(7) M. S. Wrighton, *Chem. Rev.*, **74**, 401 (1974).
(8) M. A. Mathur, W. H. Myers, H. H. Sisler, and G. E. Ryschkewitsch, *Inorg. Synth.*, **15**, 128 (1975).
(9) D. Evans, J. A. Osborn, and G. Wilkinson, *Inorg. Synth.*, **11**, 99 (1971).
(10) L. Vallarino, *J. Chem. Soc.*, 2287 (1957).
(11) G. M. Intille, *Inorg. Chem.*, **11**, 695 (1972).
(12) G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, **24**, 845 (1968).
(13) K. Takao, M. Wayaku, Y. Fujiwara, T. Imanaka, and S. Teranishi, *Bull. Chem. Soc. Jpn.*, **43**, 3898 (1970).
(14) G. W. Dudley, G. Read, and P. J. C Walker, *J. Chem. Soc., Dalton Trans.*, 1926 (1974).
(15) (a) J. P. Collman, M. Kubota, and J. W. Hosking, *J. Am. Chem. Soc.*, **89**, 4809 (1967); (b) J. E. Lyons and J. O. Turner, *J. Org. Chem.*, **37**, 2881 (1972).
(16) J. P. Birk, J. Halpern, and A. L. Pickard, *J. Am. Chem. Soc.*, **90**, 4491 (1968).
(17) G. L. Geoffroy, D. A. Denton, and C. W. Eigenbrot, Jr., *Inorg. Chem.*, **15**, 2310 (1976).
(18) R. Brady, B. R. Flynn, G. L. Geoffroy, H. B. Gray, J. Peone, Jr., and L. Vaska, *Inorg. Chem.*, **15**, 1485 (1976).
(19) G. L. Geoffroy, M. S. Wrighton, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **96**, 3105 (1974).
(20) G. Malouf and P. C. Ford, *J. Am. Chem. Soc.*, **96**, 601 (1974).

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Synthesis and Reactivity of Cationic Pentacoordinate Nitrosyl Complexes

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The syntheses of two new series of cationic pentacoordinate nitrosyl complexes of iridium and rhodium are described. Their physical properties and spectroscopic data are reported. The bonding modes of the nitrosyl ligand and the geometries around the metal are discussed in comparison with x-ray structures of known compounds and molecular orbital theories. The possibility that the nitrosyl ligand acts as an electron pair sink and pump by interconversion of the bonding modes is considered.

Introduction

There has been a great deal of interest in the synthesis,[1] structure,[2] bonding,[3] and reactivity[3] of pentacoordinate nitrosyl complexes. It is well known that nitric oxide coordinates to transition metal complexes in a linear or bent manner. From a structural point of view the linear arrangement has been viewed in terms of NO^+ and the bent arrangement in terms of NO^-. For the pentacoordinate species the predominant geometries are the square pyramid with a strongly bent apical nitrosyl and a triagonal bipyramid with a linear equatorial nitrosyl. Recently evidence has been reported for the existence of conformational equilibria between the two pentacoordinate forms of metal nitrosyls, whereby the coordination geometry about the metal changes as the metal and the nitrosyl undergo a formal redox reaction.[4] Further studies of these conformational equilibria are being carried out in our laboratories.[5] In this paper we report the synthesis and the characterization of some pentacoordinate cationic nitrosyl complexes of rhodium and iridium and their reactions with neutral ligands. The novel compounds obtained are consistent with (i) present theories of the stability and the geometries of the pentacoordinate nitrosyl complexes[3] and (ii) the capacity of the nitrosyl ligand to act as an electron sink or pump.[4-6]

Experimental Section

All the reactions and subsequent operations were performed in an atmosphere of nitrogen which had been purified by passing it down a column of R 3-11 BASF deoxygenating catalyst and then drying over molecular sieves. All solvents were deoxygenated prior to use and the transfers were carried out with the flexible needle technique or the syringe technique. Acetonitrile was purified as described by Coetzee et al.;[7] absolute ethanol was dried over 3 Å molecular sieves; reagent grade diethyl ether and hexane were purified by distillation from Na. All other chemicals and ligands used were readily available reagent grade chemicals and were used throughout. $RhCl_3 \cdot 3H_2O$ and $Na_2IrCl_6 \cdot 6H_2O$ were purchased from Johnson and Matthey Ltd. Infrared spectra were recorded with a Perkin-Elmer 180 (4000–180 cm^{-1}). The solid samples were run as KBr or CsI pellets. Conductivity measurements were carried out with a Jones 0.1-cm cell and a LKB 5300B Conductolyzer conductivity bridge. Proton NMR spectra were obtained using a Varian Associates XL-100 spectrometer with tetramethylsilane as internal standard. ^{31}P NMR spectra were recorded in 10-mm tubes using the Fourier transform technique at 40.5 MHz, employing a Varian XL-100 spectrometer. All spectra employed white-noise proton decoupling. ^{31}P chemical shifts are with respect to external 85% H_3PO_4, downfield shifts being negative. NMR samples were prepared by deoxygenating the solids and the solvents with argon separately and using the needle technique for mixing. The elemental analyses were determined by the Microanalysis Laboratory of the Istituto di Farmacia dell'Università di Pisa, Pisa, Italy.

The starting complexes $IrI_2(NO)(P(C_6H_5)_3)_2$ (**1a**) and $RhI_2(NO)(P(C_6H_5)_3)_2$ (**1b**) were prepared as described in the literature.[8,9]

Preparation of $(M(NO)(CH_3CN)_2(P(C_6H_5)_3)_2)(PF_6)_2$ (2a, M = Ir; 2b, M = Rh). To a suspension of 0.7 mmol of the appropriate iodide complex in 20 ml of acetonitrile was added 1.4 mmol of silver hexafluorophosphate in 10 ml of acetonitrile and the mixture was magnetically stirred at room temperature for 15 min. The silver iodide precipitate was removed by filtration in a Schlenk tube. The green solution was concentrated to a small volume under reduced pressure. Slow addition of a 20-ml syringe of ethanol led to the precipitation of the nitrile complexes **2** as green crystals. The precipitate was filtered, washed with ethanol and ether, and dried under vacuum: yield 70% **2a**, 85% **2b**. Anal. Calcd for (**2a**) $C_{40}H_{36}F_{12}IrN_3OP_4$: C, 42.94; H, 3.24; N, 3.75. Found: C, 43.01; H, 3.26; N, 3.70. Calcd for (**2b**) $C_{40}H_{36}F_{12}N_3OP_4Rh$: C, 46.66; H, 3.52; N, 4.08. Found: C, 46.80; H, 3.48; N, 4.10.

Preparation of $(Ir(NO)(N–N)(P(C_6H_5)_3)_2)(PF_6)_2$ (3a, N–N = 2,2′-Bipyridine; 4a, N–N = 1,10-Phenantroline). (i) To a suspension of 0.1 mmol of **2a** in 5 ml of ethanol was added the stoichiometric amount of the bidentate ligand in 2 ml of ethanol. The mixture was stirred under reflux for 10 min. After cooling the light brown precipitate was filtered, washed with ethanol and hexane, and dried under vacuum. The crude products were recrystallized from methylene chloride–ethanol to give light brown microcrystals (quantitative yield).

(ii) The same complexes can be obtained in low yields from **1a** in ethanol by reaction with a stoichiometric amount of ligand in ethanol and fourfold excess of ammonium hexafluorophosphate in ethanol. The mixture was stirred at room temperature for 7 days. The light brown precipitate was filtered, washed with ethanol and hexane, and dried under vacuum.

(iii) The same complexes can be obtained in quantitative yield from **5** by reaction with a stoichiometric amount of ligand in ethanol solution in the presence of perchloric acid. Anal. Calcd for (**3a**) $C_{46}H_{38}F_{12}IrN_3OP_4$: C, 46.31; H, 3.20; N, 3.52. Found: C, 45.80; H, 3.26; N, 3.51. Calcd for (**4a**) $C_{48}H_{38}F_{12}IrN_3OP_4$: C, 47.50; H, 3.12; N, 3.45. Found: C, 48.00; H, 3.10; N, 3.49.

Preparation of $(Rh(NO)(N–N)(P(C_6H_5)_3)_2)(PF_6)_2$ (3b, N–N = 2,2′-Bipyridine; 4b, N–N = 1,10-Phenantroline). (i) These compounds were prepared from **2b** using the analogous procedure described above for the iridium analogues except that the reactions were carried out

Table I. Physical Data of Nitrosyl Complexes

	Compd	ν(NO),[a] cm^{-1}	Other freq[a] ν, cm^{-1}	NMR data	Λ_M,[b] Ω^{-1} cm^2 mol^{-1}
(**1a**)	$IrI_2(NO)(P(C_6H_5)_3)_2$	1560 vs			
(**1b**)	$RhI_2(NO)(P(C_6H_5)_3)_2$	1630 vs			
(**2a**)	$Ir(NO)(CH_3CN)_2(P(C_6H_5)_3)_2{}^{2+}$	1540 s	2285 w (C≡N)	τ (H) 7.8 (6, methyl),[c] ^{31}P 13.27 ppm $P(C_6H_5)$[d]	178.0
(**2b**)	$Rh(NO)(CH_3CN)_2(P(C_6H_5)_3)_2{}^{2+}$	1730 vs	2310 w (C≡N)	τ (H) 7.9 (6, methyl),[c] ^{31}P 22.39 ppm $P(C_6H_5)$,[d] $^1J_{Rh-P} = 97$ Hz	187.5
(**3a**)	$Ir(NO)(bpy)(P(C_6H_5)_3)_2{}^{2+}$	1790 vs			197.3
(**3b**)	$Rh(NO)(bpy)(P(C_6H_5)_3)_2{}^{2+}$	1820 vs			167.5
(**4a**)	$Ir(NO)(o\text{-phen})(P(C_6H_5)_3)_2{}^{2+}$	1805 vs			195.9
(**4b**)	$Rh(NO)(o\text{-phen})(P(C_6H_5)_3)_2{}^{2+}$	1830 vs			175.1
(**5**)	$Ir(OH)(NO)(P(C_6H_5)_3)_2{}^{+}$	1850 vs	3545 m (OH)		90.6
(**6**)	$Ir(NO)(P(C_6H_5)_3)_3$	1600 s			
(**7**)	$Ir(NO)(P(p\text{-}ClC_6H_4)_3)_3$	1627 s			
(**8**)	$Ir(NO)(P(p\text{-}FC_6H_4)_3)_3$	1617 s			
	CH_3CN		2255 (C≡N)[e]		

[a] KBr pellets. [b] In CH_3NO_2 at 25 °C. [c] In CD_3NO_2, tetramethylsilane as internal standard. [d] In CH_3CN, 85% H_3PO_4 as external standard. [e] See ref 13.

at room temperature. The crude products were recrystallized from methylene chloride–ethanol to give light brown microcrystals (quantitative yield).

(ii) The analogous complexes can be obtained from **1b** in low yield using the same procedure of the iridium analogues (ii). Anal. Calcd for (**3b**) $C_{46}H_{38}F_{12}N_3OP_4Rh$: C, 50.02; H, 3.44; N, 3.80. Found: C, 50.51; H, 3.42; N, 3.85. Calcd for (**4b**) $C_{48}H_{38}F_{12}N_3OP_4Rh$: C, 51.12; H, 3.39; N, 3.72. Found C, 50.50; H, 3.41; N, 3.90.

Preparation of $(M(OH)(NO)(P(C_6H_5)_3)_2)(PF_6)$ (5, M = Ir). A suspension of 0.1 mmol of **2a** in 10 ml of aqueous (95%) ethanol was refluxed for 5 min. After cooling the orange crystals of **5** were removed by filtration, washed with ethanol and hexane, and dried under vacuum. Anal. Calcd for (**5**) $C_{36}H_{31}F_6IrNO_2P_3$: C, 47.6; H, 3.45; N, 1.55. Found: C, 47.5; H, 3.50; N, 1.60.

Preparation of $M(NO)(P(C_6H_5)_3)_3$ (6, M = Ir). (i) To a suspension of 0.1 mmol of **2a** in 10 ml of ethanol 1 mmol of triphenylphosphine was added. The mixture was refluxed for 20 min. After cooling orange crystals precipitated and were recrystalizated from benzene–ethanol, washed with ethanol and hexane, and dried under vacuum (yield 65%).

(ii) The same complex could be obtained from **5** by reaction with an excess of triphenylphosphine (1:10 ratio) in ethanol. Anal. Calcd for (**6**) $C_{54}H_{45}IrNOP_3$: C, 64.15; H, 4.58; N, 1.38. Found: C, 63.68; H, 4.50; N, 1.40.

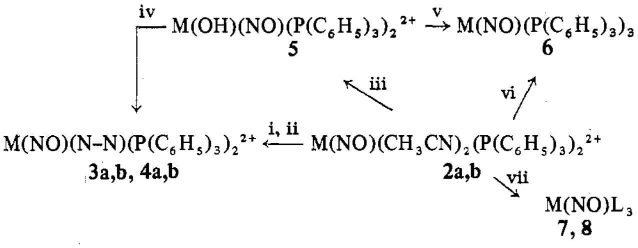
Preparation of $M(NO)L_3$ (7, M = Ir, L = $P(p\text{-}ClC_6H_4)_3$; 8, M = Ir, L = $P(p\text{-}FC_6H_4)_3$). To a suspension of 1.0 mmol of **2a** in 10 ml of ethanol 1 mmol of the appropriate triarylphosphine has been added. The mixture was refluxed for 1 h. After cooling the crude orange product was crystallized from methylene chloride–ethanol, washed with ethanol and hexane, and dried under vacuum: yield 70% **7**, 60% **8**. Anal. Calcd for (**7**) $C_{54}H_{36}Cl_9IrNOP_3$: C, 49.20; H, 2.75; N, 1.06; Cl, 24.20. Found: C, 49.13; H, 2.71; N, 1.06; Cl, 24.80. Calcd for (**8**) $C_{54}H_{36}F_9IrNOP_3$: C, 55.39, H, 3.07; N, 1.19; F, 13.47. Found: C, 56.09; H, 3.13; N, 1.22; F, 13.41.

Results and Discussion

Acetonitrile suspensions of the complexes $MI_2(NO)(P(C_6H_5)_3)_2$, (**1a**, M = Ir; **1b**, M = Rh) react almost instantly with a stoichiometric quantity of AgX (X = PF_6^-, ClO_4^-) in acetonitrile solution to give the green crystalline cationic compounds $(M(NO)(CH_3CN)_2(P(C_6H_5)_3)_2)X_2$ (**2a**, M = Ir, **2b**, M = Rh) in high yield.

$$\begin{array}{l} \mathrm{MI_2(NO)(P(C_6H_5)_3)_2 + 2AgX} \\ \quad \mathbf{1a}, \mathrm{M = Ir} \\ \quad \mathbf{b}, \mathrm{M = Rh} \\ \xrightarrow{\mathrm{CH_3CN}} \mathrm{(M(NO)(CH_3CN)_2(P(C_6H_5)_3)_2)X_2 + 2AgI} \\ \qquad\qquad \mathbf{2a}, \mathrm{M = Ir} \\ \qquad\qquad \mathbf{b}, \mathrm{M = Rh} \\ \qquad\qquad \mathrm{X = PF_6^-, ClO_4^-} \end{array}$$

Scheme I. Flow Diagram Illustrating Preparations and Reactions of Cationic Nitrosyl Complexes[a]



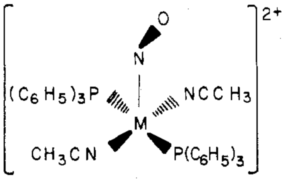
[a] i = N-N, C_2H_5OH; ii = N-N, $(C_2H_5)_2O$; iii = H_2O, C_2H_5OH; iv = N-N, H^+, C_2H_5OH; v, vi = $P(C_6H_5)_3$(ex), C_2H_5OH; vii = L(ex), C_2H_5OH. Anion PF_6^- is not shown.

The rhodium complex **2b** has been recently synthesized by Connelly et al. using a different procedure.[10] Our method seems to be generally applicable for the synthesis of cationic nitrosyl complexes containing both phosphine and two molecules of coordinating solvent in which the reaction is carried out.

Cationic rhodium complexes with two molecules of pyridine or benzonitrile have been prepared. The reactivity of the acetonitrile derivatives has been tested with a variety of reagents and has led to several novel nitrosyl complexes as shown in Scheme I.

Physical properties, selected infrared stretching frequencies, conductivity data, and NMR data for the parent complexes and their derivatives are reported in Table I.

For the cationic complexes **2** the stereochemistry around the metal can be easily established. Their proton NMR spectra in CD_3NO_2 solution exhibit a singlet for the methyl group resonance of the methyl cyanide ligands (**2a**, τ = 7.8; **2b**, τ = 7.9) and an unresolved phenyl proton resonance (τ = 2.40). The integration ratio of the methyl protons with the phenyl multiplet was found to be the expected 1:5 for the two complexes. The ^{31}P NMR spectrum of **2a** in CH_3CN at 25 °C consists of a singlet at +13.27 ppm. The ^{31}P NMR spectrum of **2b** in CH_3CN at 25 °C consists of a doublet centered at about −22.39 ppm ($^1J_{Rh-P}$ = 97 Hz). The proton and phosphorous NMR spectra reported here indicate chemical equivalence of the two phosphines and of the two acetonitrile ligands in solution. The infrared spectra, recorded as KBr pellets, show a medium weak band in the 2300-cm^{-1} region attributable to a ν(CN) stretching frequency (**2a**, 2285 cm^{-1}; **2b**, 2310 cm^{-1}) and a strong band in the region attributable to a ν(NO) stretching frequency (**2a**, 1540 cm^{-1}; **2b**, 1730 cm^{-1}). In all the cases, the ν(C≡N) band appears at higher frequency than for the ligand indicative of σ bonding through nitrogen.[11,12] Molecular orbital studies have attributed this increase primarily to an increased CN force constant. As suggested by Ford et al.[13] back-donation from the metal reduces the value of $\Delta\nu(C{\equiv}N)$ (defined as $\nu(C{\equiv}N)_{complex} - \nu(C{\equiv}N)_{free\ ligand}$) and negative values have been found for the cases where back-donation is large. Negative values can also be observed in instances when the nitrile is bonded to the metal by the π electrons, but complexes of this type are rare[14] and some are known to rearrange to the N-bonded form.[15] In the polar solvent nitromethane complexes **2a** and **2b** exibit conductances characteristic of 1:2 electrolytes[16] (**2a**, 178 Ω^{-1} cm^2 mol^{-1}; **2b**, 178.5 Ω^{-1} cm^2 mol^{-1}). The combination of all these results leads us to conclude that the dications **2a** and **2b** are five coordinate and may have square-pyramid geometry with a strongly bent axial nitrosyl with basal trans phosphine, trans nitrile ligands.



2a, M = Ir
b, M = Rh

It is noteworthy to remember that square-pyramidal geometries have been determined for the parent dihalide complexes by x-ray structures.[17,18] Though the two limiting forms of the nitrosyl group cannot be unequivocally distinguished on the basis of the ν(NO) frequencies for both limiting bond types, the nitrosyl stretching frequency of the bicationic rhodium complexes **2b** is not at unusually high energy to exclude a bent NO$^-$ coordination mode. For the monocationic complexes $IrCl(NO)(CO)(P(C_6H_5)_3)_2^+$ (ref 19), $IrI(NO)(CO)(P(C_6H_5)_3)_2^+$ (ref 20), and $RuCl(NO)_2(P(C_6H_5)_3)_2^+$ (ref 21), for which the geometries have been determined by x-ray structure, the axial bent nitrosyl stretching frequencies have been found at 1680, 1720, and 1687 cm^{-1}, respectively. The iridium complex **2a** seems to be less sensitive to the positive charge and the nitrosyl stretching frequency moves to lower energy than in the parent complex **1a**.

We have studied the reactivity of the cationic nitrosyl complexes with a variety of reagents.

During several reactions of the dications **2** the nitrosyl ligand is lost as in the cases of reaction with basic trialkylphosphines, secondary alkylphosphines, diphosphines, diarsines, phosphites, and dienes. These reactions are much more complicated than simple substitution of the coordinated nitric oxide ligand. The stoichiometry of these reactions has yet to be established although phosphine oxide appears to be present in the reaction mixtures. Further research is being conducted on the role played by the nitric oxide in these reactions and will be published separately. The reactions of the cationic nitrosyls **2a** and **2b** which take place without elimination of the nitric oxide ligand are more interesting. Collman et al.[4,6] have viewed the nitrosyl ligand as an electron pair sink and pump by interconversion of its bonding mode. It must be noted that a variation in the nitrosyl bonding mode would be expected to be accompanied by a conformational change in the coordination geometry, to reflect the implied change in the metal oxidation state.[9,22,23] Recent theoretical studies done have led to the following conclusions for pentacoordinate nitrosyls:[3] (i) the presence of several π accepting ligands favors a trigonal geometry with a linear nitrosyl group in the equatorial position, (ii) in a square pyramid the better the σ- or π-donating capability of the basal ligands the more likely is the nitrosyl to bend in the plane of the poorer donors (better acceptors). As was pointed out above the parent complexes **1a** and **1b** have square-pyramidal geometries[17,18] and for analogy we have suggested square-pyramidal geometry for the cationic nitrosyl complexes **2a** and **2b** on the basis of ir and NMR data. Reaction of **2a** with excess triphenylphosphine in dry ethanol produces the well known d^{10} complex $Ir(NO)(P(C_6H_5)_3)_3$ (**6**) for which a linear nitrosyl has been determined by the x-ray method.[24] The stoichiometry of the reaction has not yet been established. However, it can be suggested that the reduction of the iridium atom is due to the change of the nitrosyl bonding mode associated with the oxidation of a phosphine molecule. Phosphine oxide is always present in the reaction mixture. When the complex **2a** is gently refluxed in 95% ethanol the d^8 Roper's[22] hydroxo complex $Ir(OH)(NO)(P(C_6H_5)_3)_2^+$ (**5**) with a linear NO group is obtained. **5** reacts further with triphenylphosphine to give **6** and phosphine oxide.

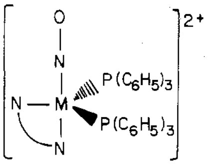
Electron-withdrawing substituted triarylphosphines tris(4-fluorophenylphosphine) and tris(4-chlorophenylphosphine) react with **2a** to give the new compounds $Ir(NO)L_3$ (**7**, L = $P(p\text{-}FC_6H_4)_3$; **8**, L = $P(p\text{-}ClC_6H_4)_3$). Phosphine oxide is always present in the reaction mixtures. For these complexes a tetrahedral geometry can by predicted by analogy with the triphenylphosphine isoelectronic complex.[9]

The cationic nitrosyl complexes **2a** and **2b** react, in alcohol or ether solution, with 2,2′-bipyridine (bpy) and 1,10-phenanthroline (*o*-phen) to give the pentacoordinate cationic nitrosyl complexes **3a**, **4a**, **3b**, and **4b**. These complexes can be obtained in low yields and with very long reaction times from the diiodide complexes **1** by reaction with the ligands in the presence of an excess of ammonium hexafluorophosphate.

In the case of iridium the complexes can also be obtained by reaction of the hydroxo complex **5** with the appropriate ligand in ethanolic solution in the presence of perchloric acid.

In the polar solvent nitromethane the complexes **3** and **4** exhibit a conductance characteristic of 1:2 electrolytes (see Table I). The infrared spectra of the complexes **3a** and **4a** show nitrosyl stretching frequency bands at 1790 cm^{-1} and 1820 cm^{-1}, respectively, which are about 250 wavenumbers higher than in the parent complex **2a**. For the rhodium complexes **3b** and **4b** the nitrosyl stretching frequencies are about 100 wavenumbers higher than in the complex **2b**. This dramatic change of ν(NO) must be the consequence of an interconversion of the nitrosyl bonding mode. The possible formation of the iridium complexes from the hydroxo compound **5** is a support of the linear bonding mode of the nitrosyl ligand in complexes **3a** and **4a**.

For the complexes **3** and **4** the most reasonable geometry around the metal is that sketched below.



3a, M = Ir; N-N = 2,2′-bipyridine
b, M = Rh; N-N = 2,2′-bipyridine
4a, M = Ir; N-N = 1,10-phenanthroline
b, M = Rh; N-N = 1,10-phenanthroline

This is a trigonal bipyramid with the metal in the d^8 configuration, the nitrosyl linearly bonded in axial position, and the bidentate ligands in the equatorial-axial position. The bite angles of the phenanthroline and bipyridine ligands with large metals such as those of the group 8[25] are certainly less than 90°. Consequently they cannot possibly occupy the equatorial position of a trigonal bipyramid.[26]

Thus the NO group is forced into the axial position of a trigonal bipyramid since it will be very difficult for the two triphenylphosphine ligands to occupy cis positions in the basal plane of a square pyramid because of unfavorably close ligand–ligand contacts. The lower yield and the longer reaction times found in the formation of **3** and **4** starting from the diiodide **1** are probably due to the lower halide scavenging capacity of the ammonium ions with respect to the silver ion. In all the reactions described above the behavior of the nitrosyl ligand is noteworthy. The net result of forcing the rhodium and iridium complexes to have trigonal-bipyramidal geometry with an axial nitrosyl group is a reduction of the central metal **2** (d^6) → **3**, **4** (d^8) due to interconversion of nitrosyl bonding mode. The further reduction to d^{10} configuration in the triphenylphosphine case can be due as pointed out above to the reducing power of the phosphine itself.

In these reactions the nitrosyl ligand is acting as an electron sink, as suggested by Collman et al.[4,6] Those observations further support the hypothesis that the higher reactivity of the nitrosyl complexes in comparison to the carbonyl analogues is probably due to the ambivalent character of the nitrosyl ligand.

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Registry No. 1a, 25544-86-9; **1b**, 40241-25-6; **2a**, 59983-15-2; **2b**, 60018-66-8; **3a**, 59983-17-4; **3b**, 59983-19-6; **4a**, 59983-21-0; **4b**, 59983-23-2; **5**, 42712-02-7; **6**, 25448-15-1; **7**, 59983-24-3; **8**, 59982-92-2.

References and Notes

(1) K. G. Caulton, *Coord. Chem. Rev.*, **14**, 317 (1975); N. G. Connelly, *Inorg. Chim. Acta, Rev.*, **6**, 48 (1972).

(2) B. A. Frenz and J. A. Ibers, *MTP Int. Rev. Sci.: Phys. Chem., Ser. One*, **11**, 33 (1972); J. A. McGinnety, *ibid.*, **5**, 229 (1972).

(3) C. G. Pierpont and R. Eisenberg, *J. Am. Chem. Soc.*, **93**, 4905 (1971); D. M. P. Mingos, *Inorg. Chem.*, **12**, 1209 (1973); J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974), and references therein; R. Hoffmann, M. L. Chen, M. Elian, A. R. Rossi, and D. M. P. Mingos, *Inorg. Chem.*, **13**, 2666 (1974), and references therein.

(4) J. P. Collman, P. Farnham, and G. Dolcetti, *J. Am. Chem. Soc.*, **93**, 1788 (1971); C. P. Brock, J. P. Collman, G. Dolcetti, P. H. Farnham, J. A. Ibers, J. E. Lester, and C. A. Reed, *Inorg. Chem.*, **12**, 1304 (1973).

(5) G. Dolcetti, M. Ghedini, and B. Giovannitti, to be published.

(6) J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Am. Chem. Soc.*, **91**, 5659 (1969).

(7) J. P. Coetzee and G. R. Padmanabhan, *J. Phys. Chem.*, **66**, 1708 (1962).

(8) C. A. Reed and W. R. Roper, *J. Chem. Soc. A*, 3054 (1970).

(9) G. Dolcetti, N. W. Hoffman, and J. P. Collman, *Inorg. Chim. Acta*, **6**, 531 (1972).

(10) N. G. Connelly, M. Green, and T. A. Kuc, *J. Chem. Soc., Chem. Commun.*, 542 (1974).

(11) H. C. Clark and K. J. Reimer, *Inorg. Chem.*, **14**, 2133 (1975); R. A. Walton, *Q. Rev., Chem. Soc.*, **19**, 126 (1965).

(12) K. F. Purcell and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 919 (1966).

(13) R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 227 (1970).

(14) H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **10**, 2699 (1971).

(15) M. F. Farona and K. F. Kraus, *Inorg. Chem.*, **9**, 1700 (1970); *J. Chem. Soc., Chem. Commun.*, 513 (1972).

(16) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

(17) S. Z. Goldberg, C. Kubiak, C. D. Meyer, and R. Eisenberg, *Inorg. Chem.*, **14**, 1650 (1975).

(18) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10** 1035 (1971).

(19) D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Am. Chem. Soc.*, **90**, 4486 (1968); D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968).

(20) D. J. Hodgson and J. A Ibers, *Inorg. Chem.*, **8**, 1282 (1969).

(21) C. G. Pierpont, D. G. Van Derveer, W. Durant, and R. Eisenberg, *J. Am. Chem. Soc.*, **92**, 4760 (1970); C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **11**, 1088 (1972).

(22) C. A. Reed and W. R. Roper, *J. Chem. Soc., Dalton Trans.*, 1014 (1973).

(23) R. Eisenberg and C. D. Meyer, *Acc. Chem. Res.*, **8**, 26 (1975).

(24) V. Albano, P. Bellon, and M. Sansoni, *J. Chem. Soc. A*, 2420 (1971).

(25) C. J. Neitzel and R. Desiderato, *Cryst. Struct. Commun.*, **4**, 333 (1975); B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, **11**, 1109 (1972); L. F. Power, *Inorg. Nucl. Chem. Lett.*, **6**, 791 (1970).

(26) B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, **14**, 2610 (1975).

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Rapid Equilibration of the Ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetatoaquochromate(III) Complex with Chromate(VI), Molybdate(VI), Tungstate(VI), and Azide. Labilization of the Aquo Ligand by the Free Carboxylate and Substitution at Chromium(III)

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Equilibration kinetic studies on the rapid complexation of ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetatoaquochromate(III), $Cr(EDTA)H_2O^-$, with chromate(VI), molybdate(VI), and tungstate(VI) have been carried out using the stopped-flow method at 25 °C, pH in the range 7.3–8.7, and $I = 1.0$ M ($LiClO_4$). Replacement of the coordinated H_2O

$$Cr(EDTA)H_2O^- + X^{n-} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Cr(EDTA)X^{(n+1)-} + H_2O \qquad (i)$$

which is labilized by the free carboxylate arm of the EDTA is observed. Temperature-jump and stopped-flow studies of (i) with X^{n-} = azide have also been carried out at pH 4.3–5.4 and pH 7.38, respectively. The hydrogen ion dependence of k_f is in all cases given by $k_1 + k_2[H^+]$, where k_2 makes ≤25% contributions with molybdate(VI) and azide and ≤10% with chromate(VI) and tungstate(VI). Rate constants k_1 ($M^{-1}\ s^{-1}$) are 3.2 ± 0.2 (CrO_4^{2-}), 21 ± 2 (MoO_4^{2-}), 27 ± 4 (WO_4^{2-}), and 98 ± 5 (N_3^-). Kinetic equilibrium constants $K_1 = k_f/k_b$ are in good agreement with those obtained spectrophotometrically.

It has been shown previously that the Cr(III)–EDTA complex is quinquedentate and contains a coordinated H_2O.[1] Unlike the case of the Co(III) analogue there is no evidence for a sexadentate EDTA complex.[2] Thus samples of $Cr(EDTA)H_2O^-$ retain the coordinated H_2O when left in a desiccator in vacuo over P_2O_5 for 7 days or when kept at ca. 100°C for 1 day.[3] Evidence for the free carboxylate group has been obtained from ir spectroscopy.[4] The complex can also be titrated with base to yield two acid dissociation constants; see (1) and (2) (EDTA = Y^{4-}). At 18 °C, pK_{a1} = 2.27, and pK_{a2} = 7.41, $I = 0.15$ M.[5] Whereas chromium(III) is normally inert to substitution and there is a vast

$$Cr(YH)H_2O \overset{K_{a1}}{\rightleftharpoons} Cr(Y)H_2O^- + H^+ \qquad (1)$$

$$Cr(Y)H_2O^- \overset{K_{a2}}{\rightleftharpoons} Cr(Y)OH^{2-} + H^+ \qquad (2)$$