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Reductive Nitrosation of Molybdenum and Tungsten Halides.

V. Preparation of Trichloro-nitrosylmolybdenum and Tungsten Derivatives

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$M(NO)Cl_3(OPPh_3)_2$ (M = Mo or W) complexes are excellent precursors of homogeneous olefin metathesis catalysts [1, 2]. These complexes were prepared originally by reaction of NOCl with molybdenum or tungsten carbonyl halides [3], or reductive nitrosation of $MCl_{5,6}$ in the presence of PPh_3 [4]. In the early seventies crystalline $[Mo(NO)Cl_3]_n$ was prepared by reaction of solid $MoCl_5$ and gaseous NO [5], that made several new $Mo(NO)Cl_3L_2$ derivatives readily available [6]. However, the preparation of the analogous tungsten derivatives could not be achieved this way. Leigh [7] contributed one to this field by preparing several types of new mononitrosyl complexes. Reacting the red nitrosyl ($WCl_{5\,or\,6}NO$) with tertiary phosphines by careful choice of reaction conditions, Leigh succeeded in isolating $W(NO)Cl_3(PR_3)_2$ derivatives (yield 7–8%) as well as large quantities of the corresponding phosphine oxide complexes.

The purpose of our present work was to find a general and simple route to mononitrosyl molybdenum and tungsten derivatives, avoiding the unwanted oxidation of co-ligands such as tertiary phosphines and arsines. In this we were successful by the method described below.

Experimental

All manipulations were carried out under argon or nitric oxide. The solvents were dried and degassed before use. Nitric oxide was dried and freed from NO_2. The compounds were identified by their IR spectra and elemental analysis.

Preparation of $W(NO)Cl_3(CH_3CN)_2$, (I)

The reaction was carried out in a three necked 150 ml Erlenmeyer flask equipped with a gas inlet and magnetic stirrer. The flask was swept with argon and 0.8 g (2 mmol) WCl_6, 30 cm^3 CH_2Cl_2 and 0.21 cm^3 (4 mmol) CH_3CN were introduced. The reaction mixture was stirred and bubbled with NO at room temperature until its purple colour turned to dark violet (about 1 h). The solution was evaporated to 10 ml and refrigerated, yielding dark violet crystals, which were filtered off, washed with pentane and dried in vacuum. Yield 90%. (Found: W, 44.9; N, 9.85; Cl, 25.69. Calcd.: W, 45.7; N, 10.44; Cl, 26.44%.

Preparation of $Mo(NO)Cl_3(CH_3CN)_2$, (II)

3.21 g (12 mmol) $MoCl_5$, 1.26 cm^3 (24 mmol) CH_3CN were dissolved in 200 cm^3 CH_2Cl_2. Nitric oxide was passed through the solution, which was stirred at room temperature until the dark purple colour of the solution turned to light greenish-yellow. The NO current was changed to argon and the mixture refluxed for 1 h to remove traces of NOCl by-product. The solution was concentrated to one third of its original volume, and addition of pentane (10 cm^3) afforded a green-yellow voluminous precipitate, which was filtered off, washed with pentane and dried in vacuum. Yield 70%. (Found: Mo,31.1; Cl, 32.7; N, 12.9. $Mo(NO)Cl_3(CH_3CN)_2$ requires Mo, 30.51; Cl, 33.83; N, 13.57%).

Preparation of $M(NO)Cl_3L_2$ (M = Mo and W) Complexes

Trichlorobis(acetonitryl)molybdenum or tungsten (1 mmol) and the coligand (L) (4 mmol) were dissolved in dichloromethane (50 cm^3). The solution was stirred for 1 h, concentrated under vacuum and refrigerated overnight. The crystals were filtered off, washed with pentane and dried under reduced pressure. Yield 80–85%. Analytical results were satisfactory for $M(NO)Cl_3L_2$. IR data of the complexes are given in Table I.

Results and Discussion

Dichloromethane solution of WCl_6 was treated with nitric oxide in the presence of acetonirile (CH_3CN/WCl_6 = ½). Following a rapid NO uptake a dark violet solution formed, from which dark lilac crystals of trichlorobis(acetonitrile)nitrosyltungsten separated in nearly quantitative yield:

$$WCl_6 + 2CH_3CN \xrightarrow[-NOCl\ 2]{NO,CH_2Cl_2} W(NO)Cl_3(CH_3CN)_2 \qquad (1)$$

(I), ν_{NO} (cm^{-1}): 1710

When $MoCl_5$ reacted with nitric oxide in analogous conditions $Mo(NO)_2Cl_2(CH_3CN)_2$ formed as a final product. Following the course of the reaction by IR spectroscopy two reaction intermediates were detect-

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TABLE I. Properties of Trichloronitrosylmolybdenum and Tungsten Complexes.

Complex	Colour	IR spectrum, cm^{-1}		
		ν_{NO}	ν_{PO}	ν_{CN}
$W(NO)Cl_3(CH_3CN)_2$	Dark violet	1710^b		$2286-90^b$
$W(NO)Cl_3(PPh_3)_2$	Green	1667^b	–	
$W(NO)Cl_3(AsPh_3)_2$	Green	1670^b		
$W(NO)Cl_3[P(c\text{-}C_6H_{11})_3]_2$	Green	1635^b	–	
$W(NO)Cl_3(OPPh_3)_2$	Yellow	1642^b	1170–60, 1140	
$Mo(NO)Cl_3(CH_3CN)_2$	Yellow	1740^a		2288
$Mo(NO)Cl_3(PPh_3)$	Yellowish green	1700^b	–	
$Mo(NO)Cl_3(OPPh_3)_2$	Green	1710^b	$1170, 1120^c$	
$Mo(NO)Cl_3(AsPh_3)_2$	Green	1720^b		
$Mo(NO)Cl_3(DMF)_2$	Dark green	1712^b	$\nu_{CO} = 1650$	
$Mo(NO)Cl_3(DMSO)_2$	Dark green	1692^b		

Medium: a, nujol, b, CH_2Cl_2; c, KBr.

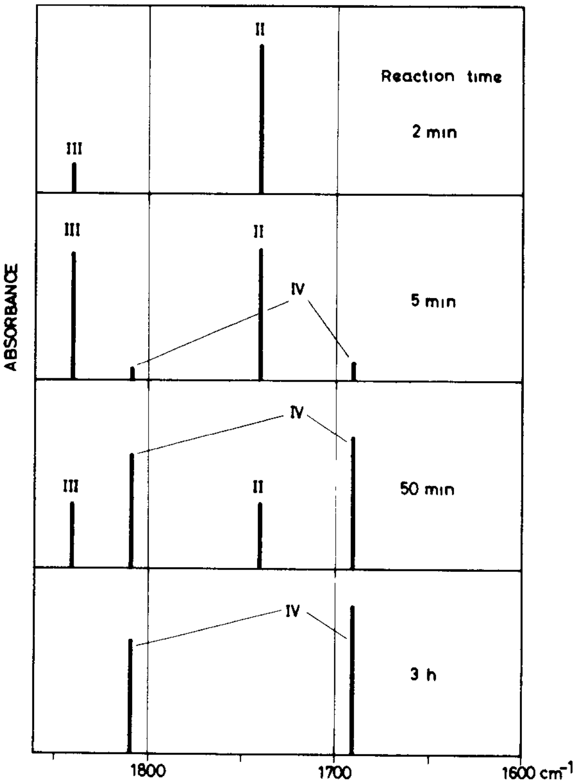

Fig. 1. IR spectra of $MoCl_5 + CH_3CN + NO$ reaction mixture in CH_2Cl_2 (ν_{NO} frequency of NOCl at 1850 cm^{-1} is omitted).

ed (Fig. 1). The dark solution of $MoCl_5$ turned to light green on NO treatment within a few minutes, and the strong absorption of $Mo(NO)Cl_3(CH_3CN)_2$ (II) at 1740 cm^{-1} appeared in the IR spectrum of the reaction mixture.

$$MoCl_5 + CH_3CN + NO \xrightarrow[\text{rapid}]{CH_2Cl_2} No(NO)Cl_3(CH_3CN)_2 + NOCl \quad (2)$$

II, ν_{NO} (cm^{-1})· 1740

Consequently another ν_{NO} band of a new compound (III) could be observed at 1840 cm^{-1}. The ν_{NO} intensities of compound (II) and (III) soon became nearly equal. while their absolute value slowly decreased, their ratio remained constant. Compound (II) can easily be separated from the reaction mixture on addition of pentane. Compound (III) could not be isolated in pure form. Based on preliminary analytical data it is assumed to be dichlorotris(acetonitrile)nitrosylmolybdenum·

$$Mo(NO)Cl_3(CH_2CN)_2 + NO + CH_3CN \rightleftharpoons Mo(NO)Cl_2(CH_3CN)_3 + NOCl \quad (3)$$

III, ν_{NO} (cm^{-1}): 1840

The equilibrium character of reaction (3) is further emphasized by the observation that the reaction rate is increased by occasional removal of NOCl or application of higher concentration of acetonitrile.

Formation of the dinitrosyl derivative (IV) from compound (III) is relatively slow, but the final yield is high.

$$Mo(NO)Cl_2(CH_3CN)_3 + NO \rightarrow Mo(NO)_2Cl_2(CH_3CN)_2 + CH_3CN \quad (4)$$

IV, ν_{NO} (cm^{-1}). 1808m, 1690s

Compounds I and II are convenient starting materials. They are readily converted into other mononitrosyl derivatives in a simple ligand exchange reaction·

$$M(NO)Cl_3(CH_3CN)_2 + 2L \xrightarrow{CH_2Cl_2} M(NO)Cl_3L_2 + 2CH_3CN \quad (5)$$

(M = Mo or W; L = PPh_3; $AsPh_3$, $OPPh_3$, DMF, DMSO, EtCN *etc.*)

The yield of reaction (5) is high. No oxidation of tertiary phosphines was detected by IR measurements.

References

1 Part IV. J. Kohán, S. Vastag and L. Bencze, *Inorg. Chim. Acta, 14,* L1 (1975).

2 R. Taube and K. Seyferth, *Z. Chem., 14,* 284 (1974).

3 R. Davis, B. F. G. Johnson and K. H Al-Obaidi, *J Chem. Soc Dalton,* 508 (1972).

4 L. Bencze, *Proc XVth ICCC, Moscow, 2,* 111 (1971). L. Bencze, J. Kohán, B. Mohai and L. Markó, *J. Organometal Chem., 70,* 421 (1974).

5 H. Hein (JENA), personal communication (1971).

6 R. Taube and K. Seyferth, *Z Anorg Allg. Chem., 437,* 213 (1977).

7 F. King and G. J. Leigh, *J. Chem. Soc Dalton,* 429 (1977).