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REDUCTIVE NITROSATION OF MOLYBDENUM AND TUNGSTEN HALIDES. A NEW ROUTE TO DICHLORODINITROSYLMOLYBDENUM, DICHLORODINITROSYLTUNGSTEN AND THEIR DERIVATIVES

L. BENCZE

Department of Organic Chemistry, Veszprém University of Chemical Engineering, Veszprém (Hungary)

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SUMMARY

Complexes of the type $[M(NO)_2Cl_2]_n$ and $M(NO)_2Cl_2(PPh_3)_2$ ($M=Mo$ or W) have been prepared by the action of nitric oxide on tungsten hexachloride and molybdenum pentachloride.

INTRODUCTION

Several methods have been described for the preparation of molybdenum and tungsten halo nitrosyls starting from different carbonyl complexes of these metals[1-5]. We have now found that the action of nitric oxide on $MoCl_5$ and WCl_6 in methylene dichloride also yields halo nitrosyl complexes of Mo and W. This method may be termed reductive nitrosation, since NO acts both as a reducing and coordinating agent in these reactions.

RESULTS AND DISCUSSION

The preparation of molybdenum and tungsten chloro carbonyls by the reductive carbonylation of tungsten and molybdenum chlorides under atmospheric CO pressure was described recently[6]. In our first experiments a similar method was used for the preparation of the analogous chloro nitrosyl compounds: WCl_6 was suspended in n-hexane under one atmosphere pressure of nitric oxide and $EtAlCl_2$ added in hexane solution (W/Al $\frac{1}{4}$). A fast reaction occurred and three sharp bands appeared at 1827 s, 1733 s and 1665 w cm^{-1} in the IR spectrum of the yellow-green reaction mixture, these absorptions were assigned to $W(NO)_2Cl_2 \cdot Et_nCl_{3-n}$ ($n=0$ or 1). Addition of an excess of PPh_3 to the mixture caused a yellow-green material to separate, and after this had been left in the air for several hours $W(NO)_2Cl_2(PPh_3)_2$ was isolated by recrystallization from benzene. $MoCl_5$ reacted similarly. The IR spectra of the reaction mixtures indicated that the degrees of conversion were good, but the actual yields of the $M(NO)_2Cl_2(PPh_3)_2$ derivatives remained comparatively low (about 15%) because of experimental difficulties caused by the large quantities of aluminium salts.

$MoCl_4(PPh_3)_2$ reacted in hexane suspension with NO and $EtAlCl_2$ at a molar ratio of Mo/Al $\frac{1}{2}$ to give $Mo(NO)_2Cl_2(PPh_3)_2$ in 25% yield.

These reactions can be represented by the following equations:

$$MCl_{5,6} \xrightarrow[\text{Hexane}]{\text{NO+EtAlCl}_2} M(NO)_2Cl_2 \cdot Et_nAlCl_{3-n} \xrightarrow{\text{PPh}_3} M(NO)_2Cl_2(PPh_3)_2$$

(M=Mo or W; n=0 or 1)

$$MoCl_4(PPh_3)_2 \xrightarrow[\text{Hexane}]{\text{NO+EtAlCl}_2} Mo(NO)_2Cl_2(PPh_3)_2$$

It was found, however, that the presence of organoaluminium compounds is not necessary for the reductive nitrosation of molybdenum and tungsten chlorides. When nitric oxide was passed into a dichloromethane solution of $MoCl_5$, green crystals (I) formed in almost quantitative yield and the dark solution became clear. The product was filtered off and dried under vacuum. The IR spectrum of the product in Nujol showed the bands characteristic of $[Mo(NO)_2Cl_2]_n$, as listed by Johnson and Cotton[2]. For confirmation of the structure (I) was treated with PPh_3 at a molar ratio of 1/2 in benzene, and gave $Mo(NO)_2Cl_2(PPh_3)_2$ (II) in 75% yield.

The reaction of nitric oxide with WCl_6 in dichloromethane gave a green powder (IV) which did not have the clean IR spectrum of $[W(NO)_2Cl_2]_n$, but showed a very broad band between 1600 and 1900 cm^{-1}, with a maximum at about 1800 cm^{-1}. From analytical data (IV) was formulated as $[W(NO)_{1.3}Cl_{2.7}]_n$, and is thought to be a mixture of various nitrosyl compounds, mostly $[W(NO)_2Cl_2]_n$ and $[W(NO)Cl_3]_n$. We have not been able to separate this mixture, but it is useful as a source of $[W(NO)_2Cl_2]_n$; thus it reacts with triphenyl phosphine $W(NO)_2Cl_2(PPh_3)_2$ to give (V) in 35% yield. The reactions can be represented as follows:

$$MCl_z \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{NO}} [M(NO)_2Cl_2]_n \xrightarrow[\text{benzene}]{\text{PPh}_3} M(NO)_2Cl_2(PPh_3)_2$$

(M=Mo or W; z=5 or 6)

TABLE 1

NITROSYL STRETCHING FREQUENCIES (IN NUJOL)

Compound	*Ref.*	*$\nu(NO)(cm^{-1})$*					
$[Mo(NO)_2Cl_2]_n$	1	1805 s(br)	1690 s	1600 vw			
$[W(NO)_2Cl_2]_n$	1	1800	1680	1600			
(I)		1805 s(br)	1690s	1600 vw			
(IV)		1900	1800	[1900–1600(br)]			
		Isomer A		*Isomer B*		*Isomer C*	
$Mo(NO)_2Cl_2(PPh_3)_2$	4	1783	1660	1774	1652	1753	1643
$W(NO)_2Cl_2(PPh_3)_2$	4			1748	1635	1743	1630
(II)				1755 s	1655 s		
(III)				1755 s	1655 s		
(V)				1748 s	1638 s		
(VI)				1748 s	1638 s		

We also prepared $Mo(NO)_2Cl_2(PPh_3)_2$ (III) and $W(NO)_2Cl_2(PPh_3)_2$ (VI) by Johnson and Cotton's method. IR spectra (Table 1) showed that (II) was identical with (III), and (V) was identical with (VI).

EXPERIMENTAL

All manipulations were carried out under argon or nitric oxide at room temperature. The solvents were dried and degassed before use.

Nitric oxide was prepared by the interaction of sodium nitrate and acidified ferrous sulphate solutions. The gas was dried and freed from NO_2 by passage over NaOH pellets.

IR spectra were recorded on a double beam Carl Zeiss UR 20 spectrophotometer.

$[Mo(NO)_2Cl_2]_n$, (*I*)

The reaction was carried out in a three-neck 150 ml Erlenmeyer flask equipped with magnetic stirrer. The flask was swept with argon, and molybdenum pentachloride (1 g) and dichloromethane (20 ml) were introduced. The mixture was stirred and flushed with nitric oxide several times until the dark colour of the solution disappeared and a dark green powder precipitated. The solid product was separated by filtration, washed with dichloromethane, and dried in vacuum.

$Mo(NO)_2Cl_2(PPh_3)_2$, (*II*)

$[Mo(NO)_2Cl_2]_n$ (1.15 g; 0.005 mol) and 2.65 g triphenylphosphine (0.01 mol) were refluxed together in 100 ml benzene under argon for 15 min. The solution was decanted, the solvent partially removed in vacuum, and pentane added. The product was filtered off, washed with pentane, and dried in vacuum. (Found: Mo, 12.8. Calcd.: 12.9%.) Yield 75%.

$W(NO)_2Cl_2(PPh_3)_2$, (*V*)

WCl_6 (1.98 g; 0.005 mol) in 50 ml dichloromethane was treated with nitric oxide as described above. The green powder (IV) which separated was filtered off and dried in vacuum. (Found: Cl, 30.1.$[W(NO)Cl_3]_n$ Calcd.: Cl, 33.2; $[W(NO)_2Cl_2]_n$ calcd.: Cl, 22.5%.) Triphenylphosphine (2.65 g; 0.01 mol) was refluxed in 100 ml benzene with (IV) for 15 min. The benzene solution was concentrated in vacuum, and pentane was added to precipitate $W(NO)_2Cl_2(PPh_3)_2$. (Found: W, 20.5. Calcd.: W, 21.9%.) Yield 35%.

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