Journal of Organometallic Chemistry, 70 (1974) 421—425

REDUCTIVE NITROSATION OF MOLYBDENUM AND TUNGSTEN HALIDES

II*. ONE-STAGE SYNTHESIS OF PHOSPHINE OXIDE SUBSTITUTED MONONITROSYLTRICHLORO-, AND DINITROSYLDICHLORO-MOLYBDENUM DERIVATIVES**

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(Received October 12th, 1973)

Summary

The reductive nitrosation of $MoCl_5$ with NO in the presence of PPh_3 in CH_2Cl_2 solution gives $Mo(NO)Cl_3(OPPh_3)_2$ as an intermediate and $Mo(NO)_2Cl_2\cdot(OPPh_3)_2$ as a final product. In benzene solution the final product of the reaction is $Mo(NO)_2Cl_2(OPPh_3)_2\cdot 2C_6H_6$.

Introduction

$M(NO)_2Cl_2L_2$ (where M = Mo or W and L = donor molecule such as PPh_3, $OPPh_3$) complexes have aroused considerable interest recently following their successful application in combination with aluminium alkyls as homogeneous olefin disproportionation and polymerization catalysts by Zuech and his coworkers [1, 2, 3]. $M(NO)_2Cl_2L_2$ and $M(NO)Cl_3L_2$ derivatives were first prepared from carbonyl derivatives and nitrosyl halides by oxidative nitrosation [4—7]. Later we observed that $MoCl_5$ and WCl_6 reacted with NO by reductive nitrosation to give halo nitrosyl derivatives. $[Mo(NO)_2Cl_2]_n$ may be obtained in high yields by this latter method but the reductive nitrosation of WCl_6 results in a mixture of mono and dinitrosyl derivatives [8] which, similarly to $[W(NO)_2Cl_2]_n$ prepared from $W(CO)_6$ [9], may absorb further NOCl molecules. Both products can be used as a source of $M(NO)_2Cl_2$ and their reactions with donor molecules give $M(NO)_2Cl_2L_2$ complexes.

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* For Part I, see ref. 8.

** Parts of this work were reported at the IVth Polish—German Colloquium on Organometallic Chemistry, Meissen, (October 18th, 1972).

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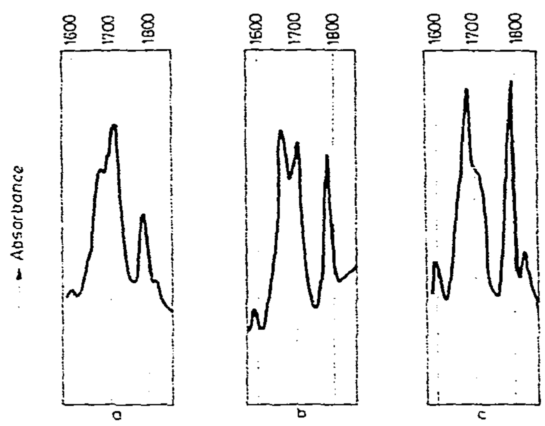

Fig. 1. IR spectra in the NO stretching region of a reaction mixture of $MoCl_5$, PPh_3 and NO in dichloromethane with increasing reaction time. (a) 15 min; (b) 1 h; (c) 5 h.

Results and discussion

As complexes of the type $Mo(NO)_2Cl_2L_2$ ($L = OPPh_3, PPh_3, Py$) were essential components of Zuech's homogeneous olefin disproportionation catalysts [2] a simple one-step synthesis for their preparation was attempted.

A mixture of $MoCl_5$ and PPh_3 (Mo/P 1/2) was treated with a solution of nitric oxide in dichloromethane. The color of the solution turned from yellow to green and new absorption bands characteristic of coordinated nitric oxide appeared in the IR spectrum of the reaction mixture. First a fast growing peak appeared at 1705 cm^{-1} ; this was later followed by two other peaks at 1665 and 1783 cm^{-1} which finally dominated the spectrum of the reaction mixture (Fig. 1). The spectrum remained unchanged on further treatment with NO. On concentrating the solution, green crystals of $Mo(NO)_2Cl_2(OPPh_3)_2$ (II) separated in 90% yield. The transient absorption band at 1705 cm^{-1} in the IR spectrum of the reaction mixture was attributed to $Mo(NO)Cl_3(OPPh_3)_2$ (I), an intermediate of reductive nitrosation. To isolate (I) the admission of NO was stopped at an early stage of the reaction and the solvent was evaporated. The solid residue thus obtained gave, on recrystallisation from acetone, (I) in 60% yield contaminated by 5—10% (II).

$Mo(NO)Cl_3(OPPh_3)_2$ was also prepared from PPh_3 and $[Mo(NO)Cl_3]_n$ obtained from $Mo(CO)_4Cl_2$ and NOCl by Johnson's method [7]. This product contained about 30% (II) as contaminant. The IR spectra of the two samples prepared by two rather different routes supported the identity of the mononitrosyl derivatives (Table 1).

This sequence of reactions in which NO is simultaneously an oxidizing, reducing and coordinating agent is summarized in eqns. (1—3).

$$PPh_3 + 2NO \xrightarrow[CH_2Cl_2]{} OPPh_3 + N_2O \tag{1}$$

TABLE 1

IR DATA OF THE COMPLEXES (I)—(V) AND THE TWO COMPLEXES USED AS REFERENCE MATERIALS

Complex	Medium	ν(NO), (cm^{-1})	Method of preparation
$Mo(NO)Cl_3(OPPh_3)_2$	Nujol	[ν(P=O), 1120, 1156] 1703 s	Ref. 7
	KBr	1702 s	
(I)	CH_2Cl_2	1708 s	Reductive nitrosation in CH_2Cl_2
	Nujol	1703 s	Reductive nitrosation in benzene
	KBr	1702 s	
$Mo(NO)_2Cl_2(OPPh_3)_2$	Nujol	1656 s (br), 1773 m, 1781 m	Ref. 7
	Nujol	1656 s (br), 1773 m, 1781 m	Reaction of $[Mo(NO)_2Cl_2]_n$ [a] and Ph_3PO in xylene
(II)	CH_2Cl_2	1665 s (br), 1783 m	Reductive nitrosation in CH_2Cl_2
	Nujol	1656 s (br), 1773 m, 1781 m	Recrystallization from xylene
(III)	Nujol	1659 s (br), 1775 w, 1784 m	Both by reductive nitrosation in benzene and by reaction of $[Mo(NO)_2Cl_2]_n$ and Ph_3PO in benzene
	KBr	1662 s, 1784 s	
(IV)	KBr	1656 s (br), 1773 m, 1782 m	By decomposition of (III) at 120°
(V)	KBr	1665 s, 1777 s	(II) or (IV) eluted from an alumina column by CH_2Cl_2

[a] Ref. 8.

$$MoCl_5 + 2\,OPPh_3 \xrightarrow[CH_2Cl_2]{NO} Mo(NO)Cl_3(OPPh_3)_2 \qquad (2)$$

$$Mo(NO)Cl_3(OPPh_3)_2 \xrightarrow[CH_2Cl_2]{NO} Mo(NO)_2Cl_2(OPPh_3)_2 \qquad (3)$$

When the reaction was carried out in benzene (I) separated as an oily layer. This oil re-dissolved during the course of the reaction and finally a light green crystalline material was deposited which was found to be $Mo(NO)_2Cl_2(OPPh_3)_2 \cdot 2C_6H_6$ (III), a benzene solvate of (II). This solvate was fairly stable but slowly lost benzene in the presence of benzene acceptors. Its IR spectrum therefore changed with time in a Nujol mull and could be determined reliably only in KBr pellets. (III) was stable up to 100° when it lost both benzene molecules in one endothermic step (Fig. 2). The residue (IV) contained two isomers of (II), both of which were stable up to 300° and could be easily isolated as a mixture.

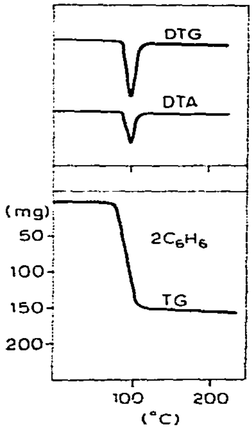

Fig. 2. TG (DTG) and DTA curves of $Mo(NO)_2Cl_2(OPPh_3)_2 \cdot 2C_6H_6$.

Chromatography of this mixture on an alumina column with xylene and dichloromethane gave only one compound (V) the IR spectrum of which was not identical, however, to that of any of the starting compounds. (III) can also be prepared from $[Mo(NO)_2Cl_2]_n$ (made either by Johnson's method or by reductive nitrosation) and $OPPh_3$ (1/3) in benzene or by simply recrystallizing (II) from benzene. Attempts to prepare benzene solvates of (I) and $Mo(NO)_2Cl_2(PPh_3)_2$ failed.

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 nitrite and acidified ferrous sulphate solutions. The gas was dried and freed from NO_2 by passage over NaOH pellets. IR reference materials were prepared as described in the literature. IR spectra were recorded on a double beam Carl Zeiss UR 20 spectrophotometer. TG and DTA analyses were made using a MOM G-425 type derivatograph.

The compounds were identified by comparing their IR spectra with those of known materials and by thermogravimetric analysis followed by GLC of the gases evolved. GLC analysis was carried out on a 4 m × 0.04 m column packed with Porapak Q. Argon was used as carrier gas in conjunction with a thermal conductivity detector (Carlo Erba).

$Mo(NO)Cl_3(OPPh_3)_2$ *(I)*

The reaction was carried out in a three necked 150 ml Erlenmeyer flask equipped with a magnetic stirrer. The flask was swept with argon and molybdenum pentachloride (273 mg, 1 mmole), triphenylphosphine (524 mg, 2 mmole) and benzene (20 ml) were introduced. The stirred mixture was flushed with nitric oxide several times until a dark green oily layer was deposited. This oil was separated and washed with ether; on addition of acetone green crystals formed. The solid product was recrystallized from acetone and dried in vacuum (yield 60%). This material was estimated to be about 92% pure based on its IR spectrum and the amount of N_2O (1.9% N) evolved on thermolysis.

$Mo(NO)_2Cl_2(OPPh_3)_2$ *(II)*

Reductive nitrosation was carried out as described above, using CH_2Cl_2 instead of benzene. The mixture remained homogeneous throughout the reaction. After the band at 1705 cm^{-1} had disappeared from the IR spectrum of the reaction mixture (a light green solution) the solvent was partly removed; on standing overnight light green crystals of (II) separated (yield 90%). (Found: NO, 7.6. Calcd.: NO, 7.67%.)

$Mo(NO)_2Cl_2(OPPh_3)_2 \cdot 2C_6H_6$ *(III)*

A similar procedure to that described for (I) was used but the oily layer was not separated and the reaction mixture was further treated with NO until a homogeneous light green benzene solution had formed. Light green crystals of (III) were deposited on concentrating the solution (yield 80%). (Found: C_6H_6, 16.5; NO, 6.78. Calcd.: C_6H_6, 16.6; NO, 6.38%.)

Acknowledgement

The authors thank K. Gőgös for experimental assistance.

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