Transition-metal Nitrosyl Compounds. Part VI.[1] Mononitrosyltrichloromolybdenum, Mononitrosyltrichlorotungsten, and Some Related Derivatives

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Nitrosyl chloride reacts with $Mo_2(CO)_8Cl_4$ and $W_2(CO)_8Cl_4$ to give the new mononitrosyl derivatives tentatively formulated as $[Mo(NO)Cl_3]_n$ and $[W(NO)Cl_3]_n$ together with small amounts of $[Mo(NO)_2Cl_2]_m$ and $[W(NO)_2Cl_2]_m$. $[Mo(NO)Cl_3]_n$ reacts with triphenylphosphine, triphenylphosphine oxide, 2,2′-bipyridyl, or NaS_2CNR_2 to give the mononitrosyl derivatives $Mo(NO)Cl_3(Ph_3PO)_2$, $Mo(NO)Cl_3(bipy)$, or $Mo(NO)(S_2CNR_2)_3$ which have been fully characterised.

REPORTS have appeared recently on the preparation of molybdenum complexes containing a basic $Mo(NO)^{3+}$ unit. King has reported the cyclopentadienyl (cp) complexes $(cp)Mo(NO)I_2$,[2] $(cp)_2Mo(NO)I$ [3] and some of their derivatives and Cotton and Legzdins [4] have prepared $(cp)_3Mo(NO)$.

The nitrosyl halides, XNO (X = Cl or Br), are suitable reagents for the preparation of transition-metal nitrosyl compounds.[5] It has been shown that ClNO or BrNO readily react with $Mo(CO)_6$ and $W(CO)_6$ to produce, in good yields, $[Mo(NO)_2X_2]_m$ (1) and $[W(NO)_2X_2]_m$ (2) (X = Cl or Br).[5,6] We now report that ClNO reacts with $Mo_2(CO)_8Cl_4$ [7] and $W_2(CO)_8Cl_4$ [8] to give new mononitrosyl-derivatives tentatively formulated as $[Mo(NO)Cl_3]_n$ (3) and $[W(NO)Cl_3]_n$ (4) together with varying amounts of $[Mo(NO)_2Cl_2]_m$ and $[W(NO)_2Cl_2]_m$. The mononitrosyl compounds are convenient starting materials for a range of complexes containing the $M(NO)^{3+}$ system, some of which are reported here.

RESULTS AND DISCUSSION

On addition of nitrosyl chloride to $Mo_2(CO)_8Cl_4$ at −40° carbon monoxide is evolved and a green-black solid is produced. In the i.r. spectrum of this solid three bands are observed in the region 1590—1805 cm^{-1}. Two of these (1690 and 1805 cm^{-1}) are weak and may be assigned to ν_{NO} of the previously reported $[Mo(NO)_2Cl_2]_m$ (1),[5] whereas the third band (1590 cm^{-1}) is very strong and is assigned to a new mononitrosyl compound which is presumed to be $[Mo(NO)Cl_3]_n$ (3). We have been unable to isolate (3) as a pure sample. The reaction always produces samples contaminated with small amounts of $[Mo(NO)_2Cl_2]_m$ and separation has not been achieved since the properties of $[Mo(NO)Cl_3]_n$ and $[Mo(NO)_2Cl_2]_m$ are very similar.† Thus, they both dissolve only in solvents with which they react and they are involatile. The tentative formulation of the new compound as a mononitrosyl trichloride is based mainly

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† We estimate, on the basis of N and Cl analysis, that the black-green reaction product consists of $[Mo(NO)Cl_3]_n$ (95%) and $[Mo(NO)_2Cl_2]$ (5%).

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on i.r. data and on its reactions with triphenylphosphine, triphenylphosphine oxide, 2,2′-bipyridyl, or sodium *NN*′-dialkyldithiocarbamates to give the mononitrosyl derivatives, $Mo(NO)Cl_3(Ph_3PO)_2$ (5), $Mo(NO)Cl_3(bipy)$ (6), or $Mo(NO)(S_2CNR_2)_3$ [9] which have been fully characterised.

Dichlorotetracarbonyltungsten dimer is considerably less stable than the molybdenum analogue [7,8] and in its reaction with ClNO a mixture of products was obtained. On the basis of i.r. data two of these are thought to be $[W(NO)_2Cl_2]_m$ and $[W(NO)Cl_3]_n$ but the other components of the mixture which do not contain NO groups were not identified. Again it was not possible to separate the components of this mixture but the mixture may be employed as a convenient source of the $W(NO)^{3+}$ unit, reacting with triphenylphosphine, for example, to give $W(NO)Cl_3(Ph_3PO)_2$ (7) and $W(NO)_2Cl_2(Ph_3PO)_2$ (8) which may be readily separated as pure products.

In contrast to the behaviour of ClNO with $Mo_2(CO)_8Cl_4$ and $W_2(CO)_8Cl_4$ the corresponding reactions of BrNO with $Mo_2(CO)_8Br_4$ [10] and $W_2(CO)_8Br_4$ gave $[Mo(NO)_2Br_2]_m$ and $[W(NO)_2Br_2]_m$ as the sole products and the bromo-compounds $[M(NO)Br_3]_n$ have not been observed.

Mononitrosyltrichloro-molybdenum and -tungsten are hygroscopic, oxygen sensitive, black-green powders. They are soluble in oxygen-free donor solvents such as alcohols, acetone, or acetonitrile without loss of nitric oxide but are completely insoluble in all non-donor solvents. Their thermal stability is high (>150 °C) and they are involatile.

The derivatives $M(NO)Cl_3(Ph_3PO)_2$ (M = Mo or W) have been prepared from the reaction of the parent compound with triphenylphosphine. Although these reactions were carried out in deoxygenated solvents and under an oxygen-free nitrogen atmosphere, oxidation of the phosphine occurred in each case. It is significant that triphenylphosphine is oxidised by nitric oxide under similar conditions and, in the reactions described above, yields of $M(NO)Cl_3(Ph_3PO)_2$ are comparatively low (*ca.* 70%) suggesting that some decomposition of the parent compound occurs during the reaction. In air, complex (5) rapidly decomposes to give large yellow-green crystals of $MoOCl_3(Ph_3PO)_2$. Complex (5) has also been prepared from the reaction of (3) with triphenylphosphine oxide. In this case the yields are relatively high (*ca.* 70%). The same mononitrosyl derivatives, (5) and (7), have also been prepared from the reactions of ClNO with $M(CO)_4(Ph_3P)_2$, $M(CO)_3Cl_2(Ph_3P)_2$ (M = Mo or W), or $Mo(CO)_3(Ph_3P)_3$. They are non-electrolytes and diamagnetic. $[Mo(NO)Cl_3]_n$ reacts with 2,2′-bipyridyl to give $Mo(NO)Cl_3(bipy)$ (6) as a yellow-green solid. Complex (6) is unstable in air, rapidly oxidising to green $MoOCl_3(bipy)$.

In the i.r. spectra of the mononitrosyl complexes (Table 1) a single strong NO band is observed in the range 1800—1590 cm^{-1}; this is close to the values found for the related compounds $(cp)Mo(NO)I_2L'$ [$L' = Ph_3P, (PhO)_3P$, or py],[2] $(cp)_2Mo(NO)I$,[3] $(cp)_2Mo(NO)CH_3$, and $(cp)_3Mo(NO)$ [4] and we therefore consider that in the new compounds the NO group may be regarded as a three-electron donor. The phosphine oxide and bipyridyl derivatives are only slightly soluble in organic solvents and for this reason molecular weight values have not been obtained. However on the basis of the effective atomic number rule a dimeric formulation involving two halogen bridges is reasonable.

TABLE 1

Infrared spectra (ν_{NO}) and (ν_{PO}) of the mononitrosyl derivatives; in cm^{-1}; Nujol mulls

	Compound	ν_{NO}	ν_{PO}	
(3)	$[Mo(NO)Cl_3]_n$	1590		
(4)	$[W(NO)Cl_3]_n$	1590		
(5)	$Mo(NO)Cl_3(Ph_3PO)_2$	1710	1180	1130—1140
(6)	$Mo(NO)Cl_3(bipy)$	1705		
(7)	$W(NO)Cl_3(Ph_3PO)_2$	1650	1170	1140

The structure of $[Mo(NO)Cl_3]_n$ and $[W(NO)Cl_3]_n$ may be discussed in terms of their chemical behaviour. Since they are insoluble in non-co-ordinating solvents and are involatile we conclude that they are polymeric. A probable structure is one in which all the chlorine atoms are bridging and the NO group occupies a terminal position. In this manner each metal achieves a noble-gas electronic configuration.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer using NaCl plates. Analyses were determined by the analytical department of University College, London; the analytical department, University Chemical Labs., Cambridge, and Herr A. Bernhardt, Max Planck Institute, Mulheim, Germany, and reported in Table 2.

All solvents were degassed before use and all reactions and manipulations carried out in an atmosphere of dry, oxygen-free nitrogen. The molybdenum and tungsten hexacarbonyls were freshly sublimed before use.

Nitrosyl chloride was obtained from K & K Chemical Inc. and nitrosyl bromide was prepared by the literature method.[14] Both were freshly distilled before use. Tetracarbonylbis(triphenylphosphine)metal complexes, $M(CO)_4(Ph_3P)_2$ (M = Mo or W) were prepared as described in the literature [15] by direct interaction of triphenylphosphine and hexacarbonylmetal.

Halogenocarbonyls of Molybdenum and Tungsten.—$M_2(CO)_8X_4$ (M = Mo [7] or W,[8]; X = Cl or Br) were prepared by the action of the halogens on the hexacarbonylmetal at −78 °C.

Preparation of Mononitrosyltrichloromolybdenum(II).—Hexacarbonylmolybdenum (1·0 g) was suspended in an excess of liquid chlorine at −78 °C for 5 h. The temperature was then raised to −40 °C and the excess of

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chlorine was allowed to evaporate. Nitrosyl chloride (2·0 ml) was added to the residue and the mixture was maintained at −40 °C for 1 h. The temperature was then raised to 20 °C and the excess of nitrosyl chloride was removed in a fast stream of nitrogen. The black solid residue was found to be a mixture of $[Mo(NO)_2Cl_2]_m$ and $[Mo(NO)Cl_3]_n$ (identified by their i.r. spectra).

Bis(triphenylphosphine oxide)trichloromononitrosylmolybdenum(II).—This compound was prepared by the following methods: (a) *By the reaction of* $[Mo(NO)Cl_3]_n$ *with triphenylphosphine.* An excess of triphenylphosphine (2·5 g) was dissolved in benzene (80 ml) and $[Mo(NO)Cl_3]_n$ (1 g) was added to the solution. The mixture was heated under reflux for 15 min to give a yellow-green solution and an oily layer (settled to the bottom of the flask). The solution was decanted and the benzene removed *in vacuo.* Recrystallisation of the yellow-green residue, from acetone, gave the complex $Mo(NO)_2Cl_2(Ph_3P)_2$.

TABLE 2

Analytical and other data for complexes

	Compound	Colour	Found % C	Calc. % C	Found % H	Calc. % H	Found % N	Calc. % N	Found % Cl	Calc. % Cl
(5)	$Mo(NO)Cl_3(Ph_3PO)_2$ [a]	Yellow-green	54·8	54·8	3·7	3·8	1·3	1·7	13·7	13·5
	$Mo(NO)Cl_3(Ph_3PO)_2$ [b]	Yellow-green	54·8	54·8	4·0	3·8	1·6	1·7	14·0	13·5
	$Mo(NO)Cl_3(Ph_3PO)_2$ [c]	Yellow-green	55·0	54·8	4·0	3·8	1·7	1·7	13·5	13·5
	$Mo(NO)Cl_3(Ph_3PO)_2$ [d]	Yellow-green	55·0	54·8	3·7	3·8	1·5	1·7	14·1	13·5
(6)	$Mo(NO)Cl_3(bipy)$	Yellow-green	30·6	30·8	1·9	2·01	11·2	10·8	27·1	26·7
(7)	$W(NO)Cl_3(Ph_3PO)_2$ [a]	Green	49·4	49·3	3·8	3·4	1·5	1·6	12·6	12·1

[a] From $M(CO)_4(Ph_3P)_2$ and NOCl. [b] From $[Mo(NO)Cl_3]_n$ and Ph_3P. [c] From $Mo(CO)_3(Ph_3P)_2Cl_2$ and NOCl. [d] From $Mo(NO)Cl_3$ and Ph_3PO.

The oily layer was washed with ether and dissolved in acetone. On concentration of this solution, yellow crystals of $Mo(NO)Cl_3(Ph_3PO)_2$ (5) separated. They were filtered off, washed with small portions of acetone and pentane, and dried (yield 30%).

(b) *By the reaction of* $Mo(CO)_4(Ph_3P)_2$ *with nitrosyl chloride.* $Mo(CO)_4(Ph_3P)_2$ (0·5 g) was suspended in dichloromethane (90 ml) and nitrosyl chloride (1·0 ml) added dropwise; the $Mo(CO)_4(Ph_3P)_2$ dissolved immediately with an evolution of carbon monoxide. The solution was stirred for 30 min and the dichloromethane was removed under reduced pressure. The yellow-green residue was dissolved in acetone. On concentration *in vacuo* yellow-green crystals separated; these were filtered off, washed with acetone and pentane, and dried (yield 60%).

(c) *By the reaction of* $Mo(CO)_3(Ph_3P)_2Cl_2$ *with nitrosyl chloride.* $Mo(CO)_3(Ph_3P)_2Cl_2$ (0·7 g) was suspended in degassed dichloromethane (50 ml). Nitrosyl chloride (1 ml) in dichloromethane (4 ml) was added dropwise when the solid dissolved immediately. Evaporation to dryness gave a yellow-green solid which on recrystallisation, from acetone, gave the required product.

(d) *By the reaction of* $Mo(CO)_3(Ph_3P)_3$ *with nitrosyl chloride.* $Mo(NO)Cl_3(Ph_3PO)_2$ was prepared by a procedure similar to that described above in (c); yellow-green crystals obtained from acetone were filtered and dried. They were identified by their i.r. spectra.

(e) *By the reaction of* $[Mo(NO)Cl_3]_n$ *with triphenylphosphine oxide.* A slight excess of triphenylphosphine oxide (2·18 g) was dissolved in benzene (100 ml) and $[Mo(NO)Cl_3]_n$ (0·88 g) was added. The resulting green solution was refluxed for 5 min during which time a crop of pale green crystals was obtained. These were shown by i.r. spectroscopy and analysis to be a mixture of $Mo(NO)Cl_3(Ph_3PO)_2$ and $Mo(NO)_2Cl_2(Ph_3PO)_2$. The remaining solution was cooled for 1 h in ice and the resulting yellow-green crystals of (5) were filtered off, washed with small portions of pentane, and dried (yield 73%).

2,2′-Bipyridyltrichloromononitrosylmolybdenum(II).— An excess of 2,2′-bipyridyl (0·65 g) was dissolved in benzene (100 ml). The solution was cooled in ice and $[Mo(NO)Cl_3]_n$ (0·88 g) was added. On stirring, the resulting yellow solution for 30 min, a crop of yellow-green crystals was obtained. These were shown by i.r. spectroscopy and analysis to be a mixture of $Mo(NO)Cl_3(bipy)$ and a small amount of $Mo(NO)_2Cl_2(bipy)$. The remaining yellow solution was set aside for 2 h; the yellow-green solid (6) which was deposited was filtered off, washed with pentane and dried *in vacuo* (yield 65%).

Bis(triphenylphosphine oxide)trichloromononitrosyltungsten(II).—This compound was best obtained by the two following methods: (a) *By the reaction of* $W(CO)_4(Ph_3P)_2$ *with nitrosyl chloride.* The procedure outlined in (b) above was followed. Green $W(NO)Cl_3(Ph_3PO)_2$ in 50% yield was obtained.

(b) *By the reaction of* $W(CO)_3Cl_3(Ph_3P)_2$ *and nitrosyl chloride.* $W(NO)Cl_3(Ph_3PO)_2$ was prepared from $W(CO)_3Cl_2(Ph_3P)_2$ and NOCl by a procedure similar to that described in (c) above for the analogous molybdenum derivative. The compound was identified by its i.r. spectrum.

Reaction between Nitrosyl Bromide and Tetracarbonyldibromomolybdenum(II).—$Mo_2(CO)_8Br_4$ was prepared as described previously.[10] The temperature of the reaction was raised from −78 °C to −40 °C and distilled nitrosyl bromide was admitted; after 1 h a green product was precipitated. It was identified by its i.r. spectrum as $[Mo(NO)_2Br_2]_m$.

Reaction of Nitrosyl Bromide with Tetracarbonyldibromotungsten(II).—A similar procedure to that described above was followed. The compound $[W(NO)_2Br_2]_m$ was obtained (as identified by its i.r. spectrum).

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