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TRANSITION METAL NITROSYLS AS NITROSYLATION AGENTS

II *. PHOTO-NITROSYLATION OF η^5-$C_5H_5V(CO)_3L$ (L = CO, PZ_3) BY $[Co(NO)_2Br]_2$

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Summary

η^5-$C_5H_5V(NO)_2CO$ is prepared in 40% yield by the photo-reaction between η^5-$C_5H_5V(CO)_4$ and $[Co(NO)_2Br]_2$. η^5-$C_5H_5V(NO)_2CO$ reacts by an S_N1 mechanism with various phosphines PZ_3 to yield η^5-$C_5H_5V(NO)_2PZ_3$. The phosphine complexes are also obtained by photo-induced ligand interchange between η^5-$C_5H_5V(CO)_3PZ_3$ and $[Co(NO)_2Br]_2$, or η^5-$C_5H_5V(CO)_4$ and $Co(NO)_2Br(PZ_3)$. In all cases, the main cobalt species formed is $Co(NO)(CO)_3$. 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 $\delta(^{51}V)$ (—1328 to —973 ppm rel. $VOCl_3$) decrease in the order $PF_3 > CO > P(OR)_3 > P(alkyl)_3 > PPh_3 > PPh(NEt_2)_2$, reflecting the decreasing π-acceptor ability of the ligands. $\delta(^{51}V)$ also decreases in the series of alkylphosphines PR_3 (R = Me, Et, Pr^n, Bu^i, Pr^i, 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 $Co(NO)(dmg)_2$ (dmg = dimethylglyoxime) [1], $Co(NO)(PPh_3)_3$ [2], and $[Co(NO)(NH_3)_5]^{2+}$ [3] have been employed mostly in nitrosylation reactions of transition metal complexes containing the Cl^- and phosphine ligands. Other transition metal nitrosyls, such as $Ru(NO)_2(PPh_3)_2$ [4] and $Rh(NO)(PPh_3)_3$ [2] react similarly, and there are at least two examples in the literature in which the transfer reagent and the substrate are identical

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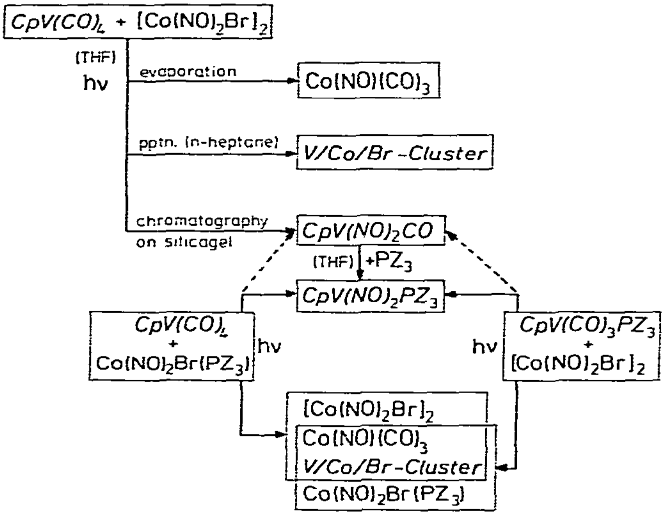
* See ref. 9 for communication I.

($[Fe(NO)CO(PPh_3)_2]^+$ [6] and $Co(NO)(tac)_2$ (tac = dithioacetylacetonate) [5]).

Photo-reaction of $Co(NO)(CO)_3$ in CH_2Br_2 has been reported by Seel to give $[Co(NO)_2Br]_2$ [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 $Cr(CO)_6$ to yield $Cr(NO)X_2(THF)_n$ (X = Cl, Br, I) and $Co(NO)(CO)_3$ [9]. Three ligands (X, CO, NO) are interchanged in this reaction. We have now investigated nitrosylation in the system $CpV(CO)_4/[Co(NO)_2Br]_2/PZ_3$.

Results and discussion

The results are summarized in Scheme 1. In the reaction between $CpV(CO)_4$ and $[Co(NO)_2Br]_2$, about 70% of the cobalt is converted into the volatile $Co(NO)(CO)_3$ (I). 40% of the vanadium can be recovered in the form of $CpV(NO)_2CO$ (II), while about 50% is incorperated in a vanadium-cobalt-bromine cluster (III) of unknown geometry (characteristic data are: V/Co/Br = 2.5/1/2; $\delta(^{51}V) = -509$ ppm rel. $VOCl_3$; $\delta(^{59}Co) = 3200$ ppm rel. $[Co(CN)_6]^{3-}$; IR: 1690 and 1582 cm^{-1}).



SCHEME 1

Complex II was previously prepared by direct nitrosylation of $CpV(CO)_4$, $[CpV(CO)_3CN]^-$, or $Cp_2V_2(CO)_7$ 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 $CpV(NO)_2PZ_3$ (IV). The average reaction time for almost complete removal of CO is 10 hours, except for PBu^t_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 $CpMn(CO)_3$ [12] and $CpV(CO)_4$ [13,14]. IR

TABLE 1

IR AND ^{51}V NMR DATA FOR $CpV(NO)_2L$ COMPLEXES ($L = CO, PZ_3$)

Ligand L	Cone Angle of L (°) [a]	ν(NO) [b] (cm^{-1})	$\delta(^{51}V)$ [c] (ppm)	^1J(VP) [d] (Hz)	$\Delta\nu_{1/2}$ [e] (Hz)
CO	ca 95	1725 1636 [f]	—1294	—	260
PF_3	106	1783	—1328	[g]	
$P(OMe)_2CH_2$- [h]	115	1692 1595	—1213	512	195
$P(OPr^i)_3$	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
$PPh(NEt_2)_2$	120	1686 1588	—1075	476	180
PMe_3	118	1685 1584	—1169	403	190
$P(Pr^n)_3$	132	1682 1582	—1160	409	135
$P(Bu^i)_3$	145	1683 1585	—1127	391	180
$P(Pr^i)_3$	160	1682 1584	—1115	402	150
$P(Bu^t)_3$	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] $\nu(CO) = 2048$ cm^{-1}. [g] Unresolved. [h] $CpV(NO)_2(MeO)_2PCH_2CH_2P(OMe)_2$.

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

$$PF_3 > P(OPr^i)_3 > PEt_3 > PPh_2Et > PPh_3 > PPh(NEt_2)_2 \qquad (A)$$

and

$$PMe_3 > P(Pr^n)_3 > P(Bu^i)_3 > P(Pr^i)_3 > P(Bu^t)_3 \qquad (B)$$

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 $CpV(CO)_3PZ_3$ and $[V(CO)_5PZ_3]^-$ 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 $CpV(CO)_3PZ_3$ [18]. It is of interest in this context that the (NO)V(NO) angles calculated from the relative intensities of the ν(NO) bands [20] are alike for PMe_3, PEt_3 and $P(Pr^n)_3$ (108°), while for the bulkier $P(Bu^i)_3$ and $P(Pr^i)_3$, for which the ^{51}V shielding attains smaller values, this angle amounts to 99° and 97°, respectively.

Experimental

1.90 g $CpV(CO)_4$ (8.3 mmol) and 1.62 g $[Co(NO)_2Br]_n$ (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 $CpV(CO)_4$ (2027 and 1917 cm^{-1}) and $[Co(NO)_2Br]_2$ (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 $CpV(CO)_4$ 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 × 2.5 cm; eluant: heptane (ca 1.5 l, elution time 2.5 hours)). The first, red fraction is $CpV(CO)_4$, 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 $PZ_3 = P(OPr^i)_3$, PPh_2Et, PPh_3, $P(NEt_2)_2Ph$ and PR_3 (R = Me, Et, Pr^n, Bu^i), and mixtures of IV and II for PPr^i_3 and PBu^t_3. $CpV(NO)_2PF_3$ 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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