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REACTIONS OF *cis*-[DICARBONYLBIS(1,2-BIS(DIMETHYLPHOSPHINO)-ETHANE)METAL] COMPOUNDS OF CHROMIUM AND MOLYBDENUM WITH ORGANIC ELECTRON ACCEPTORS: TETRACYANOETHENE, 1,2,4,5-TETRACYANOBENZENE AND 1,3,5-TRINITROBENZENE *

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Summary

Reaction between *cis*-[$Mo(CO)_2(dmpe)_2$] (dmpe = $Me_2PCH_2CH_2PMe_2$) and organic π-acids tetracyanoethene (TCNE), 1,2,4,5-tetracyanobenzene (TCNB) and 1,3,5-trinitrobenzene (TNB) proceeds via electron transfer from the metal complex, which is oxidised to the 17-electron *trans*-[$Mo(CO)_2(dmpe)_2]^+$ ion, to the organic acceptor which is reduced to the radical anion. The final products of the reactions are characterised as *cis*-[$Mo\{C_2(CN)_3\}(CO)_2(dmpe)_2$] [CN], *cis*-[$Mo\{C_6H_2(CN)_4\}(CO)_2(dmpe)_2$] [$C_6H_2(CN)_4]_8$ and [$Mo(CO)_2(dmpe)_2 \cdot 2\ C_6H_3(NO_2)_3$] by analysis and spectroscopic (IR, NMR, ESR) measurements which are compared with those of *cis*-[$MoX(CO)_2(dmpe)_2$]X (X = Cl, Br, I) and *fac, fac*-[$Mo_2Cl_4(CO)_4(dmpe)_3$]. The reaction of *cis*-[$Cr(CO)_2(dmpe)_2$] with TCNE gives *trans*-[$Cr(CO)_2(dmpe)_2]^+$ [TCNE]$^-$ only.

Introduction

Studies of the reaction between *cis*-[$M(CO)_2(dmpe)_2$] (M = Cr, Mo; dmpe = $Me_2PCH_2CH_2PMe_2$) and alkyl halides, RX, in solution have shown that an electron is readily transferred from the metal complex to produce the 17-electron cation, *trans*-[$M(CO)_2(dmpe)_2]^+$ and the radical anion $RX^{-\cdot}$. It is suggested that this redox process is of the outer sphere type [1]. Characterisation of the radical anions, $RX^{-\cdot}$ is hampered by the ease with which these dissociate to form the radical $R^\cdot$, and the halide ion, X^-. We were able to detect $R^\cdot$ by ESR spectroscopy and to trap it in certain cases with nitrosodurene. The anion was captured by the metal.

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* No reprints available.

We report on reactions between *cis*-[M(CO)$_2$(dmpe)$_2$] and other organic electron acceptors which form more stable radical anions. These experiments provide evidence to support the proposed outer sphere electron transfer mechanism. They also show that the radical anions may undergo a variety of subsequent reactions in forming the final product.

Results and discussion

Reaction with tetracyanoethene

Addition of tetracyanoethene, TCNE, to a colourless solution of *cis*-[Mo(CO)$_2$(dmpe)$_2$] in methyl cyanide produces a golden yellow colour. The electronic spectrum of this solution shows the characteristic absorption band centered at 435 nm which is associated [2] with the radical anion, TCNE$^{-\cdot}$. The ESR spectrum of the golden yellow solution provided unambiguous evidence of TCNE$^{-\cdot}$ (g 2.0036; a_N 1.55 gauss) [3]. The intense signal of the radical anion obscured the weaker signal of the molybdenum(I) cation (g 2.053; a_P 25 gauss). Pale yellow crystals were deposited from the golden yellow solution on standing at room temperature over a period of 3—6 h. Analytical and spectroscopic data for this pale yellow crystalline solid indicate that it is the σ-tricyanoethenyl/molybdenum(II) complex, *cis*-[Mo{$C_2(CN)_3$}(CO)$_2$(dmpe)$_2$][CN]. The infrared spectrum (Fig. 1a; KBr disc) shows two ν(CO) absorptions (1950vs, 1900s cm^{-1}) typical of cationic molybdenum(II) complexes of the type *cis*-[MoX(CO)$_2$(dmpe)$_2$]$^+$ (see below, Table 2). Additionally, the solid state infrared spectrum shows the presence of both anionic cyanide (2082 cm^{-1}) and covalent cyanide (2210w, 2170m, 2160m cm^{-1}). The latter vibrations can be assigned to the σ-tricyanoethenyl ligand by analogy with the corresponding absorptions in the spectrum of the neutral molybdenum(II) complex [Mo{$C_2(CN)_3$}(C_5H_5)(CO)$_3$] [4]. The contrast between *cis*-[Mo{$C_2(CN)_3$}(CO)$_2$(dmpe)$_2$][CN] and a compound such as [VBr(C_5H_5)$_2$(TCNE)] in which the TCNE ligand is known (X-ray structure) to be bound to the metal through one nitrogen atom [5], and a com-

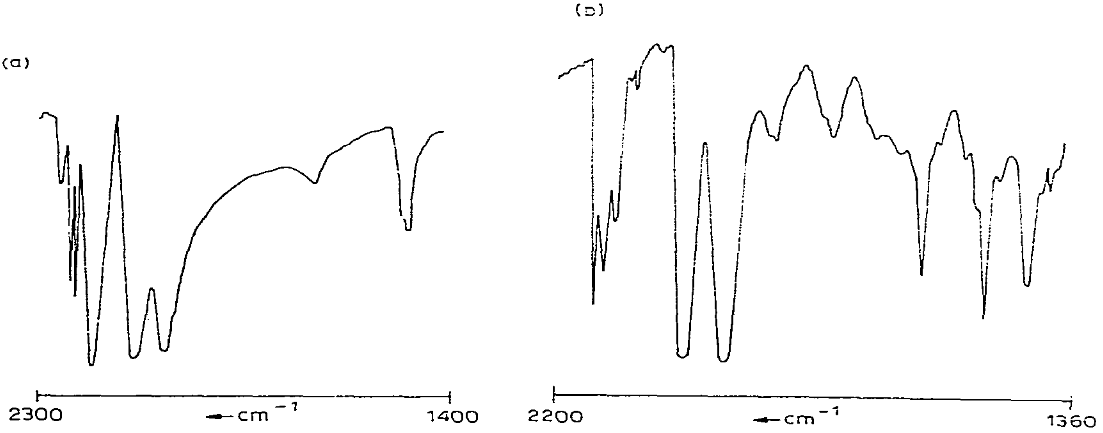

Fig. 1. IR spectrum (KBr disc) in the region 2300—1400 cm^{-1} of (a) *cis*-[Mo{$C_2(CN)_3$}(CO)$_2$(dmpe)$_2$][CN] and (b) *cis*-[Mo{$C_6H_2(CN)_4$}(CO)$_2$(dmpe)$_2$][TCNB]$_8$.

TABLE 1

INFRARED ABSORPTIONS (ν, cm^{-1}) IN TCNE AND CERTAIN COMPLEXES CONTAINING TCNE OR THE TRICYANOETHENYL $[C_2(CN)_3]$ LIGAND

	ν(CN)				ν(C=C)	ref.
$[Pt(PMe_3)_2(TCNE)]$	2220	2165			1191	6
$[VBr(TCNE)(C_5H_5)_2]$	2211	2192	2152	2128	1400	5
$[Fe(dmpe)_2(TCNE)]$	2183	2175	2145	2095		7
$[Mo\{C_2(CN)_3\}(CO)_3(C_5H_5)]$	2231	2209	2190		1472	4
$[Mo\{C_2(CN)_3\}(CO)_2(dmpe)_2][CN]$	2210	2170	2160	2082	1435	this work
TCNE	2260	2225			1570	5
$TCNE^-$	2200	2175			1370	5
$Cl\cdot C(CN)=C(CN)_2$	2244	2238			1565	4

pound such as $[Pt(PPh_3)_2(TCNE)]$ in which the TCNE ligand is bonded to the metal through the central carbon—carbon link [6] is emphasized by their CN-stretching frequencies. These frequencies are given in Table 1, together with the appropriate data for the insoluble emerald green complex $[Fe(dmpe)_2(TCNE)]$, which were reported recently [7]. Table 1 also gives the vinylic ν(C=C) absorption frequency in *cis*-$[Mo\{C_2(CN)_3\}(CO)_2(dmpe)_2]$ [CN] which re-emphasizes the similarity to $[Mo\{C_2(CN)_3\}(CO)_3(C_5H_5)]$. We were unable to record the ^1H or ^{13}C NMR spectra or to measure the conductivity of *cis*-$[Mo\{C_2(CN)_3\}(CO)_2(dmpe)_2][CN]$ in solution because the solid is insufficiently soluble in any suitable solvent.

This tricyanoethenylation reaction of TCNE is unusual in transition metal chemistry, although such a reaction is well known in organic chemistry. For example, *N*,*N*-dimethylbenzenamine reacts with TCNE to form 4-(tricyanoethenyl)-*N*,*N*-dimethylbenzenamine and hydrogen cyanide. The mechanism of the reaction has been studied in detail and is known to involve the rate-determining conversion of a donor—acceptor π complex into an ion pair which subsequently undergoes elimination [8]. A reaction which is formally similar to that reported here occurs as a result of oxidative addition of *trans*-1,2-dicyanohexafluorobut-2-ene to $[Pt(PPh_3)_2(PhCH{=}CHPh)]$ which gives *trans*-$[Pt(PPh_3)_2\{C(CF_3)C(CN)(CF_3)\}(CN)]$ [9].

The reaction of *cis*-$[Cr(CO)_2(dmpe)_2]$ with TCNE in methyl cyanide solution was monitored spectroscopically. Both IR and ESR spectra showed the formation of *trans*-$[Cr(CO)_2(dmpe)_2]^+$ ion (ν(CO) 1840 cm^{-1}; g 2.003, a_p 30 gauss) [10]. The ESR spectrum also showed the formation of the radical anion, $TCNE^{-\cdot}$ (g 2.0036, a_N 1.55 gauss). The solution was stable in a sealed system. The tricyanoethenylation reaction observed with *cis*-$[Mo(CO)_2(dmpe)_2]$ did not occur in the chromium case. The reaction which gives *trans*-$[Cr(CO)_2(dmpe)_2]^+$ $[TCNE]^-$ is formally similar to the reaction between $[Cr(C_6H_6)_2]$ and TCNE which has been shown by ESR spectroscopy to produce $[Cr(C_6H_6)_2]^+$ $[TCNE]^-$ [11].

These observations are important for the light they throw on the redox reactions involving *cis*-$[M(CO)_2(dmpe)_2]$. They show that it is possible to observe the oxidised and the reduced product simultaneously in the presence of one another. They indicate that when the acceptor is an alkyl halide, the intervention of the molecular radical anion $RX^{\cdot -}$ as a labile intermediate [1] is a strong possibility.

Reaction with 1,2,4,5-tetracyanobenzene (TCNB)

Addition of TCNB (1 mol) to a solution of *cis*-[Mo(CO)$_2$(dmpe)$_2$] (1 mol) in dry, degassed methyl cyanide produces a golden yellow colour. Both the electronic absorption spectrum and the ESR spectrum of this golden yellow solution indicate the presence of the radical anion $TCNB^{\cdot -}$ [2,12]. The infrared spectrum of this solution showed that a large proportion of the *cis*-[Mo(CO)$_2$(dmpe)$_2$] had not reacted. Further TNB was added and the reaction was monitored by IR spectroscopy. A total of approximately 10 mol of TCNB was required to consume all of the *cis*-[Mo(CO)$_2$(dmpe)$_2$], at which point the reaction solution was deep purple. A powdery purple solid (85% yield) was isolated and shown by microanalysis to have the composition corresponding to [Mo(CO)$_2$(dmpe)$_2$(TCNB)$_9$].

The IR spectrum of the solid (KBr disc) shows two ν(CO) absorptions (1950vs, 1890vs cm^{-1}) typical of a cationic molybdenum(II) complex of *cis* stereochemistry. The spectrum (Fig. 1b) also shows three absorptions due to ν(CN) (2240s, 2208s, 2160m cm^{-1}), the first of which is also present in the IR spectrum of pure TNCB. The remaining two bands suggest the presence of either the $TCNB^-$ ion or, more probably, vinylic cyano groups in this complex. There was no indication of the presence of anionic cyanide in the complex (no absorption at ca. 2080 cm^{-1}). The presence of a vinylic system is supported by the observation of two absorptions (1584m, 1486s cm^{-1}), of which only the latter is also present in the IR spectrum of pure TCNB. The electronic absorption spectrum of the pure solid recorded in ethanol solution shows four bands (λ_{max}, nm (log ϵ)) 546 (3.47), 348 (4.20), 316 (4.38) 304 (4.27)). The two highest energy bands are also present in the electronic spectrum of pure TCNB. The mass spectrum of the purple solid (70 eV) showed m/e 452 (assigned to [Mo(CO)$_2$(dmpe)$_2$]$^+$) as the highest mass peak. There was no evidence for the presence of free TCNB in the mass spectrum. Attempts to remove any unreacted starting materials (either Mo(CO)$_2$(dmpe)$_2$ or TCNB both of which are volatile) by sublimation from the purple solid in a high vacuum (10^{-4} torr at 320 K) gave negative results, although we could show that an excess of either component added separately to the purple solid was easily removed by sublimation under these conditions.

The ^{1}H NMR spectrum (acetone-d_6) shows the broad signals (δ 1.85 ($C\underline{H}_3$); 2.25 ($C\underline{H}_2$) ppm) due to the protons of the dmpe ligand, and a complex series of signals centered around δ 8.9 ppm (Fig. 2) due to the aromatic protons of the TCNB component. Integration of these signals showed the ratio 2 dmpe : 9 TCNB in agreement with microanalytical results. The proton resonance of pure TCNB appears at δ 8.33 ppm. The very intense resonance (δ 8.89 ppm; Fig. 2) in the NMR spectrum of the complex integrates as approximately 16 protons ($\equiv$8 TCNB), showing a substantial (0.56 ppm) downfield shift from the free molecule and providing further evidence that no free TCNB is present in the violet complex.

On the basis of this information, it would appear that the violet compound is a seven coordinate molybdenum(II) complex of the type *cis*-[MoX(CO)$_2$-

Fig. 2. NMR spectrum (300 MHz, acetone-d_6) in the region δ 7.5—9.5 ppm of *cis*-[Mo{$C_6H_2(CN)_4$}$(CO)_2$-$(dmpe)_2$][TCNB]$_8$.

$(dmpe)_2$]Y. We suggest that the group X may be a tetracyanocyclohexadienyl group, and that the remaining eight TCNB molecules constitute the anion, Y. The exact form of Y is unknown. Several attempts to grow crystals of the purple solid which would be suitable for X-ray diffraction have been unsuccessful. In the presence of transition metals, TCNB is known to polymerise forming deeply coloured phthalocyanine-type metal complexes [13]. Recently it has been shown that TCNB reacts with strong base (LiOPr/PrOH) to form a simple, phthalocyanine-like tetramer [14]. The stacking of cyanocarbons in charge transfer complexes such as [1,2-bis(1-benzyl-4-pyridinio)ethane]$^{2+}$ [1,2,4,5-tetracyanoquinodimethane)$_5$]$^{2-}$ is well known [15]. In these compounds the cation occupies the space between columns of the oligomeric anion in the lattice. Following this model, we propose a structure for the purple molybdenum(II) complex in which *cis*-[Mo(tetracyanocyclohexadienyl)$(CO)_2(dmpe)_2$]$^+$ ions occupy the lattice sites between columns of eight TCNB molecules which form an anion, [$(TCNB)_8$]$^-$.

Reaction with 1,3,5-trinitrobenzene (TNB)

The addition of TNB (2 moles) to a colourless solution of *cis*-[$Mo(CO)_2$-$(dmpe)_2$] in methyl cyanide at room temperature immediately produced a brownish-red colour. The ESR spectrum of this brown-red solution showed resonances due to both *trans*-$[Mo(CO)_2(dmpe)_2]^+$ (g 2.053; a_P 25 gauss) and the radical anion $TNB^{-\cdot}$ (g 2.0046; a_N 2.24 gauss) [16]. The IR spectrum of the solution showed an absorption at 1858 cm^{-1} attributable to *trans*-$[Mo(CO)_2(dmpe)_2]^+$ ion [10] as well as two absorptions (1838, 1756 cm^{-1}) due to the starting material *cis*-$[Mo(CO)_2(dmpe)_2]$.

Admission of a very small quantity of oxygen to the solution resulted in a rapid colour change from brown-red to deep cherry red. Removal of the solvent and crystallisation of the residue from acetone/hexane produced a deep red solid. The IR spectrum of the solid (KBr disc) showed two absorptions at 1930, 1873 cm^{-1}. The red solid is paramagnetic ($g = 2.000$, powder). Microanalysis indicates that the solid has the composition $[Mo(CO)_2(dmpe)_2(TNB)_2]$. Charge transfer complexes of TNB with aromatic hydrocarbons are well known [17], as are also the 1 : 1 complexes formed between TNB and $[(\eta^6\text{-arene})Cr(CO)_3]$ complexes [18].

The identification of both *trans*-$[Mo(CO)_2(dmpe)_2]^+$ ion and $TNB^{-\cdot}$ in the absence of oxygen indicates the redox (electron transfer) reaction has taken place. Electron transfer has also been invoked to explain the formation of $[(C_6H_6)_2Cr]$-$[TNB]$ in the reaction between TNB and $[(C_6H_6)_2Cr]$; in that case ESR evidence was obtained for the chromium-containing cation, but no signals were observed for $TNB^{-\cdot}$ [11].

The role of oxygen in the subsequent reaction of the *trans*-$[Mo(CO)_2(dmpe)_2]^+$ $[TNB]^-$ ion pair is not known; it appears that oxygen may act by sensitising the molybdenum complex to oxidation, because the red solid shows ν(CO) absorptions which are similar to those observed in *cis*-dicarbonylmolybdenum(II) compounds, but some 20 cm^{-1} to lower frequency (see below). It is possible that the red solid contains the structure *cis*-$[Mo(C_6H_3(NO_2)_3)(CO)_2(dmpe)_2]^+$ $[TNB]^-$, in which the seven-coordinate cation includes the 1,3,5-trinitrocyclohexadienyl anion, but we are unable to bring confirmatory evidence for this proposal in the absence of a determination of the crystal structure.

Spectroscopic properties of some seven-coordinate molybdenum(II) cations

The IR spectra of the complex cations *cis*-$[MoX(CO)_2(dmpe)_2]^+$ (X = Cl, Br, I) (Table 2) show two intense ν(CO) absorptions in solution at higher frequ-

TABLE 2

INFRARED ABSORPTIONS IN THE REGION 2000—1700 cm^{-1} OF THE COMPLEXES *cis*-$[MoX(CO)_2(dmpe)_2]X$ AND RELATED COMPOUNDS IN SOLUTIONS (CH_2Cl_2) AND THE SOLID STATE (NUJOL, KBr)

	Solution CH_2Cl_2	Solid dispersion in	
		Nujol	KBr
cis-$[MoCl(CO)_2(dmpe)_2]Cl$	1952vs, 1890s	1943, 1936; 1889, 1876	1940; 1888, 1880
cis-$[MoBr(CO)_2(dmpe)_2]Br$	1952vs, 1890s	1947, 1938; 1876, 1857	1945; 1872, 1854
cis-$[MoI(CO)_2(dmpe)_2]I$	1952vs, 1886s	1956, 1948; 1878, 1856	1945; 1875, 1853
cis-$[Mo(CO)_2(dmpe)_2]$	1838vs, 1766vs	1835, 1770	1835, 1765
trans-$[MoH(CO)_2(dmpe)_2]HCl_2$ [a]	1871vs	1850, 1840	1850, 1840

[a] ν(Mo—H) 1962 cm^{-1} (KBr).

ency ($\Delta\nu$ ca. 120 cm^{-1}) than those of the six-coordinate molybdenum(0) precursor, *cis*-[$Mo(CO)_2(dmpe)_2$]. Solid state spectra in the region 2000—1700 cm^{-1} show that there is a splitting of the ν(CO) absorptions; in KBr discs only the lower frequency absorption is split, but in the case of Nujol mull spectra both of the absorptions are split. The splitting of the carbonyl absorptions, which probably arises from differences in site symmetry in the solid state, decreases in the order X = I ($\Delta\nu$ 22 cm^{-1}) > Br > Cl ($\Delta\nu$ 13 cm^{-1}). The single ν(CO) absorption band in the spectrum of *trans*-[$MoH(CO)_2(dmpe)_2$]$^+$ ion is also split ($\Delta\nu$ 10 cm^{-1}) in the solid state. No splitting is observed in the solid state IR spectra of *cis*-[$Mo(CO)_2(dmpe)_2$].

Some absorptions in the IR spectra of the molybdenum(II) cations show a slight dependence upon the nature of the anion in the coordination sphere of the seven-coordination species; these, and some other absorptions (which do not show dependence on the anion), are sensitive to the formal oxidation state of the molybdenum. These observations are summarised in Table 3. Other absorptions which do not show significant changes in either respect are observed as follows in the IR spectra of the molybdenum(II) cations: 1420m, 1310m, 1288m, 1240w, 1000w, 805m, 747m, 712m, 640w, 528w, 450w cm^{-1} (X = Cl). While not attempting a detailed assignment, it would appear that the frequencies of many vibrations of the dmpe ligand increase as a result of oxidation, whereas the frequencies of the molybdenum—ligand bond vibrations, in particular ν(Mo—C), decrease as a result of oxidation of the metal. In general, these changes are not highly significant.

The dynamic stereochemistry of seven-coordinate complexes of the general type [$MX(CO)(P—P)_2$] have been examined in detail by NMR spectroscopy recently [19]. The cations *cis*-[$MoX(CO)_2(dmpe)_2$]$^+$ have a monocapped trigonal prismatic structure [19,20] and undergo *cis/trans* isomerism by a non-dissociative twist mechanism [19,21]. We have observed that the transition (coalescence) temperature, T_C, of *cis*-[$MoX(CO)_2(dmpe)_2$]$^+$ ions is sensitive to the halide, X, and decreases in the order X = I (T_C 253 K) > Br ($\leq$200 K), Cl. The nature of the halide, X, has a slight influence upon the chemical shift of both the CH_2 and the CH_3 protons of the dmpe ligands in the cationic complexes. Other features

TABLE 3

INFRARED ABSORPTIONS IN THE RANGE 1450—250 cm^{-1} FOR THE CATIONS [$MoX(CO)_2(dmpe)_2$]$^+$ (X = Cl, Br, I(*cis*); H(*trans*)) AND NEUTRAL *cis*-[$Mo(CO)_2(dmpe)_2$].

[$MoX(CO)_2(dmpe)_2$]$^+$				*cis*-[$Mo(CO)_2(dmpe)_2$]	$\Delta\nu^a$ (cm^{-1})
X = Cl	X = Br	X = I	X = H		
1132m	1135m	1138m	1131m	1120m	15
955s	955s	950s	945s	935s	18
946vs	938vs	932vs	940vs	925vs	13
928s	928s (sh)	925s (sh)	920m	908m	18
912s	911s	908s	905m	885s	25
655m	650m	645m	650m	638s	12
597m	595m	595m	605m	610m	—14
567m	563m	558s		589m	—26
510m	507m	502m		523m	—17

[a] $\Delta\nu = \{\Sigma\nu_i([MoX(CO)_2(dmpe)_2]^+)/3\} - \nu_i[Mo(CO)_2(dmpe)_2]$ for X = Cl, Br, I.

of the NMR spectra of the seven-coordinate cations are in accord with expectation in that the value of ^1J(PH) increases on oxidation and the shift to lower field on oxidation is greater for the methylene than for the methyl protons of the dmpe ligands [20].

Experimental

All reactions were performed under an atmosphere of deoxygenated dry nitrogen using conventional vacuum line and Schlenk tube techniques. Solvents were thoroughly dried, deaerated and distilled under an atmosphere of nitrogen prior to use. Melting points were recorded on a hot stage block using capillary tubes sealed under nitrogen. IR spectra were recorded in a variety of solvents using 1.0 mm solution cells, or as mulls (NaCl plates) in Nujol or hexachlorobutadiene, or else as dispersions in KBr (ca. 2% w/w) using either a PE 257 or PE 225 spectrometer. Calibration of IR spectra was achieved using the 1602 cm^{-1} peak of polystyrene. Electronic spectra were recorded on a Unicam SP 800 spectrometer in a variety of solvents. Proton NMR spectra were recorded on a PE R12 (60 MHz), PE R32 (90 MHz), Varian HA100 (100 MHz) or on a Varian SC300 (300 MHz) using a variety of deuterated solvents. Tetramethyl silane provided an internal reference. ESR spectra were recorded on either a Varian V4502 Q-band (35 GHz) or on a Varian E4 X-band (9.5 GHz) spectrometer using solids or solutions in various solvents. Microanalyses were performed by Mr. M. Hart and his staff of this department. Conductivity measurements were made on approximately 10^{-3} M solutions of the solid complexes in nitromethane using a Phillips PR 9500 conductivity bridge. Under these conditions 1 : 1 and 1 : 2 electrolytes have conductivities in the ranges 75—95 and 160—190 S cm^3 mol^{-1} respectively [22].

Tetracyanoethene and TCNB were generous gifts from Dr. M.A.J. Rodgers. TNB was reagent grade (BDH). The complexes *cis*-[M(CO)$_2$(dmpe)$_2$] (M = Cr, Mo) were prepared [20] by published methods.

cis[Dicarbonylchlorobis(1,2-bis(dimethylphosphino)ethane) molybdenum(II)] chloride

Carbon tetrachloride (10 cm^3) was frozen (77 K) in a Schlenk tube. The cooling bath was removed and the tube allowed to warm slowly until the CCl_4 became molten at which point solid *cis*-[Mo(CO)$_2$(dmpe)$_2$] (0.34 g, 0.75 mmol) was added and the mixture was stirred rapidly. A transient bright yellow colour appeared at first which faded and, as the solution warmed to room temperature, a fawn solid precipitated from the solution. The solid was isolated by filtration and twice recrystallised from CH_2Cl_2/hexane to give a fawn powder, m.p. 518 K (dec.), 70% yield. Microanalysis: found: C, 33.4; H, 6.1; Cl, 12.8; Mo, 17.7; P, 26.4. $C_{14}H_{32}Cl_2MoO_2P_4$ calcd.: C, 32.1; H 6.1; Cl, 13.6; Mo, 18.3; P, 23.7%. $\Lambda(MeNO_2)$: 67 S cm^3 mol^{-1}. $\delta(^1H)$: 1.69 (quintet, N, 2 Hz), 2.28 (br) (CD_3CN) ppm.

trans-[Dicarbonylhydridobis(1,2-bis(dimethylphosphino)ethane) molybdenum-(II) iodide

A solution containing *cis*-[Mo(CO)$_2$(dmpe)$_2$] (0.38 g, 0.84 mmol) and 2-iodo-

2-methylpropane (0.16 g, 0.84 mmol) in methyl cyanide (20 cm^3) was heated at reflux for 2.5 h. The resulting yellow solution was concentrated to ca. 10 cm^3 and excess diethyl ether added to precipitate a pale yellow powder. Recrystallisation (CH_2Cl_2/Et_2O) at 273 K gave the product as pale yellow needles, in 85% yield. $\Lambda(MeNO_2)$: 86 S cm^3 mol^{-1}. Microanalysis: found: C, 28.5; H, 5.8; I, 22.3; Mo, 16.2; P, 21.8. $C_{14}H_{33}IMoO_2P_4$ calcd.: C, 28.9; H, 5.7; I, 21.9; Mo, 16.5; P, 21.4%. $\delta(^1H)$: 1.80 (d, ^2J 9 Hz), 1.74 (d, ^2J 7 Hz), 2.10 (br), −7.4 (tt, ^2J 69 and 8 Hz) ($CDCl_3$) ppm.

fac,fac-[Tetracarbonyltetrachlorotris(1,2-bis(dimethylphosphino)ethane)dimolybdenum(II)]

Tetrachloromethane (0.5 cm^3) was added to a solution containing *fac,fac*-[$Mo_2(CO)_6(dmpe)_3$] (0.3 g, 0.3 mmol) [20] in dichloromethane (20 cm^3) whereupon the colour of the solution became a deeper yellow and slight gas evolution was observed. The solution was stirred for 0.5 h, after which time addition of hexane caused precipitation of a pale yellow solid which was recrystallised from CH_2Cl_2/hexane to give the product as yellow microcrystals, m.p. 473 K (dec.). Λ ($MeNO_2$): <20 S cm^3 mol^{-1}. 90% yield. Microanalysis: found: C, 29.3 H, 5.5; Cl, 15.6; P, 19.8. $C_{22}H_{48}Cl_4Mo_2O_4P_6$ calcd.: C, 29.5; H, 5.4; Cl, 15.8; P, 20.7%. $\delta(^1H)$: 1.54 (d, ^2J 8.3 Hz), 1.59 (d, ^2J 9.0 Hz), 1.64 (d, ^2J 9.6 Hz)), 2.0, 2.15 (CD_2Cl_2) ppm.

cis-[Dicarbonyl(tricyanoethenyl)bis(1,2-bis(dimethylphosphino)ethane)molybdenum(II)]cyanide

Freshly sublimed tetracyanoethene (0.026 g, 0.2 mmol) was added to stirred solution of *cis*-[$Mo(CO)_2(dmpe)_2$] (0.09 g, 0.2 mmol) in methyl cyanide (10 cm^3). The resulting yellow solution was left to stand (273 K, 3 h) during which time a pale yellow microcrystalline product was deposited from the mixture. The yellow solid was collected by filtration, washed with cold methyl cyanide (5 cm^3) and dried under vacuum, m.p. 393 K (dec.), 80% yield. Microanalysis: found: C, 41.5; H, 5.6; Mo, 16.2; N, 9.9; P, 20.7. $C_{20}H_{32}MoN_4O_2P_4$ calcd.: C, 41.4; H, 5.5; Mo, 16.6; N, 9.7; P, 21.3%. The solid was insufficiently soluble to record either the conductivity or the NMR spectrum in solution.

Reaction between cis-[Mo(CO)$_2$(dmpe)$_2$] and 1,2,4,5-tetracyanobenzene

Freshly recrystallised 1,2,4,5-tetracyanobenzene (0.39 g, 2.2 mmol) was added in small portions over a period of 0.5 h to a solution containing *cis*-[$Mo(CO)_2(dmpe)_2$] (0.1 g, 0.22 mmol) in methyl cyanide. The mixture was heated at reflux for 24 h, to produce a deep purple solution which was filtered hot. The solvent was evaporated under reduced pressure to leave a deep purple solid which was twice reprecipitated from dichloromethane by the addition of hexane. Microanalysis: found: C, 60.2; H, 2.4; Mo, 3.7; N, 24.4; P, 5.3. $C_{102}H_{50}MoN_{30}O_2P_4$ calcd.: C, 60.8; H, 2.4; Mo, 4.7; N, 24.5; P, 6.0%. Yield 85%.

Reaction between cis-[Mo(CO)$_2$(dmpe)$_2$] and 1,3,5-trinitrobenzene

Solid TNB (0.324 g, 1.52 mmol) was added to a solution of *cis*-[$Mo(CO)_2(dmpe)_2$] (0.34 g, 0.76 mmol) in methyl cyanide (15 cm^3) to give a brownish-red solution immediately. Passage of oxygen gas through the rapidly stirred solution resulted in an immediate colour change to cherry red which did not alter if the gas was passed for a longer period (5 min) than a few seconds. The solvent was evaporated under reduced pressure and the residue was crystallised from acetone/hexane at 273 K to give a deep red solid product. Microanalysis: found: C, 34.7; H, 4.7; N, 10.2; Mo, 11.1; P, 16.7. $C_{26}H_{38}MoN_6O_{14}P_4$ calcd.: C, 35.5; H, 4.3; N, 9.6; Mo, 10.9; P, 14.1%.

cis-[Bromodicarbonylbis(1,2-bis(dimethylphosphino)ethane)molybdenum(II)]-bromide

Benzyl bromide (0.34 g, 1.99 mmol) and *cis*-[Mo(CO)$_2$(dmpe)$_2$] (0.44 g, 0.98 mmol) were sealed in an evacuated Carius tube (volume ca. 100 cm^3) and heated at 303 K for 15 h. The tube was opened and the content extracted with CH_2Cl_2 (10 cm^3). Evaporation of the solvent under reduced pressure left a residue which was extracted with diethyl ether (2 × 10 cm^3). The solid remaining after extraction was redissolved in methylene chloride and crystallised by the addition of ether at 273 K to give a pale yellow powder, m.p. 520 K (dec.), 75% yield. Microanalysis; found: C, 27.6; H, 5.2; Br, 25.8; P, 20.7. $C_{14}H_{32}Br_2MoO_2P_4$ calcd.: C, 27.5; H, 5.2; Br, 26.1; P, 20.3%. $\Lambda(MeNO_2)$: 97 S cm^3 cm^{-1}. $\delta(^1H)$ 1.74 (quintet, N, 2 Hz), 2.30 (br) ($CDCl_3$) ppm.

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