

Halogen Oxidation and Nitrosylation of Mixed Ligand Molybdenum and Tungsten Tricarbonyls

S. C. TRIPATHI*, S. C. SRIVASTAVA, D. P. PANDEY and P. K. SRIVASTAVA

Department of Chemistry, University of Gorakhpur, Gorakhpur-273 001

(L-L)(Ph₃E)Mo(CO)₃ (L-L = *o*-phen or 2,2'-bipy; E = As or Sb) after bromine or iodine oxidation yield [(L-L)(Ph₃E)Mo(CO)₂X]X (X = Br, I) derivatives. Under similar conditions Ph₃P is displaced from (L-L)(Ph₃P)Mo(CO)₃ to produce dimeric (L-L)Mo(CO)₂X₂. Chlorine swept benzene displaces both CO and Ph₃P from (L-L)(Ph₃P)Mo(CO)₃ and only CO from (L-L)(Ph₃E)Mo(CO)₃ to yield (L-L)MoCl₂ and [(L-L)(Ph₃E)MoCl₂]Cl, respectively. Nitrosylation of (L-L)(Ph₃E')M(CO)₃ (M = Mo, W; E' = P, As, Sb) using NOCl gives a mixture of (L-L)M(NO)₂Cl₂ and [(L-L)M(CO)₂(NO)₂Cl]Cl; while [(L-L)M(CO)₂(NO)]₂ derivatives are recovered when free NO is used.

The complexes have been characterised by elemental analysis, ir, conductivity and magnetic measurements.

SEVERAL studies have been made on the halogen oxidation of penta- and tetra-carbonyls of group VI metals but relatively little attention^{1,2} has been paid to tricarbonyls, particularly to those containing two different non-carbonyl ligands. A few recent investigations on some (L-L)LM(CO)₃ (L-L = *o*-phen or 2,2'-bipy; L = amine molecule; M = Mo, W) derivatives exhibited very striking results due to the formation of complexes of unusual stoichiometry^{3,4}. These products are thought to be either seven-coordinate complexes with bidentate ligands (L-L) acting as monodentate or seven-coordinate 1:1 adducts with (L-L)LM(CO)₃ species acting as Lewis bases and molecular halogens as Lewis acids. To examine the nature of products formed as a result of chlorination, bromination and iodination of analogous Ph₃P, Ph₃As and Ph₃Sb derivatives, the complexes (L-L)(Ph₃E')Mo(CO)₃ (E' = P, As or Sb) have been used in the present investigation.

To explore the possibility of formation of nitrosyl carbonyl derivatives of group VI metals, nitrosylation of these mixed ligand derivatives and analogous tungsten complexes has also been attempted using both nitrosonium cation (NO⁺) and free NO.

Experimental

General: All the experiments were performed in dry nitrogen. (L-L)M(CO)₃ derivatives were prepared by the methods given in literature^{8,9}. Nitrosyl chloride was prepared by the method described in literature¹⁰ and nitric oxide was prepared by the action of sodium nitrite on acidified ferrous sulphate solution and was purified by passing through 50% NaOH solution. Halogens were estimated gravimetrically by precipitating the corresponding silver salt. Conductivity measurements were made on a Toshniwal conductivity bridge (model 302) using nitrobenzene or acetone

as solvent. Magnetic measurements were done with polytronic Electromagnetic Type EM-100, SR No 113 using Keroy magnetic balance with sensitivity 10⁻⁶g. IR spectra were recorded on a Perkin-Elmer spectrophotometer model 337 in KBr discs.

Reaction of *o*-phenanthroline(triphenylphosphine)tricarbonylmolybdenum(O) with iodine: A benzene solution of iodine (0.13 g) was added dropwise to a solution *o*-phenanthroline(triphenylphosphine)tricarbonylmolybdenum(O) (0.30 g) in benzene (75 ml) under nitrogen at ambient temperature with constant stirring of the reaction mixture. A grey precipitate slowly appeared and the reaction mixture was set aside for further 4 hr to ensure complete precipitation. Liberation of CO did not take place during the reaction. The precipitate was filtered and washed well with several 10 ml portions of benzene to remove traces of iodine or parent carbonyl, if left unreacted. The product was dried *in vacuo*. Yield 55.5%. Anal. Found: C, 30.2; H, 2.0; N 4.8; I, 40.1. C₃₀H₁₈Mo₃N₄O₆I₄ requires C, 29.3; H, 1.3; N, 4.6; I, 41.3%.

Colour, yield, ν_{C-O} , mol. conductivity and analytical data of different halocomplexes prepared under similar conditions (but by using different halogens and appropriate carbonyls) are given in Table 1.

Reaction of *o*-phenanthroline(triphenylphosphine)tricarbonylmolybdenum(O) with NOCl: A dilute benzene solution of NOCl was added drop by drop on solid *o*-phenanthroline(triphenylphosphine)tricarbonylmolybdenum(O) (0.2 g) under nitrogen at room temperature with constant stirring of the reaction mixture. Slow dissolution of the solid mass took place followed by the precipitation of a yellow red solid. After 1 hr of stirring the colour of the supernatant liquid became paddy green and the solid (product A) settled down at the bottom of the reaction vessel. The supernatant liquid was

TABLE 1—CHARACTERISTIC, PHYSICAL AND ANALYTICAL DATA OF HALOCOMPLEXES

Complexes	Colour	Yield %	$\nu_{\text{CO}}(\text{cm}^{-1})$ (KBr disc)	$\Delta m \text{ ohm}^{-1}$ cm^2 (acetone)	Analysis (%) Found(Calcd.)			
					C	H	N	X
$[(o\text{-phen})\text{Mo}(\text{CO})_2\text{Br}_2]$	brown	48.4	2040wsh, 2030s, 1975s, 1950s, 1940s, 1910w, 1898s		35.8 (34.6)	1.9 (1.5)	5.2 (5.4)	28.2 (30.7)
$[(2,2'\text{-bipy})\text{Mo}(\text{CO})_2\text{I}_2]$	grey	56.8	2040wsh, 2028s, 1972s, 1950s, 1920vw, 1915m, 1892s		26.9 (26.1)	1.8 (1.3)	4.3 (4.7)	42.5 (43.0)
$[(2,2'\text{-bipy})\text{Mo}(\text{CO})_2\text{Br}_2]$	brown	49.3	2045wsh, 2028s, 1980s, 1942s, 1920vw, 1910w, 1905s		30.3 (31.5)	1.4 (1.6)	5.2 (5.6)	30.8 (32.2)
$[(o\text{-phen})(\text{Ph}, \text{As})\text{Mo}(\text{CO})_2\text{I}]\text{I}$	grey	57.3	2030s, 1958s, 1905s	60.4	42.2 (43.0)	2.1 (2.5)	2.9 (3.0)	26.1 (27.6)
$[(o\text{-phen})(\text{Ph}, \text{As})\text{Mo}(\text{CO})_2\text{Br}]\text{Br}$	yellow	48.3	2055s, 1978s, 1915s	63.8	46.1 (47.9)	2.2 (2.7)	3.5 (3.3)	18.8 (19.4)
$[(o\text{-phen})(\text{Ph}, \text{Sb})\text{Mo}(\text{CO})_2\text{I}]\text{I}$	grey	56.2	2040s, 1978m, 1898vs	61.2	39.8 (40.8)	2.1 (2.4)	2.5 (2.9)	25.2 (26.3)
$[(o\text{-phen})(\text{Ph}, \text{Sb})\text{Mo}(\text{CO})_2\text{Br}]\text{Br}$	brown	49.2	2055s, 1975s, 1910vs	65.3	43.2 (45.3)	2.4 (2.6)	2.9 (3.2)	17.5 (18.3)
$[(2,2'\text{-bipy})(\text{Ph}, \text{As})\text{Mo}(\text{CO})_2\text{I}]\text{I}$	grey	56.6	2020ms, 1955s, 1905s	59.6	38.6 (41.5)	2.2 (2.5)	2.5 (3.1)	27.2 (28.3)
$[(2,2'\text{-bipy})(\text{Ph}, \text{As})\text{Mo}(\text{CO})_2\text{Br}]\text{Br}$	orange	46.3	2055vs, 1980s, 1915s	64.8	44.8 (46.3)	1.9 (2.8)	3.1 (3.4)	16.3 (17.1)
$[(2,2'\text{-bipy})(\text{Ph}, \text{Sb})\text{Mo}(\text{CO})_2\text{I}]\text{I}$	grey	57.5	2020s, 1952ms, 1900ms	56.8	37.3 (39.3)	2.1 (2.4)	3.4 (3.9)	24.1 (26.9)
$[(2,2'\text{-bipy})(\text{Ph}, \text{Sb})\text{Mo}(\text{CO})_2\text{Br}]\text{Br}$	orange	45.3	2050s, 1975s, 1922s	65.6	41.6 (43.8)	2.2 (2.7)	2.8 (3.3)	17.5 (18.8)
$(o\text{-phen})\text{MoCl}_4$	yellow	74.2			32.6 (34.4)	1.5 (1.9)	6.2 (6.6)	30.2 (33.9)
$[(o\text{-phen})(\text{Ph}, \text{As})\text{MoCl}_2]\text{Cl}$	yellow	75.3		60.4	48.1 (47.7)	2.5 (3.2)	3.1 (3.8)	18.2 (19.6)
$[(2,2'\text{-bipy})(\text{Ph}, \text{As})\text{MoCl}_2]\text{Cl}$	yellow	73.8		62.2	52.1 (53.2)	3.2 (3.3)	4.8 (4.1)	19.8 (20.3)
$[(o\text{-phen})(\text{Ph}, \text{Sb})\text{MoCl}_2]\text{Cl}$	yellow	72.3		60.2	45.5 (46.7)	2.1 (2.0)	3.5 (3.6)	17.6 (18.1)
$[(2,2'\text{-bipy})(\text{Ph}, \text{Sb})\text{MoCl}_2]\text{Cl}$	yellow	74.3		62.3	46.3 (49.8)	2.3 (3.1)	3.2 (3.7)	18.9 (19.0)

TABLE 2—CHARACTERISTIC, PHYSICAL AND ANALYTICAL DATA OF VARIOUS COMPLEXES

Complex	Colour	Yield %	$\nu_{\text{CO}}(\text{cm}^{-1})$ (KBr disc)	$\nu_{\text{NO}}(\text{cm}^{-1})$	$\Delta m \text{ ohm}^{-1}$ cm^2 (in acetone)	Analysis (%) Found(Calcd.)			
						C	H	N	Cl
$[(\text{Ph}, \text{As})\text{Mo}(\text{CO})_2(\text{NO})_2\text{Cl}]\text{Cl}$	Yellow-red	40.2	2040s, 1930s	1785s, 1660s	65.5	38.7 (40.8)	2.1 (2.5)	4.5 (4.8)	11.5 (12.0)
$[(\text{Ph}, \text{Sb})\text{Mo}(\text{CO})_2(\text{NO})_2\text{Cl}]\text{Cl}$	Yellow-red	41.7	2035s, 1925s	1780s, 1660s	68.7	35.3 (37.3)	2.0 (2.3)	4.0 (4.1)	10.7 (11.0)
$[(\text{Ph}, \text{P})\text{W}(\text{CO})_2(\text{NO})_2\text{Cl}]\text{Cl}$	Yellow	38.5	2030s, 1925s	1780s, 1660s	82.2	35.3 (38.0)	2.0 (2.4)	4.0 (4.4)	10.7 (11.2)
$[(\text{Ph}, \text{As})\text{W}(\text{CO})_2(\text{NO})_2\text{Cl}]\text{Cl}$	Yellow	38.2	2030s, 1920s	1780s, 1665s	78.0	33.1 (35.5)	1.8 (2.2)	3.2 (3.1)	9.1 (10.5)
$[(\text{Ph}, \text{Sb})\text{W}(\text{CO})_2(\text{NO})_2\text{Cl}]\text{Cl}$	Yellow	40.0	2030s, 1920s	1779s, 1652s	80.5	31.0 (33.1)	1.3 (1.7)	2.9 (2.9)	9.0 (9.8)
$[(2,2'\text{-bipy})\text{Mo}(\text{NO})_2\text{Cl}_2]$	Green	30.8-42.4		1775s, 1660s, 1625sh	5.8	28.3 (30.7)	2.8 (2.1)	13.1 (14.6)	17.5 (18.5)
$[(o\text{-phen})\text{W}(\text{NO})_2\text{Cl}_2 \cdot]$	Green	27.0-34.3		1745s, 1645s, 1635sh	7.0	27.3 (29.1)	2.0 (1.6)	10.1 (11.3)	12.8 (14.3)
$[(2,2'\text{-bipy})\text{W}(\text{NO})_2\text{Cl}_2 \cdot]$	Green	30.4-36.0		1745s, 1650s, 1640s	6.2	24.0 (25.5)	2.0 (1.7)	11.0 (11.9)	14.8 (15.1)

* reported $\nu_{\text{N-O}}$ 1790s, 1695s (Ref. 11)

** IR bands in nujol mull (others in KBr).

decanted out under nitrogen. A paddy green solid (product B) was precipitated from this solution by adding hexane (60 ml). Product B was washed several times with hexane and was dried *in vacuo*. It was shown to be dichloro (*o*-phenanthroline)

dinitrosylmolybdenum(II). Anal. Found: C, 32.3; H, 2.2; N, 12.9; Cl, 17.0. $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_2\text{MoCl}_2$ requires C, 35.4; H, 2.0; N, 13.0; Cl, 17.4%. $\nu_{\text{N-O}}$: 1785s, 1688s, 1655sh cm^{-1} , reported bands¹¹ 1790s, 1685s cm^{-1} .

Product A was washed several times with benzene to remove parent *o*-phenanthroline (triphenylphosphine)tricarbonylmolybdenum(O) (practically nil) and dichloro(*o*-phenanthroline)dinitrosylmolybdenum(II) and was dried *in vacuo*. It was shown to be chloro(triphenylphosphine)dinitrosyldicarbonylmolybdenum(II) chloride: (yield 0.074 g, 42.2%). Anal. Found: C, 41.2; H, 2.4; N, 5.3; P, 5.2; Cl, 12.5. $C_{20}H_{15}O_4N_2PMoCl_2$ requires C, 44.0; H, 2.8; N, 5.1; P, 5.7; Cl, 13.0%; m.p. 163-55° d in sealed capillary, ν_{C-O} 2035s, 1920s cm^{-1} , ν_{N-O} : 1778s, 1640s cm^{-1} , $\Delta_M = 70.2 \text{ ohm}^{-1} \text{ cm}^2$ (in acetone). It dissolved only in polar solvents like acetone, methanol, dichloromethane and chloroform and was fairly stable.

Colour, yield, ν_{C-O} , ν_{N-O} , molecular conductivity and analytical data of other derivatives are given in Table 2.

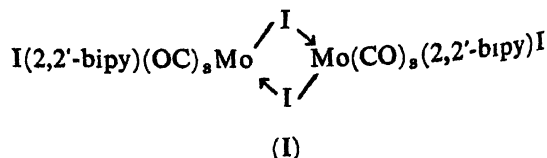
Reaction of *o*-phenanthroline(triphenylphosphine)tricarbonylmolybdenum(O) with nitric oxide: Nitric oxide, free from nitrogen peroxide, was absorbed in benzene and the solution was added dropwise on solid *o*-phenanthroline(triphenylphosphine)tricarbonyl(O) (0.2 g) at room temperature under an atmosphere of nitrogen with constant stirring of the reaction mixture. The violet colour of the solid mass disappeared slowly with the dissolution of the parent carbonyl and precipitation of an yellow solid took place. The reaction mixture was set aside for 2 hr and then the precipitate was filtered, washed and dried *in vacuo*. It could not be recrystallised due to its unstable nature in solution. It was shown to be bis(*o*-phenanthroline)dinitrosyltetra carbonyldimolybdenum(I), $[(C_{15}H_9N_2)_2Mo(CO)_4(NO)]_2$, prepared by an alternative method⁷. Anal. Found: C, 44.1; H, 2.4; N, 11.0. $C_{30}H_{18}N_4O_6Mo_2$ requires C, 46.4; H, 2.2; N, 11.6%.

Under similar conditions analogous triphenylarsine and triphenylstibine derivatives yielded the identical compounds.

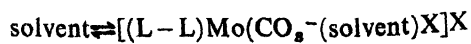
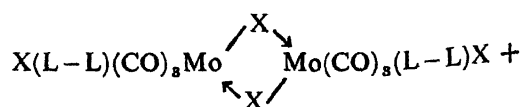
Results and Discussion

Halogen oxidation: Compared to triphenylarsine and triphenylstibine containing complexes, triphenylphosphine derivatives, $(L-L)(Ph_3P)Mo(CO)_3$ behaved differently when subjected to halogen oxidation. They yielded products of stoichiometry $(L-L)Mo(CO)_3X_2$ (X=Br or I) when treated with a benzene solution of bromine or iodine at ambient temperature in nitrogen atmosphere with constant stirring of the reaction mixture. Evolution of CO did not take place in any case. The ir spectra of the resulting complexes exhibited seven bands in the C-O region but the bands of coordinated triphenylphosphine molecule were not present. The appearance of seven CO bands cannot be attributed to any geometry of mononuclear formulation and the possibility of formation of simple $(L-L)Mo(CO)_3X_2$ derivatives is ruled out. Except two extra very weak bands, which might arise due to enhanced molecular interactions in solid state

(KBr discs), the spectra are almost identical to that reported by Stiddard⁸ for the iodo-bridged dinuclear complex:



prepared by the action of iodine on $(2,2'\text{-bipy})Mo(CO)_3$ in chloroform at 0° (ν_{CO} : 2040, 2018, 1976, 1935 and 1888 cm^{-1} in $CHCl_3$). Moreover, they resembled the complex (I) in the conductivity behaviour. Although, assuming dimeric structures, the complexes are expected to exhibit non-ionic behaviour, they gave conducting solutions in nitrobenzene (20.3-21.74 $ohm^{-1} \text{ cm}^2$). These values are in comparatively lower range than expected for uni-univalent metal halocarbonyls. Such electrolytic behaviour may be accounted for the well established solvent attack⁸ according to the following equilibrium:



Under similar conditions $(L-L)(Ph_3E)Mo(CO)_3$ (E=As or Sb) gave $[(L-L)(Ph_3E)Mo(CO)_3X]X$ (X=Br or I) after bromine or iodine oxidation. The ir spectra of the products exhibited three strong bands in the CO region (Table 1) alongwith the bands of coordinated Ph_3As or Ph_3Sb . The appearance of these ligand bands clearly indicate that, in contrast to the Ph_3P analogues, Ph_3As and Ph_3Sb molecules remain intact through the metal atom even after halogen attack. The molecular conductivity data (Table 1) together with diamagnetic character of these derivatives are in full accordance with their hepta-coordinate cationic structures having molybdenum in the II oxidation state.

Chlorine swept benzene displaced both Ph_3P and CO from $(L-L)(Ph_3P)Mo(CO)_3$ to yield $(L-L)MoCl_4$. The absence of Ph_3P bands from the spectra, their non-electrolytic behaviour and an μ_{eff} of 2.64 B.M. (for both *o*-phen and 2,2'-bipy substituted derivatives) established the neutral and hexacoordinate formulation for the resulting complexes.

It is noteworthy that, similar to bromination and iodination, Ph_3E (E=As, Sb) ligands remained intact through the metal atom in case of chlorination also and products having composition $(L-L)(Ph_3E)MoCl_4$ were isolated in all cases. Such complexes are of rare occurrence; they had not been synthesised hitherto by the action of halogens on metal carbonyl species. The synthesis of a few resembling complexes⁹, $ML_2L'X_4$ (M=Mo, W; L=PPhMe₃, PPhEt₃ and L'=PPhMe₃,

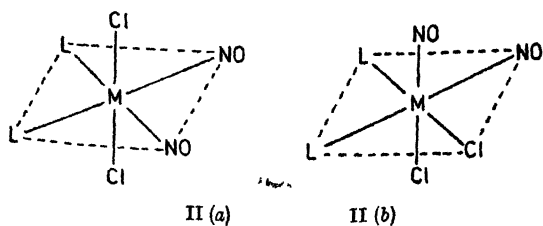
PPh_3Me), has been achieved via another route, i.e., by the action of L' on ML_2X_4 derivatives under forcing conditions (protracted reflux).

Although these complexes are fairly stable under nitrogen, their slow conversion into unidentified red substances has been noted on exposure to air. In nitrogen swept acetone they exhibited molecular conductivity attributable to uni-univalent electrolytic behaviour (Table 1).

Nitrosylation: Nitrosylation of the mixed ligand tricarbonyls of both molybdenum and tungsten has been studied using both $NOCl$ and free NO .

$(L-L)(Ph_3E')M(CO)_3$ ($M=Mo, W$; $E'=P, As, Sb$; $L-L=o$ -phen, 2,2'-bipy) reacted with a benzene solution of nitrosyl chloride at room temperature under nitrogen to give a mixture of two products $[Ph_3E']M(CO)_2(NO)_2Cl$ and already known $(L-L)M(NO)_2Cl_2$ (details of separation are given in the experimental section). $[(Ph_3E')M(CO)_2(NO)_2Cl]Cl$ derivatives are yellow-red crystalline solids, soluble in polar solvents like dichloromethane, acetone and methanol but do not dissolve in hydrocarbon solvents and light petroleum (40-60°). The nature and number of CO and NO bands in their ir spectra (Table 2), their uni-univalent electrolytic behaviour ($\Delta_m=65.5-87.5 \text{ ohm}^{-1}\text{cm}^2$) and diamagnetic character suggested them to be the hexacoordinate cationic complexes of metal (II).

$(L-L)M(NO)_2Cl_2$ were isolated in the form of an unseparable mixture of two isomers (II a and b):



The ir spectra of $(L-L)M(NO)_2Cl_2$ exhibited two strong and one shoulder bands in the N-O

stretching region. On the basis of usual π -bonding effect isomer (a) is expected to show higher ν_{N-O} than the isomer (b). Intensities of these bands further suggest that isomer (a) predominates in case of molybdenum while isomer (b) for tungsten complexes.

Nitrosylation of analogous mixed amine-molybdenum tricarbonyls, $(L-L)$ (amine) $Mo(CO)_3$ (amine = $C_4H_9NH_2$, $C_6H_{11}NH_2$, $C_6H_{11}N$ and C_4H_9NO) (solid carbonyl), with a benzene solution of $NOCl$ gave only isomeric mixture of $(L-L)Mo(NO)_2Cl_2$ and compounds of the type $[(\text{amine})Mo(CO)_2(NO)_2Cl]Cl$ could not be isolated.

On attempting nitrosylation of $(L-L)(Ph_3E')M(CO)_3$ with a benzene solution of nitric oxide yellow crystalline dinuclear products $[(L-L)M(CO)_2(NO)]_2$ were isolated. Synthesis of identical compounds has already been reported⁷ by the action of nitric oxide on $(L-L)M(CO)_4$ or carbonyl-bridged molybdenum derivative $[(2,2'\text{-bipy})Mo(CO)]_2$.

References

1. I. V. HOWELL and L. M. VERNANZI, *Inorg. Chim. Acta*, 1969, 3, 121.
2. S. C. TRIPATHI, S. C. SRIVASTAVA and A. K. SHRIMAL, *Inorg. Chim. Acta*, 1976, 18, 231.
3. D. N. PATHAK, *Indian J. Chem.*, 1978, 16A, 158.
4. S. C. TRIPATHI, S. C. SRIVASTAVA and C. P. SINGH, *Transston Metal Chem.*, 1977, 2, 198.
5. M. H. B. STIDDARD, *J. Chem. Soc.*, 1962, 4712.
6. "Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands", (Ed.) C. A. McAULIFFE, The Macmillan Press Ltd., 1973, p. 47.
7. S. C. TRIPATHI, S. C. SRIVASTAVA and A. K. SHRIMAL, *J. Organometal. Chem.*, 1976, 118, 325.
8. L. W. HOUK and G. R. DOBSON, *Inorg. Chem.*, 1966, 5, 2119.
9. S. C. TRIPATHI and S. C. SRIVASTAVA, *J. Organometal. Chem.*, 1970, 25, 193.
10. J. R. MORTON and H. W. WILCOX, *Inorg. Synth.*, 1953, 4, 48.
11. F. CANZIANI, U. SARTORRELLI and F. CARIATI, *Annali. Chim.*, 1964, 54, 1954.