

SYNTHESIS OF SUBSTITUTED CARBONYL NITROSYL HALIDES OF MOLYBDENUM AND TUNGSTEN

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SUMMARY

The reaction of $(\text{CO})_3\text{M}(\text{CH}_3\text{CN})_3$ ($\text{M} = \text{Mo}$ or W) in THF successively with NOCl and a Lewis base was used in the preparation of $\text{M}(\text{CO})_2(\text{NO})(\text{Diphos})\text{Cl}$, $\text{M}(\text{CO})_2(\text{NO})(\text{Bipy})\text{Cl}$, $\text{M}(\text{CO})_2(\text{NO})(\text{Phen})\text{Cl}$, $\text{Mo}(\text{CO})(\text{NO})(\text{CH}_3\text{CN})(\text{PPh}_3)_2\text{Cl}$ and $\text{Mo}(\text{CO})_2(\text{NO})(\text{DPM})\text{Cl}$.

Molybdenum and tungsten dinitrosyl dichloride may be prepared¹ by the reaction of the respective hexacarbonyl with nitrosyl chloride in dichloromethane. However, the reaction of $\text{M}(\text{CO})_3(\text{CH}_3\text{CN})_3^2$ ($\text{M} = \text{Mo}$ or W) in tetrahydrofuran with sufficient nitrosyl chloride to just dissolve the insoluble metal carbonyl produces a dark brown solution, (I), from which may be isolated either $\text{M}(\text{CO})_2(\text{NO})\text{L}_2\text{Cl}$ or $\text{M}(\text{CO})(\text{NO})(\text{CH}_3\text{CN})\text{L}_2\text{Cl}$ by addition of the appropriate ligand. The individual compounds isolated and their infrared spectra and analyses are presented in Table 1. Since mixed carbonyl nitrosyl derivatives of molybdenum and tungsten are limited to $(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{NO})^{3,4}$ and their derivatives; $\text{RB}(\text{Pz})_3\text{M}(\text{CO})_2\text{NO}^{5,6}$; $[\text{Mo}(\text{CO})_2(\text{NO})\text{Bipy}]_2^6$; and $[(\text{HO})\text{Mo}(\text{CO})_2(\text{NO})]_4$ and its hydrogen bonded derivatives with Lewis bases^{7,8}, these carbonyl nitrosyl halides constitute derivatives of a hitherto unreported class of metal carbonyl nitrosyl compounds.

The reaction of (I) prepared from either $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$ or $\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3$ with 1,2-bis(diphenylphosphino)ethane (Diphos), 1,10-phenanthroline monohydrate, or 2,2'-bipyridine produces $\text{M}(\text{CO})_2(\text{NO})\text{L}_2\text{Cl}$ where $\text{M} = \text{Mo}$ or W and L_2 is one of the bidentate ligands. All of these materials appear to contain *cis* carbonyl groups since their infrared spectra contain two pronounced CO absorptions in addition to an NO absorption.

Other evidence consistent with the formulation of these compounds as indicated is available from chemical, conductometric, and molecular weight studies. The reaction of $\text{W}(\text{CO})_2(\text{NO})(\text{Bipy})\text{Cl}$ with nitrosyl chloride in dichloromethane proceeds smoothly giving a quantitative yield of $\text{W}(\text{NO})_2\text{Cl}_2(\text{Bipy})$ as expected for the replacement of two CO groups. Conductivity studies of $\text{W}(\text{CO})_2(\text{NO})(\text{Bipy})\text{Cl}$ and $\text{Mo}(\text{CO})_2(\text{NO})(\text{Diphos})\text{Cl}$ in acetonitrile indicate that these compounds are nonionic, while their molecular weights in acetone are consistent with monomeric species in solution.

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** Pz = pyrazolyl.

TABLE I
 INFRARED SPECTRA AND ANALYSES

Compound	IR Spectra in THF (cm^{-1})	Analysis found (calcd.)				
		C	H	N	P	Cl
Mo(CO) ₂ (NO)(Diphos)Cl	2040 s, 1972 vs, 1648 m	54.5 (54.6)	4.13 (3.39)		9.90 (10.1)	5.56 (5.76)
W(CO) ₂ (NO)(Diphos)Cl	2024 s, 1953 vs, 1634 m	47.9 (47.8)	3.59 (3.44)		8.70 (8.80)	4.84 (5.04)
Mo(CO) ₂ (NO)(Bipy)Cl	2023 s, 1938 vs, 1646 m	38.7 (38.6)	2.43 (2.16)	11.0 (11.2)		9.21 (9.49)
W(CO) ₂ (NO)(Bipy)Cl	2008 s, 1918 vs, 1632 m	31.2 (31.2)	1.81 (1.75)	9.20 (9.10)		7.80 (7.68)
Mo(CO) ₂ (NO)(Phen)Cl · H ₂ O	2025 s, 1938 vs, 1646 m	41.0 (40.5)	2.59 (2.42)	10.0 (10.1)		8.31 (8.53)
W(CO) ₂ (NO)(Phen)Cl	2008 s, 1918 vs, 1632 m	34.8 (34.6)	1.83 (1.66)	8.41 (8.65)		7.60 (7.30)
Mo(CO)(NO)(CH ₃ CN)- [P(C ₆ H ₅) ₃] ₂ Cl	1928 vs, 1617 m	61.8 (62.0)	4.65 (4.40)	3.61 (3.71)	7.90 (8.20)	4.87 (4.70)
Mo(CO)(NO)Py ₂ P(C ₆ H ₅) ₃ Cl	1912 vs, 1595 s	57.2 (57.1)	4.23 (4.13)	6.66 (6.89)	5.36 (5.07)	6.00 (5.81)
Mo(CO) ₂ (NO)(DPM)Cl	1920 vs, 1632 s ^a	53.8 (53.8)	4.02 (3.68)	2.34 (2.35)		5.81 (5.89)

^a Spectrum obtained in KBr.

The reaction of triphenylphosphine with (I) prepared from Mo(CO)₃(CH₃CN)₃ produces Mo(CO)(NO)(CH₃CN)[P(C₆H₅)₃]₂Cl. The infrared spectrum of this material exhibits only one carbonyl band in addition to a single NO absorption. Although no CN stretching frequency is observed in the infrared spectrum of Mo(CO)(NO)(CH₃CN)[P(C₆H₅)₃]₂Cl, there is a pronounced peak at *m/e* 41.0 attributable to CH₃CN⁺ in its mass spectrum, and an NMR spectrum shows aromatic and methyl hydrogen signals with a ratio of 10/1. Reaction of Mo(CO)(NO)(CH₃CN)[P(C₆H₅)₃]₂Cl with pyridine produces Mo(CO)(NO)Py₂P(C₆H₅)₃Cl which also exhibits only one CO absorption and one NO absorption in the infrared. There is no indication of an acetonitrile peak at *m/e* 41.0 in the mass spectrum of this compound. A third compound with only one carbonyl stretching frequency in its infrared spectrum may be prepared by the addition of bis(diphenylphosphino)methane, DPM, to (I) prepared from Mo(CO)₃(CH₃CN)₃. However, this compound analyses as Mo(CO)₂(NO)(DPM)Cl and probably contains the two CO groups in a *trans* configuration. A second nitrosyl compound from the reaction of (I) with Diphos, although not yet isolated in a pure state, also exhibits one CO stretching frequency at 1947 cm^{-1} and an NO frequency at 1610 cm^{-1} . This may be the *trans* isomer of Mo(CO)₂(NO)(Diphos)Cl.

EXPERIMENTAL

Compounds were isolated, as indicated below, from the dark solution, (I), prepared by bubbling nitrosyl chloride into a suspension of 2 g of Mo(CO)₃(CH₃-

$\text{CN})_3^2$ or $\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3^2$ in about 20 ml of deoxygenated tetrahydrofuran. Nitrosyl chloride addition was stopped when the carbonyl was just dissolved. At this point, no $\text{M}(\text{CO})_3(\text{CH}_3\text{CN})_3$ bands were present in an infrared spectrum of the solution.

Except where noted, the following solid compounds are stable in air, and solutions can be handled in air for short periods without appreciable decomposition. Chromatographic separations, for example, were run in air.

$\text{M}(\text{CO})_2(\text{NO})(\text{Bipy})\text{Cl}$

Addition of a stoichiometric amount of 2,2'-bipyridine to (I) resulted in the precipitation of the desired compound after about 15–30 min. The orange molybdenum compound was purified by recrystallization from THF with pentane. The orange tungsten compound was loaded into a silica gel column with dichloromethane, washed with dichloromethane, then eluted with THF or acetone.

$\text{M}(\text{CO})_2(\text{NO})(\text{Phen})\text{Cl}$

Addition of a stoichiometric amount of 1,10-phenanthroline monohydrate to (I) resulted in precipitation of the desired compound in 3–5 min. Both the orange molybdenum and orange tungsten compounds were recrystallized from THF with pentane. The molybdenum compound crystallized with one water of hydration.

$\text{M}(\text{CO})_2(\text{NO})(\text{Diphos})\text{Cl}$

Addition of a stoichiometric amount of 1,2-bis(diphenylphosphino)ethane to (I), reduction of the volume of the solution, and addition of pentane produced the product as an impure brown powder. The molybdenum compound was loaded into a silica gel column in dichloromethane, washed with dichloromethane, and eluted with acetone. The acetone eluate was passed through an alumina column giving a solution of the pure product which was recovered by evaporation. The tungsten compound was extracted with pentane, and an acetone solution of the solid residue was passed through an alumina column giving the pure yellow product upon evaporation of the acetone eluate.

$\text{Mo}(\text{CO})(\text{NO})(\text{CH}_3\text{CN})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}$

Addition of a stoichiometric amount of triphenylphosphine to (I) from $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$ produced a golden yellow precipitate within 35 min. This solid was filtered under nitrogen, washed with THF and pentane, then dried in vacuum. The solid is very air sensitive when damp with THF, and the dry compound slowly decomposes in air.

$\text{Mo}(\text{CO})(\text{NO})\text{Py}_2\text{P}(\text{C}_6\text{H}_5)_3\text{Cl}$

Stirring $\text{Mo}(\text{CO})(\text{NO})(\text{CH}_3\text{CN})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}$ (1 g) in deoxygenated pyridine (20 ml) resulted in solution of the starting material after about 1.5 h. Addition of pentane produced orange crystals of the product which were filtered from the reaction mixture, washed with pentane and dried in vacuum. The compound slowly decomposes in air.

$\text{Mo}(\text{CO})_2(\text{NO})(\text{DPM})\text{Cl}$

Addition of a stoichiometric amount of bis(diphenylphosphino)methane to

(I) from $\text{Mo}(\text{CO})_3(\text{C}\bar{\text{H}}_3\text{CN})_3$ produced an insoluble red precipitate after about 3 days. This was isolated, washed with THF, and dried. The compound is insoluble in all common organic solvents.

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