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Reductive Nitrosylation of Group VIIIb Compounds[1]

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Nitric oxide in the presence of base and alcohol is shown to function as a reducing agent and nitrosylating agent toward $FeCl_2$ and $CoCl_2$. The reaction products are alkyl nitrite and an equilibrium mixture of $[M(NO)_2Cl]_2$ and $M(NO)_2Cl_2^-$. Addition of potential ligands either before or after reductive nitrosylation yields salts of formula $Co(NO)_2L_2^+$ where L = $P(C_6H_5)_3$, $^1/_2(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$, or $^1/_2(CH_3)_2N(CH_2)_2N(CH_3)_2$; $Fe(NO)_2Cl_2^-$ reacts with $P(C_6H_5)_3$ to yield $Fe(NO)_2(P(C_6H_5)_3)Cl$ and $Fe(NO)_2(P(C_6H_5)_3)_2$. Evidence is presented supporting the idea that the reaction proceeds by nucleophilic attack by alcohol or alkoxide on coordinated NO.

Introduction

Despite the formal similarity between transition metal complexes of nitric oxide and carbon monoxide, some interesting differences exist. Foremost among these is the existence of "bent" metal nitrosyls.[3] In contrast to CO, nitric oxide may function as an oxidizing agent toward metals as well as phosphine ligands. Some hint of the exceptional versatility of NO as a redox reagent is provided by the report that methemoglobin (Fe^{3+}) and hemoglobin (Fe^{2+}) both react with nitric oxide to yield the same nitrosylhemoglobin.[4] Similar observations have been made on cytochrome *c*.[5] Reduction by nitric oxide was postulated but the fate of NO^+ was not determined.

$$(\text{heme FeNO})^{3+} \rightarrow (\text{heme Fe})^{2+} + NO^+$$

It is generally true that stoichiometry with respect to NO has rarely been investigated. Thus, the preparation, from Co(II), of salts containing $Co(NO)_2L_2^+$ has been reported[6] with no mention of the stoichiometry or other nitrogenous products.

In an attempt to prepare the *N,N,N',N'*-tetramethylethylenediamine (TMEDA) analog of the ethylenediamine (en) nitrosyl complex, $Co(en)_2(NO)Cl_2$, it was found that the infrared spectrum of the deep green solution (*vs.* the expected red color) contained not one but two stretches in the region of 2000-1600 cm^{-1}, characteristic of nitrosyl compounds. We present here an investigation of this reaction, which provides the first definitive evidence for NO functioning as a reducing and nitrosylating agent.[1b]

Experimental Section

Materials and Analysis. All reactions and subsequent work-ups were performed in an atmosphere of prepurified nitrogen in Schlenk glassware. Methanol was distilled from $Mg(OCH_3)_2$, while absolute ethanol was dried over 3A molecular sieves. Ethyl ether and hexane were distilled from Na-K alloy. Triethylamine was distilled from KOH and TMEDA from BaO. Anhydrous cobalt(II) chloride was prepared by heating the commercial hexahydrate under vacuum at 60-80° for 10-16 hr.[7] Anhydrous iron(III) chloride and nickel(II) chloride were prepared using thionyl chloride,[8] while iron(II) chloride was prepared from $FeCl_3$ and chlorobenzene.[9] NO (Matheson) was purified by passing the gas through a −78° trap. All other reagents were used as received.

Authentic samples were prepared as referenced. The elemental analyses were determined by Huffman Microanalytical Laboratories, Wheatridge, Colo., and Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Infrared spectra were measured on a Perkin-Elmer 137-G grating spectrophotometer. Mass spectra were measured on an AEI Model MS-9 high-resolution mass spectrometer.

A. Stoichiometric Measurements. Measurements of gas uptake and evolution were determined in a glass vacuum system, using standard vacuum techniques. In a typical determination, reagents, except NO, were charged in a reaction flask. The solution (25 ml of alcohol) was degassed to a pressure of less than 10^{-2} mm at −196° using the freeze–thaw method. The measured quantity of NO was condensed into the reaction flask; upon warming, the reaction started as the solvent melted. Initial reaction pressures were approximately 1 atm. After 20–24 hr of reaction time, unreacted NO and the volatile products were removed from the solvent and purified *via* trap-to-trap separation prior to measurement. The nonvolatile products were removed from the vacuum system and handled under nitrogen in Schlenk glassware. Identity and purity of volatile components were established using infrared and mass spectra. Characterization of methyl and ethyl nitrite[10] included exact mass determinations (calculated (found)): for $CH_3O_2{}^{14}N$, 61.0164 (61.0156); for $C_2H_5O_2{}^{14}N$, 75.0320 (75.0312). The results are summarized in Table I.

B. Reactions with Excess NO. The purified NO was bubbled through the reaction solution in a three-neck flask equipped with a reflux condenser. When NO uptake was complete and prior to any subsequent addition of reagents, dissolved NO was removed by degassing.

1. $Co(NO)_2TMEDA^+X^-$. (a) From Excess TMEDA. TMEDA (3.6 ml, 24.0 mmol) was slowly added to a solution of 12.0 mmol of $CoCl_2$ in 75 ml of methanol. After NO was passed through the solution for 8 hr, 9.0 g of $NaB(C_6H_5)_4$ (26.0 mmol) dissolved in 50 ml of methanol was added to the deep green solution. The precipitate was filtered, washed with methanol, and dried under vacuum. Recrystallization from dichloromethane–ethanol yielded a mixture of black and white crystals. The black crystals of $Co(NO)_2TMEDAB(C_6H_5)_4$ (6.12 g) were obtained by Soxhlet extraction with methanol. *Anal.* Calcd for $C_{30}H_{36}BCoN_4O_2$: C, 64.98; H, 6.55; Co, 10.63; N, 10.11. Found: C, 64.98; H, 6.68; Co, 10.43; N, 9.99. The filtrate from the methanol extraction, upon cooling, yielded white crystals of *N,N,N',N'*-tetramethylethylenediammonium tetraphenylborate ($HTMEDAB(C_6H_5)_4$). *Anal.* Calcd for $C_{28}H_{27}BN_2$: C, 83.58; H, 6.78; N, 6.96. Found: C, 81.38; H, 8.64; N, 6.45. Reducing the amount of TMEDA to 12.0 mmol halved the yield. $Co(NO)_2TMEDAPF_6$[11] was isolated as small brown-green crystals, when KPF_6 was added to the reaction solution. *Anal.* Calcd for $C_6H_{12}CoF_6N_4O_2P$: C, 18.21; H, 4.25; N, 14.74. Found: C, 18.96; H, 4.43; N, 13.16.

(b) From Triethylamine. Triethylamine (1.7 ml, 12.0 mmol) was added to a solution of 12.0 mmol of $CoCl_2$ and 12.0 mmol of TMEDA in 75 ml of methanol. $Co(NO)_2TMEDAB(C_6H_5)_4$ (5.17 g) was isolated as in (a) above. *Anal.* Found: Co, 10.61. Triethylammonium tetraphenylborate ($HNEt_3B(C_6H_5)_4$) was also isolated; mp 172–175° (lit. mp[12] 172–174°). *Anal.* Calcd for $C_{30}H_{36}BN$: C, 85.49; H, 8.62; N, 3.28. Found: C, 84.64; H, 8.56; N, 3.28.

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(1) (a) Presented in part at the American Chemical Society Division of Inorganic Chemistry Summer Symposium on Coordination and Activation of Small Molecules by Transition Metals, Buffalo, N. Y., June 19-21, 1972. (b) See D. Gwost and K. G. Caulton, *J. Chem. Soc., Chem. Commun.*, 64 (1973).

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(7) The above-mentioned reagents may be used without purification but with a reduction in yield, especially for $(Co(NO)_2Cl)_2$.

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Table I. Stoichiometric Measurements of Reductive Nitrosylation

Amt, mmol							
Initial				Final			
Metal	Ligand	Base	NO	RONO[a]	Complex[b] (yield,[c] %)	Unreacted NO	% recovery of N (all forms)
4.0 (Co)	4.0 (TMEDA)	4.0 (NEt_3)	12.0	4.1	2.5 (65[d])	0.7	82
4.0 (Co)	2.2 (TMEDA)	2.2 (TMEDA)	12.0	2.8	2.1 (79[e])	4.0	80
3.1 (Co)	3.2 (TMEDA)	3.1 ($NaOCH_3$)	9.3	3.0	1.9 (65)	0.6	92
4.0 (Co)		4.3 (NEt_3)	12.0	2.7	0.7 (55)	4.3	82
4.0 (Co)		8.7 (NEt_3)	12.0	3.3	1.0 (65)	2.8	84
4.0 (Co)		20.0 (NEt_3)	12.0	3.6	2.4[f] (73)	2.2	88
4.0 (Co)	8.0 ($P(C_6H_5)_3$)	4.3 (NEt_3)	12.0	0.6	0.8[g] (7)	4.3[h]	94
4.5 (Fe)		4.6 (NEt_3)	13.6	1.6		6.6	
5.1 (Ni)		5.1 (NEt_3)	15.3	0.7[i]	0.0 (0)	14.0	>96
		4.0 (NEt_3)	12.0	Trace		11.9	99
		6.0 (diphos)	12.0			5.9[h]	98

[a] Includes trace amounts of N_2O (infrared). [b] Recrystallized or sublimed dinitrosyl complex. [c] Based on NO consumed. [d] 3.9 mmol of $HNEt_3B(C_6H_5)_4$ also isolated. [e] 95% yield based on amount of TMEDA able to function as ligand (*cf.* Table II). [f] Isolated as $Co(NO)_2(P(C_6H_5)_3)_2B(C_6H_5)_4$; 4.0 mmol of $HNEt_3B(C_6H_5)_4$ also isolated. [g] 0.5 mmol of $Co(P(C_6H_5)_3)_2Cl_2NO$ and 3.7 mmol of $HNEt_3B(C_6H_5)_4$ also isolated. [h] N_2O from $R_3P + 2NO \rightarrow R_3PO + N_2O$. [i] Mixture of CH_3ONO and N_2O.

(c) **From Sodium Methoxide.** A solution of 14.0 mmol of TMEDA and 14.0 mmol of $CoCl_2$ (or $CoTMEDACl_2$[13]) in 75 ml of methanol was added to 0.756 g of $NaOCH_3$ (14.0 mmol). The slurry immediately darkened upon exposure to NO. After NO was bubbled through the reaction mixture for 10 hr, the solution was filtered and a 50% excess of $NaB(C_6H_5)_4$ (7.2 g) was added. Recrystallization from dichloromethane–ethanol yielded 4.46 g of black crystals.

2. $Co(NO)_2(P(C_6H_5)_3)_2B(C_6H_5)_4$. (a) Triethylamine (1.7 ml, 12.0 mmol) was added to a blue slurry of 6.3 g of $P(C_6H_5)_3$ (24.0 mmol) and 12.0 mmol of $CoCl_2$ (or $Co(P(C_6H_5)_3)_2Cl_2$[14]) in 75 ml of ethanol. Initial reaction with NO resulted in a green solution and brown solid. After NO was bubbled through the reaction mixture for 8.5 hr, no solid was found on filtration. A solution of 9.0 g of $NaB(C_6H_5)_4$ (24.0 mmol) in 50 ml of ethanol was added to give a brown precipitate. The solid was washed with ethanol, water, and ethanol. Extraction with chloroform yielded a brown filtrate, which was taken to dryness and recrystallized from chloroform–methanol–ethyl ether to yield 1.21 g of $Co(NO)_2(P(C_6H_5)_3)_2B(C_6H_5)_4$[15] as brown crystals. *Anal.* Calcd for $C_{60}H_{50}BCoN_2O_2P_2$: C, 74.84; H, 5.24; Co, 6.12; N, 2.91. Found: C, 74.29; H, 5.22; Co, 6.33; N, 2.73. $HNEt_3B(C_6H_5)_4$ (4.33 g, 10.3 mmol) was isolated from the white residue of the chloroform extraction by recrystallization from acetone–methanol–water.

(b) When NO was bubbled through a solution of $CoCl_2$ and triethylamine, but with no $P(C_6H_5)_3$ present, a red-brown solution was formed (*i.e.*, $(Co(NO)_2Cl)_2$; see below). Addition of 7.0 g of $P(C_6H_5)_3$ (27.0 mmol) and $NaB(C_6H_5)_4$ as before results in 3.65 g of $Co(NO)_2(P(C_6H_5)_3)_2B(C_6H_5)_4$ (32% yield).

3. $CoNO(P(C_6H_5)_3)_2Cl_2$. Reaction of $CoCl_2$, $P(C_6H_5)_3$, and NEt_3 in 75 ml of ethanol in a 1:2:1 molar ratio with NO for 15 min resulted in the formation of a brown solid, as mentioned previously. The infrared spectrum of the dried solid (KBr pellet) showed bands at 1728 (m) and 1638 (s) cm^{-1}, characteristic of $Co(NO)(P(C_6H_5)_3)_2Cl_2$.[16] *Anal.* Calcd for $C_{36}H_{30}Cl_2CoNOP_2$: C, 63.17; H, 4.43; Cl, 10.37; N, 2.04. Found: C, 57.07; H, 4.50; Cl, 10.74; N, 2.04.

4. $Co(NO)_2diphosB(C_6H_5)_4$. Triethylamine (1.7 ml, 12.0 mmol) was added to a green slurry of 7.79 g (12.0 mmol) of 1,2-bis(diphenylphosphino)ethane (diphos) and 12.0 mmol of $CoCl_2$ in 75 ml of ethanol. After NO was bubbled through the slurry for 6 hr, 2.67 g of $[(Co(NO)_2Cl)_2diphos]$[15] was filtered off as a brown powder (3.8 mmol). *Anal.* Calcd for $C_{26}H_{24}Cl_2Co_2N_4O_4P_2$: C, 44.15; H, 3.43; Cl, 10.02; N, 7.92. Found: C, 44.54; H, 3.80; Cl, 10.40; N, 7.82. Infrared spectrum (KBr pellet): ν_{NO} 1812 (s) and 1748 (vs) cm^{-1}. $NaB(C_6H_5)_4$ (9.0 g) in 50 ml of ethanol was added to the filtrate. The resulting orange solid was filtered, washed with ethanol, and extracted with chloroform. Methanol was added to the concentrated solution to yield 2.05 g of $Co(NO)_2diphosB(C_6H_5)_4$[15] (2.4 mmol) as orange plates. *Anal.* Calcd for $C_{50}H_{44}BCoN_2O_2P_2$: C, 71.77; H, 5.31; Co, 7.04; N, 3.35. Found: C, 69.98; H, 5.48; Co, 6.96; N, 3.19. When the $NaB(C_6H_5)_4$ solution was added with no filtration, 5.75 g of $Co(NO)_2diphosB(C_6H_5)_4$ and 3.02 g of $HNEt_3B(C_6H_5)_4$ (7.2 mmol) were isolated.

5. $(Co(NO)_2Cl)_2$. (a) **From Triethylamine.** Triethylamine (1.7 ml, 12.0 mmol) was added to a blue solution of 12.0 mmol of $CoCl_2$ in 75 ml of methanol, resulting in a pink solution. Exposure to NO immediately darkened the reaction mixture. After NO was passed through the solution for 10 hr, the red-black solution was concentrated under vacuum to give a dark green oil. Attempts to sublime $[Co(NO)_2Cl]_2$ from this oil resulted in decomposition. The oil was extracted with 50 ml of ethyl ether for 12 hr and filtered. The blue-green solid was washed with ether until the washings were colorless. The infrared spectrum (KBr pellet) of the blue-green solid showed no peaks in the 2000–1600-cm^{-1} region. The ether from the extraction and washings was removed under vacuum to give black crystals. Sublimation under vacuum (10^{-1} mm) at 50–70° resulted in the isolation of 0.47 g of $(Co(NO)_2Cl)_2$[17] (25% yield). Mol wt for $Co_2N_4O_4{}^{35}Cl_2$: calcd, 307.7962; found, 307.7997. When 8.3 ml of triethylamine was used (5:1 molar ratio to $CoCl_2$), 0.76 g of black crystals was obtained.

(b) **From Triethylamine in Methanol-Ethyl Ether.** NO was bubbled through a solution of 4.0 mmol of $CoCl_2$ and 4.0 mmol of triethylamine in 10 ml of methanol and 50 ml of ethyl ether for 14.5 hr. The reaction solution was filtered and cooled to −10° for 12 hr. The green solution darkened and small white crystals of $HNEt_3Cl$ (infrared) formed and were filtered. Removing the solvent from the filtrate under vacuum and subliming the residue resulted in the sublimation of a small amount of black crystals.

(c) **From Sodium Methoxide.** The addition of 10.4 mmol of $CoCl_2$ in 75 ml of methanol to 0.564 g of $NaOCH_3$ (10.4 mmol) formed a pink solid.[18] After NO was bubbled through the slurry for 11 hr, 0.33 g of $(Co(NO)_2Cl)_2$ was isolated as in (a) above.

6. $Fe(NO)_2Cl_2HNEt_3$. (a) Triethylamine (1.37 ml, 9.85 mmol) was added to a solution of 1.25 g of $FeCl_2$ (9.85 mmol) in 75 ml of methanol; a white precipitate formed immediately. When exposed to NO the solution immediately darkened; after 9 hr of bubbling NO, the solution was deep red. An infrared spectrum of the degassed reaction solution showed peaks at 1780 (s), 1711 (vs) cm^{-1} (methanol reference). After filtration, the solution was concentrated under vacuum to give a red oil, which could not be solidified or sublimed under vacuum without decomposition. There was no change in the infrared spectrum on removal of the solvent. Attempts to precipitate the $Fe(NO)_2Cl_2^-$ anion with tetraphenylarsonium chloride or benzyltriphenylphosphonium chloride in methanol or acetone also failed.

(b) When NO was bubbled through a methanol solution of $FeCl_2$ with no triethylamine, the solution turned dark green and gas uptake was complete in 1 hr. This solution (methanol reference) showed only one peak (1802 cm^{-1})[19] in the region from 2000 to 1600 cm^{-1}.

(c) To a filtered solution of $Fe(NO)_2Cl_2^-$ (12.3 mmol of $FeCl_2$), 3.23 g of $P(C_6H_5)_3$ (12.3 mmol) in 50 ml of ethanol was added dropwise. After 15 min of stirring, a sample of the deep purple crystals

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Table II. Nitrosyl Complexes Formed *via* Reductive Nitrosylation

Complex	Base	Yield,[a] %	Appearance	ν_{NO}, cm^{-1}
$Co(NO)_2(TMEDA)B(C_6H_5)_4$	TMEDA	94	Black crystals	1869, 1792[b]
	NEt_3	79		
	$NaOCH_3$	58		
$Co(NO)_2(TMEDA)PF_6$	TMEDA	63	Green crystals	1876, 1818[b]
$Co(NO)_2(P(C_6H_5)_3)_2B(C_6H_5)_4$	NEt_3	10	Brown crystals	1855, 1795[b]
$Co(NO)_2(diphos)B(C_6H_5)_4$	NEt_3	58	Orange plates	1838, 1789[b]
$(Co(NO)_2Cl)_2$	NEt_3	41	Black crystals	1866, 1792[c]
	$NaOCH_3$	20		
$Fe(NO)_2Cl_2HNEt_3$	NEt_3		Red oil	1779, 1706[d]

[a] Yield of recrystallized or sublimed product. [b] KBr disk. [c] Nujol mull. [d] Neat sample.

of $Fe(NO)_2(P(C_6H_5)_3)Cl$[20] was withdrawn from the solution, filtered, washed with ethanol, and dried. *Anal.* Calcd for $C_{18}H_{15}ClFeN_2O_2P$: C, 52.27; H, 3.66; Cl, 8.57; N, 6.77. Found: C, 52.78; H, 3.71; Cl, 8.68; N, 6.98 [ν_{NO} 1786, 1724 cm^{-1} (KBr disk)].

An additional 6.46 g of $P(C_6H_5)_3$ (24.6 mmol) in 60 ml of ethanol was added as a slurry to the reaction mixture. After 24 hr of stirring, filtration yielded 4.06 g of $Fe(NO)_2(P(C_6H_5)_3)_2$ (6.34 mmol, 52% yield based on $FeCl_2$) as yellow-brown crystals. *Anal.* Calcd for $C_{36}H_{30}FeN_2O_2P_2$: C, 67.51; H, 4.73; Fe, 8.72; N, 4.37. Found: C, 67.43; H, 4.77; Fe, 8.90; N, 4.39 [ν_{NO} 1712, 1667 cm^{-1} (KBr disk)].

7. **Attempted Preparation of $(Ni(NO)Cl)_x$.**[20] Triethylamine (2.1 ml, 15.7 mmol) was added to a solution of 1.93 g of $NiCl_2$ (14.8 mmol) in 90 ml of methanol to yield a slightly cloudy, green solution. After NO was bubbled through the solution for 9 hr, the solution was still green, but clear. Infrared spectra of the degassed reaction solution (methanol reference) and the solid residue (Nujol mull), remaining after removing the solvent under vacuum, showed no absorption in the region 2000–1600 cm^{-1}.

8. **Attempted Preparation of $Rh(P(C_6H_5)_3)_3NO$.**[21] Triethylamine (0.05 ml, 0.4 mmol) was added to a slurry of 0.37 g of $Rh(P(C_6H_5)_3)_3Cl$[22] in 20 ml of methanol. After NO was bubbled through the solution for 12 hr, a tan solid was isolated and dried. The infrared spectrum (KBr pellet) of the solid showed no band at 1610 cm^{-1}, characteristic of $Rh(P(C_6H_5)_3)_3NO$.

9. **Attempted Preparation of $Co(NO)(DMG)_2$.**[23] $Co(DMG)_2(P(C_6H_5)_3)Cl$[24] (1.10 g, 2.0 mmol), DMG = dimethylglyoximate monoanion, was slurried in 100 ml of methanol. Addition of 0.3 ml of NEt_3 caused no color change. NO was passed through this solution for 1.5 hr. The infrared spectrum of the filtered solid was identical with that of $CoCl(DMG)_2(P(C_6H_5)_3)$; there were no absorptions indicative of coordinated NO or $(C_6H_5)_3PO$.

10. **$Co(TMEDA)Cl_2$.** The addition of 4.0 mmol of TMEDA to a blue solution of 4.0 mmol of $CoCl_2$ in 10 ml of methanol resulted in the formation of an intensely blue solution. The blue compound $Co(TMEDA)Cl_2$[13] was isolated by filtration after the addition of ethyl ether and hexane. *Anal.* Calcd for $C_6H_{16}Cl_2CoN_2$: C, 28.81; H, 6.57; Cl, 28.81; Co, 23.95. Found: C, 28.83; H, 6.34; Cl, 28.59; Co, 23.67. The addition of a second 4.0-mmol portion of TMEDA (2:1 molar ratio of TMEDA:Co) caused no additional color change. Again, $Co(TMEDA)Cl_2$ was isolated. *Anal.* Found: C, 28.29; H, 6.5.

11. **Reaction of Triethylamine and Alcohol.** A 1.5-g sample of $NaB(C_6H_5)_4$ (4.4 mmol) was added to a solution of 0.6 ml of triethylamine (4.3 mmol) in 25 ml of ethanol. No precipitate was formed. An infrared spectrum (KBr pellet) of the solid residue, formed after removing the ethanol under vacuum, was identical with that of $NaB(C_6H_5)_4$.

Results

Passage of NO through a solution of $CoCl_2$ and TMEDA (1:2 molar ratio) in anhydrous methanol yields a solution of the cation $Co(NO)_2TMEDA^+$, which can be quantitatively precipitated as its PF_6^- or $B(C_6H_5)_4^-$ salt. Trap-to-trap fractionation of the volatiles after the reaction is complete yields 1 mol of methyl nitrite for every 3 mol of NO consumed. The $Co(NO)_2TMEDA^+$ cation is isolated in agreement with the reaction

$$CoCl_2 + 2TMEDA + 3NO \xrightarrow[CH_3OH]{(1)\ \text{room temp}} \xrightarrow{(2)\ NaB(C_6H_5)_4} Co(NO)_2(TMEDA)B(C_6H_5)_4 + CH_3ONO + H(TMEDA)^+B(C_6H_5)_4^- + 2NaCl \quad (1)$$

The monoammonium salt of TMEDA, $H(TMEDA)^+B(C_6H_5)_4^-$, has been isolated as a reaction product. Other proton acceptors (B) function equally well, the general reaction being

$$CoCl_2 + L\text{-}L + B \xrightarrow[ROH]{\text{room temp}} Co(NO)_2(L\text{-}L)^+Cl^- + RONO + B\cdot HCl \quad (2)$$

where L-L = TMEDA, diphos, or $2P(C_6H_5)_3$, and B = TMEDA, NEt_3, or $NaOCH_3$ (Table II). When triethylamine functions as the base, a stoichiometric amount of triethylammonium salt is isolated. Amine oxides, nitrite salts, or other oxides of nitrogen are not found after completion of the reaction. Yields for the reactions done at atmospheric pressure and at reduced pressure are virtually the same (Tables I and II).

$Co(NO)_2(L\text{-}L)^+$ Complexes. The yield of recrystallized $Co(NO)_2TMEDA^+$ is quantitative when TMEDA is also the proton acceptor; if triethylamine is the base, yields are reduced due to difficulty in separating the triethylammonium salt from the dinitrosyl complex. The yields of phosphine-dinitrosyl complexes are low due to the oxidation of phosphine to phosphine oxide. Uncoordinated diphos is oxidized by NO (Table I) with quantiative formation of nitrous oxide. Oxidation of coordinated phosphine by NO has not yet been demonstrated; therefore, phosphine dissociation may occur, either in the starting material

$$CoCl_2(P(C_6H_5)_3)_2 \rightleftarrows CoCl_2(P(C_6H_5)_3) + P(C_6H_5)_3$$

or in the product[15]

$$Co(NO)_2(P(C_6H_5)_3)_2^+ + Cl^- \rightleftarrows Co(NO)_2(P(C_6H_5)_3)Cl + P(C_6H_5)_3$$

The improved yield of $Co(NO)_2diphos^+$ may reflect tighter binding of the chelate ligand. However infrared evidence for an oxide of diphos in this reaction and the isolation of $[(Co(NO)_2Cl)_2diphos]$, where diphos functions as a bridging ligand, indicates that diphos also is susceptible to oxidation *via* partial dissociation. Improved yields of phosphine-dinitrosyl complexes can be achieved by addition of the phosphine ligand to the reaction solution of Co(II) and base only after the reaction with NO is complete (see Experimental Section).

In addition to oxidation of phosphines by NO, alkyl nitrites are known[25] to oxidize phosphines to phosphine oxides. This is demonstrated in the less-than-stoichiometric yield of ethyl nitrite (0.6 mmol) to metal complex (0.8

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Table III. Infrared Study of $(Co(NO)_2Cl)_2 + 2HNEt_3Cl \rightleftarrows 2Co(NO)_2Cl_2HNEt$

Sample	ν_{NO}, cm^{-1}	ν_{NO}, cm^{-1}, for $(Co(NO)_2Cl)_2$ [a]	Ref compd and ν_{NO}, cm^{-1}
Reaction mixture (dilute in CH_3OH)	1845, 1754	1842, 1757	
Reaction mixture (concd in CH_3OH)	1835, 1748, 1704		
Green oil (Nujol)	1833, 1745	1866, 1792	$Co(NO)_2Br_2NEt_4$ [a] 1826, 1742
Green oil, redissolved (dilute in CH_3OH)	1839, 1758	1842, 1757	
Green oil, dissolved (dilute in $CHCl_3$)	1848, 1764	1866, 1795	$Co(NO)_2Cl_2P(C_6H_5)_4$ [a] 1835, 1750 $Co(NO)_2Br_2NEt_4$ [a] 1840, 1760

[a] Authentic sample[17] in specified solvent.

mmol) and the high yield of isolated $HNEt_3B(C_6H_5)_4$. The triethylammonium salt is not formed from the reaction of amine and alcohol even in the presence of NO. A high yield of $HNEt_3B(C_6H_5)_4$, when compared to the amount of dinitrosyl complex formed, may also be explained by NO functioning as a reducing agent without subsequent nitrosylation.

$$M^q + NO + B + ROH \rightarrow M^{q-1} + BH^+ + RONO$$

The reaction of Ni(II) with base and NO (Table I) results in the formation of a small amount of alkyl nitrite, but there is no infrared evidence for nitrosylation of the metal. The simple reductive ability of NO is now being investigated.

$(Co(NO)_2Cl)_2$ and $Fe(NO)_2Cl_2^-$. In the absence of potential ligands, $(Co(NO)_2Cl)_2$ can be isolated from the reaction of Co(II) and triethylamine or sodium methoxide with NO.[26] Infrared evidence presented in Table III shows that, as the red-brown reaction solution is concentrated, the nitrosyl frequencies shift to lower energies and become more complicated. This is consistent with the formation[17] of $Co(NO)_2Cl_2^-$.

$$[Co(NO)_2Cl]_2 + 2Cl^- \rightleftarrows 2Co(NO)_2Cl_2^-$$

The green oil, formed after all the solvent has been removed, redissolves in methanol to form a red-brown solution of the dimer; however in chloroform the green oil dissolves to form a green solution. The infrared spectrum of the chloroform solution exhibits nitrosyl frequencies shifted to lower energies than those for $(Co(NO)_2Cl)_2$ ($\Delta\nu_{NO} = 18$, 31 cm^{-1}) in the same solvent. These values are similar to those for other $Co(NO)_2Cl_2^-$ salts. Attempts to precipitate salts of $Co(NO)_2Cl_2^-$ from the green chloroform solution result in darkening of the solution and the formation of solid decomposition products whose infrared spectrum contains no absorptions characteristic of a nitrosyl complex. The equilibrium between the dinitrosyl dimer and dichloride anion is further demonstrated when the dimer is prepared in the mixed solvent methanol-ethyl ether. When the green reaction solution of the anion is cooled, the solution becomes black and triethylammonium chloride precipitates; the dimer can be isolated from the black solution.

The dinitrosyl dimer is best separated from the green oil containing the anion by extracting the oil with ethyl ether, filtering away the ammonium salt, and subliming the black residue of the filtrate. Although the yield of alkyl nitrite increases with an increase in the concentration of the base (Table I), the yield of dimer is limited by the physical process of extraction and isolation. However, if other ligands (*e.g.*, triphenylphosphine) are added to the reaction solution to form the cationic dinitrosyl, the yield of isolated dinitrosyl compound is improved. Thus, the addition of 2 mol of triphenylphosphine per mole of Co(II) taken initially increases the yield of dinitrosyl compound from 25% ($(Co(NO)_2Cl)_2$) to 32% ($(Co(NO)_2(P(C_6H_5)_3)_2{}^+)$).

Reductive nitrosylation of $FeCl_2$ yields a solution exhibiting only two NO stretching frequencies; these are unchanged as the solution is concentrated. These frequencies are similar to those of $[Fe(NO)_2Cl]_2$ (ν_{NO} 1826, 1764 cm^{-1}) and $Fe(NO)_2(CN)_2^-$ (ν_{NO} 1808, 1730 cm^{-1})[27] and are consistent with those of $Fe(NO)_2(CN)_2^-$ considering that CN^- is a better π acid than Cl^-. This suggests that bridge splitting of the iron dimer

$$[Fe(NO)_2Cl]_2 + 2Cl^- \rightleftarrows 2Fe(NO)_2Cl_2^-$$

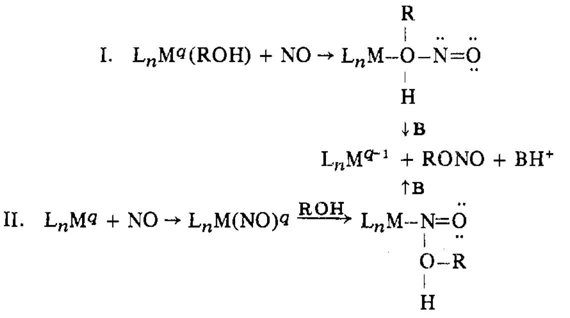
is more favorable than in the cobalt analog. Although it is not possible to isolate the $Fe(NO)_2Cl_2^-$ anion from the reaction mixture, the formulation $Fe(NO)_2Cl_2HNEt_3$ is made on the basis of infrared data, isolation of alkyl nitrite, and the similar nitrosyl chemistry of Co(II) and Fe(II).[20] Reaction of $Fe(NO)_2Cl_2^-$ with 1 mole of $P(C_6H_5)_3$ yields $Fe(NO)_2(P(C_6H_5)_3)Cl$, while additional $P(C_6H_5)_3$ effects reduction to $Fe(NO)_2(P(C_6H_5)_3)_2$.[28] The oxidized form of $P(C_6H_5)_3$ is

$$Fe(NO)_2Cl_2^- + P(C_6H_5)_3 \rightarrow Fe(NO)_2(P(C_6H_5)_3)Cl + Cl^- \xrightarrow{2P(C_6H_5)_3} Fe(NO)_2(P(C_6H_5)_3)_2 + (C_6H_5)_3PO$$

isolated as triphenylphosphine oxide ($(C_6H_5)_3PO$).

Discussion

Formally, reductive nitrosylation involves a one-electron oxidation of NO followed by nitrosylation of the reduced metal species. Oxidation of NO is reasonable based on the low ionization potential of NO, 9.26 eV.[29] Oxidation of NO is probably intimately associated with coordination to the metal, but two mechanisms must be considered, *i.e.*, (L = other ligands)



$$\text{I.}\quad L_nM^q(ROH) + NO \rightarrow L_nM\text{—}\overset{\overset{\textstyle R}{|}}{\underset{\underset{\textstyle H}{|}}{O}}\text{—}N{=}O \xrightarrow{B} L_nM^{q-1} + RONO + BH^+$$

$$\text{II.}\quad L_nM^q + NO \rightarrow L_nM(NO)^q \xrightarrow{ROH} L_nM\text{—}\underset{\underset{\underset{\textstyle H}{|}}{\textstyle O\text{—}R}}{|}{N}{=}O \xrightarrow{B} L_nM^{q-1} + RONO + BH^+$$

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Path I involves electrophilic attack by NO on coordinated alcohol, while path II involves nucleophilic attack by alcohol (or alkoxide) on coordinated NO. Path II is analogous to the well-studied[30] reductive carbonylation of metal salts in basic solutions

$$M^q + CO + 2OH^- \rightarrow M^{q-2} + CO_2 + H_2O$$

and requires the formation of a nitrosyl complex by the oxidized form of the metal.

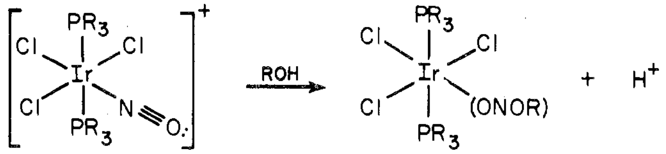
We find that an alcoholic solution of Fe(II), in the absence of base, forms a mononitrosyl complex, $Fe(NO)(MeOH)_xCl_y{}^{2-y}$, consistent with path II.[31] Addition of base to this solution, followed by further treatment with NO, is an alternative route to $Fe(NO)_2Cl_2{}^-$. Isolation of $CoNOCl_2(P(C_6H_5)_3)_2$ early in the reductive nitrosylation of $CoCl_2(P(C_6H_5)_3)_2$, coupled with the fact that this mononitrosyl is consumed as $Co(NO)_2(P(C_6H_5)_3)_2{}^+$ is formed, is also consistent with path II. The failure of NO or amine to react with an alcoholic solution of $NiCl_2$ to give the known cluster $[Ni(NO)Cl]_x$ suggests that only path II is operative; Ni(II) has no demonstrated affinity for NO. Reductive nitrosylation is not observed with $Rh(P(C_6H_5)_3)_3Cl$ and $Co(DMG)_2(P(C_6H_5)_3)Cl$

$$Rh(P(C_6H_5)_3)_3Cl + 2NO + ROH + B \nrightarrow Rh(P(C_6H_5)_3)_3NO + BH^+Cl^- + RONO$$

$$Co(DMG)_2(P(C_6H_5)_3)Cl + 2NO + ROH + B \nrightarrow Co(NO)(DMG)_2 + BH^+Cl^- + RONO$$

$Rh(P(C_6H_5)_3)_3Cl$ is two electrons short of saturation (NO being a three-electron donor), while $Co(DMG)_2(P(C_6H_5)_3)Cl$ is coordinatively saturated and kinetically inert.

Although nucleophilic attack on coordinated CO is a well-known reaction, the reactivity of coordinated NO has only recently come under investigation. Hydroxide attacks NO in linear nitrosyl complexes,[32] while alcohols react with the relatively electropositive (ν_{NO} 1925 cm^{-1}) nitrosyl nitrogen of $IrCl_3(PR_3)_2NO^+$ to yield isolable alkyl nitrite complexes[33]



Class A *vs.* B Compounds. The reactions of an alcoholic solution of Co(II) and various ligands (L) in a 1:4 molar ratio with NO have been reported[6] to give two classes of compounds depending on the ligand: "class A" compounds of general formula $CoL_4(NO)X_2$ and "class B" compounds of general formula $CoL_2(NO)_2X$. Thus when L = 1/2en, $Co(en)_2NO(ClO_4)_2$ is formed while L = aniline yields to $Co(aniline)_2(NO)_2(ClO_4)$. No explanation was offered for this anomalous behavior.

The work reported here shows that class B ligands allow NO to act as a stoichiometric one-electron reducing agent, with the oxidized form of NO, the alkyl nitrite, separable from the metal. Class A ligands yield complexes where there is at best an intramolecular redox reaction. This disparate behavior depends on the coordinating ability of the particular ligand. Class A ligands (aziridine, en, pyridine, *o*-phenylenediamine) form six-coordinate complexes with Co(II). Thus, $Co(en)_2(NO)Cl_2$ has been made from a complex claimed to be $Co(en)_2Cl_2$.[34] Equilibrium constant measurements[35] suggest the existence of substantial quantities of $Co(en)_n{}^{2+}$ (n = 2, 3) even for low ratios of total [en] to [Co^{2+}]. Likewise, in the cobalt-pyridine system, the major component is the six-coordinate complex.[36]

The only isolable complexes of $CoCl_2$ with class B ligands are four-coordinate.[37] For example, when TMEDA is treated with $CoCl_2$ even in a molar ratio of 2:1, only four-coordinate $Co(TMEDA)Cl_2$ is isolated. The formation of the coordinatively unsaturated four-coordinated species facilitates initial coordination of NO as a three-electron ligand. A linear M-NO geometry, with a more electropositive nitrogen than in bent[38] $Co(en)_2NOCl^+$, is more susceptible to nucleophilic attack by alcohol or alkoxide; this is characteristic of path II, above. In contrast to the reductive nitrosylation of mononitrosyls with class B ligands (*e.g.*, $CoCl_2(P(C_6H_5)_3)_2NO$), $Co(en)_2(NO)Cl_2$ reacts with excess NO in an oxidative manner to yield $Co(en)_2(NO_2)Cl_2$.[39]

Conclusion. On the basis of the work reported here, the formation of nitrosylhemoglobin from methemoglobin must stand as an example of reductive nitrosylation in aqueous solution (NO^+ reacting with water to form HNO_2). More recently it was reported[40] that NO reduces $MoCl_5$ and $MoOCl_3$ in aprotic solvents; nitrosyl chloride was identified as the oxidized form of NO. Thus the ability of NO to function as a reducing agent toward transition metals has clearly been established.

Similarly, the oxidized form of NO, the nitrosonium ion (NO^+), has been shown to be an oxidizing agent toward certain transition metal complexes. For example, ferrocene is oxidized to ferricinium ion without nitrosylation[41]

$$Fe(C_5H_5)_2 + NO^+ \rightarrow Fe(C_5H_5)_2{}^+ + NO$$

The reductive ability of NO, coupled with the oxidative capacity of NO^+, establishes a potentially important synthetic method

$$M^q + NO \rightleftarrows (MNO)^q \rightleftarrows M^{q-1} + NO^+$$

Registry No. $Co(NO)_2TMEDA[B(C_6H_5)_4]$, 40804-51-1; $Co(NO)_2(P(C_6H_5)_3)_2[B(C_6H_5)_4]$, 24507-62-8; $Co(NO)(P(C_6H_5)_3)_2Cl_2$, 41150-63-4; $[(Co(NO)_2Cl)_2diphos]$, 15672-42-1; $Co(NO)_2diphos[B(C_6H_5)_4]$, 24533-59-3; $(Co(NO)_2Cl)_2$, 39302-64-2; $Fe(NO)_2P(C_6H_5)_3Cl$, 40813-55-6; $Fe(NO)_2(P(C_6H_5)_3)_2$, 14056-98-5; $Co(TMEDA)Cl_2$, 15380-92-4; $Co(NO)_2(TMEDA)PF_6$, 40813-80-7; $Fe(NO)_2Cl_2HNEt_3$, 40813-56-7; $Co(NO)_2Cl_2HNEt_3$, 40804-54-4.

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