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Reductive Nitrosation of Molybdenum and Tungsten Halides.
IV.[1] Synthesis of Dichlorodinitrosyltungsten and its Derivatives

J. KOHAN, S. VASTAG and L. BENCZE

Department of Organic Chemistry, Veszprém University of Chemical Engineering, 8201 Veszprém, Hungary

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Several halo nitrosyl complexes have been reported as products of the reaction of nitric oxide and tungsten hexachloride but no clean formation of $[W(NO)_2Cl_2]_n$ was achieved this way up till now[2,3,4].

The product available by reductive nitrosation of tungsten hexachloride in dichloro methane suspension at room temperature is a green powder (I) which, based on analytical data, was thought to be a mixture of various nitrosyl complexes, mostly $W(NO)Cl_3$ and $W(NO)_2Cl_2$ associated with NOCl molecules[3,5]. The IR spectrum of I also suggests it to be a mixture (Fig. 1a). I is insoluble in cold dichloro methane and the liquid phase of the reaction mixture shows only one strong absorption of NOCl formed as byproduct (νNO 1850 cm^{-1}) in the NO stretching frequency region.

Since NOCl was shown to coordinate to $W(NO)_2Cl_2$ [6] this coordinated NOCl was regarded as the cause of the insolubility of the product and thus the lack of further reduction of intermediates or starting materials enclosed inside the crystals. To verify this assumption the reaction mixture obtained in the preparation of I described earlier[4] was refluxed for two hours in a current of NO. This procedure diminished the amount of NOCl absorbed in the liquid and the green solid (I) gradually dissolved giving a greenish black solution. Solid materials isolated from the reaction mixture from time to time showed significantly different IR spectra (Figs. 1a - d). The nearly horizontal absorption level of I between 1600 and 1800 cm^{-1} (Fig. 1a) first turned into a broken line (Fig. 1b) and later a quite clean spectrum of at least two compounds with five NO absorptions could be observed among which the peaks of $W(NO)_2Cl_2$ could be easily recognized at 1797 and 1696 cm^{-1} (Fig. 1c). On further treatment the additional peaks disappeared and crystals of $[W(NO)_2Cl_2]_n$ (II) (Fig. 1d) began to precipitate on cooling (yield 70%). Reductive nitrosation of WCl_6 has to be carried out therefore in a strongly diluted suspension to avoid the trapping of starting material and intermediates. In this way the complete reduction to W^{II} is rapidly accomplished and the N/W ratio of the crude product varies between 2 and 4 depending on the drying conditions which determine the amount of NOCl remaining in the solid material.

However, the equilibrium

$$W(NO)_2Cl_2 \cdot nNOCl \rightleftharpoons W(NO)_2Cl_2 + nNOCl$$

may be easily shifted to the right by simply refluxing the reaction mixture in an argon current.

Compound II was reacted with donor molecules. Its reactions with PPh_3 and $OPPh_3$ gave $W(NO)_2Cl_2(PPh_3)_2$ (III) and $W(NO)_2Cl_2(OPPh_3)_2$ (IV) respectively. The same compounds were also prepared from $[W(NO)_2Cl_2]_n$ obtained from $W(CO)_6$ and NOCl. The IR spectra of the parallel compounds were identical between 700 and 3200 cm^{-1} as well as their TG, DTG and DTA curves[1]. While the formation[8] and thermal behaviour[1] of IV have already been described its IR data are published here for the first time (Table I). Although, the formation of a benzene solvate in the case of IV was not detected it was isolated as a mixture of two isomers like the molybdenum analog prepared from $Mo(NO)_2Cl_2(OPPh_3)_2 \cdot 2C_6H_6$ by thermal decomposition[5].

Reaction of II with P(cyclohexyl)$_3$ and OP(cyclohexyl)$_3$ in benzene solution gave $W(NO)_2Cl_2[P(C_6H_{11})_3]_2$ (V) and $W(NO)_2Cl_2[OP(C_6H_{11})_3]_2 \cdot 2C_6H_6$ (VI) respectively. The solvate (VI) was stable up to 100 °C. The benzene free product contained only one *cis* isomer of $W(NO)_2Cl_2[OP(C_6H_{11})_3]_2$ (VII). Neomenthyl diphenyl phosphine oxide gave $W(NO)_2Cl_2[OPPh_2(neomenthyl)]_2$ (VIII). Formation of benzene solvates or isomers could not be detected in this case.

Experimental

Analytical grade solvents (Reanal) were dried and degassed before use. All manipulations were carried out in argon or nitric oxide atmosphere.

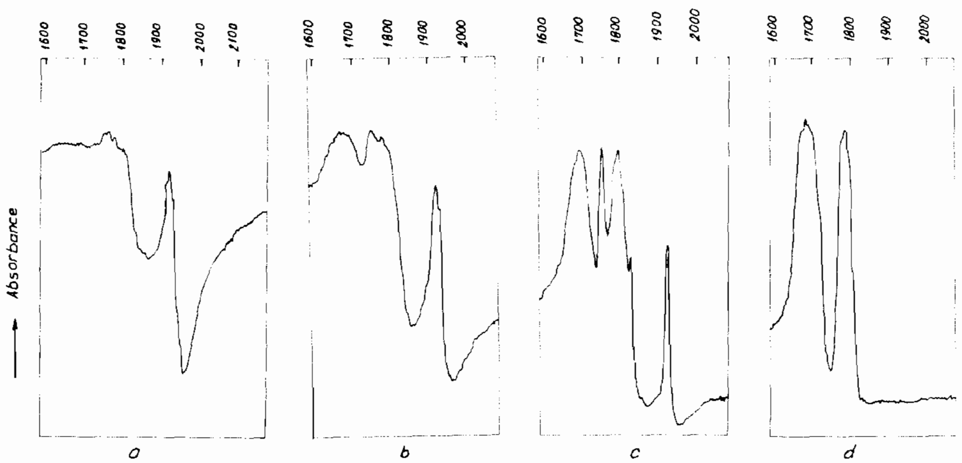

Fig. 1. IR spectra (in Nujol) of the solid product formed in the reaction of I and NO in CH_2Cl_2 with increasing reaction times. (a) 0 min; (b) 15 min; (c) 60 min; (d) 120 min.

TABLE I. Nitrosyl Stretching Frequencies of New and Reference Compounds.

Compound		References	ν(NO), cm^{-1}	Medium
$[W(NO)_2Cl_2]_n$		7	1805 s, 1690 s	Nujol
I		3, 4	1900 s, 1800 (1800 - 1600 s, br)	Nujol
$[W(NO)_2Cl_2]_n$	II		1797 s, 1696 s	Nujol
$W(NO)_2Cl_2(PPh_3)_2$	III		1748 s, 1638 s	KBr
$W(NO)_2Cl_2(OPPh_3)_2$	IV		1746 w, 1742 m, 1656 m, 1631 s	KBr
$W(NO)_2Cl_2[P(C_6H_{11})_3]_2$	V		1742 s, 1633 s	KBr
$W(NO)_2Cl_2[OP(C_6H_{11})_3]_2 \cdot 2C_6H_6$	VI		1739 s, 1623 s	KBr
$W(NO)_2Cl_2[OP(C_6H_{11})_3]_2$	VII		1739 s, 1622 s	KBr
$W(NO)_2Cl_2[OPPh_2(neomenthyl)]_2$	VIII		1746 m, 1631 s	KBr

Neomenthyl diphenyl phosphine oxide (m.p.: 213 - 215 °C; $[\alpha]_D^{20}$ = +51 ± 1, *c.* 9.45 EtOH) was made by the method of R. E. Burnett[9].

The compounds were identified by their IR spectra, elemental and thermogravimetric analysis. IR spectra were recorded on a double beam Carl Zeiss UR 20 spectrophotometer.

Thermal analyses were kindly made by B. Mohai, Department of General and Inorganic Chemistry, Veszprém University of Chemical Engineering, using a MOM G-425 type derivatograph.

$[W(NO)_2Cl_2]_n$ (II)

The reaction was carried out in a three necked 150 ml Erlenmeyer flask equipped with magnetic stirrer. The flask was swept with argon and 1 g tungsten hexachloride and 50 ml dichloro methane were introduced. The mixture was stirred continuously and flushed with NO several times at room temperature until the NO uptake ceased, the dark solution cleared up and a green powder of I precipitated. Following this the mixture was refluxed in a current of argon until the argon effluent contained no more NOCl. On cooling an olive green powder separated from the light green solution. The solid product was filtered off and dried under vacuum. Found: W, 57.1; Cl, 23.1. Calcd.: W, 58.4; Cl, 22.6%. Yield 79%.

$W(NO)_2Cl_2(PPh_3)_2$ (III)

$[W(NO)_2Cl_2]_n$ (1.58 g, 0.005 mol) was suspended in benzene (200 ml) and PPh_3 (2.62 g, 0.01 mol) was added to the suspension. The mixture was stirred for one hour at room temperature and heated under reflux for 15 min. The solution was decanted, the solvent partially removed until crystallization started and left overnight. The solid product was filtered off and pumped dry. Found: W, 22.0; N, 3.41; P, 7.2. Calcd.: W, 21.9; N, 3.34; P, 7.39%. Yield 72%.

The same general technique was applied for complexes IV - VIII. The solvate free material was prepared from VI by heating it briefly to 120 °C under vacuum.

Satisfactory W, N and P analyses were obtained for all of the compounds.

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