Cationic Transition metal Complexes. Part IV.[1] Molybdenum and Tungsten Dinitrosyl Complexes

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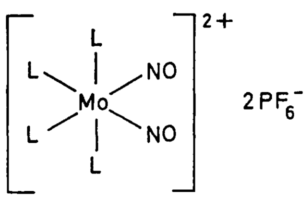
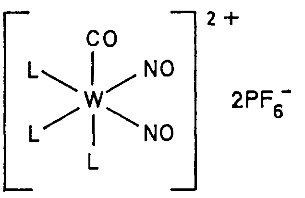
Treatment of $[Mo(MeCN)_3(CO)_3]$ with $NOPF_6$–MeCN gives *cis*-$[Mo(NO)_2(MeCN)_4]^{2+}[PF_6^-]_2$, (I). The corresponding reaction of $[W(MeCN)_3(CO)_3]$ affords *cis*-$[W(NO)_2(CO)(MeCN)_3]^{2+}[PF_6^-]_2$, (III). Reaction of (I) and (III) with sodium diethyldithiocarbamate gives the known complexes *cis*-$[M(NO)_2(S_2CNEt_2)_2]$ (M = Mo or W), whereas, reaction with acetylacetone–Na_2CO_3 gives the new compounds *cis*-$[M(NO)_2(acac)_2]$ (M = Mo or W).

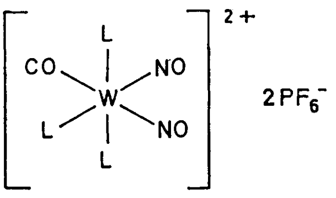
THE oxidative-reaction of nitrosyl halides and more recently nitrosyl hexafluorophosphate with low-valent transition metal complexes has been widely used as a route to nitrosyl complexes. In the Group VIB triad the molybdenum and tungsten dinitrosyl dihalides $[M(NO)_2X_2]$ (X = Cl or Br) have been prepared by reaction of nitrosyl halide with the corresponding hexacarbonyl,[2,3] whereas, the chromium dication *trans*-$[Cr(NO)_2(MeCN)_4]^{2+}$ has been obtained by treatment of tricarbonyl(toluene)chromium with nitrosyl hexafluorophosphate in acetonitrile solution.[4] With a view to developing a more versatile synthetic route to dinitrosyl molybdenum and tungsten species we have examined the reaction of tris(acetonitrile)tricarbonyl-molybdenum and -tungsten with nitrosyl hexafluorophosphate. It was thought that since one of the factors controlling the rate of oxidative-addition reaction is considered to be the electron density on the metal atom, that the trisacetonitrile species $[M(MeCN)_3(CO)_3]$ (M = Mo[5] or W[6,7]) would, relative to the hexacarbonyl or arenetricarbonyl complexes, show enhanced reactivity towards $NO^+PF_6^-$. The new compounds described in this paper were characterized by elemental analysis, mass spectroscopy, and i.r. and ^1H n.m.r. spectroscopy.



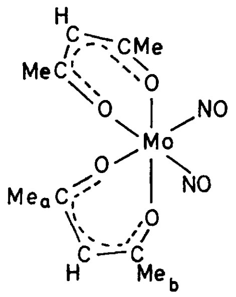
(I, L = MeCN)



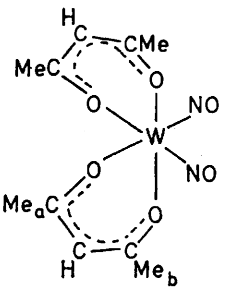
(IIIa, L = MeCN)



(IIIb, L = MeCN)



(VII)



(VI)

Addition of a solution of nitrosyl hexafluorophosphate in acetonitrile to a suspension of tris(acetonitrile)tricarbonylmolybdenum led to the evolution of carbon monoxide. The addition of diethyl ether to the reaction mixture gave a dark green solid, which on fractional crystallisation from diethyl ether–acetonitrile gave dark green crystals of complex (I). The i.r. spectrum showed two nitrosyl stretching frequencies at 1863 and 1780 cm^{-1} in agreement with the illustrated structure, in which the nitrosyl groups have a *cis*-configuration.

In addition the spectrum showed two strong bands at 2320 and 2300 cm^{-1} which are assigned[8] to co-ordinated acetonitrile, the increase in ν(CN) on co-ordination implies the absence of backbonding from filled metal *d*-orbitals into nitrile π^* orbitals. The ^1H n.m.r. spectrum showed

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only a single resonance for co-ordinated acetonitrile, whereas, for the suggested octahedral structure two CH_3CN proton environments might have been expected, corresponding to acetonitrile *cis*- and *trans*- to the nitrosyl ligands. The single resonance could be due to coincidence of the chemical shifts. In CD_3CN as the solvent the ^1H n.m.r. signal of the co-ordinated acetonitrile only slowly ($t_{1/2}$ *ca.* 10 h) decreased in intensity, demonstrating the absence of a dissociative exchange process. The apparent equivalence of the CH_3CN environments could alternatively be due to an intramolecular exchange process, *i.e.* a polytopal rearrangement; however, the solubility of complex (I) limited low-temperature n.m.r. measurements.

Further fractional crystallisation afforded variable small yields of a yellow crystalline compound (II), which could not be assigned a reasonable structure on the basis of the available evidence.

A similar reaction of tris(acetonitrile)tricarbonyltungsten with $NOPF_6$ in acetonitrile led to rapid carbon monoxide evolution and the formation of dark green prisms of complex (III). The i.r. spectrum of (III) showed in addition to two acetonitrile and two nitrosyl stretching frequencies (1867 and 1775 cm^{-1}) a strong band at 2159 cm^{-1}, which is assigned to a terminal carbonyl band of a cationic complex. The ^1H n.m.r. spectrum measured in CD_3NO_2 showed two bands with relative intensities 2 : 1 assignable to co-ordinated acetonitrile. These observations are consistent with either of the *cis*-dinitrosyl structures (IIIa) or (IIIb).

It is interesting to compare these results with the recent report[9] that reaction of tris(acetonitrile)tricarbonylmolybdenum or -tungsten in tetrahydrofuran with NOCl gives dark brown solutions from which may be isolated either $[M(CO)_2(NO)L_2Cl]$ or $[M(CO)(NO)(MeCN)L_2Cl]$ by addition of the appropriate ligand (L). Although attempts were made in this work to isolate mono-nitrosyl cationic species this was not successful, but transient brown-red colours were noted during the addition of nitrosyl hexafluorophosphate.

Treatment of both (I) and (III) with sodium diethyldithiocarbamate afforded respectively the neutral dithiocarbamato-complexes (IV) $[Mo(NO)_2(S_2CNEt_2)_2]$ and (V) $[W(NO)_2(S_2CNEt_2)_2]$,[10] thus providing further evidence as to the identity of (I) and (III).

Treatment of (I) and (III) with acetylacetone in the presence of sodium carbonate gave the new stable crystalline complexes (VII) *cis*-dinitrosylbis(acetylacetonato)molybdenum and (VI) *cis*-dinitrosylbis(acetylacetonato)tungsten. Complexes of this type have not been previously described. The i.r. spectra showed in addition to two nitrosyl bands characteristic of a *cis*-dinitrosyl complex, bands typical[11] of an oxygen bonded acetylacetonato-ligand. At 25°C the ^1H n.m.r. spectra of $[Mo(NO)_2(acac)_2]$ and $[W(NO)_2(acac)_2]$ exhibited three singlet resonances with relative intensities of 1 : 3 : 3, which are assigned respectively to *CH*, Me$_a$, and Me$_b$. This indicates that the complexes exist in a single configuration in solution at this temperature, *cis*-orientated as indicated by the i.r. spectrum. The two methyl groups are not equivalent because the symmetry of the presumed octahedral molecule is low (C_2). It has been previously shown[12] that the inequivalent methyl resonance of the related complex $[Mo(NO)_2(S_2CNMe_2)_2]$ collapses to a singlet at 100 °C; this being ascribed to partial dissociation of the dithiocarbamato-ligand. Examination of the ^1H n.m.r. spectrum of (VII) in *p*-dichlorobenzene to 160 °C, and (VI) in chlorobenzene to 140 °C, showed no evidence of collapse of the acetylacetonate methyl resonances. This indicates the stability of these six-co-ordinate systems and demonstrates the absence of an intramolecular polytopal rearrangement.

Correlation diagrams have been described[13] for the bonding of nitrosyls in five- and six-co-ordinate complexes. A simple application of these concepts to the molybdenum and tungsten complexes described here, which are 22 electron systems, would suggest that all of these complexes have linear nitrosyl ligands. As pointed out by Pierpont and Eisenberg,[13] ν(NO) is an unreliable criteria for assessing the bonding mode of co-ordinated NO.

EXPERIMENTAL

^1H N.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100 MHz; chemical shifts are relative to Me_4Si (τ 10·00). I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer using CaF_2 cells. All operations were carried out in a dry oxygen-free atmosphere. Solvents were dried by established methods. Tris(acetonitrile)tricarbonyl-molybdenum(0) and -tungsten(0) were prepared by the standard method, *i.e.* refluxing the carbonyl in an excess of acetonitrile. By following the reactions by i.r. spectroscopy, it was found necessary in preparing the tungsten compound to increase the reaction time to 60—70 h. The common impurity was $[W(CO)_4(MeCN)_2]$. Melting points were carried out *in vacuo*.

Reaction of Nitrosyl Hexafluorophosphate with Tris(acetonitrile)tricarbonylmolybdenum.—A solution of nitrosyl hexafluorophosphate (3·0 g, 17·1 mmol) in acetonitrile (20 ml) was added dropwise with stirring (room temperature) to a suspension of tris(acetonitrile)tricarbonylmolybdenum (2·4 g, 7·9 mmol) in acetonitrile (25 ml). The colour of the solution changed through brown-purple to green with evolution of carbon monoxide. After 10 min, diethyl ether (150 ml) was added and the precipitated solid washed with diethyl ether and dried *in vacuo*. Fractional crystallisation from acetonitrile–diethyl ether gave dark green prisms of *tetrakis(acetonitrile)dinitrosylmolybdenumbishexafluorophosphate*, (I) (2·4 g, 50%) m.p. 204—207° (Found: C, 16·0; H, 2·1; N, 13·5. $C_8H_{12}F_{12}MoN_6O_2P_2$ requires C, 15·8; H, 2·0;

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N, 13·8%), ν (CH_3CN soln.) 1863s (NO), 1761s (NO) cm^{-1}, ν (Nujol) 2320m (CH_3CN), 2300s (CH_3CN), 1863s (NO), 1780s (NO) and 830br, s (PF_6) cm^{-1}. The ^1H n.m.r. spectrum (CD_3CN) showed a resonance at τ 7·46 (s, 12H, CH_3CN); on standing the intensity of the peak decreased. Further crystallisation afforded yellow *crystals* of compound (II) (0·5 g., 15%, variable yields), m.p. 230—235° dec. (Found: C, 19·8; H, 2·3. $C_{14}H_{18}F_{12}Mo_2N_8O_4P_2$ requires C, 19·9; H, 2·2%), ν (CH_3CN soln.) 1712br,s cm^{-1}, ν (Nujol) 2320m (CH_3CN), 2300s (CH_3CN), 1705s and 835br,s (PF_6) The ^1H n.m.r. spectrum (CD_3NO_2) showed a resonance at τ 8·00 (s, 18H, CH_3CN).

Reaction of Nitrosyl Hexafluorophosphate with Tris(acetonitrile)tricarbonyltungsten.—Similarly, slow addition of nitrosyl hexafluorophosphate (1·2 g, 6·9 mmol) in acetonitrile (15 ml) to a stirred suspension of tris(acetonitrile)-tricarbonyltungsten (1·1 g, 2·8 mmol) in acetonitrile (25 ml) led to carbon monoxide evolution and a dark green colouration. Addition of diethyl ether (150 ml) gave a precipitate, which was recrystallised from acetonitrile–diethylether to give very dark green prisms of *tris(acetonitrile)carbonyldinitrosyltungsten bishexafluorophosphate,* (III) (1·5 g, 71%), m.p. 209—211° (Found: C, 12·5; H, 1·3; N, 10·6. $C_7H_9F_{12}N_5O_3P_2W$ requires C, 12·3; H, 1·3; N, 10·2%), ν (CH_3CN soln.) 2164 (CO), 1861s (NO), 1776s (NO) cm^{-1}, ν (Nujol) 2319s (CH_3CN), 2295 (CH_3CN), 2159s (CO), 1867s (NO), 1775s (NO) and 835br,s (PF_6) cm^{-1}. The ^1H n.m.r. spectrum (CD_3NO_2) showed resonances at τ 7·30 (s, 6H, CH_3CN), 7·40 (s, 3H, CH_3CN) and 8·02 (s, free CH_3CN).

Reaction of Sodium Diethyldithiocarbamate with Tetrakis(acetonitrile)dinitrosylmolybdenum Bishexafluorophosphate, Complex (I).—A solution of $NaS_2CNEt_2,3H_2O$ (0·03 g, 0·15 mmol) in nitromethane (5 ml) was added with stirring (room temperature) to a solution of complex (I) (0·038 g, 0·06 mmol) in nitromethane (2 ml). After 18 h the solvent was removed *in vacuo* and the diethyl ether soluble material recrystallised from methanol to give golden-brown crystals of complex (IV) (0·02 g, 73%), m.p. 127—128° (lit.[10] m.p. >300°) (Found: C, 27·0; H, 4·4; N, 12·2. Calc. for $C_{10}H_{20}MoN_4O_2S_4$: C, 26·7; H, 4·4; N, 12·4%), ν (Nujol) 1745s (NO), 1630s (NO), 1500s (CN) cm^{-1} [lit.[10] ν (Nujol) 1745s, 1630s and 1505s cm^{-1}].

Reaction of Sodium Diethyldithiocarbamate with Tris(acetonitrile)carbonyldinitrosyltungsten Bishexafluorophosphate, Complex (III).—Similarly reaction of complex (III) (0·087 g, 0·13 mmol) with $NaS_2CNEt_2,3H_2O$ (0·065 g, 0·29 mmol) in acetonitrile (15 ml) gave after 18 h at room temperature a diethyl ether soluble material, which on recrystallisation from methanol gave dark green rhombic crystals of complex (V) (0·045 g, 57%), m.p. 148—152° (Found: C, 22·4; H, 3·8. Calc. for $C_{10}H_{20}N_4O_2S_4W$: C, 22·2; H, 3·7%), ν (Nujol) 1723s (NO), 1612s (NO), and 1503s (CN) cm^{-1}.

Reaction of Acetylacetone with Tris(acetonitrile)carbonyldinitrosyltungsten Bishexafluorophosphate, Complex (III).—Acetylacetone (10 ml, an excess) was added to complex (III) (0·116 g, 0·17 mmol) and anhydrous sodium carbonate (0·02 g, 0·18 mmol). After stirring at room temperature for 12 h the excess of acetylacetone was removed *in vacuo* and the residue extracted with hot hexane (200 ml). Reduction of the volume (to 5 ml) *in vacuo* gave green rhombic crystals of *bis(acetylacetonato)dinitrosyltungsten*(0), (VI) (0·055 g, 75%), m.p. 181—182° (Found: C, 27·7; H, 3·2; N, 6·1. $C_{10}H_{14}N_2O_6W$ requires C, 27·2; H, 3·2; N, 6·3%), ν (Nujol) 1735s (NO), 1629s (NO), 1557s (acac), and 1538s (acac) cm^{-1}. The mass spectrum showed peaks at *m/e* 442 (*P*), 412 (*P* – NO), and 382 (*P* – 2NO); a high resolution mass spectrum confirmed the formula $C_{10}H_{14}N_2O_6W$. The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 4·36 (s, 2H, CH), 7·78 (s, 6H, CH_3), and 8·02 (s, 6H, CH_3).

Reaction of Acetylacetone with Tetrakis(acetonitrile)dinitrosylmolybdenum Bishexafluorophosphate, Complex (I).—Similarly, a solution of complex (I) (0·25 g, 0·41 mmol) and sodium carbonate (0·07 g, 0·66 mmol) in acetylacetone (10 ml, an excess) was stirred at room temperature for 12 h. The solvent was removed *in vacuo* and the residue extracted with hot hexane (200 ml). Reduction of the volume (to 5 ml) *in vacuo* gave green crystals of *bis(acetylacetonato)dinitrosylmolybdenum*(0), (VII) (0·095 g, 68%), m.p. 146—147° (Found: C, 33·7; H, 4·2; N, 7·3. $C_{10}H_{14}MoN_2O_6$ requires C, 33·9; H, 4·0; N, 7·9%), ν (Nujol) 1763s (NO), 1645s (NO), 1555s (acac), and 1517s (acac) cm^{-1}. The mass spectrum showed peaks at *m/e* 356 (*P*), 326 (*P* – NO), and 296 (*P* – 2NO). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 4·40 (s, 2H, CH), 7·80 (s, 6H, CH_3), and 8·02 (s, 6H, CH_3).

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