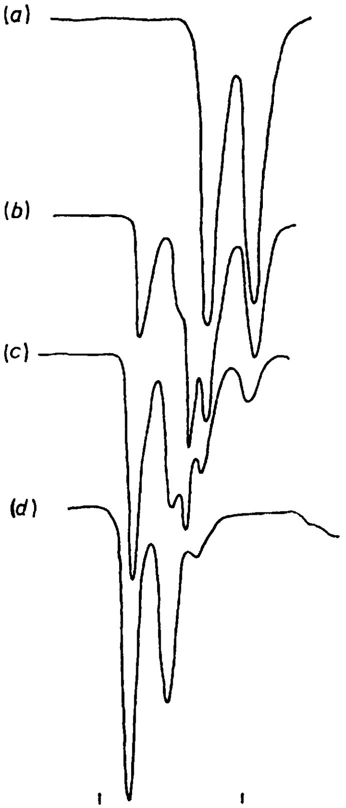

FIGURE 1 Infrared spectra (1 700—2 050 cm^{-1}) of the reaction between CCl$_4$ and *cis*-[Mo(CO)$_2$(dmpe)$_2$] in acetonitrile solution at various times: t = 0 (*a*), 300 (*b*), 600 (*c*), and 3 600 s (*d*)

(b) *Reactions with Bromoalkanes*.—The reaction between CBr$_4$ and *cis*-[Mo(CO)$_2$(dmpe)$_2$] in acetonitrile solution at room temperature gave *cis*-[Mo(CO)$_2$(dmpe)-Br]Br quantitatively; once again *trans*-[Mo(CO)$_2$-(dmpe)$_2$]$^+$ ion was observed as an intermediate in the reaction by means of i.r. spectroscopy. The reaction was more rapid (*ca.* 10^3 times) than the corresponding reaction with CCl$_4$. The bromocarbon products were not identified.

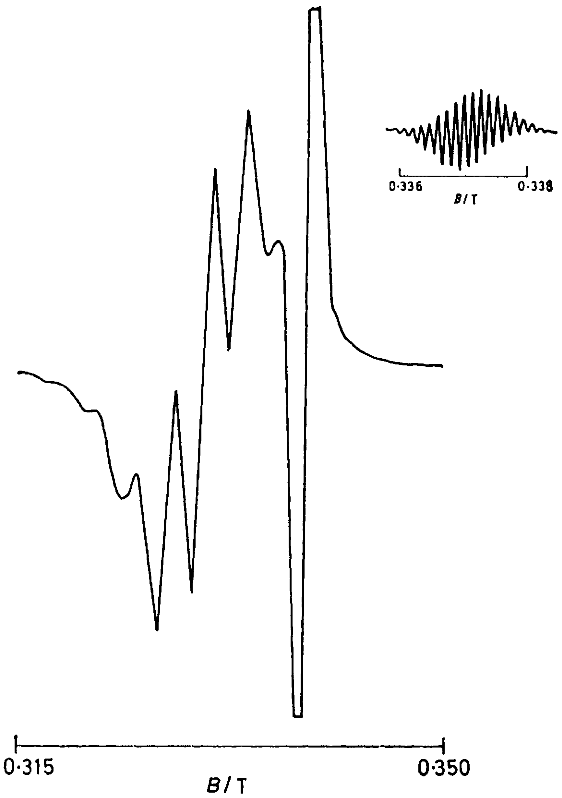

FIGURE 2 E.s.r. spectrum of the reaction between Ph$_3$CCl and *cis*-[Mo(CO)$_2$(dmpe)$_2$] in acetonitrile solution showing the presence of *trans*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ (g 2.053) and the $^{\bullet}$CPh$_3$ radical. Inset: scale expansion for 0.336—0.338T region

The compound *cis*-[Mo(CO)$_2$(dmpe)$_2$Br]Br is also formed by reaction of *cis*-[Mo(CO)$_2$(dmpe)$_2$] with benzyl bromide, 4-nitrobenzyl bromide, bromodiphenylmethane, and 3-bromoprop-1-ene. In each case the reaction proceeds through *trans*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ ion as an intermediate. When the reactions with PhCH$_2$Br and with Ph$_2$CHBr were carried out in the presence of the radical trap, 1,2,4,5-tetramethyl-6-nitrosobenzene (nitrosodurene, QNO), signals attributable to the spin-trapped radicals QN(R)O$^{\bullet}$ (R = CH$_2$Ph or CHPh$_2$) were

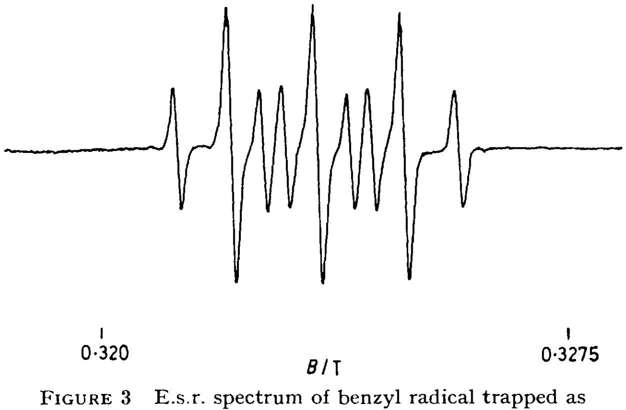

FIGURE 3 E.s.r. spectrum of benzyl radical trapped as benzyl(2,3,5,6-tetramethylphenyl)aminyl oxide

observed in the e.s.r. spectra in addition to those of *trans*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ (Figures 3 and 4). There is no reaction between QNO and *cis*-[Mo(CO)$_2$(dmpe)$_2$] or between QNO and *cis*-[Mo(CO)$_2$(dmpe)$_2$Br]Br in the presence of excess of RBr. The hydrocarbon product derived from PhCH$_2$Br was shown to be 1,2-diphenylethane. Further evidence for the intervention of benzyl radicals was obtained when the reaction between PhCH$_2$Br and *cis*-[Mo(CO)$_2$(dmpe)$_2$] was monitored by n.m.r. spectroscopy. This showed the operation of CIDNP effects which perturbed the aromatic proton resonances, as also observed[6] in the reaction between PhCH$_2$Br and [Pt(PEt$_3$)$_3$] which produces *trans*-[Pt(PEt$_3$)$_2$Br$_2$]. Monitoring the i.r. spectrum in the 1 700—2 050 cm^{-1} region showed that the rate of conversion of *cis*-[Mo(CO)$_2$(dmpe)$_2$] into *trans*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ ion was approximately the same for both PhCH$_2$Br and 4-NO$_2$C$_6$H$_4$CH$_2$Br; the subsequent conversion of *trans*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ ion to *cis*-[Mo(CO)$_2$(dmpe)$_2$Br]Br was approximately five times faster for 4-NO$_2$C$_6$H$_4$CH$_2$Br than for PhCH$_2$Br at 300 K.

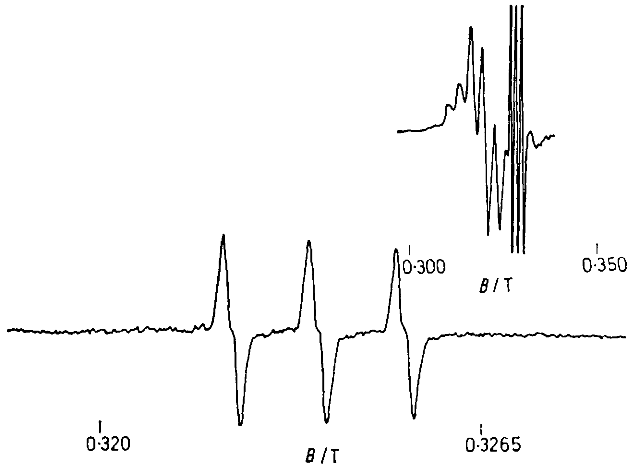

FIGURE 4 E.s.r. spectrum of diphenylmethyl radical trapped as (diphenylmethyl)(2,3,5,6-tetramethylphenyl)aminyl oxide. Inset: complete spectrum showing the presence of *trans*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ ion

(c) *Reactions with Iodoalkanes.*—Whereas benzyl iodide reacts smoothly with *cis*-[Mo(CO)$_2$(dmpe)$_2$] in acetonitrile at 290 K to give *cis*-[Mo(CO)$_2$(dmpe)$_2$I]I and 1,2-diphenylethane, reaction with 2-iodo-2-methylpropane (310 K) produced the hydrido-complex *trans*-[MoH(CO)$_2$(dmpe)$_2$]I.

(d) *Reactions of cis*-[Cr(CO)$_2$(dmpe)$_2$].—The addition of an excess of either CCl$_4$ or PhCH$_2$Br to *cis*-[Cr(CO)$_2$(dmpe)$_2$] in acetonitrile solution at room temperature resulted in the formation of *trans*-[Cr(CO)$_2$(dmpe)$_2$]$^+$ ion [ν(CO) at 1 840 cm^{-1}, *g* 2.003, a_P 3.0 × 10^{-3} T] as the only chromium-containing product; no further oxidation was observed.

(e) *Reactions of cis*-[Mo(CO)$_2$(dppe)$_2$].—The reaction between *cis*-[Mo(CO)$_2$(dppe)$_2$] and various alkyl halides (Ph$_3$CCl, Ph$_2$CHBr, or PhCH$_2$Br) in acetonitrile gave *trans*-[Mo(CO)$_2$(dppe)$_2$]$^+$ ion [ν(CO) at 1 878 cm^{-1}, *g* 2.05] as the only molybdenum-containing product in each case. No further oxidation was observed and the reactions did not appear to be photosensitive. Reaction in the presence of QNO produces signals in the e.s.r. spectrum which can be assigned to the spin-trapped benzyl and diphenylmethyl radicals in QN(R)O$^{\bullet}$ (R = CH$_2$Ph or CHPh$_2$), as well as *trans*-[Mo(CO)$_2$(dppe)$_2$]$^+$ ion.

(f) *Kinetic Measurements.*—The rate of the reaction between CCl$_4$ and *cis*-[Mo(CO)$_2$(dmpe)$_2$] under pseudo-first-order conditions was measured in acetonitrile solution using i.r. spectrophotometry. The observed rate constants for the conversion of *cis*-[Mo(CO)$_2$(dmpe)$_2$] (ν at 1 766 cm^{-1}, Figure 1) into *trans*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ ion (ν at 1 858 cm^{-1}) at various initial concentrations of CCl$_4$ are given in Table 1(*a*). A plot of $k_{obs.}$ against CCl$_4$ concentration is linear and passes through the origin, implying a first-order dependence on CCl$_4$ concentration. The rate law for this step of the reaction is (1). Least-squares analysis of the data in Table 1(*a*) gives a value for the second-order rate constant k_1 = (2.1 ± 0.1) × 10^{-2} dm^3 mol^{-1} s^{-1}. Rate constants for the conversion of the intermediate ionic species *trans*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ into the final molybdenum-containing product *cis*-[Mo(CO)$_2$(dmpe)$_2$Cl]Cl (ν at 1 948 cm^{-1}) indicate [Table 1(*b*)] a direct transformation of the former into the latter. A plot of $k_{obs.}$ against CCl$_4$ concentration is linear and passes through the origin. Although deviations from the line are substantial, particularly at higher concentrations of CCl$_4$, the rate law for this second step of the reaction is (2)

$$-\mathrm{d}[cis\text{-Mo(CO)}_2(\text{dmpe})_2]/\mathrm{d}t = k_1[\text{Mo(CO)}_2(\text{dmpe})_2][\text{CCl}_4] \quad (1)$$

$$\mathrm{d}[cis\text{-}\{\text{Mo(CO)}_2(\text{dmpe})_2\text{Cl}\}\text{Cl}]/\mathrm{d}t = -\mathrm{d}[trans\text{-Mo(CO)}_2(\text{dmpe})_2{}^+]/\mathrm{d}t = k_2[\text{Mo(CO)}_2(\text{dmpe})_2{}^+][\text{CCl}_4] \quad (2)$$

TABLE 1

Rate of reaction $k_{obs.}$ (±0.2) between *cis*-[Mo(CO)$_2$(dmpe)$_2$] (5 × 10^{-3} mol dm^{-3}) and CCl$_4$ in acetonitrile solution at 307 K

(*a*) Disappearance of *cis*-[Mo(CO)$_2$(dmpe)$_2$] (ν at 1 766 cm^{-1})

10^2[CCl$_4$]/mol dm^{-3}	10^3$k_{obs.}$/s^{-1}
50	10.5
40	8.2
30	5.7
20	3.8
10	1.9
5	1.0

(*b*) Disappearance of *trans*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ ion and appearance of *cis*-[Mo(CO)$_2$(dmpe)$_2$Cl]Cl

	10^3$k_{obs.}$/s^{-1}	
10^2[CCl$_4$]/mol dm^{-3}	*a*	*b*
50	3.0	3.5
40	3.0	2.9
30	3.3	3.3
20	2.5	2.5
10	1.3	1.3
5	0.9	0.9

[a] For appearance of *cis*-[Mo(CO)$_2$(dmpe)$_2$Cl]Cl (ν at 1 948 cm^{-1}). [b] For disappearance of *trans*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ ion (ν at 1 858 cm^{-1}).

with a second-order rate constant k_2 *ca.* 1×10^{-2} dm^3 mol^{-1} s^{-1}. Measurements monitoring the change in absorbance at 447 nm due to *trans*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ by stopped-flow techniques gave similar results. When applied to the reaction between Ph$_3$CCl and *cis*-[Mo(CO)$_2$(dmpe)$_2$], the rate of the first step was measured as $k_1 > 10^4$ dm^3 mol^{-1} s^{-1} and the value of k_2 *ca.* 2 dm^3 mol^{-1} s^{-1}.*

(g) *Mechanism of Reaction.*—The mechanism we propose for the reaction between alkyl halides and *cis*-[Mo(CO)$_2$(dmpe)$_2$] is shown in Scheme 1. In the first step, an electron is transferred from the molybdenum complex to the organic substrate (addend), RX. The relative ease with which the molybdenum complex undergoes one-electron oxidation is indicated both by the reduction potential in solution measured by cyclic voltammetry, and the first ionization potential measured by photoelectron spectroscopy (Table 2). This electron transfer would be expected to produce the *cis*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ ion, however it is the *trans* isomer which is observed directly. The isomerization process *cis*- ⟶ *trans*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ could not be observed. This isomerization is known to be rapid, as shown by double-potential-step chronoamperometric measurements [7] on the analogous dppe complex, *cis*-[Mo(CO)$_2$(dppe)$_2$]$^+$, for which the rate of conversion into the *trans* isomer is 32.7 s^{-1} at 298 K ($\Delta H^\ddagger$ 24.6 ± 2.1 kJ mol^{-1}, $\Delta S^\ddagger$ −133 ± 8 J K^{-1} mol^{-1}). Recent experiments have led to the synthesis of *trans*-[Mo(CO)$_2$(dmpe)$_2$] from the reaction between *trans*-[MoH(CO)$_2$(dmpe)$_2$][SFO$_3$] and K(OBu^t). The rate of *trans* ⟶ *cis* isomerization has been measured [8] ($k = 0.305$ s^{-1} at 329 K). Electrochemical measurements [7] on the isomerization of *trans*-[Mo(CO)$_2$(dppe)$_2$] have shown that the rate of conversion into the *cis* isomer is 0.10 s^{-1} at 298 K. The activation parameters for isomerization ($\Delta H^\ddagger$ 36.8 ± 1.3 kJ mol^{-1}, $\Delta S^\ddagger$ −146 ± 15 J K^{-1} mol^{-1}) are consistent with a twist [7] rather than a dissociative [9] mechanism for both the cationic and the neutral species, irrespective of the metal or diphosphine ligand.[7] Using the known carbonyl stretching frequencies, ν(CO), in the [Mo(CO)$_2$(dmpe)$_2$]$^{Z+}$ system (Table 3) it is possible to estimate (±5 cm^{-1}) the wavenumbers which would be expected for the unknown *cis*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ ion as 1 890 and 1 825 cm^{-1}. These are sufficiently close to absorptions (Figure 1) of *cis*-[Mo(CO)$_2$(dmpe)$_2$X]$^+$ and *cis*-[Mo(CO)$_2$(dmpe)$_2$], respectively, for the *cis*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ ion not to be recognizable by i.r. spectroscopy because of rapid isomerization.

$$cis\text{-}[\mathrm{Mo(CO)_2(dmpe)_2}] + \mathrm{RX} \longrightarrow cis\text{-}[\mathrm{Mo(CO)_2(dmpe)_2}]^+ + \mathrm{RX}^{-\bullet}$$

$$\big\downarrow$$

$$trans\text{-}[\mathrm{Mo(CO)_2(dmpe)_2}]^+ + \mathrm{X}^- + \mathrm{R}^\bullet$$

$$trans\text{-}[\mathrm{Mo(CO)_2(dmpe)_2}]\mathrm{X} + \mathrm{RX} \longrightarrow cis\text{-}[\mathrm{Mo(CO)_2(dmpe)_2X}]\mathrm{X} + \mathrm{R}^\bullet$$

$$\mathrm{R}^\bullet + \mathrm{R}^\bullet \longrightarrow \mathrm{R{-}R}$$

Overall reaction:

$$cis\text{-}[\mathrm{Mo(CO)_2(dmpe)_2}] + 2\mathrm{RX} \longrightarrow cis\text{-}[\mathrm{Mo(CO)_2(dmpe)_2X}]\mathrm{X} + \mathrm{R{-}R}$$

SCHEME 1

TABLE 2

Half-wave oxidation potentials, $E_{\frac{1}{2}}^{\mathrm{ox}}$(V), in solution and first vertical ionization potential (eV) for [Mo(CO)$_m$(dmpe)$_n$] ($m = 6$, $n = 0$; $m = 4$, $n = 1$; $m = 2$, $n = 2$)

Complex	$E_{\frac{1}{2}}^{\mathrm{ox}}$/V *vs.* s.c.e.	Ref.	I.p./eV	Ref.
[Mo(CO)$_6$]	1.53	*a*	8.50	*b*
cis-[Mo(CO)$_4$(dmpe)]	0.61	3	7.20	*c*
cis-[Mo(CO)$_2$(dmpe)$_2$]	−0.23	3	6.00	*c*

[a] C. J. Pickett and D. Pletcher, *J.C.S. Dalton*, 1975, 879.
[b] D. R. Lloyd and E. W. Schlag, *Inorg. Chem.*, 1969, **8**, 2544.
[c] D. R. Lloyd, unpublished work.

The alkyl halide RX reacts very rapidly with the electron (k *ca.* 10^{10} dm^3 mol^{-1} s^{-1} in a polar solvent [10]) transferred from *cis*-[Mo(CO)$_2$(dmpe)$_2$] to give RX$^{-\bullet}$ which is not observed directly. However, when tetracyanoethylene, tcne, is added to *cis*-[Mo(CO)$_2$(dmpe)$_2$] in solution, e.s.r. spectra show the presence of both the radical anion tcne$^{-\bullet}$ and *trans*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ ion, which lends strong support to the proposal that RX$^{-\bullet}$ is formed. The final product of the reaction with tcne is the σ-tricyanovinyl complex,[11a] *cis*-[Mo(CO)$_2$(dmpe)$_2${C$_2$(CN)$_3$}][CN]. The RX$^{-\bullet}$ species is not observed because electron capture results in very rapid dissociation to R$^\bullet$ radicals and halide ions. Measurements in the gas phase have shown that the cross section for dissociative electron capture is dependent upon the halogen (decreasing in the order CH$_3$I > CH$_3$Br > CH$_3$Cl) and upon the number of halogen atoms (decreasing in the order CCl$_4$ > CHCl$_3$ > CH$_2$Cl$_2$).[10]

TABLE 3

Carbonyl stretching bands (cm^{-1}) for [Mo(CO)$_2$(dmpe)$_2$]$^{Z+}$ (Z = 0—2)

	$Z = 0$	Ref.	$Z = 1$	Ref.	$Z = 2$	Ref.
cis	1 838, 1 766	5	(1 890, 1 825)	est.	1 948, 1 886	2
trans	1 815	8	1 858	2	(1 905)	est.

est. = Estimated.

Evidence for the dissociation of RX$^{-\bullet}$ to give R$^\bullet$ in these reactions with *cis*-[Mo(CO)$_2$(dmpe)$_2$] is drawn from the observations that the radical R$^\bullet$ can be trapped by nitrosodurene when R = CH$_2$Ph or CHPh$_2$, and that $^\bullet$CPh$_3$ can be detected by e.s.r. spectroscopy. We have been unable to trap $^\bullet$CCl$_3$ radicals which are presumed to be formed in the reaction between CCl$_4$ and *cis*-[Mo(CO)$_2$(dmpe)$_2$], and there was no signal which might be assigned to $^\bullet$CCl$_3$ in the e.s.r. spectrum. The possibility that *both* chloride ions in the final molybdenum(II) product might come from the same molecule of CCl$_4$ and that dichlorocarbene might therefore be involved in the reaction was tested by carrying out the reaction between CCl$_4$ and *cis*-[Mo(CO)$_2$(dmpe)$_2$] in the presence of cyclohexene. The yield of 7,7-dichlorobicyclo[4.1.0]heptane was 2% (g.l.c.) on the assumption that CCl$_4$ is quantitatively

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* Further details of the kinetic measurements are available as Supplementary Publication No. SUP 22532 (12 pp.). See Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

converted into dichlorocarbene. Since the chlorocarbon products of the reaction include C_2Cl_6 (which is itself a substrate), it seems likely that the small amount of CCl_2 which is intercepted could arise from the decay, prior to their dimerization, of $^{\bullet}CCl_3$ radicals, which is well documented.[11b] The formation of C_2Cl_4 as the major product of the reaction with CCl_4 suggests the following scheme for which there is ample precedent: [10]

$$CCl_4 \xrightarrow{e} CCl_4^{-\bullet} \longrightarrow Cl^- + {}^{\bullet}CCl_3$$

$$2{}^{\bullet}CCl_3 \longrightarrow C_2Cl_6 \xrightarrow{e} C_2Cl_6^{-\bullet} \longrightarrow Cl^- + {}^{\bullet}C_2Cl_5$$

$${}^{\bullet}C_2Cl_5 \longrightarrow C_2Cl_4 + Cl \xrightarrow{e} Cl^-$$

SCHEME 2

The halide ion produced by dissociation of $RX^{-\bullet}$ provides the anion for the molybdenum(I) cation. It does not enter the co-ordination sphere of the molybdenum.

The observations are most closely related to those made on the reaction of 4-nitrobenzyl halides with the six-co-ordinate cobalt(II) complex [Co(salmeen)$_2$] [salmeen = *N*-methyl-*N'*-(salicylidene)ethylenediaminate] which proceeds by outer-sphere electron transfer because radical capture is precluded.[12]

The subsequent reaction of the *trans*-$[Mo(CO)_2(dmpe)_2]^+$ ion to give the final molybdenum(II) product involves a simple inner-sphere atom-transfer reaction. This conclusion is supported by the observation of overall second-order kinetics for the conversion of the molybdenum(I) intermediate into *cis*-$[Mo(CO)_2(dmpe)_2X]X$ (X = Cl, Br, or I), by the observed inverse dependence of the rate of reaction upon the strength of the carbon–halogen bond among the benzyl halides ($PhCH_2I > PhCH_2Br > PhCH_2Cl$), and by the observed enhancement of the reaction rate by an electron-withdrawing substituent ($4\text{-}NO_2C_6H_4CH_2Br$). This atom-abstraction process is particularly favoured by the requirement for the six-co-ordinate high-spin molybdenum(I) to become seven-co-ordinate low-spin molybdenum(II) in the product.

This mechanistic step is exactly similar to that proposed for the reaction of alkyl halides with chromium(II), equation (3),[13] and with cobalt(II), equation (4).[14] Both

$$RX + 2Cr^{II} \longrightarrow [CrX]^{2+} + [CrR(OH_2)_5]^{2+} \quad (3)$$

$$RX + 2[Co(CN)_5]^{3-} \longrightarrow [Co(CN)_5X]^{3-} + [CoR(CN)_5]^{3-} \quad (4)$$

these reactions involve halogen-atom abstraction from RX in an inner-sphere, bridged, transition state. In the case of the reactions discussed here, this could be represented by (A). The formation of the hydrido-

$$[(dmpe)_2(OC)_2Mo \cdots X \cdots R] \quad (A)$$

molybdenum(II) complex, *trans*-$[MoH(CO)_2(dmpe)_2]I$, from the reaction between Me_3CI and *cis*-$[Mo(CO)_2(dmpe)_2]$ is consistent with the atom-transfer mechanism in that a hydrogen atom is abstracted from a CMe_3 radical in place of an iodine atom from Me_3CI. A similar observation was made [15] in the reaction between pentacyanocobaltate(II) ion and Me_3CI.

An alternative path for the consumption of the molybdenum(I) intermediate, which would account for the constant rate of reaction observed at high concentrations of CCl_4 [Table 1(*b*)], would suppose an equilibrium to be very rapidly established between *trans*-$[Mo(CO)_2(dmpe)_2]^+$ and RX to form an adduct $[Mo(CO)_2(dmpe)_2(RX)]^+$. This adduct would decay by a first-order process, k_3, to give *cis*-$[Mo(CO)_2(dmpe)_2X]^+$. If the equilibrium constant, K, in favour of the adduct is large (say, $\geqslant 10^3$), the rate law (5) for the process is

$$d[Mo^{II}]/dt = k_3K[RX]/(1 + K[RX]) \quad (5)$$

simplified, and is independent of the concentration of RX, so that, in the case of CCl_4 at high concentration, k_3 *ca.* 3×10^{-3} s^{-1}. The major disadvantage of this proposal is that we have no physical evidence (*e.g.* from spectroscopy) for the formation of the supposed seven-co-ordinate molybdenum(I) adduct, which is in all other respects identical to the intermediate (A) involved in the inner-sphere halogen-atom transfer. Following Occam's principle, this alternative is rejected.

The observation that reactions between alkyl halides and *cis*-$[Cr(CO)_2(dmpe)_2]$ do not proceed beyond the chromium(I) stage is taken to show the reduced compulsion for chromium(II) to achieve seven-co-ordination, as well as the greater oxidation potential for the process $[Cr(CO)_2(dmpe)_2]^+ \longrightarrow [Cr(CO)_2(dmpe)_2]^{2+}$. Support for the latter conclusion is provided by the observations that *cis*-$[Mo(CO)_2(dppe)_2]$ ($E_{\frac{1}{2}}^1 = -0.02$, $E_{\frac{1}{2}}^2 > 1.6$ V; ref. 3) reacts with $PhCH_2Br$ and Ph_2CHBr to give *trans*-$[Mo(CO)_2(dppe)_2]Br$ only, whereas with *cis*-$[Mo(CO)_2(dmpe)_2]$ ($E_{\frac{1}{2}}^2 = +0.82$ V) oxidation to give *cis*-$[Mo(CO)_2(dmpe)_2Br]Br$ occurs.

(h) *Relationship to Other Work.*—The one-electron transfer to the addend molecule demonstrated here, which produces a metal-centred paramagnetic cation, can be applied to other systems undergoing oxidative addition. A restriction operates in the present instance in that seven-co-ordinate molybdenum(II) is co-ordinatively saturated (18-electron system [16]), so that oxidation of *cis*-$[Mo(CO)_2(dmpe)_2]$ by RX can result in the co-ordination of either R or X but not of both. This restriction is relaxed in complexes of d^8 and d^{10} metals, many of which are four-co-ordinate, allowing both R and X to bond to the metal atom.

A generalized scheme for the reaction of alkyl halides with $[M(PPh_3)_n]$ (M = Pd or Pt; n = 3 or 4) has been proposed [6] in which a radical pair (M^I–X,R$^{\bullet}$) is an intermediate. Presumably the formation of this radical pair is preceded by electron transfer.

Although metal-centred paramagnetic intermediates (Ir^{II}, Pd^I, or Pt^I) have been invoked in oxidative additions to d^8 and d^{10} metal complexes, there is no direct evidence for their existence.[1] Indeed, well characterized examples of these intermediates are rare.[17] Recently a platinum(I) complex has been spin-trapped, indicating that Pt^I is an intermediate in the insertion reaction of acetylenes with platinum hydride complexes.[18] It is reasonable to suggest that reactions such as the oxidative addition [19] of chlorocarbons to [Pt$(PPh_3)_4$], the free-radical polymerizations [20] which are catalyzed by a variety of organometallic complexes with CCl_4, and the free-radical addition of CCl_4 to terminal olefins which is catalyzed [21] by [$Ru(PPh_3)_2Cl_2$] may all involve an initial electron transfer from the metal.

Finally, we refer to the contrast between the reactions of *cis*-[$Mo(CO)_2(dmpe)_2$] and *cis*-[$Mo(CO)_2(dppe)_2$] on the one hand, and those of *trans*-[$Mo(N_2)_2(dppe)_2$] on the other. The compound *trans*-[$Mo(N_2)_2(dppe)_2$] reacts with CCl_4 and with CH_2Cl_2 to give [$Mo(dppe)_2Cl_2$] and C_2Cl_6 or 1,2-dichloroethane.[22] Rather in contrast to this, alkyl halides react with *trans*-[$Mo(N_2)_2(dppe)_2$] to produce alkyldiazenido-complexes,[23] diazoalkane-N^2 complexes,[24] or diazobutanol-N^2 complexes [25] depending upon the alkyl halide and solvent. It has been shown that these reactions proceed through a rate-controlling loss of one dinitrogen ligand, co-ordination of the alkyl halide giving [$Mo(RX)(N_2)(dppe)_2$], homolytic splitting of the C–X bond, and attack of the $R^{\bullet}$ radical upon the co-ordinated dinitrogen ligand. Electron transfer to the alkyl halide is not involved.[26] The first reduction potential [27] of *trans*-[$Mo(N_2)_2(dppe)_2$] ($E_{\frac{1}{2}} = -0.16$ V *vs.* standard calomel electrode) is similar to that of *cis*-[$Mo(CO)_2(dmpe)_2$], so that if stereochemical differences are ignored it appears that the principal distinction between the carbonyl and dinitrogen complexes resides in the relatively easy dissociation of the metal–dinitrogen bond.

(i) *Conclusions.*—The reaction between *cis*-[$M(CO)_2(dppe)_2$] (M = Cr or Mo) or *cis*-[$Mo(CO)_2(dppe)_2$] and an alkyl halide RX proceeds by electron transfer from the metal, giving a paramagnetic six-co-ordinate metal(I) cation, and the radical anion $RX^{-\bullet}$ which dissociates to halide ion and the carbon-centred radical $R^{\bullet}$. This electron transfer is thought to be an outer-sphere process: nothing is known of the structure of the encounter complex within which the transfer occurs. In the case of the molybdenum(I) cation *trans*-[$Mo(CO)_2(dmpe)_2$]$^+$ a further oxidation is possible and the cation reacts with another molecule of RX. Halogen-atom transfer occurs by an inner-sphere process to form a molybdenum(II) cation, *cis*-[$Mo(CO)_2(dmpe)_2X$]$^+$, and the organic radical $R^{\bullet}$. Except where hydrogen-atom transfer is preferred, giving *trans*-[$MoH(CO)_2(dmpe)_2$]$^+$, the organic product is the dimer, R_2.

EXPERIMENTAL

Materials and methods were in general similar to those described in other papers from this laboratory. All operations were carried out under nitrogen atmospheres. Solvents were dried (CaH_2, sodium, or molecular sieves), deaerated, and distilled prior to use. Alkyl halides were of the best commercially available quality: they were dried, deaerated, and distilled prior to use.

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