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NITROSYL CARBONYL DERIVATIVES OF GROUP VI METALS

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Summary

$[M(CO)_2(NO)(o\text{-phen or }2,2'\text{-bipy})]_2$ ($M = Mo, W$) are formed when a slow stream of NO is passed through a benzene solution of $M(CO)_4(o\text{-phen or }2,2'\text{-bipy})$. Under similar conditions $M(CO)_4(Ph_2PCH_2CH_2AsPh_2)$ ($M = Cr, Mo$) gives $M(NO)_3(Ph_2PCH_2CH_2AsPh_2)$, but $W(CO)_4(Ph_2PCH_2CH_2AsPh_2)$ gives the nitrosyl carbonyl complex $W(CO)(NO)_2(Ph_2PCH_2CH_2AsPh_2)$.

Introduction

Simple nitrosyl carbonyls of Group VI metals are unknown. Recent communications [1,2] reported complete displacement of all the carbonyl groups in chromium hexacarbonyl when nitric oxide is passed through its UV irradiated pentane solution.

Preparation of substituted derivatives, mainly cationic, by nitrosylation of substituted metal carbonyls with NOCl or $NOPF_6$ has been reported [3,4]. A neutral complex, $[Mo(CO)_2(NO)(C_{10}H_8N_2)]_2$, has been reported [5] to form when NO reacts with the carbonyl bridged complex $[Mo(CO)_3(C_{10}H_8N_2)]_2$. We describe below the nitrosylation of some substituted metal carbonyls like $M(CO)_4(C_{12}H_8N_2$ or $C_{10}H_8N_2)$ or $M(CO)_4(Ph_2PCH_2CH_2AsPh_2)$($M = Cr, Mo, W$).

Results and discussion

Nitric oxide reacted with $M(CO)_4(o\text{-phen})$ and $M(CO)_4(2,2'\text{-bipy})$ at room temperature (25°C) to give the dinuclear complexes, $M_2(CO)_4(NO)_2(C_{12}H_8N_2)_2$ and $M_2(CO)_4(NO)_2(C_{10}H_8N_2)_2$ (M = Mo and W), respectively in 30—40% yield. The complexes are yellow solids, soluble in polar solvents such as acetone, methanol and dichloromethane, and insoluble in non-polar solvents such as aliphatic and aromatic hydrocarbons, including light petroleum (60—80°C). The molybdenum derivatives are more stable than their tungsten analogues. Passage of

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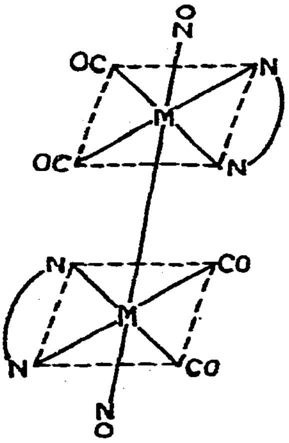
nitric oxide through a solution of $Cr(CO)_4$(*o*-phen) and $Cr(CO)_4$(2,2′-bipy) caused a similar change but the yellowish green sticky products could not be purified.

Under similar conditions nitric oxide displaced all the CO groups in $Cr(CO)_4(Ph_2PCH_2CH_2AsPh_2)$ and $Mo(CO)_4(Ph_2PCH_2CH_2AsPh_2)$ to give the trinitrosyl complexes, $Cr(NO)_3(Ph_2PCH_2CH_2AsPh_2)$ and $Mo(NO)_3(Ph_2PCH_2CH_2AsPh_2)$, respectively. $W(CO)_4(Ph_2PCH_2CH_2AsPh_2)$ reacted differently to give a substituted nitrosyl carbonyl product, $W(CO)(NO)_2(Ph_2PCH_2CH_2AsPh_2)$.

IR and molecular conductivity data for the molybdenum and tungsten derivatives, $[M(CO)_2(NO)$(*o*-phen or 2,2′-bipy)$]_2$, are shown in Table 1. All the complexes are non-electrolytes. The IR spectra exhibit two bands in the CO stretching region and four bands in the NO stretching region, of which only two are strong. Bands attributable to bridging CO and bridging NO groups were absent in all cases.

The two strong CO bands at ~2030 and 1940 cm^{-1} observed in the IR spectra of these complexes resembled closely those in the complex $[Mo(CO)_2(NO)(C_{10}H_8N_2)]_2$ which was prepared by the action of nitric oxide on the carbonyl bridged complex, $[Mo(CO)_3(C_{10}H_8N_2)]_2$. However, whereas Behrens et al. [5] reported only one strong NO band at 1653 cm^{-1} for this complex, we observed an addi-



(I)

TABLE 1

IR AND CONDUCTIVITY DATA FOR $[M(CO)_2(NO)$ (*o*-phen OR 2,2′-bipy)$]_2$ COMPLEXES

Complex	$\nu(CO)$ (cm^{-1})	$\nu(NO)$ (cm^{-1})	Molar conductivity (A.R. acetone) (ohm^{-1} cm^2)
$[Mo(CO)_2(NO)(C_{12}H_8N_2)]_2$	2040s, 1940s	1785ms, 1666s, 1638(sh), 1626(sh)	2.6
$[Mo(CO)_2(NO)(C_{10}H_8N_2)]_2$	2032s, 1932s 2028s, 1942s [5]	1785ms, 1680s, 1638(sh), 1618m 1653s [5]	2.5
$[W(CO)_2(NO)(C_{12}H_8N_2)]_2$	2020s, 1940s	1738ms, 1666(sh), 1638s	3.0
$[W(CO)_2(NO)(C_{10}H_8N_2)]_2$	2040s, 1940s	1790ms, 1666s, 1638(sh), 1618(sh)	2.8

TABLE 2

VALUES OF ν(CO) AND ν(NO) FOR NITROSYL DERIVATIVES OF Cr, Mo AND W

Complex	ν(NO)(cm^{-1})	ν(CO)(cm^{-1})
$Cr(NO)_3(Ph_2PCH_2CH_2AsPh_2)$	1793s, 1758(sh), 1662s	—
$Mo(NO)_3(Ph_2PCH_2CH_2AsPh_2)$	1770s, 1739(sh), 1652s	—
$W(CO)(NO)_2(Ph_2PCH_2CH_2AsPh_2)$	1790s, 1652s	2037 ms

tional medium strong NO band at ~1785 cm^{-1}. The diamagnetic character of the complexes suggested structure I, which includes a metal—metal bond.

The IR spectra of $Cr(NO)_3(Ph_2PCH_2CH_2AsPh_2)$ and $Mo(NO)_3(Ph_2PCH_2CH_2AsPh_2)$ exhibited one shoulder and two strong NO bands (Table 2). The absence of absorption bands in the CO region indicated complete displacement of all the carbonyl groups. In the spectrum of the tungsten complex, $W(CO)(NO)_2(Ph_2PCH_2CH_2AsPh_2)$, two strong NO bands were noted and a medium strong CO band. The diamagnetic character and non-ionic nature (in acetone) of this product support the proposed formula.

Experimental

All experiments were performed under dry nitrogen or in vacuo. (*o*-Phenanthroline, 2,2′-bipyridine and 1-diphenylphosphino-2-diphenylarsinoethane)metal tetracarbonyls (metal = Cr, Mo, W) were prepared by methods given in the literature [6—8]. Infrared spectra were recorded on a Perkin—Elmer spectrophotometer model 221 in KBr discs. Conductivity measurements were made with a Toshniwal conductivity bridge (model 302).

Preparation of di-o-phenanthrolinedinitrosyltetracarbonyldimolybdenum(I)

Nitric oxide gas, free from nitrogen peroxide, was passed through a solution of *o*-phenanthrolinemolybdenum tetracarbonyl (0.2 g in 50 ml benzene) at room temperature (25° C) with constant swirling. The red colour of the solution disappeared after half an hour and yellow crystals began to appear. After 1 h the passage of nitric oxide was stopped, and benzene was decanted off under nitrogen. The precipitate was washed several times with benzene and dried in vacuo. (Recrystallisation was not used because of the instability of the complex in solution.) The product was shown to be di-*o*-phenanthrolinedinitrosyltetracarbonyldimolybdenum(I) (yield 37%). (Found: C, 45.2; H, 2.1; N, 11.2. $C_{28}H_{16}N_6O_6Mo_2$ calcd.: C, 46.4; H, 2.2; N, 11.6%.)

Preparation of di-o-phenanthromlinedinitrosyltetracarbonylditungsten(I)

Nitric oxide reacted with *o*-phenanthrolinetungsten tetracarbonyl (0.2 g in 60 ml benzene) at room temperature to give a yellow precipitate. It was isolated in the same way as its more stable molybdenum analogue (yield 38%). (Found: C, 36.2; H, 1.6; N, 9.1. $C_{28}H_{16}N_6O_6W_2$ calcd.: C, 37.3; H, 1.7; N, 9.3%.)

Preparation of di-2,2′-dipyridinedinitrosyltetracarbonyldimolybdenum(I)

Nitric oxide reacted with 2,2′-bipyridinemolybdenum tetracarbonyl (0.2 g in

50 ml benzene) at room temperature to give di-2,2'-bipyridinedinitrosyltetracarbonyldimolybdenum(I) (yield 33%). (Found: C, 41.2; H, 2.2; N, 12.2. $C_{24}H_{16}N_6O_6Mo_2$ cald.: C, 42.6; H, 2.3; N, 12.4%.)

Preparation of di-2,2'-bipyridinedinitrosyltetracarbonylditungsten(I)

Nitric oxide reacted with 2,2'-bipyridinetungsten tetracarbonyl (0.2 g in 60 ml benzene) to give the expected product (yield 38%). (Found: C, 32.4; H, 1.8; N, 9.3. $C_{24}H_{16}N_6O_6W_2$ calcd.: C, 33.8; H, 1.8; N, 9.8%.)

Preparation of (1-diphenylphosphino-2-diphenylarsinoethane)trinitrosylchromium(0)

Nitric oxide was passed through a solution of (1-diphenylphosphino-2-diphenylarsinoethane)chromium tetracarbonyl (0.2 g in 25 ml benzene) at room temperature. No change in colour of the solution was observed, but after 15 min a yellow precipitate appeared. After a further half hour the bubbling of nitric oxide was stopped and benzene was decanted off under nitrogen. The precipitate was washed well with benzene and dried in vacuo. Analytical data and IR measurements were consistent with the formula (1-diphenylphosphino-2-diphenylarsinoethane)trinitrosylchromium(0) (yield 35%). (Found: C, 52.6; H, 4.0; N, 7.0. $C_{26}H_{24}N_3O_3Cr$ calcd.: C, 53.4; H, 4.1, N, 7.2%).

Preparation of (1-diphenylphosphino-2'-diphenylarsinoethane)trinitrosylmolybdenum(0)

Passage of nitric oxide through a solution of (1-diphenylphosphino-2-diphenylarsinoethane)molybdenum tetracarbonyl (0.2 g in 25 ml benzene) for 1 h at room temperature gave a greenish yellow precipitate, which was worked up as described for the chromium complex. It was shown to be (1-diphenylphosphino-2-diphenylarsinoethane)trinitrosylmolybdenum(0) (yield 41%). (Found: C, 48.5; H, 3.5; N, 6.5. $C_{26}H_{24}N_3O_3Mo$ calcd.: C, 49.6; H, 3.8; N, 6.6%.)

Preparation of (1-diphenylphosphino-2-diphenylarsinoethane)dinitrosylcarbonyltungsten(0)

A similar colour change was observed on passing nitric oxide gas through a solution of (1-diphenylphosphino-2-diphenylarsinoethane)tungsten tetracarbonyl (0.2 g in 25 ml benzene) for 1 h, but isolation by a similar procedure gave (1-diphenylphosphino-2-diphenylarsinoethane)dinitrosylcarbonyltungsten(0) (yield 41%) (Found: C, 44.2; H, 3.1; N, 3.8. $C_{27}H_{24}N_2O_3W$ calcd.: C, 45.3; H, 3.3; N, 3.9%.)

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