

TRANSITION METAL NITROSYLS AS NITROSYLATION AGENTS

II *. PHOTO-NITROSYLATION OF $\eta^5\text{-C}_5\text{H}_5\text{V}(\text{CO})_3\text{L}$ ($\text{L} = \text{CO}, \text{PZ}_3$) BY $[\text{Co}(\text{NO})_2\text{Br}]_2$

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Summary

$\eta^5\text{-C}_5\text{H}_5\text{V}(\text{NO})_2\text{CO}$ is prepared in 40% yield by the photo-reaction between $\eta^5\text{-C}_5\text{H}_5\text{V}(\text{CO})_4$ and $[\text{Co}(\text{NO})_2\text{Br}]_2$. $\eta^5\text{-C}_5\text{H}_5\text{V}(\text{NO})_2\text{CO}$ reacts by an $\text{S}_{\text{N}}1$ mechanism with various phosphines PZ_3 to yield $\eta^5\text{-C}_5\text{H}_5\text{V}(\text{NO})_2\text{PZ}_3$. The phosphine complexes are also obtained by photo-induced ligand interchange between $\eta^5\text{-C}_5\text{H}_5\text{V}(\text{CO})_3\text{PZ}_3$ and $[\text{Co}(\text{NO})_2\text{Br}]_2$, or $\eta^5\text{-C}_5\text{H}_5\text{V}(\text{CO})_4$ and $\text{Co}(\text{NO})_2\text{Br}(\text{PZ}_3)$. In all cases, the main cobalt species formed is $\text{Co}(\text{NO})(\text{CO})_3$. While the one-bond vanadium–phosphorus coupling constants of most of the phosphine complexes are virtually the same (ca 410 Hz), the chemical shift values $\delta(^{51}\text{V})$ (–1328 to –973 ppm rel. VOCl_3) decrease in the order $\text{PF}_3 > \text{CO} > \text{P}(\text{OR})_3 > \text{P}(\text{alkyl})_3 > \text{PPh}_3 > \text{PPh}(\text{NEt}_2)_2$, reflecting the decreasing π -acceptor ability of the ligands. $\delta(^{51}\text{V})$ also decreases in the series of alkylphosphines PR_3 ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^n, \text{Bu}^i, \text{Pr}^i, \text{Bu}^t$) as the cone angle of PR_3 increases.

Introduction

There have been few studies of intermolecular nitrosyl transfer (usually involving ligand interchange of one and more ligands in addition to NO). The cobalt complexes $\text{Co}(\text{NO})(\text{dmg})_2$ ($\text{dmg} = \text{dimethylglyoxime}$) [1], $\text{Co}(\text{NO})(\text{PPh}_3)_3$ [2], and $[\text{Co}(\text{NO})(\text{NH}_3)_5]^{2+}$ [3] have been employed mostly in nitrosylation reactions of transition metal complexes containing the Cl^- and phosphine ligands. Other transition metal nitrosyls, such as $\text{Ru}(\text{NO})_2(\text{PPh}_3)_2$ [4] and $\text{Rh}(\text{NO})(\text{PPh}_3)_3$ [2] react similarly, and there are at least two examples in the literature in which the transfer reagent and the substrate are identical

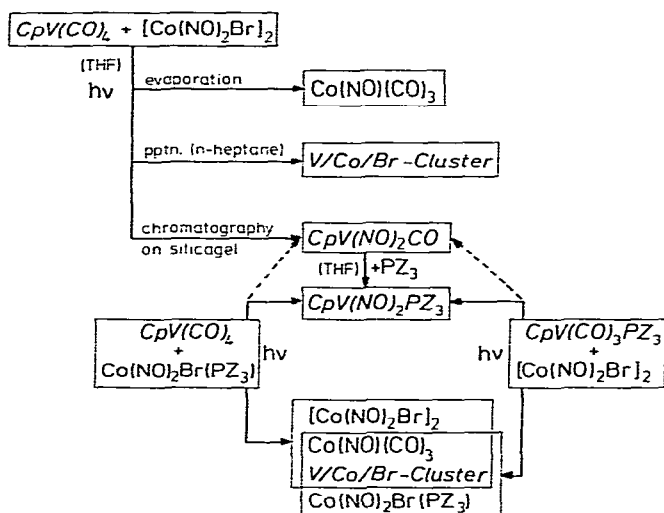
* See ref. 9 for communication I.

$([\text{Fe}(\text{NO})\text{CO}(\text{PPh}_3)_2]^+ [6] \text{ and } \text{Co}(\text{NO})(\text{tac})_2 \text{ (tac = dithioacetylacetonate) [5]}).$

Photo-reaction of $\text{Co}(\text{NO})(\text{CO})_3$ in CH_2Br_2 has been reported by Seel to give $[\text{Co}(\text{NO})_2\text{Br}]_2$ [7]. We have used this complex, and its chlorine and iodine analogues (for which a convenient synthesis is given in ref. 8) in photo-nitrosylation reactions with $\text{Cr}(\text{CO})_6$ to yield $\text{Cr}(\text{NO})\text{X}_2(\text{THF})_n$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $\text{Co}(\text{NO})(\text{CO})_3$ [9]. Three ligands ($\text{X}, \text{CO}, \text{NO}$) are interchanged in this reaction. We have now investigated nitrosylation in the system $\text{CpV}(\text{CO})_4/[\text{Co}(\text{NO})_2\text{Br}]_2/\text{PZ}_3$.

Results and discussion

The results are summarized in Scheme 1. In the reaction between $\text{CpV}(\text{CO})_4$ and $[\text{Co}(\text{NO})_2\text{Br}]_2$, about 70% of the cobalt is converted into the volatile Co-



SCHEME 1

$(\text{NO})(\text{CO})_3$ (I). 40% of the vanadium can be recovered in the form of $\text{CpV}(\text{NO})_2\text{CO}$ (II), while about 50% is incorporated in a vanadium-cobalt-bromine cluster (III) of unknown geometry (characteristic data are: $\text{V/Co/Br} = 2.5/1/2$; $\delta(^{51}\text{V}) = -509$ ppm rel. VOCl_3 ; $\delta(^{59}\text{Co}) = 3200$ ppm rel. $[\text{Co}(\text{CN})_6]^{3-}$; IR: 1690 and 1582 cm^{-1}).

Complex II was previously prepared by direct nitrosylation of $\text{CpV}(\text{CO})_4$, $[\text{CpV}(\text{CO})_3\text{CN}]^-$, or $\text{Cp}_2\text{V}_2(\text{CO})_7$ in yields <7% [10]; a moderate yield preparation, using the highly carcinogenic *N*-methyl-*N*-nitroso-*p*-tolylsulfonamide, was reported by Herberhold [11].

Complex II reacts with various phosphines PZ_3 in THF solution and at room temperature without irradiation to form $\text{CpV}(\text{NO})_2\text{PZ}_3$ (IV). The average reaction time for almost complete removal of CO is 10 hours, except for P^tBu_3 , for which the reaction is incomplete even after one week. The reactions are of first order and hence the mechanism resembles that found for the thermally and photo-induced CO substitution in $\text{CpMn}(\text{CO})_3$ [12] and $\text{CpV}(\text{CO})_4$ [13,14]. IR

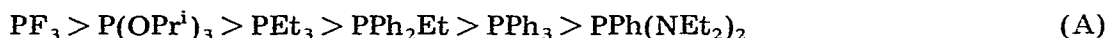
TABLE 1

IR AND ^{51}V NMR DATA FOR $\text{CpV}(\text{NO})_2\text{L}$ COMPLEXES ($\text{L} = \text{CO}, \text{PZ}_3$)

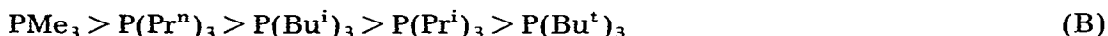
Ligand L	Cone Angle of L ($^\circ$) ^a	$\nu(\text{NO})$ ^b (cm^{-1})	$\delta(^{51}\text{V})$ ^c (ppm)	$^1J(\text{VP})$ ^d (Hz)	$\Delta\nu_{1/2}$ ^e (Hz)
CO	ca 95	1725 1636 ^f	-1294	—	260
PF_3	106	1783	-1328	^g	
$\text{P}(\text{OMe})_2\text{CH}_2$ ^h	115	1692 1595	-1213	512	195
$\text{P}(\text{OPr}^i)_3$	130	1682 1582	-1194	409	135
PET_3	132	1682 1584	-1170	400	170
PPh_2Et	140	1686 1589	-1143	409	160
PPh_3	145	1689 1592	-1115	403	170
$\text{PPh}(\text{NEt}_2)_2$	120	1686 1588	-1075	476	180
PMe_3	118	1685 1584	-1169	403	190
$\text{P}(\text{Pr}^n)_3$	132	1682 1582	-1160	409	135
$\text{P}(\text{Bu}^i)_3$	145	1683 1585	-1127	391	180
$\text{P}(\text{Pr}^i)_3$	160	1682 1584	-1115	402	150
$\text{P}(\text{Bu}^t)_3$	182	1681 1579	-973	342	155

^a Tolman's cone angle [19]. ^b 0.01 M THF. ^c Bruker WH 90, 23.66 MHz, ca 0.1 M THF at 300 K, relative to COCl_3 , absolute error ± 1 ppm. ^d One-bond ^{51}V — ^{31}P coupling constant, absolute error ± 3 Hz. ^e Peak-to-peak width of the dispersion signal, absolute error ± 10 Hz. ^f $\nu(\text{CO}) = 2048 \text{ cm}^{-1}$. ^g Unresolved. ^h $\text{CpV}(\text{NO})_2(\text{MeO})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OMe})_2$.

and ^{51}V NMR data of the complexes II and IV are compiled in Table 1. While variations in the $\nu(\text{NO})$ stretching frequencies are small, there is a consistent decrease of ^{51}V shielding (decrease of $|\delta(^{51}\text{V})|$) in the order



and



The shielding for the PF_3 complex is even greater than for II itself. Except for PF_3 , the phosphines in series A exhibit similar steric conditions (cone angles around 130° , and hence this ordering may be considered to reflect electronic factors, i.e. decreasing ligand strength; and we further conclude, from the constancy of the vanadium—phosphorus coupling constants, that π -interactions are predominant (cf. refs. 15 and 16 for a detailed analysis of ^{51}V NMR parameters). The same ordering of phosphines was found in $\text{CpV}(\text{CO})_3\text{PZ}_3$ and $[\text{V}(\text{CO})_5\text{PZ}_3]^-$ complexes [15–17]. Series B, which represents phosphines for which electronic contributions to the ^{51}V shielding should be very similar, reflects steric influences. Again, the results parallel those obtained for $\text{CpV}(\text{CO})_3\text{PZ}_3$ [18]. It is of interest in this context that the $(\text{NO})\text{V}(\text{NO})$ angles calculated from the relative intensities of the $\nu(\text{NO})$ bands [20] are alike for PMe_3 , PET_3 and $\text{P}(\text{Pr}^n)_3$ (108°), while for the bulkier $\text{P}(\text{Bu}^i)_3$ and $\text{P}(\text{Pr}^i)_3$, for which the ^{51}V shielding attains smaller values, this angle amounts to 99° and 97° , respectively.

Experimental

1.90 g $\text{CpV}(\text{CO})_4$ (8.3 mmol) and 1.62 g $[\text{Co}(\text{NO})_2\text{Br}]_n$ (8.0 mmol) dissolved in 100 ml THF were irradiated, using the irradiation apparatus DEMA 13/12

(Mangels, Bonn) fitted with a quartz immersion well and a high pressure mercury lamp (Philips HPK 125, Mangels). The irradiation was monitored by IR spectroscopy. After 50 min, the CO and NO absorptions characteristic of $\text{CpV}(\text{CO})_4$ (2027 and 1917 cm^{-1}) and $[\text{Co}(\text{NO})_2\text{Br}]_2$ (1835 and 1759 cm^{-1}) disappear to be replaced by a spectral pattern due to the components I (2110, 2045, 1806 cm^{-1}), II (2048, 1725, 1636 cm^{-1}) and III (1690, 1582 cm^{-1}). To remove I, the solution is evaporated to dryness. The residue is redissolved in 15 ml THF, treated with 70 ml n-heptane, and allowed to stand at 250 K for 1 day. Green-black III crystallizes during this time and is filtered off, washed with heptane and dried under high vacuum. The filtrate, containing II and small amounts of $\text{CpV}(\text{CO})_4$ and III, is concentrated to ca 1 ml, 2 ml of heptane are added, and the solution is chromatographed on silica gel (70–230 mesh ASTM, column dimensions 35 $\times$ 2.5 cm; eluant: heptane (ca 1.5 l, elution time 2.5 hours)). The first, red fraction is $\text{CpV}(\text{CO})_4$, the second, orange coloured fraction contains II, which is isolated as a cocoa-brown powder after removal of the solvent by evaporation at 1 Torr (room temperature). Yield: 40%.

For the preparation of the phosphine complexes IV, a solution of 150 mg of II and an equimolar amount of the phosphine in 5 ml THF is allowed to stand at room temperature for 1 day. Concentration to ca 1 ml and crystallization at 250 K after addition of 5 ml heptane yields pure IV in the case of $\text{PZ}_3 = \text{P}(\text{OPr}^i)_3$, PPh_2Et , PPh_3 , $\text{P}(\text{NEt}_2)_2\text{Ph}$ and PR_3 ($\text{R} = \text{Me}$, Et , Pr^n , Bu^i), and mixtures of IV and II for PPr^i_3 and PBu^t_3 . $\text{CpV}(\text{NO})_2\text{PF}_3$ is obtained by bubbling a weak PF_3 stream for 1 hour through a solution of II.

All operations were carried out under nitrogen and in dried and oxygen-free solvents.

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