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Dinitrogen and Carbonyl Complexes of Tungsten(I) and Molybdenum(I). The Nature of '$MoCl(N_2)$-$(dppe)_2$'

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Recent reports [1–3] on the chemical oxidation of zerovalent Group VI metal carbonyl complexes to their M(I) analogues prompt us to describe our investigation into Mo(I) and W(I) carbonyl and dinitrogen chemistry.

Iodine oxidation of *cis*-$M(CO)_2(dppe)_2$ [M = Mo, W; dppe = 1,2-bis(diphenylphosphino)ethane] and *trans*-$Mo(N_2)_2(dppe)_2$ is known to give *trans*-$\{M(CO)_2(dppe)_2\}I_3$ (M = Mo, W) [4] and *trans*-$\{Mo(N_2)_2(dppe)_2\}I_3$ [5] although the latter is very unstable and decomposes rapidly in solution [6]. Chatt *et al.* [7] have prepared the similar, but more stable tungsten(I) complex *trans*-$\{W(N_2)_2(PMePh_2)_4\}FeCl_4$ by oxidation of *trans*-$W(N_2)_2(PMePh_2)_4$ with $FeCl_3$. A different type of dinitrogen complex of a monovalent Group VI metal is the neutral *trans*-$MoCl(N_2)(dppe)_2$ which is reported to be formed by reduction of $MoOCl_2(dppe)$/dppe under N_2, [8] or by reaction of *trans*-$Mo(N_2)_2(dppe)_2$ with certain alkyl chlorides [9]. This material is the postulated intermediate in the alkylation of *trans*-$Mo(N_2)_2(dppe)_2$ by alkyl halides but a recent mechanistic study [10] has suggested that $MoX(N_2)(dppe)_2$ complexes are only stable at low temperatures and that the complex previously formulated as $MoCl(N_2)(dppe)_2$ is actually an equimolar mixture of *trans*-$MoCl_2(dppe)_2$ and *trans*-$Mo(N_2)_2(dppe)_2$.

In this present work we report a variety of reactions leading to the W(I) cations, *trans*-$\{W(L)_2(dppe)_2\}^+$ (L = N_2, CO), together with infrared and Raman data for these and their neutral W(0) analogues. Our Raman spectroscopic studies also lend support to the proposal that '$MoCl(N_2)(dppe)_2$' is in fact a cocrystallised mixture.

We find that, in contrast to the slow reaction between CH_3Br and *trans*-$W(N_2)_2(dppe)_2$ which is known to give $WBr(dppe)_2(N{=}N{-}CH_3)$ [11], CCl_3Br undergoes a rapid reaction to give an orange crystalline solid showing a single $\nu(N{\equiv}N)$ IR band at 1988 cm^{-1}, which we formulate as *trans*-$\{W(N_2)_2(dppe)_2\}Br$. Similar oxidations of *trans*-$W(N_2)_2(dppe)_2$ occur with tetracyanoethene (TCNE), I_2, and $FeCl_3$ giving the relatively air stable brown to red crystalline complexes *trans*-$\{W(N_2)_2(dppe)_2\}^+X^-$ (X = TCNE, I_3, $FeCl_4$). Analogous reactions take place with *cis*-$W(CO)_2(dppe)_2$ affording *trans*-$\{W(CO)_2(dppe)_2\}^+$. Interestingly the reaction with TCNE gives *trans*-$\{W(L)_2(dppe)_2\}$TCNE (L = N_2, CO) whereas Connor and Riley [12] obtained $\{Mo[C_2(CN)_3](CO)_2(dmpe)_2\}CN$ (dmpe = 1,2-bis(dimethylphosphinato)ethane) from *cis*-$Mo(CO)_2(dmpe)_2$ and TCNE. Formation of the TCNE radical anion in reactions of zerovalent complexes is not unusual so that, for example, *cis*-$Cr(CO)_2(dmpe)_2$ and $Cr(C_6H_6)_2$ react with TCNE to give $\{C(CO)_2(dmpe)_2\}$TCNE [13] and $\{Cr(C_6H_6)_2\}$TCNE [14] respectively.

The W(I) complexes are characterized by a very strong infrared absorption at 1988 cm^{-1} (N_2) and 1858 cm^{-1} (CO) assigned to the asymmetric (A_{2u}) $\nu(N{\equiv}N)$ and $\nu(C{\equiv}O)$ vibrations. As expected the $\nu(N{\equiv}N)$ band is some 30 cm^{-1} to higher frequency than in *trans*-$W(N_2)_2(dppe)_2$, consistent with an oxidation of the metal centre.

The *trans*-$M(N_2)_2(dppe)_2$ (M = Mo, W) complexes would be expected to exhibit a Raman active (A_{1g}) symmetric $\nu(N{\equiv}N)$ absorption and indeed we find that this is the case. These very strong bands occur at 1994 cm^{-1} (W) and 2020 cm^{-1} (Mo) while the remainder of the spectra contain the characteristic bands of dppe. It has not been possible to conclusively identify the symmetric $\nu(N{-}M{-}N)$ stretching mode for either complex, though it presumably lies in a group of medium intensity bands between 380 cm^{-1} and 550 cm^{-1}. Symmetrical $\nu(M{-}P_4)$ vibrations are observed at 180 cm^{-1} (M = W) and 170 cm^{-1} (M = Mo).

Raman spectroscopy also offers a means by which the nature of $MoCl(N_2)(dppe)_2$ can be checked. If $MoCl(N_2)(dppe)_2$ is correctly formulated as being a Mo(I) dinitrogen compound then there should be only one IR active N≡N stretching mode which should appear at the same frequency in the Raman spectrum. On the other hand, if, as has been proposed [10], $MoCl(N_2)(dppe)_2$ is a mixture of *trans*-$MoCl_2(dppe)_2$ and *trans*-$Mo(N_2)_2(dppe)_2$ then while one IR active $\nu(N{\equiv}N)$ (asymmetric) absorption should be observed, there should be a $\nu(N{\equiv}N)$ band at higher frequency in the Raman spectrum due to the symmetric vibration. We have prepared $MoCl(N_2)(dppe)_2$ and find that it gives rise to a strong IR absorption at 1966 cm^{-1} as previously reported [9]. However, this band is not observed in the Raman spectrum which instead shows a strong $\nu(N{\equiv}N)$ band at 2020 cm^{-1}, consistent with the presence of *trans*-$Mo(N_2)_2(dppe)_2$ (see above). This result therefore strongly supports the proposal that $MoCl(N_2)(dppe)_2$ should be formulated as a mixture of two complexes although admittedly the infrared band is not coincident with that in *trans*-$Mo(N_2)_2(dppe)_2$. However if *trans*-$MoCl_2(dppe)_2$ and *trans*-$Mo(N_2)_2(dppe)_2$ are cocrystallised a similar IR shift occurs in the product,

TABLE I. Selected Infrared and Raman Data (cm^{-1}).

$W(N_2)_2$-(dppe)$_2$	{$W(N_2)_2$(dppe)$_2$}-TCNE	{W(CO)$_2$(dppe)$_2$}-TCNE	$Mo(N_2)_2$-(dppe)$_2$	$MoCl(N_2)$-(dppe)$_2$	Assignment
	2180 m (w)	2180 m (w)			ν(CN), IR (R)
	2140 m	2140 m			ν(CN), IR
1996 s			2025 s	2020 m	$\nu(N_2)$, A_{1g}, R
1952 s	1966 s		1977 s	1966 m	$\nu(N_2)$, A_{2u}, IR
		1850 s			ν(CO), A_{2u}, IR
524 s			518 m	515 w	ν(MN)/$\delta(MN_2)$, R
442 s			471 m	479 w	
414 m			434 m	440 w	
179 s			169 s	171 m	ν(MP), A_{1g}, R

TABLE II. Characterisation Data for New Compounds.[a]

Compound	M.P. (°C)	C%	H%	N%
{$W(N_2)_2$(dppe)$_2$}TCNE	137 (dec.)	59.6(59.8)	4.5(4.1)	9.6(9.6)
{$W(N_2)_2$(dppe)$_2$}I_3·½(CH_2Cl_2)	164 (dec.)	43.3(43.2)	3.1(3.4)	3.0(3.8)
{$W(N_2)_2$(dppe)$_2$}$FeCl_4$	156 (dec.)	50.4(50.5)	3.7(3.9)	1.6(4.5)
{W(CO)$_2$(dppe)$_2$}TCNE	149 (dec.)			

[a]Calculated analyses are shown in parentheses.

presumably arising from a crystal packing effect and suggesting that an X-ray structure determination would prove most interesting.

Raman spectra of the new W(I) cationic complexes all exhibit bands arising from dppe and the particular anion. In TCNE complexes the spectrum is essentially that of the TCNE anion. Most unexpected however is the virtual absence of the anticipated strong bands attributable to the totally symmetric $\nu(N_2)$ and ν(CO) vibrations in most of these complexes. Extremely weak bands appear in *trans*-{$M(N_2)_2$(dppe)$_2$}I_3 at 2070 cm^{-1} (M = Mo) and 2020 cm^{-1} (M = W) but are indistinguishable in the remainder. Decomposition (with loss of N_2 and CO) can be ruled out, since the IR spectrum of a sample of *trans*-{$W(N_2)_2$(dppe)$_2$}TCNE was unchanged following 48 h irradiation by the Raman laser.

Experimental

Where necessary, reactions were carried out in Schlenk apparatus using previously dried solvents and a dry dinitrogen atmosphere. Infrared spectra were recorded on Perkin Elmer 157 and 577 instruments using nujol mulls and calibrated against a polystyrene standard. Raman spectra were obtained on an Anaspec 33 instrument modified with a 180° collection microscope accessory [15]. All measurements were made using a laser of 6471 Å wavelength. Melting points were determined on a Gallenkamp melting point apparatus in nitrogen filled capillaries and are uncorrected. Elemental analyses were carried out in this laboratory. The complexes *trans*-$W(N_2)_2$(dppe)$_2$ [16], *trans*-$Mo(N_2)_2$(dppe)$_2$ [17], $MoCl(N_2)$(dppe)$_2$ [9], *trans*-{W(CO)$_2$(dppe)$_2$}I_3 [4], *trans*-{$Mo(N_2)_2$-(dppe)$_2$}I_3 [5] were prepared according to literature procedures.

Bis-{bis(diphenylphosphino)ethane}-bis(dinitrogen)-tungsten Tetrachloroferrate

A solution containing $W(N_2)_2$(dppe)$_2$ (0.80 g) in 50 cm^3 of dichloromethane was treated with a solution of anhydrous ferric chloride (0.80 g) in 30 cm^3 of ethanol, and the mixture stirred for 5 minutes. Evaporation to *ca.* 30 cm^3 gave a brown crystalline precipitate, which was filtered off and washed with ethanol and diethyl ether. This material was recrystallised from dichloromethane/ethanol to give 0.33 g of yellow-brown crystals (35%).

Bis-{bis(diphenylphosphino)ethane}-bis(dinitrogen)-tungsten Triiodide

A solution of iodine (0.38 g, 1.5 mmol) in toluene (40 cm^3) was added dropwise, with vigorous stirring, to a solution of $W(N_2)_2(dppe)_2$ (1.04 g, 1 mmol) in dichloromethane (100 cm^3). As the last few drops of iodine solution were added, a crystalline red-orange solid began to precipitate, and the solution was then evaporated to *ca.* 50 cm^3. The solid (1.05 g, 74%) was filtered off, washed with toluene and pentane, and dried under vacuum.

Bis-{bis(diphenylphosphino)ethane}-bis(dinitrogen)-tungsten-Tetracyanoethene

A solution of tetracyanoethene (0.0514 g, 0.40 mmol) in 10 cm^3 of dry toluene was added dropwise under N_2 to a filtered solution of $W(N_2)_2(dppe)_2$ (0.414 g, 0.40 mmol) in 50 cm^3 of the same solvent. The mixture was stirred for 5 minutes, and the golden-brown precipitate was filtered off, washed with toluene, and dried under vacuum. The solid was dissolved in dry methanol, giving an orange-brown solution which rapidly deposited red-brown crystals. These were separated by decantation, washed with methanol, and dried under vacuum. The yield was 0.372 g (80%). The compound is a 1:1 electrolyte in nitromethane. The corresponding carbonyl complex was similarly obtained from *cis*-$W(CO)_2(dppe)_2$ and tetracyanoethene.

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