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SYNTHESIS, CHARACTERIZATION AND REACTIONS OF TERTIARY PHOSPHINE COMPLEXES OF COBALT DERIVATIVES OF NITROGEN OXIDES

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SYNTHESIS, CHARACTERIZATION AND REACTIONS OF TERTIARY PHOSPHINE COMPLEXES OF COBALT DERIVATIVES OF NITROGEN OXIDES

by

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GRADUATE COLLEGE

As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Clemente Diogenes Vallenilla

entitled Synthesis, Characterization and Reactions of Tertiary Phosphine Complexes of Cobalt Derivatives of Nitrogen Oxides

and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

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SIGNED: 

Dedicated to my family and friends

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ABSTRACT

$Co(NO)(NO_2)_2L_2$ complexes (L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, PEt_3, PEt_2Ph, $PEtPh_2$, $PPrPh_2$, PBu_3 and 1/2DPPPr) were prepared from the reactions of $Co(NO)X_2L_2$ (X = Cl, Br) with sodium nitrite in methanol freshly distilled from magnesium methoxide. The complexes were characterized by elemental analyses, 15-N labeling, infrared and NMR spectroscopy. The crystal structure of $Co(NO)(NO_2)_2(PMePh_2)_2$ was determined by X-ray diffraction. The cobalt atom has tetragonal pyramidal geometry. The nitrosyl group in the axial position is strongly bent. The NO_2 ligands have two different ligating geometries: one is bound to cobalt through the nitrogen atom and the other is bidentate forming an asymmetric four membered ring. The phosphine ligands are equivalent and trans to each other.

Multinuclear NMR spectroscopy (^{1}H, ^{31}P, ^{15}N and ^{14}N) was used to determine the solution structure of $Co(NO)(NO_2)_2L_2$ complexes, to study mono and bisnitrosyls of cobalt, to establish some correlations between NMR parameters and structural characteristics of these complexes and to follow their reactions in solution.

Reactions of $Co(NO)(NO_2)_2L_2$ with CO, NO and RCOX were observed to produce $Co(NO)_2XL$ complexes. Since the structure may be indicative of electronic requirements at the metal center as well as the reactivity of the compounds, the crystal structures of $Co(NO)_2Cl(PPh_3)$ and $Co(NO)_2(ONO)(PPh_3)$ were also determined. In these complexes the cobalt

atoms have pseudotetrahedral geometry. The CoNO angles are in the range considered to be linear. They are geniculated in an "atracto" conformation.

$Co(NO)(NO_2)_2L_2$ and $Co(NO)_2(ONO)L$ complexes react with oxygen in the solid state or in solution to form $Co(NO_3)_2(OL)_2$ complexes. When the reactions with O_2 were carried out in the presence of an excess of olefins, the formation of nitrates is inhibited $Co(NO_2)_2(OL)_2$ and olefin oxides are formed instead. The crystal structures of $Co(NO_3)_2(OPMePh_2)_2$ and $Co(NO_2)_2(OPMePh_2)_2$ were determined by X-ray diffraction. In these complexes, the NO_3 and NO_2 groups are bidentate. They are arranged in a cis configuration around the cobalt atom.

CHAPTER 1

INTRODUCTION

The role of transition metals and their complexes has become increasingly important in chemistry, especially in the field of catalysis. In particular, considerable interest in the reactions and catalytic activity of NO_x complexes has been generated by their unique structural and electronic properties.[1-5] A great variety of reactions are catalyzed by transition metal NO_x complexes.[6-10] For this reason, a new series of compounds containing these ligands which offer potential uses and/or applications has been prepared and characterized.

The interconvertibility of NO_x ligands has been observed in different transition metal systems. Intramolecular conversion of a nitrosyl ligand into a nitro group occurs in cis-nitro-nitrosylbisdithiocarbamato iron via a simple oxygen atom transfer.[11] Reaction of $Ni(NO_2)_2L_2$ (L = Tertiary phosphine) with CO produces $Ni(NO)(NO_2)L_2$ and CO_2. This process involves an intermediate step in which an oxygen atom is transferred from the $-NO_2$ ligand to the CO molecule.[12-14] Nitrosyl ligands can also be converted into coordinated nitro groups by reacting them with molecular oxygen.[15-17] Formation of coordinated nitrate has been observed only in a few ruthenium compounds and one cobaloxime complex.[18-20]

One of the most extensive studies of the reactions of nitrosyl with oxygen has been carried out by Clarkson and Basolo,[15] who principally studied complexes of the general type Co(L)NO, where L is a quadridentate dinegative Schiff base ligand or two bidentate dialkyldithiocarbamate ligands. In the presence of monodentate ligands B, such as pyridine and tri-n-butyl-phosphine, the reaction of Co(L)NO with oxygen produces $BCo(L)NOO_2$ species that react with another BCo(L)NO molecule to form $BCo(L)NO_2$ complexes. These reactions can be represented by the following sequence:

$$CoL_4NO + B \underset{\text{fast}}{\rightleftharpoons} BCoL_4NO$$

$$BCoL_4NO + O_2 \xrightarrow[\text{slow}]{} BCoL_4N\begin{matrix}O\\ \diagdown\\ O-O\end{matrix}$$

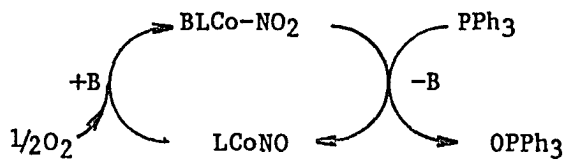
$$BCoL_4N\begin{matrix}O\\ \diagdown\\ O-O\end{matrix} + BCoL_4NO \longrightarrow BCoL_4-N\begin{matrix}O\\ \diagdown\\ O-O\end{matrix}\begin{matrix}O\\ \diagup\\ N-CoL_4B\end{matrix}$$

$$BCoL_4N\begin{matrix}O\\ \diagdown\\ O-O\end{matrix}\begin{matrix}O\\ \diagup\\ N-CoL_4B\end{matrix} \xrightarrow{\text{fast}} 2CoL_4(NO_2)B$$

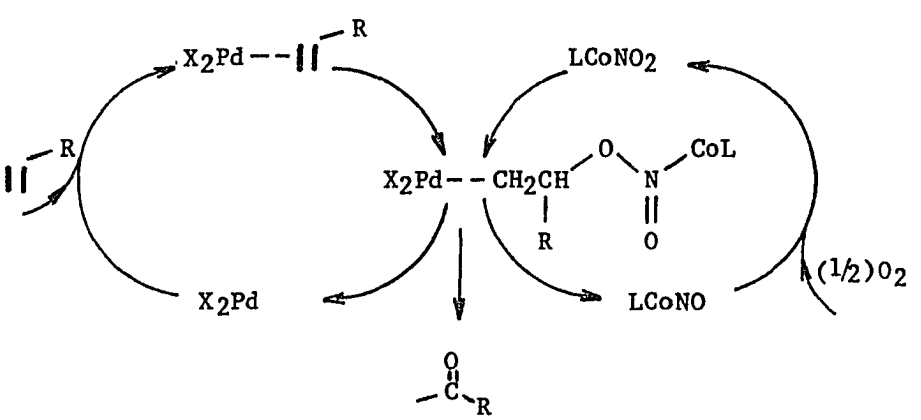
In other cases, the transition-metal nitro-nitrosyl redox couple is used for the catalytic oxidation of different substrates, among them, carbon monoxide, nitric oxide and olefins.[10,11,13,14,21-23]

Tovrog, Diamond and Mares[8,16,17,24] have reported different systems which involve oxidation of organic substrates via an oxygen atom

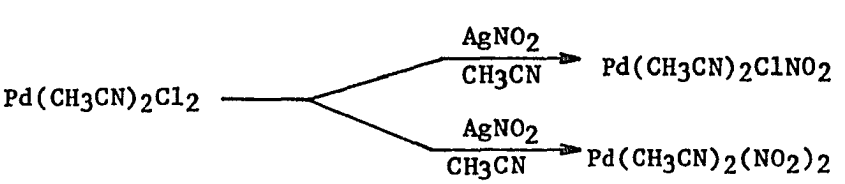
transfer from a ligand of the metal complex. The reduced ligand would then be reoxidized by molecular oxygen to complete the catalytic cycle. The following scheme shows one of these cycles:

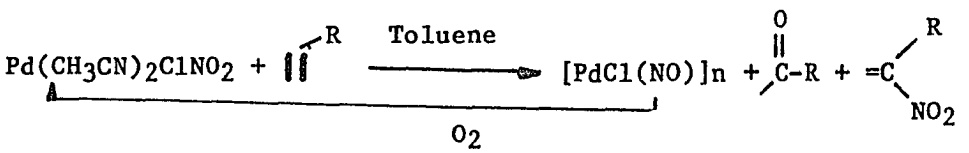


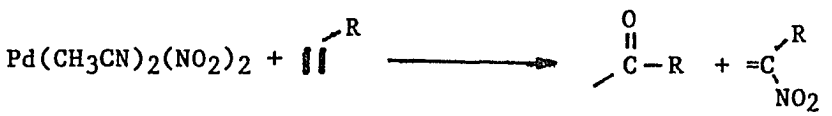
These systems also oxidize olefins by oxygen atom transfer from nitrocomplexes. The olefins were activated by coordinating them with other transition metals such as palladium. This activated olefin could then be attacked by the weak, oxygen centered nucleophile nitroligand. Some of these results are shown in the following scheme:(17)



Similar oxidations have been reported by M. A. Andrews.(7) Evidence for oxygen atom transfer from nitro groups to olefins was obtained by using ^{18}O enriched nitro compounds. Some of the reactions are as follows:







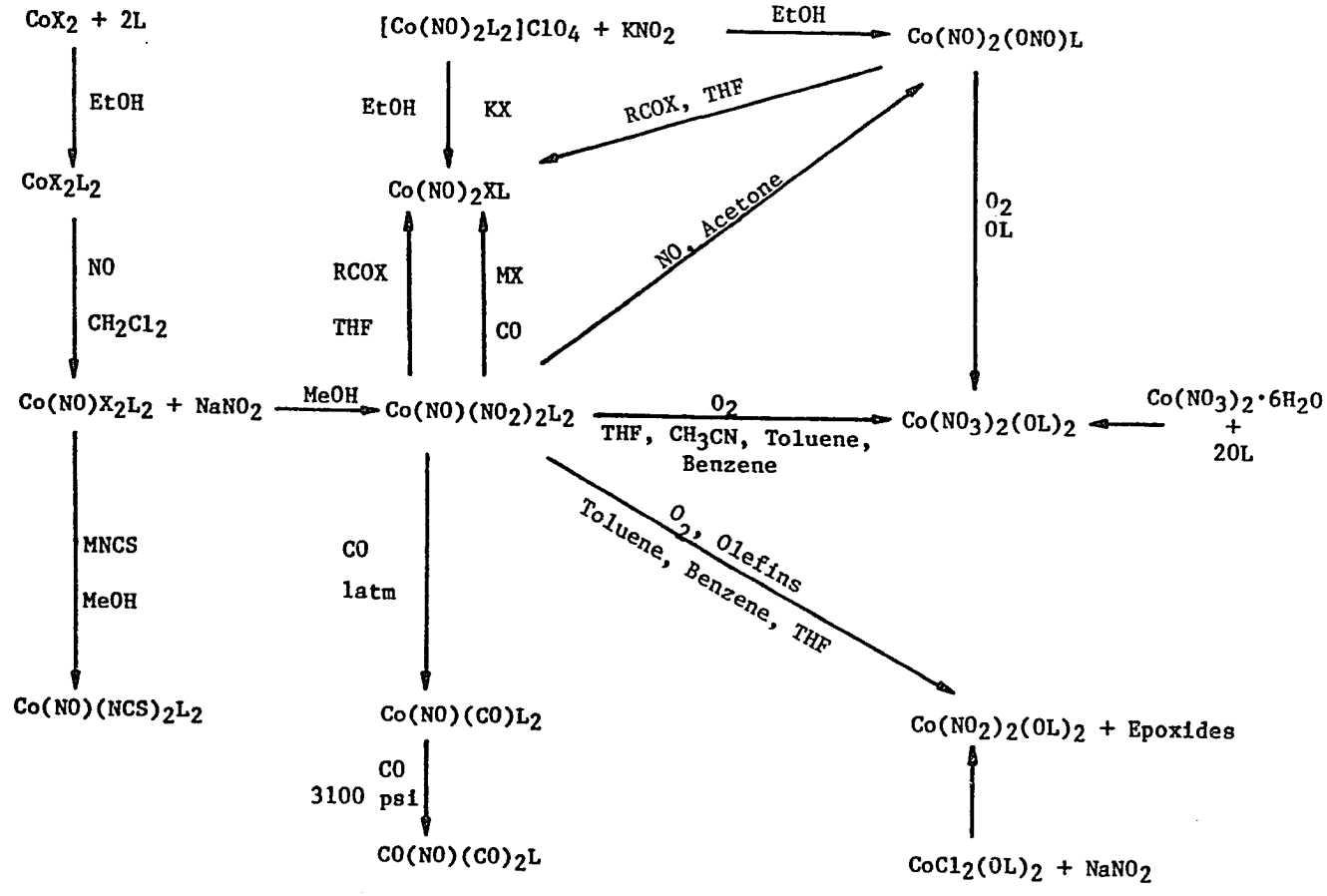
PhMe	1	:	11
Me_2CO	7	:	1

Cobalt complexes and cobalt salts are observed to be catalysts in many other series of reactions including olefin, alcohol and ketone oxidations to alcohols, ketones, epoxides, acids and aldehydes. Some of the specific reactions are: 1) The oxidation of cyclohexanone to glutaric and succinic acids by oxygen in the presence of $Co(OAc)_3$.[25] 2) Oxidations of hindered phenols and ketones by adducts of cobalt (II)bis[3-salicylideneamino)propyl]methylamine and dioxygen.[6] 3) Allylic oxidation of various olefins in acetic acids by cobalt(III) acetate.[26] 4) Catalytic oxidations of terminal olefins by cobalt(II)-Schiff base complexes.[27]

Consideration of these previous studies led us to investigate the preparation of cobalt nitro complexes that could be transformed into nitrosyl species. Chapter 2 discribes the synthesis and characterization of $Co(NO)(NO_2)_2L_2$ (L=PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, PEt_3, PEt_2Ph, $PEtPh_2$, $PPrPh_2$, PBu_3 and $\frac{1}{2}$DPPPr). This series of complexes was prepared from the reaction of $Co(NO)X_2L_2$ (X=Cl, Br) with $NaNO_2$. A detailed infrared study of these complexes indicated that they contained similar coordination spheres. The crystal structure determination of

$Co(NO)(NO_2)_2(PMePh_2)_2$ confirmed the infrared predictions and agreed well with the structure reported previously for $Co(NO)(NO_2)_2(PMe_2Ph)_2$. The solution structures of $Co(NO)(NO_2)_2L_2$ complexes were determined by multinuclear NMR spectroscopy (^1H, ^{31}P, ^{15}N and ^{14}N) as discussed in Chapter 3. This investigation required the NMR study of several $Co(NO)_x$ complexes to understand fully the relationships between structural characteristics of these complexes and NMR parameters.

The reactions of $Co(NO)(NO_2)_2L_2$ with CO, NO and RCOX which yield $Co(NO)_2XL$ complexes and were characterized by X-ray crystallography (X = Cl, ONO^-; L = PPh_3) are discussed in Chapter 4. In the final chapter, the reactions of $Co(NO)(NO_2)_2L_2$ with oxygen are discussed. These compounds react with molecular oxygen to produce a series of intense violet $Co(NO_3)_2(OL)_2$ complexes. When reactions with oxygen were carried out in the presence of an excess of olefins, the formation of nitrates is inhibited, and instead $Co(NO_2)_2(OL)_2$ and olefin oxides are formed. This chapter also contains the crystal structures of representatives of these series of bisnitrates and bisnitrito compounds: $Co(NO_3)_2(OPMePh_2)_2$ and $Co(NO_2)_2(OPMePh_2)_2$. A summary of all of the reactions in this study are shown in Figure 1.1.



X : Cl^-, Br^- M: Na^+, K^+ R: CH_3^-, $CH_3(CH_2)_2CH_2^-$, $CH_3(CH_2)_3CH_2^-$, $C_6H_5^-$

L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, PEt_3, PEt_2Ph, $PEtPh_2$, $PPrPh_2$.

Figure 1.1 Scheme of the reactions studied.

CHAPTER 2

PREPARATION AND CHARACTERIZATION OF $Co(NO)(NO_2)_2L_2$ COMPLEXES: THE CRYSTAL STRUCTURE OF $Co(NO)(NO_2)_2(PMePh_2)_2$

Introduction

In recent years, considerable interest in the reactions and catalytic activity of NO_x complexes has been generated by their unique structural and electronic properties.[1-5] One unique reaction of these NO_x ligands is the facile transfer of oxygen atoms to oxidizable substrates.[7,8,17,24,28] The transfer of an oxygen atom from a coordinated NO_2 group to form a nitrosyl complex is of particular importance since the process can be catalytic.[8,16,17,29] Although the mechanism of this reaction has been explored for square planar nickel and palladium complexes,[13,30,31] the reactions, reaction products, and reaction mechanisms of the corresponding cobalt complexes have been only briefly mentioned.[8,16,24] Cobalt complexes afford more diversified reactions since their coordination number, d electron count, and number and type of accessible nitrosyl complexes are more diverse than those of nickel and palladium. Cobalt derivatives of NO_x ligands can be conveniently prepared from tertiary phosphine complexes of divalent cobalt.[23,31-34]

This chapter describes the synthesis and characterization of $Co(NO)(NO_2)_2L_2$ complexes as well as the crystal structure of $Co(NO)(NO_2)_2(PMePh_2)_2$.

Experimental

$Co(NO)(NO_2)_2L_2$ complexes were prepared from the reaction of $Co(NO)X_2L_2$ (X = Cl, Br; L = tertiary phosphine) with sodium nitrite in methanol freshly distilled from magnesium methoxide.[35] All of the reactions were carried out under an atmosphere of purified nitrogen using Schlenk techniques.[36-37] The individual preparations are described below. The elemental analyses for these and other cobalt complexes are shown in Table 2.1. Microanalyses were carried out by Atlantic Microlabs, Atlanta, Georgia and The University of Arizona Analytical Center. NMR spectra were obtained using a Bruker WM 250 spectrometer. Infrared spectra were obtained using a Perkin-Elmer 983 spectrophotometer. The infrared frequencies[38-43] for NO and $-NO_2$ ligands in $Co(NO)(NO_2)_2L_2$ complexes are shown in Table 2.2.

Preparation of Complexes

A. Preparation of $Co(NO)(NO_2)_2(PEt_3)_2$.

Dichloro(nitrosyl)bis(triethylphosphine)cobalt, $[CoCl_2(NO)(PEt_3)_2]$[23] (0.400 mmoles) was mixed with sodium nitrite (2.00 mmoles) in 8.0 ml of methanol. The reaction mixture was stirred for one hour. The solvent was removed by flowing nitrogen slowly through the reaction vessel. Ten ml of CH_2Cl_2 were added to

dissolve the complex. Insoluble solids were removed by filtration. Fifteen ml of hexane was added to the brown solution which was then cooled to -10 °C. After one day, a dark brown crystalline material had precipitated. The mother liquor was removed via syringe, the solid washed with n-pentane and vacuum dried.

B. Preparation of $Co(NO)(NO_2)_2(PBu_3)_2$.

Dichloro(nitrosyl)bis(tri(n-butyl)phosphine)cobalt, (0.500 mmoles) was mixed with $NaNO_2$ (2.50 mmoles) in 7.0 ml of methanol. The reaction mixture was stirred for two hours. The solvent was removed by flowing nitrogen through the system. The resulting brown oil was dissolved in hexane and the solution filtered to remove white solids. This brown solution was cooled for six hours at -78 °C, resulting in a brown crystalline material and a light yellow solution. The liquid was removed, and the crystals were quickly washed with cold n-pentane and immediately vacuum dried. At room temperature this compound turns oily. $Co(NO)(NO_2)_2(PBu_3)_2$ can be also prepared from the reaction between $Co(NO)(Br)_2(PBu_3)_2$ and $NaNO_2$ in MeOH.

C. Preparation of $Co(NO)(NO_2)_2(PMePh_2)_2$.

Dichloro(nitrosyl)bis(methyldiphenylphosphine)cobalt, (0.535 mmoles) was mixed with sodium nitrite (2.677 mmoles) in 10 ml of methanol. The black solution was stirred and after one hour a brown solid had formed. The solid was removed by filtration,

washed twice with MeOH, then with well degassed distilled water and again with MeOH. Crystals of $Co(NO)(NO_2)_2(PMePh_2)2$ were obtained from a 1:1 toluene:pentane solution of the complex. X-Ray diffraction studies of this material revealed its molecular structure (Figure 2.1).

D. Preparation of $Co(NO)(^{15}NO_2)_2(PMePh_2)_2$.

The preparation was carried out as described above using 0.268 mmoles of $Co(NO)Cl_2(PMePh_2)_2$ and 1.00 mmoles of $Na^{15}NO_2$ in 3.0 ml of MeOH. The infrared spectrum (KBr) showed that ^{15}N was not incorporated into the NO ligand. The expected shifts for the $-^{15}NO_2$ ligands were observed while ν_{NO} remains the same as that for unlabeled $Co(NO)(NO_2)_2(PMePh_2)_2$.

E. Preparation of $Co(NO)(NO_2)_2(PMe_2Ph)_2$.[31]

The preparation was carried out as described above using 0.100 g. of $Co(NO)Cl_2(PMe_2Ph)_2$ (0.229 mmoles), 0.0790 g. of $NaNO_2$ (1.149 mmoles) and 3.0 ml of methanol.

F. Preparation of $Co(NO)(^{15}NO_2)_2(PMe_2Ph)_2$.

The preparation was carried out as described above using 0.229 mmoles of $Co(NO)Cl_2(PMe_2Ph)_2$ (0.100 g), $Na^{15}NO_2$ (0.070 g.) and 3.0 ml of methanol.

G. Preparation of $Co(NO)(NO_2)_2(PMe_3)_2$

Dichloro(nitrosyl)bis(trimethylphosphine)cobalt, $[CoCl_2(NO)(PMe_3)_2]$ (1.350 mmoles) was mixed with sodium nitrite (4.920 mmoles) in 10 ml of methanol. The reaction mixture was stirred for two hours. The solvent was removed by flowing nitrogen slowly through the reaction vessel. Ten ml of water were added to dissolve the excess of $NaNO_2$ and NaCl. The insoluble $Co(NO)(NO_2)_2(PMe_3)_2$ was filtered and vacuum dried.

H. Preparation of $Co(NO)(NO_2)_2(PPh_3)_2$.

Dichloro(nitrosyl)bis(triphenylphosphine)cobalt, $[Co(NO)Cl_2(PPh_3)_2]$ (0.585 mmoles) was mixed with $NaNO_2$ (2.922 mmoles) in 10 ml of MeOH. The reaction mixture was stirred for 18 hours. After this time, a brown material was removed by filtration, washed with 20.0 ml of water, and several times with methanol. Two NO stretching frequencies (1664(m) and 1646(vs) cm^{-1}) are observed in the infrared spectrum (KBr) of this compound. $Co(NO)(NO_2)_2(PPh_3)_2$ can also be prepared by reacting $Co(NO)Br_2(PPh_3)_2$ and $NaNO_2$ in MeOH.

I. Preparation of $Co(NO)(^{15}NO_2)_2(PPh_3)_2$.

The preparation was carried out as described above using 0.0750 g. of $Co(NO)Cl_2(PPh_3)_2$ (0.1096 mmoles), 0.0384 g. of $Na^{15}NO_2$ (0.5479 mmoles) and 2.0 ml of methanol. The specific labeling of the nitro groups is observed. The ν_{NO} of the labeled compound was the same as that for the unlabeled material.

J. Preparation of $Co(NO)(NO_2)_2(PEtPh_2)_2$.

Dichloro(nitrosyl)bis(ethyldiphenylphosphine)cobalt, (0.068 mmoles) was mixed with sodium nitrite (0.272 mmoles) in 2.0 ml of methanol. The solution was stirred for two hours. A brown solid was isolated by filtration and washed several times with 2.0 ml portions of MeOH, then with 5.0 ml of n-pentane.

K. Preparation of $Co(NO)(NO_2)_2(PPrPh_2)_2$.

The preparation was carried out as described above using 0.330 mmoles of $Co(NO)Cl_2(PPrPh_2)_2$ (0.2042 g.), 0.323 mmoles of $NaNO_2$ and 3.0 ml of methanol.

L. Preparation of $Co(NO)(NO_2)_2$ DPPPr.

The preparation was carried out as described previously using 2.0 mmoles of $Co(NO)Cl_2$ DPPPr (1.15 g), 7.97 mmoles of $NaNO_2$ and 12.0 ml of methanol.

Table 2.1 ELEMENTAL ANALYSES OF $Co(NO)(NO_2)_2L_2$

COMPOUND	%C		%H		%N	
	Calc.	Found	Calc.	Found	Calc.	Found
$Co(NO)(NO_2)_2(PPh_3)_2$	61.28	60.96	4.29	4.54	5.96	5.80
$Co(NO)(NO_2)_2(PMe_3)_2$	21.63	21.55	5.45	5.70	12.61	5.78
$Co(NO)(NO_2)_2(PMe_2Ph)_2$	42.03	42.00	4.85	4.87	9.19	9.30
$Co(NO)(NO_2)_2(PMePh_2)_2$	53.71	54.01	4.51	4.34	7.23	6.96
$Co(NO)(NO_2)_2(PEt_3)_2$	34.54	34.68	7.25	7.28	10.07	10.01
$Co(NO)(NO_2)_2(PEt_2Ph)_2$	46.79	46.92	5.89	6.19	8.19	8.24
$Co(NO)(NO_2)_2(PEtPh_2)_2$	55.18	55.00	4.96	4.85	6.90	6.72
$Co(NO)(NO_2)_2(PPrPh_2)_2$	56.52	56.60	5.38	5.43	6.59	6.55
$Co(NO)(NO_2)_2(PBu_3)_2$	49.22	49.30	9.30	9.33	7.18	7.26

Infrared Spectra Of $Co(NO)(NO_2)_2L_2$

Infrared spectra of the complexes were recorded with a Perkin-Elmer 983 equipped with remote data station, in the frequency range from 3100 to 300 cm^{-1}.

The spectra of the compounds $CoCl_2L_2$, $Co(NO)Cl_2L_2$ and $Co(NO)(NO_2)_2L_2$ were compared for L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, PEt_3, PEt_2Ph, $PEtPh_2$, $PPrPh_2$, PBu_3 and DPPPr. Based on these comparisons and ^{15}N substitution, assignments were made for the NO_2 and nitrosyl vibrations.[38-43] Comparison of the spectra of $Co(NO)(Cl)_2L_2$ and $Co(NO)(NO_2)_2L_2$ clearly defines the bands due to the $-NO_2$ ligand. Analysis of these frequencies indicate the presence of two different sets of $-NO_2$ frequencies in those molecules (Table 2.2). The X-ray diffraction studies show that one NO_2 ligand is bonded to the metal through the nitrogen atom and the other NO_2 ligand is bidentate, bonded to the cobalt through the two oxygen atoms in an asymmetric four-membered ring. $^{15}NO_2$ labeling in this series of compounds shows the predicted shifts in the infrared bands. The infrared results are in complete accord with the X-ray results for $Co(NO)(NO_2)_2L_2$, (L = $PMePh_2$ and PMe_2Ph).

For $Co(NO)(NO_2)_2L_2$, the asymmetric stretching frequencies ($\nu_{N-O}as$) for the NO_2 groups range from 1349 to 1397 cm^{-1}. The symmetric N-O stretch ($\nu_{N-O}sym$) is between 1291 and 1328 cm^{-1}, δNO_2 (bending mode) ranges from 806 to 816 cm^{-1} and the wagging mode [$\rho w(M-NO_2)$] that is characteristic of the N-bound nitro group, varies from 577 to 602 cm^{-1}. For the chelate NO_2 group, $\nu N-O_{as}$ ranges from 1264 to 1309 cm^{-1}, νN-Osym lies between 1121 to 1180 cm^{-1} and δONO ranges from 866 to 876 cm^{-1}.

Table 2.2 INFRARED SPECTRA (KBr) OF $Co(NO)(NO_2)_2L_2$.

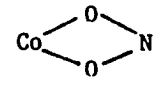
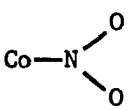
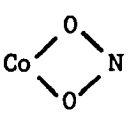
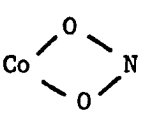
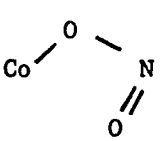
	Co-NO_2							CoNO
COMPOUND	$\upsilon_{N-O_{as}}$	$\upsilon_{N-O_{sym}}$	δNO_2	$\rho_w(NO_2)$	$\upsilon_{N-O_{as}}$	$\upsilon_{N-O_{sym}}$	δONO	υ_{N-O}
$Co(NO)(NO_2)_2(PPh_3)_2$	1397(s)	1320(m)	816(m)	591(w)	1309(s)	1142(m)	876(vw)	1663(m) 1646(vs)
$Co(NO)(^{15}NO_2)_2(PPh_3)_2$	1369(s)	1300(m)	810(m)	577(w)	1287(s)	1121(m)	868(vw)	1663(m) 1646(vs)
$Co(NO)(NO_2)_2(PMe_3)_2$	1378(s)	1319(m)	815(m)	594(m)	1302(s)	1165(m) 1153(m)	867(w)	1660(vs)
$Co(NO)(NO_2)_2(PMe_2Ph)_2$	1376(s)	1316(s)	815(m)	594(w)	1296(s)	1173(m) 1160(m)	870(vw)	1663(vs)
$Co(NO)(^{15}NO_2)_2(PMe_2Ph)_2$	1349(s)	1305(s)	808(m)	578(w)	1279(s)	1142(m)	866(vw)	1663(vs)
$Co(NO)(NO_2)_2(PMePh_2)_2$	1386(s)	1306(s)	813(m)	595(w)	1290(s)	1172(m) 1159(m)		1653(vs)
$Co(NO)(^{15}NO_2)_2(PMePh_2)_2$	1361(s)	1281(s)	806(m)	580(w)	1281(s)	1160(m) 1144(m)		1653(vs)
$Co(NO)(NO_2)_2(PEt_3)_2$	1376(s)	1306(s)	816(m)	596(w)	1264(m)	1180(m) 1160(m)	872(vw)	1650(vs)
$Co(NO)(NO_2)_2(PEt_2Ph)_2$	1392(s) 1377(s)	1315(s)	816(m)	594(w)	1297(s)	1179(m) 1160(m)	870(vw)	1666(vs) 1650(vs)
$Co(NO)(NO_2)_2(PEtPh_2)_2$	1385(s) 1374(s)	1328(m)	818(m)	578(w)	1308(s)	1150(m) 1160(m)	870(vw)	1645(vs)
$Co(NO)(NO_2)_2(PPrPh_2)_2$	1392(s)	1325(m)	816(m)	591(w)	1307(s)	1160(m) 1144(m)	870(vw)	1657(vs)

TABLE 2.3 ASSIGNMENT OF VIBRATIONAL FREQUENCIES OF NO_2 GROUPS.

Vibrational frequency (cm^{-1}) / Ligand Geometry	$\upsilon_{N-O_{As.}}$	$\upsilon_{N-O_{Sym.}}$	δ_{NO_2}	ρ_{Co-NO_2}
	1397	1320	816	591
	1262	1200 1179	859	
	1309	1142	876	
	1401	1095	757	

Collection and reduction of the X-ray intensity data:

Dark-brown crystals of $Co(NO)(NO_2)_2(PMePh_2)_2$ suitable for diffraction were obtained from toluene-hexane or toluene-pentane solutions after two days at -10°C. Several crystals were selected for X-ray diffraction studies. All of the preliminary photographic data obtained for these crystals revealed that the material belongs to the triclinic system (Laue symmetry 1 or $\bar{1}$).[44-45] Cell constants were obtained in three different experiments by least squares refinement of 25 reflections centered and indexed by a NOVA 1200 series computer that controlled the Syntex $P2_1$ four circle diffractometer where the intensity data were collected.[46] These cell dimensions and other crystallographic data for one of the crystals studied are compiled in Table 2.4. Intensity data for the half sphere $h \pm k \pm \ell$ were collected using the $\theta - 2\theta$ technique. The intensity of two standard reflections were measured every 98 reflections. No change in the intensity of the standards was observed. The data were reduced to F_o^2 and $\sigma(F_o^2)$ by published methods.[47] Lorentz and Polarization factors were calculated on the assumption of 50% mosaicity and 50% perfection of the monochromator crystal. The factor to prevent overweighting of strong reflections, P, was set equal to 0.03.

Solution and refinement of the structure:

Attempts to solve the structure were made using the space group $P\bar{1}$. The heavy atom method provided the position of two cobalt atoms when $P\bar{1}$ was the space group used. These Co positions were refined and successive difference electron density maps calculated. All non-

hydrogen atoms were determined for the $Co(NO)(NO_2)_2(PMePh_2)_2$ molecule with the cobalt atom in the general position. For the Co atom in the special position (a, 000) one of the phosphine ligands was completely determined and a series of peaks around the metal in a plane almost perpendicular to the Co-P bond were found. Trying to make some chemical sense of these peaks (assigning the most probable NO and NO_2 groups) resulted in a model that after three cycles of anisotropic least squares refinement gave an R = 12.6.[45] Additional difference electron density maps resulted in a series of peaks that indicated that the space group was P1 instead of $P\bar{1}$ and this Co atom was located on a center of inversion. The other molecule remained unchanged. At this stage, the P1 (No. 1) space group was used in the calculations. Two complete molecules of $Co(NO)(NO_2)_2(PMePh_2)_2$ and half a molecule without O and N atoms resulted from the difference in the electron density maps. Three dimensional electron density maps were calculated and plotted in the space centered on the cobalt atom at the origin. All of the possible area occupied by the coordination sphere of this molecule was analyzed. The result of this study showed electron density regions with $\bar{1}$ symmetry (a ring of electron density around the metal) as if two molecules were superimposed on one Co atom. Several attempts were made to break the symmetry and different disorder models were also explored. Calculations of the structure factors for the different models showed no improvements in the R factors. At this point, the best model was taken and the molecules in the general positions were refined isotropically to give the structure shown in Figure 2.1.

TABLE 2.4 SUMMARY OF CRYSTALLOGRAPHIC DATA FOR $Co(NO)(NO_2)_2(PMePh_2)_2$.

Compound	$Co(NO)(NO_2)_2(PMePh_2)_2$
Formula	$CoN_3O_5P_2C_{26}H_{26}$
Formula weight	581.373
Crystal shape	Triangular prism
Crystal color	Dark brown
Space system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Cell dimensions[b]	
a, Å	10.123(4)
b, Å	10.977(5)
c, Å	19.302(6)
α, deg.	89.79(3)
β, deg.	89.08(3)
γ, deg.	71.36(3)
V, $Å^3$	2032(1)
Z	3
Temperature, °C	22
$d_{obs.}$[c], $g.cm^{-3}$	1.395(5)
$d_{calc.}$, $g.cm^{-3}$	1.453(5)
Radiation, Å	MoK_α, = 0.71069

TABLE 2.4 continued

Monochromator	Graphite crystal
Data collection method	$\theta - 2\theta$ scan
Portion of the sphere collected	$h \pm k \pm \ell$
Scan speed, deg/min	Variable (3-20)
Scan range, deg.	1.4 below $K\alpha_1$ to 1.4 above $K\alpha_2$
Scan to background time	2.0
Decomposition	Not significant
Max. shift during least squares (Δ/σ)	0.01
Number of unique data	7184
Number of data used in calculations	4570

[a]This data corresponds to the crystal studied in more detail. The standard deviation of the least significant figure is given in parenthesis.

[b]Cell dimensions were obtained from a least-squares refinement of setting angles of 25 reflections with $14° < 2\theta < 23°$.

[c]Density was determined by flotation using carbon tetrachloride-hexane.

Results and Discussion

Complexes of the formula $Co(NO)(NO_2)_2L_2$

$Co(NO)(NO_2)_2L_2$ complexes have been prepared from the reaction of $Co(NO)X_2L_2$ (X=Cl, Br; L=PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, PEt_3 PEt_2Ph, $PEtPh_2$, $PPrPh_2$, PBu_3 and $\frac{1}{2}$DPPPr) with sodium nitrite in methanol. The infrared spectra of these complexes clearly shows the coordination of strongly bent nitrosyls in these complexes.[1,2,4] The ν_{NO} stretching frequencies were observed between 1682 and 1645 cm^{-1}. 15-N substitution at the NO_2 positions defined the vibrational frequencies of these ligands. Analysis of these vibrations indicated the presence of two different sets of NO_2 frequencies in these molecules (Table 2.2). One set corresponds to a nitrogen bonded nitro group and the other set to a bidentate NO_2 ligand, bonded to the cobalt through the two oxygen atoms.

The room temperature proton NMR spectra of $Co(NO)(NO_2)_2(PMe_xPh_{3-x})_2$, (x=1-3) shows well defined 1:2:1 triplets in the methyl region. This is an example of deceptively simple spectra usually observed in trans tertiary phosphine complexes.[48,49] Free phosphines and phosphine oxides resonances are not observed in the spectra of any of the complexes. These observations show that the compounds are pure and that the phosphine ligands do not dissociate in solution.

Structure of $Co(NO)(NO_2)_2(PMePh_2)_2$.

An ORTEP drawing of $Co(NO)(NO_2)_2(PMePh_2)_2$ is shown on Figure 2.1 Tables 2.5 and 2.6 list important bond lengths, angles and atomic positions for this compound. In many respects, this molecule resembles

$Co(NO)(NO_2)_2(PMe_2Ph)_2$ reported earlier[31] and is in agreement with the solution structures inferred from infrared and NMR studies of this compound. The cobalt atom has tetragonal pyramidal geometry. The nitrosyl group in the axial position is strongly bent [Co-N(1)-O(1) angle of 129.0(1)°], a geometry that has been observed for all six-coordinate $\{MNO\}^8$ complexes.[1] The Co-N(1) distance [1.757 (11) Å], N(1)-O(1) distance [1.180 (2)Å] and the Co-N(1)-O(1) angle are similar to the values observed for other five and six-coordinate complexes of cobalt with a strongly bent CoNO group. The NO_2 ligands have two different ligating geometries: one is bound to cobalt through the nitrogen atom and the other is bidentate forming an asymmetric four membered ring. In the nitro group, the Co-N(2), [1.883 (12)Å], N(2)-O(12), [1.218 (14)Å], N(2)-O(11), [1.230 (2)Å] distances and the O(11)-N(2)-O(12), [123.0(1)°] angle resemble those of other nitro complexes of cobalt.[31] The Co-O(21) distance of 2.392 (11)Å is significantly larger than the Co-O(22) distance of 2.009 (10)Å and is attributed to the trans effect of the bent NO ligand.[5] The O(22)-Co-O(21) angle of 55.7(4)° compares well with the bite angle of the corresponding nitrito group in $Co(NO)(NO_2)_2(PMe_2Ph)_2$ [56.0(4)°].[31] The cobalt-phosphorus distances are similar to Co-P distances found in other five coordinate and six coordinate complexes of cobalt. The P(2)-Co-P(3) angle is 168.8°(1) which is of about the same value as in the PMe_2Ph analog.[31]

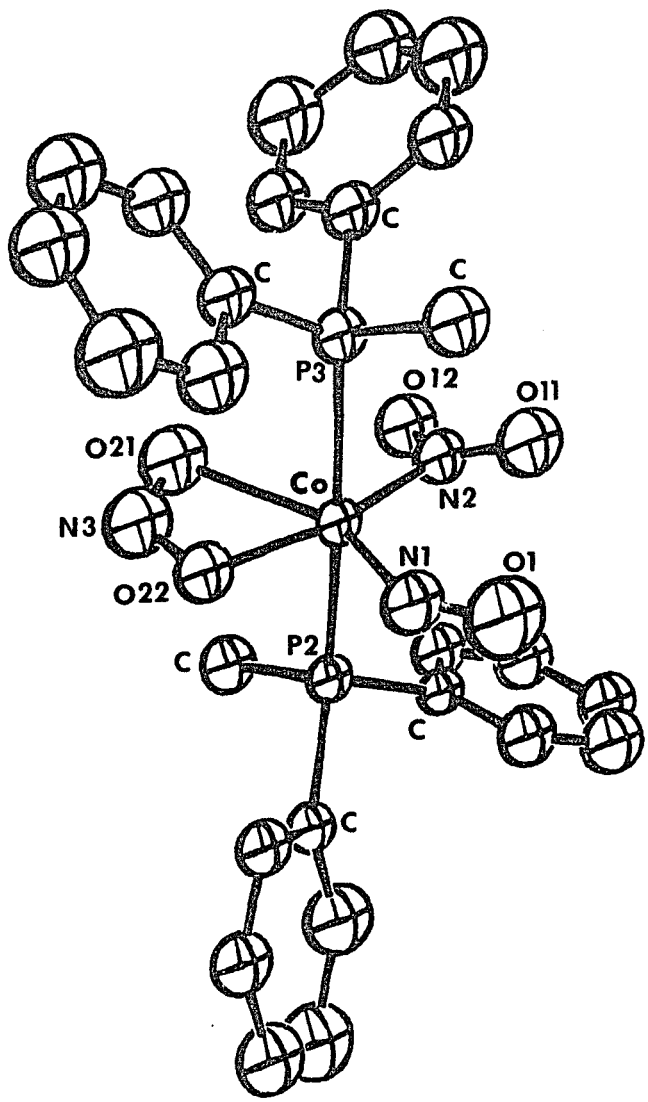


Figure 2.1. Perspective view of $Co(NO)(NO_2)_2(PMePh_2)_2$.

TABLE 2.5 SELECTED INTERATOMIC DISTANCES AND ANGLES FOR $Co(NO)(NO_2)_2(PMePh_2)_2$.

		Distances	
Co-P2	2.297(3)	P3-C11	1.836(14)
Co-P3	2.304(3)	P3-C21	1.836(15)
Co-O21	2.392(11)	P3-C31	1.810(2)
Co-O22	2.009(10)	O1-N1	1.180(2)
Co-N1	1.757(11)	O11-N2	1.230(2)
Co-N2	1.883(12)	O12-N2	1.218(14)
P2-C41	1.838(12)	O21-N3	1.250(2)
P2-C51	1.825(14)	O22-N3	1.225(15)
P2-C61	1.817(15)		
		Angles	
Co-O21-N3	85.1(8)	P2-Co-P3	168.8(1)
Co-O22-N3	104.6(9)	P2-Co-O21	90.5(3)
Co-N1-O1	129.0(1)	P2-Co-O22	92.1(3)
Co-N2-O11	124.4(9)	P2-Co-N1	93.6(4)
Co-N2-O12	112.8(9)	P2-Co-N2	88.2(3)
O11-N2-O12	123.0(9)	P3-Co-O21	83.3(3)
O21-N3-O22	115.0(9)	P3-Co-O22	92.0(3)
O22-Co-N1	90.7(5)	P3-Co-N1	96.7(4)
O22-Co-N2	167.0(4)	P3-Co-N2	85.5(3)
N1-Co-N2	102.3(5)	O21-Co-O22	55.7(4)
		O21-Co-N1	146.4(5)
		O21-Co-N2	111.2(4)

Numbers in parentheses are estimated standard deviations in the least significant digits.

TABLE 2.6 POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Co(NO)(NO_2)_2(PMePh_2)_2$.

Atom	x	y	z
Co	0.3465(3)	-0.0498(3)	0.3178(3)
P2	0.2200(3)	0.0864(3)	0.4025(3)
P3	0.5072(3)	-0.1973(3)	0.2488(3)
O1	0.2547(3)	0.1296(3)	0.2217(3)
O11	0.5163(3)	0.0947(3)	0.2808(3)
O12	0.5471(3)	0.0042(3)	0.3808(3)
O21	0.3863(3)	-0.2286(3)	0.3950(3)
O22	0.2243(3)	-0.1623(3)	0.3249(3)
N1	0.2448(3)	0.0381(3)	0.2503(3)
N2	0.4848(3)	0.0298(3)	0.3264(3)
N3	0.2777(3)	-0.2406(3)	0.3700(3)
C11	0.6852(3)	-0.2422(3)	0.2821(3)
C12	0.7116(3)	-0.2971(3)	0.3460(3)
C13	0.8448(3)	-0.3264(3)	0.3762(3)
C14	0.9475(3)	-0.2854(3)	0.3343(3)
C15	0.9190(3)	-0.2340(3)	0.2732(3)
C16	0.7882(3)	-0.2116(3)	0.2426(3)
C21	0.4726(3)	-0.3482(3)	0.2307(3)
C22	0.3493(3)	-0.3338(3)	0.1945(3)
C23	0.3139(3)	-0.4477(3)	0.1791(3)
C24	0.4102(3)	-0.5684(3)	0.2003(3)
C25	0.5265(3)	-0.5800(3)	0.2363(3)
C26	0.5584(3)	-0.4668(3)	0.2528(3)
C31	0.5140(3)	-0.1298(3)	0.1636(3)
C41	0.0302(3)	0.1480(3)	0.3909(3)
C42	-0.0382(3)	0.0826(3)	0.3532(3)
C43	-0.1797(3)	0.1219(3)	0.3483(3)
C44	-0.2565(3)	0.2321(3)	0.3813(3)
C45	-0.1959(3)	0.3019(3)	0.4233(3)
C46	-0.0424(3)	0.2570(3)	0.4254(3)
C51	0.2708(3)	0.2302(3)	0.4139(3)
C52	0.3554(3)	0.2378(3)	0.4670(3)
C53	0.3978(3)	0.3497(3)	0.4717(3)
C54	0.3579(3)	0.4469(3)	0.4247(3)
C55	0.2739(3)	0.4359(3)	0.3696(3)
C56	0.2306(3)	0.3261(3)	0.3642(3)
C61	0.2375(3)	0.0092(3)	0.4868(3)

[a]Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $8PI^2(U_{11} + U_{22} + U_{33})/3$.

Conclusions

A series of $Co(NO)(NO_2)_2L_2$ complexes have been synthesized and characterized. The nitrosyl groups are strongly bent and the NO_2 ligands are coordinated in different ways. One is a nitrogen bonded $-NO_2$ ligand and the other is a chelate NO_2 bonded to the cobalt through the oxygen atoms to form an asymmetric four-membered ring. Solution ^1H NMR studies in the CH_3 region show that the compounds do not dissociate. The structure of one of these complexes, $Co(NO)(NO_2)_2(PMePh_2)_2$, has been determined by X-ray crystallography. This structure compares well with the structure of $Co(NO)(NO_2)_2(PMe_2Ph)_2$ reported previously and is in agreement with all the spectroscopic studies performed on this series of compounds.

CHAPTER 3

NMR STUDY OF $CoNO_x$ COMPLEXES

Introduction

Nuclear magnetic resonance spectroscopy has become firmly established as one of the major methods available to the chemist for solution structure determination and for obtaining physico-chemical information about molecular dynamics.[50-51] Recent years have seen several major developments of the technique. In particular, multinuclear studies are becoming more feasible and popular.[52-55] In this study, multinuclear NMR spectroscopy (^{1}H, ^{31}P, ^{15}N and ^{14}N) was used to determine the solution structure of $Co(NO)(NO_2)_2L_2$ complexes, to study mono and bisnitrosyls of cobalt, to establish geometric characteristics of these compounds, and to follow their reactions in solution.

Proton NMR spectra in the methyl region was used to study the coordination geometry of phosphine ligands in $Co(NO)Cl_2L_2$ and $Co(NO)(NO_2)_2L_2$ complexes [$L=PMe_xPh_{3-x}$ (x=1-3)]. $^{31}P\{^{1}H\}$ NMR studies of these compounds also were carried out to add to the information obtained from ^{1}H NMR. ^{31}P has a nuclear spin of $I=1/2$ and is found in 100 percent natural abundance.[56] Although the receptivity of this nucleus is only ca. 7 per cent that of ^{1}H, the use of pulsed NMR techniques in conjunction with broadband ^{1}H decoupling allows the observation of this nucleus in the majority of its compounds. Since there are few magneti-

cally inequivalent phosphorus atoms in most molecules, one readily obtains interpretable spectra.[57-59] Additional structural information about the coordination spheres of $CoNO_x$ complexes has been obtained with nitrogen NMR.

Despite the wealth of transition metal complexes containing nitrogen ligands, there are only a few reports containing ^{15}N-NMR ($I=1/2$) data for coordinated ligands.[60-65] This stems primarily from the low natural abundance (0.36%) and sometimes unfavorable spin-lattice relaxation characteristics of this nucleus.[66] Further, signal nulling has been observed under condition of broadband ^{1}H-decoupling when the nuclear Overhauser effect approaches minus one. Of those complexes for which ^{15}N-measurements have been made, the iron derivatives have received the most attention due to their biological relevance.[62] However, there have also been reports for platinum[67], rhodium[68], cadmium[69], titanium[70], and cobalt[65] complexes.

The ^{14}N nucleus is nearly 100% abundant but has a quadrupole moment ($I = 1$).[60] It has a low magnetogyric ratio ($\gamma = 1.933 \times 10^7$ rad $T.^{-1}S^{-1}$) compared with 26.752×10^7 for ^{1}H. The sensitivity relative to ^{1}H is then 10^{-3} for ^{14}N. The receptivity at natural abundance, relative to ^{13}C, is 5.7. ^{14}N has a resonance frequency of 18.1 MHz at 5.87 T. ^{14}N NMR is dominated by quadrupolar relaxation, since the nuclear electric quadrupole is coupled to the nuclear spin. As the molecule tumbles, the change in the electric field gradient (q) around the ^{14}N nucleus relaxes the electric quadrupole, which also relaxes the spin.

The lower the local symmetry about the nitrogen, and the larger is q, the faster the quadrupolar relaxation and the broader the line. The ^{14}N quadrupole moment however, is relatively small ($Q = 1.55 \times 10^{26}$ cm about 5 times the value for ^{2}H). High-resolution work is thus very difficult unless the local symmetry is sufficiently high. The combination of these studies provides useful generalization about the geometry of NO_x ligands in these cobalt complexes.

Experimental

All NMR spectra were obtained using a Bruker WM 250 spectrometer. Proton NMR studies were performed in deoxygenated CD_2Cl_2 previously distilled from P_4O_{10} under dry, oxygen-free nitrogen. ^{31}P and ^{15}N studies were carried out in 10% CD_2Cl_2/CH_2Cl_2 purified by standard procedures just before preparing the samples.[35] All transfers were made in glove bags filled with purified nitrogen. The caps of the 10 mm NMR tubes were sealed to the glass with cyanoacrylate adhesive or carefully covered with parafilm tape to prevent air contamination of the sample. If these experimental conditions are not maintained rigorously, decomposition of the $Co(NO)(NO_2)_2L_2$ complexes occurs with the formation of paramagnetic Co(II) species. These decomposition products were found to be $CoCl_2L_2$ complexes when the solvent was not purified properly and $Co(NO_3)_2(OL)_2$ when oxygen was not completely excluded from the NMR samples.

Several NMR experiments (^{1}H and ^{31}P) were performed by using either toluene-d_8 or benzene-d_6 as solvents. Due to the sensitivity of the $Co(NO)(NO_2)_2L_2$ complexes to traces of oxygen, only a few experiments produced useful data. Formation of $Co(NO_3)_2(OL)_2$ complexes always occurred in the unsuccessful experiments carried out in aromatic hydrocarbons.

Results and Discussion

^{1}H NMR Spectra.

Proton NMR spectra of $Co(NO)Cl_2L_2$, $Co(NO)(NO_2)_2L_2$ (L = PMe_3, PMe_2Ph and $PMePh_2$), the free phosphine ligands and the corresponding phosphine oxides were obtained at 250.12 MHz.[33,48,56] The proton NMR spectra of the ligands in CD_2Cl_2 consist of a complex multiplet at ca. 7.5 ppm due to phenyl hydrogens and a very sharp 1:1 doublet near 1.7 ppm due to coupling of the methyl hydrogens with ^{31}P.[48] Oxidation to the phosphine oxide increases the ^{1}H-^{31}P coupling to ca. 13 Hz (Table 3.1). The large increase in $^{2}J_{P-H}$ may be due to greater s-character in the phosphorous-methyl bond of the phosphine oxide. In three coordinated phosphorous compounds, phosphorus uses mainly the three p-orbitals, while in four coordinated compounds it is primarily sp^3 hybridized.

In $Co(NO)(NO_2)_2(PMe_xPh_{3-x})_2$, (x = 1-3), the ^{1}H NMR signals of the methyl groups are well defined 1:2:1 triplets (Figure 3.1). This is an example of deceptively simple spectra often observed for trans tertiary phosphine complexes.[48,49] In this series of complexes the two

trans phosphorus atoms (I = 1/2) are strongly coupled to give $I(e_{ff})=1$. Table 3.2 lists the chemical shifts and coupling constants of $Co(NO)(NO_2)_2(PMe_xPh_{3-x})_2$ and $Co(NO)Cl_2(PMe_xPh_{3-x})_2$, (x = 1-3). Free phosphine and phosphine oxide resonances were not observed in any of the spectra of the complexes. These data indicate that these complexes are pure and that the phosphine ligands do not dissociate in solution.

When unpurified solvents were used to prepare solutions of $Co(NO)(NO_2)_2L_2$, three sets of well defined 1:2:1 triplets were observed in the $-CH_3$ region. One of these triplets (δ = 1.76 ppm) corresponds to the methyl groups of $Co(NO)(NO_2)_2L_2$, one to the methyl groups of $Co(NO)Cl_2L_2$ (δ = 2.37 ppm) and the third is assigned to $Co(NO)Cl(NO_2)L_2$. The latter complex could not be isolated. Addition of pure $Co(NO)Cl_2L_2$ complexes to these solutions increased the intensity of the triplet at 2.37 ppm, but left the other two triplets unchanged over period of several hours. These results show that equilibrium between $Co(NO)(NO_2)_2L_2$, $Co(NO)Cl(NO_2)L_2$ and $Co(NO)Cl_2L_2$ was not established during the experiment.

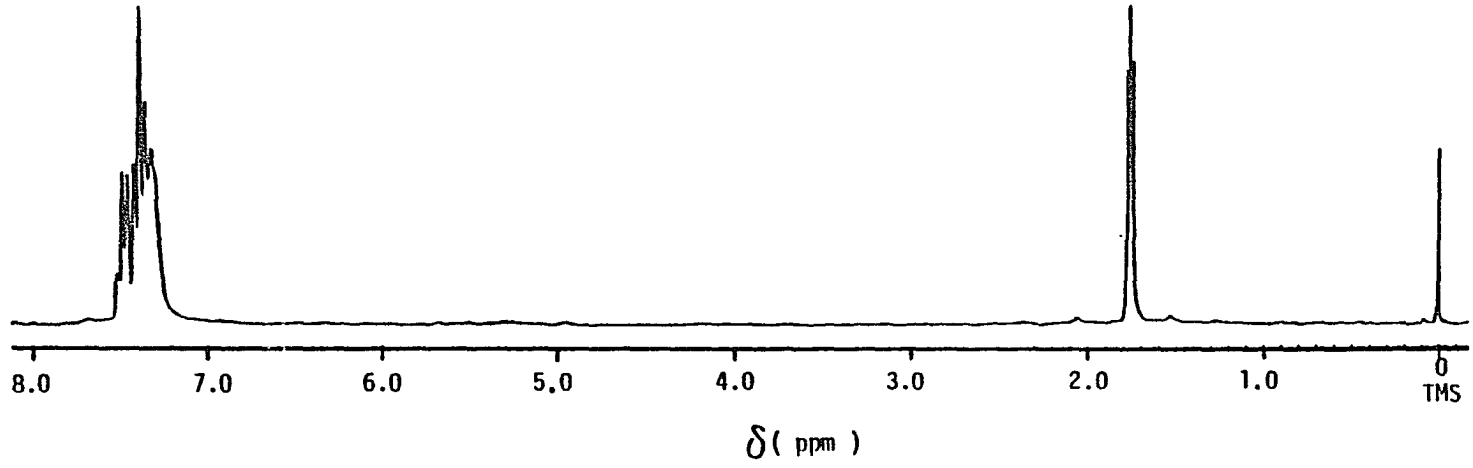


Figure 3.1. ^{1}H NMR spectrum of $Co(NO)(NO_2)_2(PMePh_2)_2$.

TABLE 3.1 ^{1}H NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS $^{2}J_{(P-H)}$ FOR THE METHYL PROTONS OF PHOSPHINES AND PHOSPHINE OXIDES.

Compound	δ (ppm)[a]	$^{2}J_{(P-H)}$(Hz)
PMe_3	0.96	1.44
$OPMe_3$	1.50	12.86
PMe_2Ph	1.31	2.30
$OPMe_2Ph$	1.74	12.98
$PMePh_2$	1.62	3.33
$OPMePh_2$	2.00	13.19

a. Chemical shifts relative to TMS.

TABLE 3.2 ^{1}H NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS $^{2}J_{(P-H)}$ FOR THE METHYL PROTONS OF $Co(NO)(NO_2)_2L_2$ AND $Co(NO)Cl_2L_2$

Complex	δ (ppm)[a]	$^{2}J_{(P-H)}$(Hz)
$Co(NO)(NO_2)_2(PMe_3)_2$	1.14	4.90
$Co(NO)(NO_2)(PMe_2Ph)_2$	1.41	4.65
$Co(NO)Cl_2(PMe_2Ph)_2$	2.04	4.81
$Co(NO)(NO_2)_2(PMePh_2)_2$	1.76	4.54
$Co(NO)Cl_2(PMePh_2)_2$	2.37	4.85

a. Chemical shifts relative to TMS.

$^{31}P\{^{1}H\}$ NMR Measurements. Temperature Study.

Phosphorus-31 NMR spectra of $Co(NO)(NO_2)_2(PMe_x\ Ph_{3-x})_2$, $Co(NO)Cl_2(PMe_xPh_{3-x})_2$, (x = 1-3) and $Co(NO)Cl_2DPPPr$ were measured over the temperature range from +30 to -90°C in 10% CD_2Cl_2/CH_2Cl_2. The proton decoupled spectra of $Co(NO)(NO_2)_2L_2$ complexes consist of a single line that sharpened as the temperature was lowered. Except the $PMePh_2$ derivative, similar spectra were obtained for the bischloro nitrosyl complexes. For $Co(NO)Cl_2(PMePh_2)_2$ the ^{31}P NMR signal was relatively sharp at room temperature ($\Delta\nu_{(1/2)}$ = 40 Hz) when the sample was cooled to -60°C the NMR signal became broad ($\Delta\nu_{(1/2)}$ ~ 300 Hz). Several spectra were recorded between -45 and -65°C, but no splitting of the signal was observed. At lower temperature (-90°C) the singlet again sharpened (30 Hz). The process was reversible. Table 3.3 shows the chemical shifts with respect to TMP. Figures 3.2 - 3.4 show the spectra at different temperatures for $Co(NO)Cl_2(PMePh_2)_2$, $Co(NO)(NO_2)_2(PMe_2Ph)_2$ and $Co(NO)Cl_2DPPPr$. $^{31}P\{^{1}H\}$ NMR measurements were also made for $Co(NO)(^{15}NO_2)_2L_2$ complexes at -80°C. The only change observed due to the labeling was a slight broadening of the ^{31}P signal to 40 Hz. The chemical shifts remained unchanged. $^{2}J_{(^{15}N-^{31}P)}$ was not observed due to the width of the signal.

TABLE 3.3 $^{31}P\{^{1}H\}$ NMR CHEMICAL SHIFTS.

Complex	20°C		-80°C	
	δ(ppm)[a]	$\Delta\nu_{(1/2)}$(Hz)	δ(ppm)[a]	$\Delta\nu_{(1/2)}$(Hz)
$Co(NO)(NO_2)_2(PMe_3)_2$	-136.0	~1200	-134.2	35
$Co(NO)Cl_2(PMe_3)_2$	-130.0	~ 850	-127.1	25
$Co(NO)(NO_2)_2(PMe_2Ph)_2$	-132.9	~ 850	-128.8	35
$Co(NO)Cl_2(PMe_2Ph)_2$	-131.9	~ 900	-126.2	30
$Co(NO)(NO_2)_2(PMePh_2)_2$	-126.4	~1000	-123.1	30
$Co(NO)Cl_2(PMePh_2)_2$	-130.3	40	-112.4	30
$Co(NO)Cl_2$DPPPr	-125.0	1000	-123.0	25

a. Positive shifts are downfield from TMP

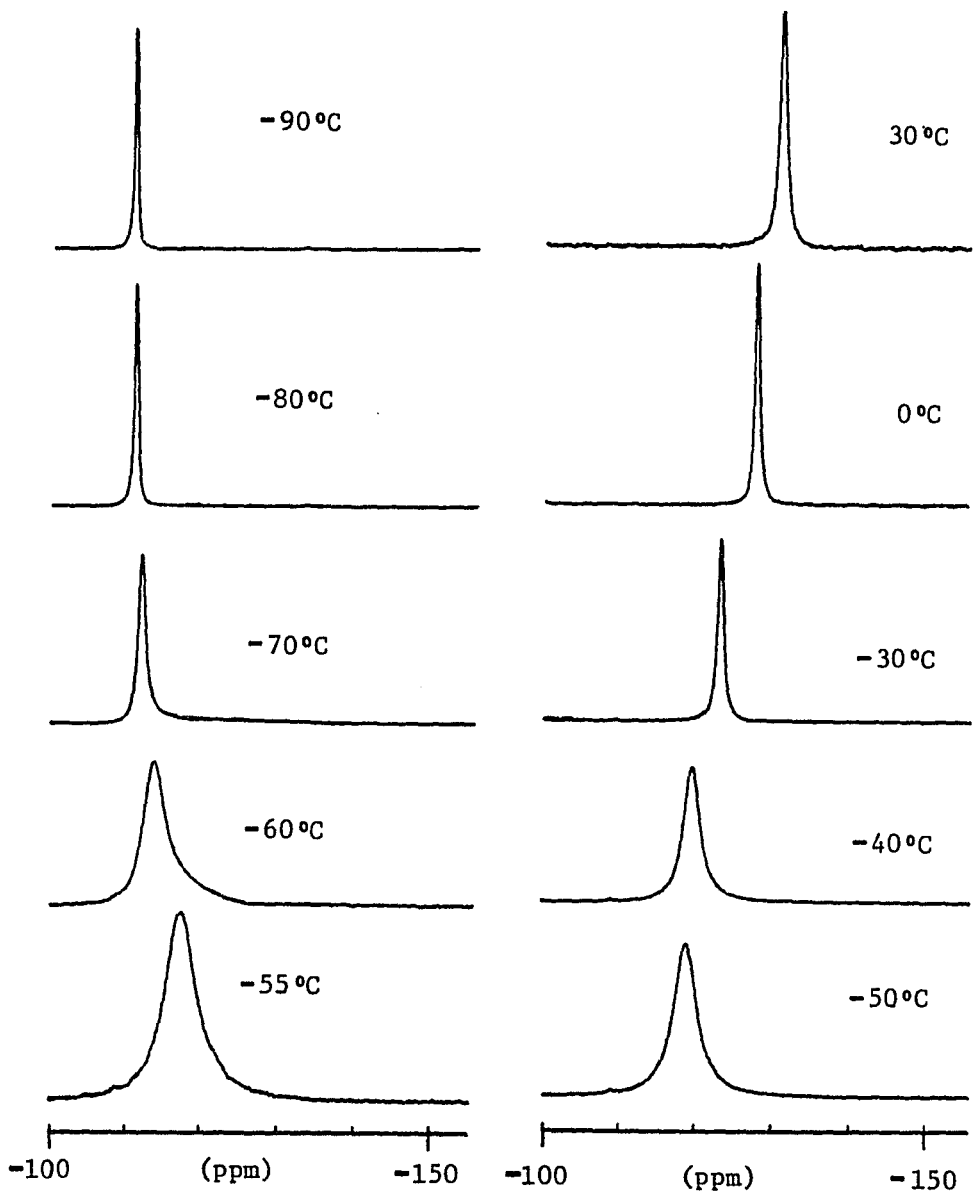


Figure 3.2. ^{31}P NMR spectra of $Co(NO)Cl_2(PMePh_2)_2$ at different temperatures. (Ref. TMP)

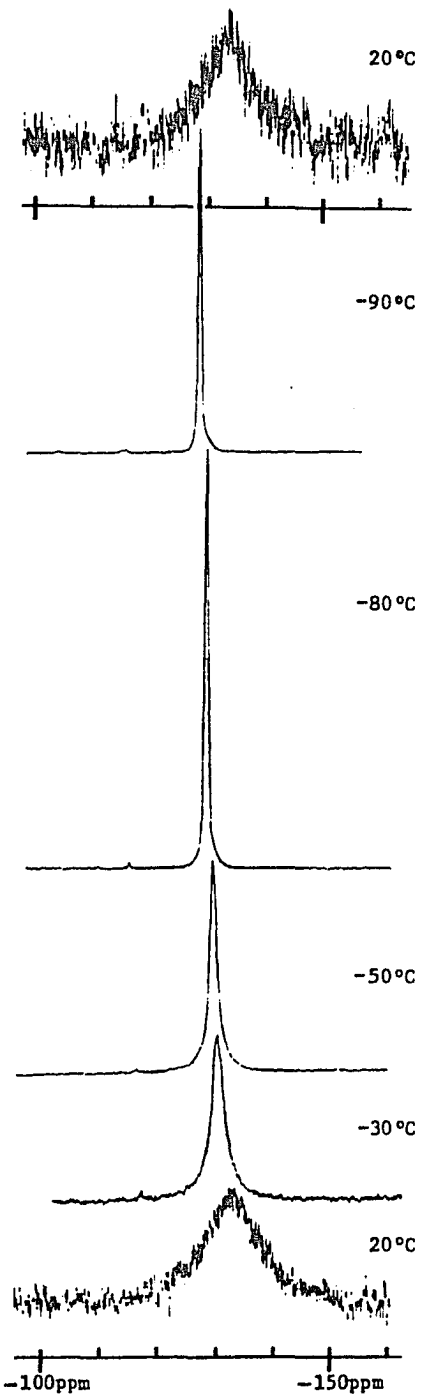


Figure 3.3. ^{31}P NMR spectra of $Co(NO)(NO_2)_2(PMe_2Ph)_2$ at different temperatures. (Ref. TMP).

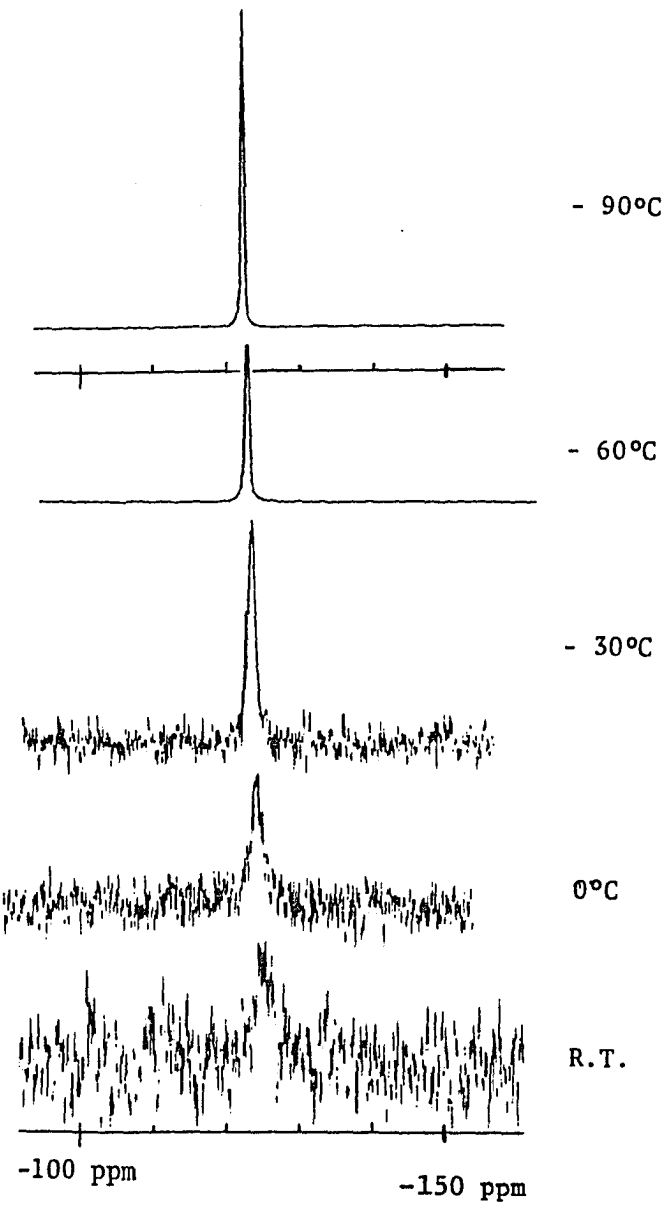


Figure 3.4. ^{31}P N.M.R. spectra of $Co(NO)Cl_2DPPPr$ at different temperatures. (Ref. TMP).

^{15}N NMR Spectra.

Nitrogen-15 NMR spectra were measured for $Co(NO)(^{15}NO_2)_2L_2$ (95.3% ^{15}N enriched) (L = PMe_3, PMe_2Ph and $PMePh_2$) over the temperature range +30 to -80°C in 90% CH_2Cl_2, 10% CD_2Cl_2. $^{31}P\{^1H\}$ NMR measurements on the labeled compounds were made to check consistency with the previous ^{31}P NMR spectra of the unlabelled materials.

At low temperature (-80°C), the 15-N NMR spectra consisted of a sharp singlet due to the $^{15}NO_2$ group bonded to the cobalt though the oxygen atoms and a well defined 1:2:1 triplet due to the $-^{15}NO_2$ nitrogen bonded to the cobalt atom (Figures 3.5,3.6:B,C). The triplet is due to the strong coupling of the two trans phosphorous atoms with the nitrogen atom of the $-NO_2$ ligand. The two signals have the expected integrated relative intensity. Several spectra were recorded with and without ^1H decoupling, but no differences were observed. The best spectra were obtained by using 90° pulses and a delay of 5 seconds to allow for relaxation of the ^{15}N nuclei.(53) Under these conditions the ^{15}N NMR signals were clearly observed after only 70 pulses. With 300 scans a spectrum with excellent signal to noise was obtained. Figure 3.5:B shows the spectrum of $Co(NO)(^{15}NO_2)_2(PMe_2Ph)_2$ at -80°C obtained under the conditions described above. Table 3.4 lists the ^{15}N chemical shift measurements with respect to nitromethane for $Co(NO)(^{15}NO_2)_2(PMe_xPh_{3-x})_2$(x = 1-3) and the $^2J_{(31P-15N)}$ coupling constants obtained at -80°C. As the temperature was raised to ambient conditions, the triplet was observed to broaden. This is shown in Figure 3.7 for $Co(NO)(^{15}NO_2)_2(PMe_2Ph)_2$.

The solution structures of $Co(NO)(NO_2)_2L_2$ (L = $PMePh_2$, PMe_2Ph) were defined by the ^{15}N NMR analyses at natural abundance of these compounds (Figures 3.5A, 3.6A).[65] The spectra were recorded at -65°C and they clearly show the three different signals for the nitrogen atoms of these complexes (Table 7). The ^{15}N nitrosyl resonances were observed at about 580 ppm downfield from nitromethane in agreement with previous results for bent nitrosyls in cobalt complexes.[72] The other two resonances agree with the results obtained for the ^{15}N labeled compounds at the NO_2 positions. Resolution of the signals could not be observed due to the poor signal to noise. As shown in Figure 3.7, the coupling between the ^{15}N and the ^{31}P is ~9.3 Hz. The $^2J_{(^{31}P-^{15}N)}$ coupling constants confirm their cis geometry. Other complexes containing both N ligands and phosphine ligands have $^2J_{(^{31}P-^{15}N)}$ coupling constants of 50-70 Hz for trans isomers and ~10 Hz for cis isomers (see Table 7). It is important to note that in the course of the natural abundance ^{15}N experiments the nitrosyl peak was observed after 3000 scans as a clearly defined signal. The signal for the chelate NO_2 ligand was observed after 5800 scans, and the $-NO_2$ signal was observed after 3000 additional scans. A series of experiments was performed to select the optimum total pulsing time. It was found that no signal could be observed by using adquisition times of 0.4096 seconds (calculated by the computer for the sweep window of 30,000 Hz) and no delay to allow the sample to relax. Nitrogen-15 is known to have long relaxation times and in $Co(NO)(NO_2)_2L_2$ it was observed that each nitro ligand has a different

relaxation time, being longer than one second in each case.[53] For total pulsing time of one second, still no signal is observed. For acquisition times of 0.4096 seconds and delays of 1.000 sec. the signals are observed to appear with different intensities, being the most intense for the nitrosyl peak (shorter relaxation time) and the weakest for the signal of the nitrogen bonded NO_2 group. When longer pulsing times were used (AT = 0.4096, Delay = 1.600 sec.), the signals for the three nitrogen atoms were observed with equal intensity. This suggests almost complete relaxation of the sample under these conditions.[73]

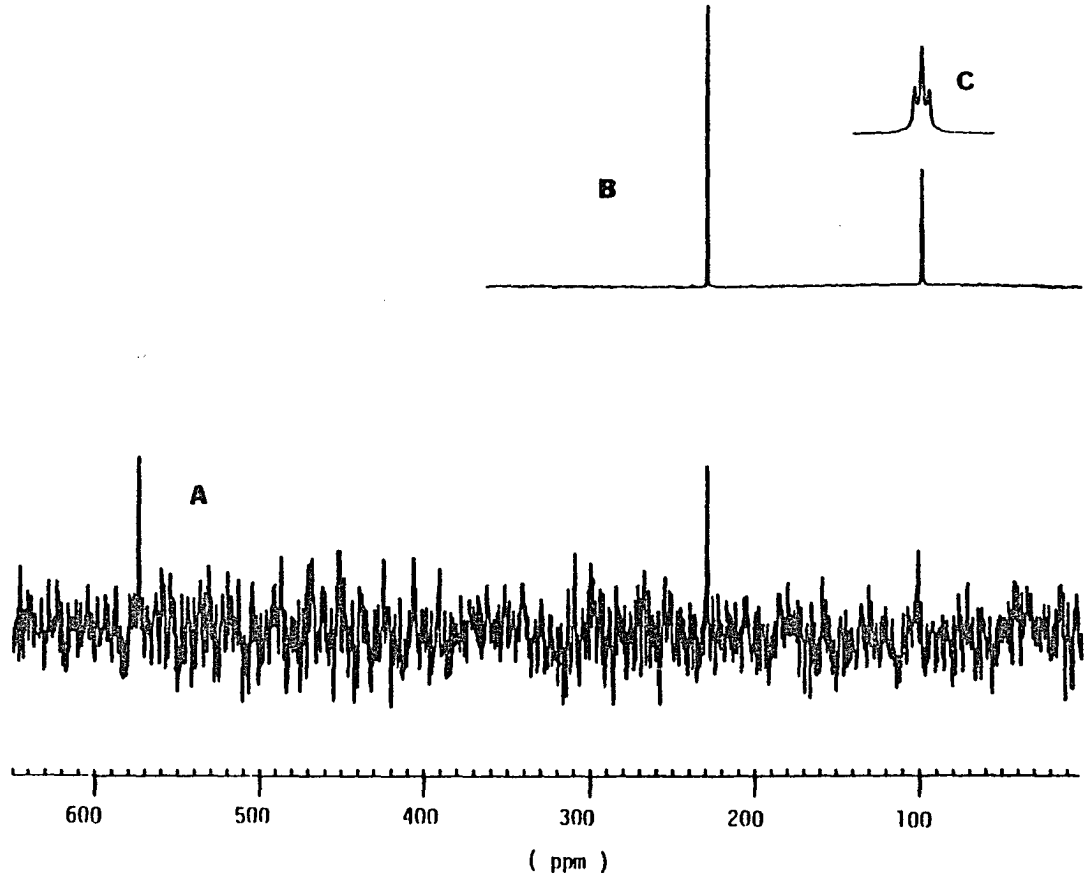


Figure 3.5. ^{15}N NMR spectra of $Co(NO)(NO_2)_2(PMe_2Ph)_2$. A. Natural abundance. B. 95.3 % enrichment of the NO_2 ligands.

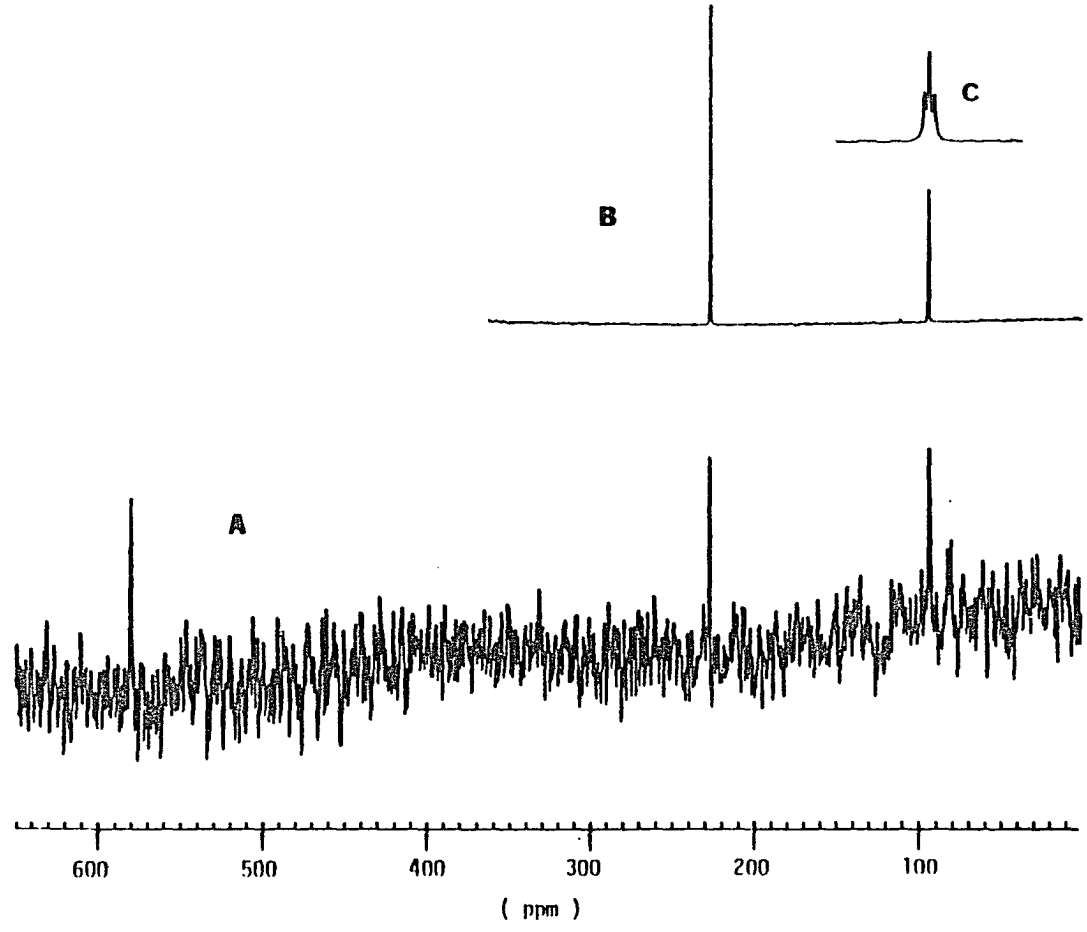


Figure 3.6. ^{15}N NMR spectra of $Co(NO)(NO_2)_2(PMePh_2)_2$. A. Natural abundance. B. 95.3% ^{15}N enrichement of the NO_2 ligands.

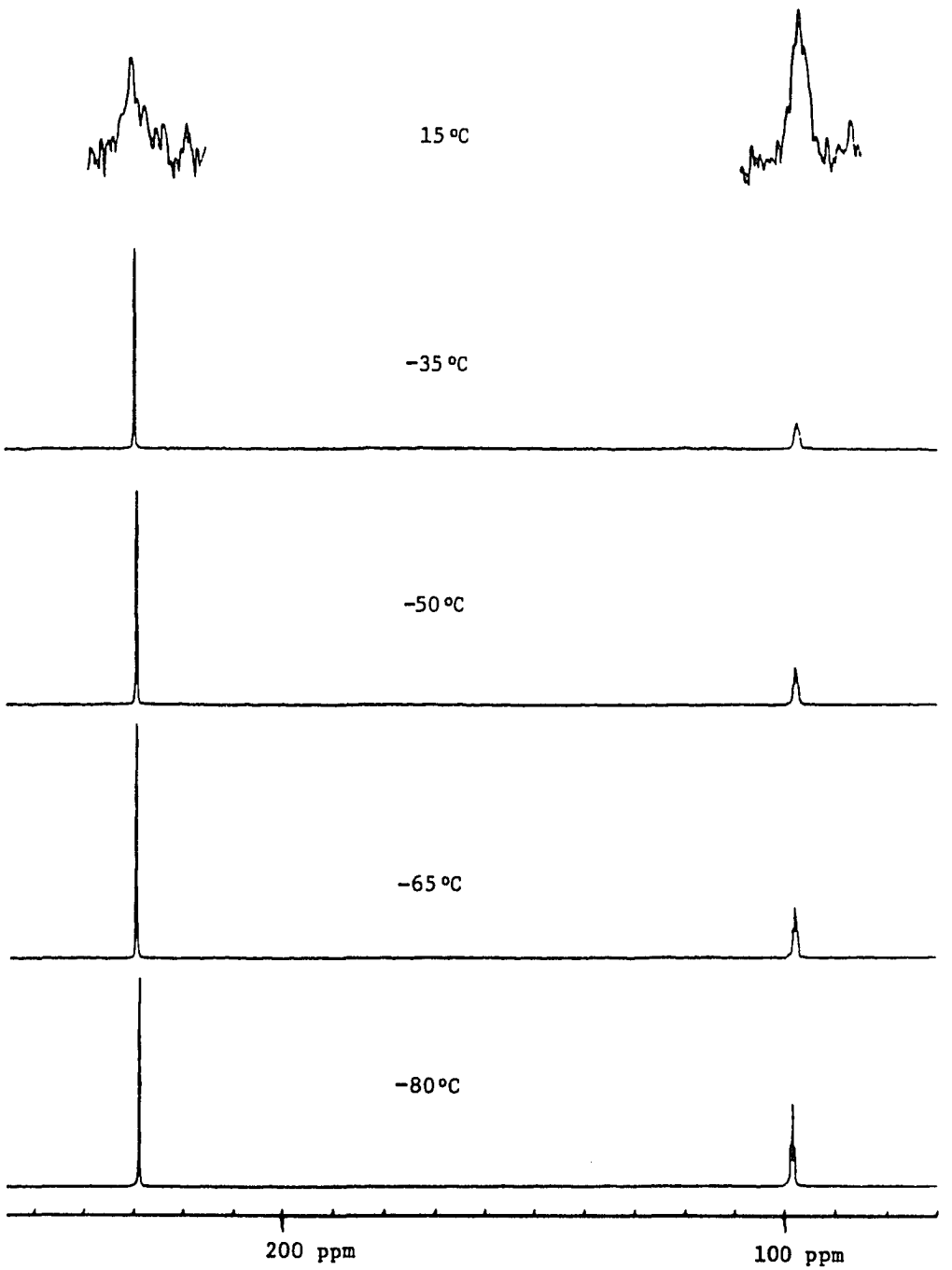


Figure 3.7. Variable temperature ^{15}N NMR study of $Co(NO)(^{15}NO_2)_2(PMe_2Ph)_2$. (Ref. CH_3NO_2).

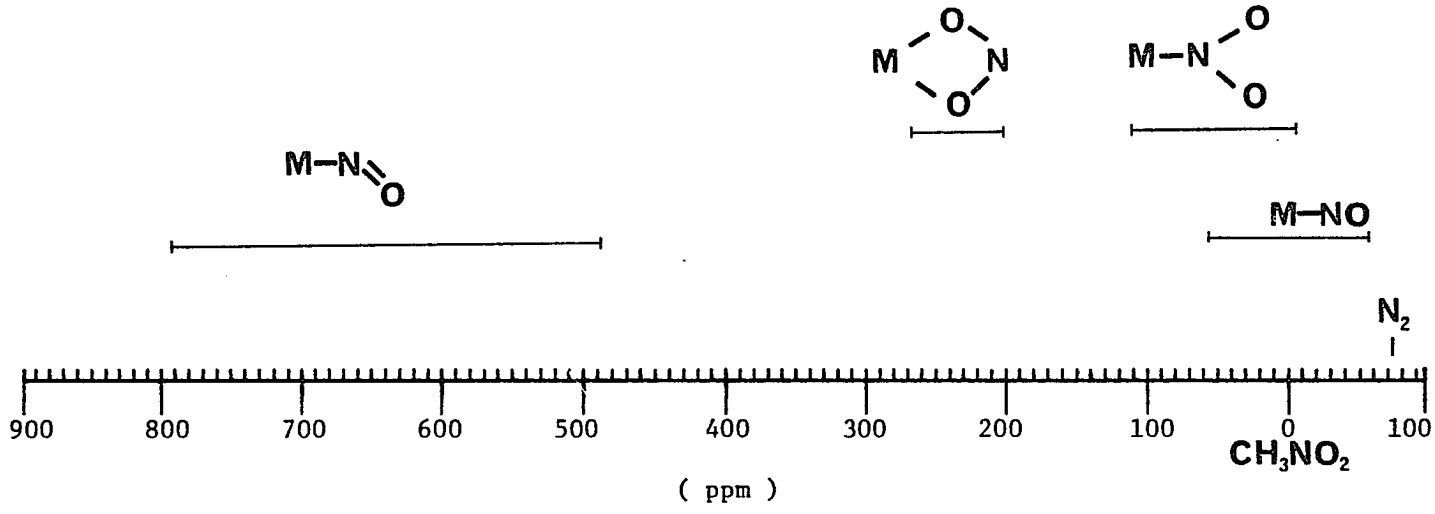
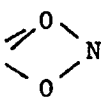
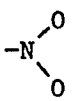


Figure 3.8. ^{15}N NMR chemical shift scale (Ref. Nitromethane).

TABLE 3.4 ^{15}N N.M.R. CHEMICAL SHIFTS AND COUPLING CONSTANTS $^{2}J_{(^{31}P-^{15}N)}$ FOR $Co(NO)(NO_2)_2L_2$. (Ref. Nitromethane).

L	$-{}^{15}N{=}O$ (ppm)	 (ppm)	 (ppm)	$^{2}J_{(^{31}P-^{15}N)}$ (Hz)
$PMePh_2$	580.37[a] 576.90[c]	226.82[a] 226.77[b]	93.26[a] 94.17[b]	9.22[b]
PMe_2Ph	574.10[a]	228.80[a] 228.82[b]	98.00[a] 98.18[b]	9.37[b]
PMe_3		220.08[b]	100.27[b]	9.46[b]

a ^{15}N NMR natural abundance (t = -65°C).

b ^{15}N NMR 95.3% labelled at NO_2 positions (t = -80°C).

c ^{15}N NMR 95.3% labelled at NO position (t = -80°C).

^{14}N NMR of cobalt complexes.

^{14}N NMR spectra were measured for $CoNO_x$ complexes and the results are shown on Table 3.5. Deshieldings up to 56 ppm (relative to neat nitromehane) were observed for linear nitrosyls. For $Co(NO)(NO_2)_2L_2$ (L = $PMePh_2$ and PMe_2Ph) with bent nitrosyls (129.(1)° and 128.(1)°) the NO resonances were found at 580 and 590 ppm respectively with $\Delta\nu_{(1/2)}$ of 2000 and 1500 Hz. These figures agree with the values of 580.37 and 574.10 obtained by ^{15}N NMR at natural abundance for these complexes. For bent nitrosyls, 20,000 to 25,000 pulses were needed to observe clearly defined signals. Linear CoNO groups produced relatively narrower lines ($\Delta\nu_{(1/2)}$ ~ 200 to 630 Hz) and were clearly observed after 1,000 scans over a period of pulsing of about 5 minutes. The crystal structures of the complexes analyzed in this ^{14}N NMR study are known. In all cases the geometry of the nitrosyl ligands was found to be the same both in solution and in solid state. These experiments show the potential of nitrogen NMR spectroscopy as a criterion of geometry, particularly in solution for nitrosyl complexes.(65-72)

TABLE 3.5 ^{14}N NMR CHEMICAL SHIFTS OF COBALT NITROSYL COMPLEXES

Complex	δ(ppm)[a]	$\Delta\nu_{(1/2)}$(Hz)
$Co(NO)(NO_2)_2(PMe_2Ph)_2$	580	2000
[$\delta(-NO_2)$]	95	1500
$Co(NO)(NO_2)_2(PMePh_2)_2$	590	2400
$Co(NO)(CO)(PMePh_2)_2$	17	196
$Co(NO)(CO)_2(PPh_3)$	16	263
$Co(NO)_2(ONO)(PPh_3)$	56	335
$Co(NO)_2I(PPh_3)$	47	348
$[Co(NO)_2(PPh_3)_2]ClO_4$	22	629

[a]Positive shifts are downfield from neat CH_3NO_2.

Conclusions

A major objective of this multinuclear NMR study was to determine the solution structure of the $Co(NO)(NO_2)_2L_2$ complexes. For comparison, $CoCl_2(NO)L_2$, cobalt bis nitrosyls and nitrosyl-carbonyl complexes were also studied. Proton NMR spectra of $Co(NO)(NO_2)_2L_2$ and $Co(NO)Cl_2L_2$ establish trans geometry for the phosphine ligands in these complexes.(47) Trans geometry is confirmed by the equivalence of the ^{31}P NMR spectra of these complexes. Nitrogen NMR provided important information about in the coordination geometry of the NO_x ligands. Figure 3.8 shows a nitrogen NMR chemical shift scale referred to neat nitromethane. Linear nitrosyls give ^{14}N signals at higher fields (50 to -50 ppm) with linewidths between 200 to 600 Hz. Deshieldings from 500 to 700 ppm were observed for bent nitrosyl ligands. These signals were broad ($\Delta\nu_{(1/2)}$ ~ 1,500 to 2,000 Hz).(72) Different coordination geometries of NO_2 ligands also gave rise to different ^{14}N NMR signals. Nitrogen bonded NO_2 groups gave resonance signals from 90 to 100 ppm. Oxygen bonded NO_2 groups have more deshielded NMR signals, above 220 ppm for chelate NO_2 groups and up to 240 ppm for -ON=O ligands as in $Co(NO)_2(ONO)(PPh_3)$. This study corroborated the power of NMR spectroscopy in determining solution structures of inorganic compounds and indicated the potential of nitrogen NMR as a criterion of geometry for NO and NO_2 ligands.

CHAPTER 4

REACTIONS OF $Co(NO)(NO_2)_2L_2$ COMPLEXES: FORMATION OF $Co(NO)_2XL$. THE CRYSTAL STRUCTURES OF $Co(NO)_2Cl(PPh_3)$ AND $Co(NO)_2(ONO)(PPh_3)$

Introduction

The presence of two powerful π-acceptor ligands in dinitrosyl complexes of transition metals stabilizes uncommon, low oxidation states and imparts other unusual properties to such complexes. The four-coordinate, pseudotetrahedral dinitrosyl complexes are especially interesting in this regard.[74-77] Several of these complexes have been shown to be effective catalysts in the reduction of nitric oxide by carbon monoxide.[78-79]

$$2NO + CO \xrightarrow[\text{"M(NO)}_2\text{"}]{} N_2O + CO_2 \qquad (4.1)$$

Many of these complexes undergo two-electron and four-electron oxidations, thereby allowing two successive oxidation-addition reactions to take place.[19,80,84] Reactions of $Co(NO)(NO_2)_2L_2$ with carbon monoxide, nitric oxide and acyl halides produce $Co(NO)_2XL$ complexes. This is a series of low valent, pseudotetrahedral dinitrosyl cobalt complexes which contains the $\{Co(NO)_2\}^{10}$ moiety.[1-2] Their structures reflect the electronic requirements of a metal center. To provide more infor-

mation about bisnitrosyl complexes, a study of the crystal structures of $Co(NO)_2Cl(PPh_3)$ and $Co(NO)_2(ONO)(PPh_3)$ was undertaken. Details of this study are contained in this chapter.

Experimental

The reactions of the $Co(NO)(NO_2)_2L_2$ complexes were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques.[36-37] Reagent grade solvents were distilled under nitrogen and purified according to published procedures immediately prior to use.[35] Microanalyses were carried out by Atlantic Microlabs, Atlanta, Georgia and The University of Arizona Analytical Center. Solid state infrared spectra were obtained from KBr pellets using a Perkin-Elmer Model 983 controlled by a remote Data Station. ^{13}C NMR spectra were obtained using a Bruker WM 250 spectromenter. Elemental analyses are shown in Table 2.1.

Reactions with Carbon Monoxide:

A. $Co(NO)(NO_2)_2(PPh_3)_2$: 0.200 g. of the complex was dissolved in 50 ml of acetone. The brown solution was stirred for two days under positive pressure of CO. The resultant brown-black mixture was filtered to remove solids and the solvent was removed with a continuous flow of nitrogen. The black oil obtained was dissolved in 15 ml of toluene and 10 ml of hexane was added. The mixture was kept at -10 °C for one day. The resultant dark brown microcrystalline solid which formed was removed by filtration,

washed with 10 ml of n-pentane and vacuum dried. Yield 0.1262 g (75%). The product was identified by elemental analysis and IR spectroscopy as $Co(NO)(CO)(PPh_3)_2$.(83) [ν_{CO}: 1940 (s) cm^{-1} and νNO:1705 (s) cm^{-1}). This product was compared with an authentic sample of $Co(NO)(CO)(PPh_3)_2$ prepared from the reaction of $Co(NO)(PPh_3)_3$ and benzoyl chloride in THF.(84) After one day of stirring, the reaction of $Co(NO)(NO_2)_2(PPh_3)_2$ (2.25 g.) in 80 ml of acetone with CO at 3100 psi of pressure produced a brown red solution of $Co(NO)(CO)_2(PPh_3)$(85) [ν_{CO}: 2036(m), 1980(s) and ν_{NO}: 1760(s) cm^{-1}, M.P. 130 °C].(83,85) Yield 1.170 g (90%).

B. $Co(NO)(NO_2)_2(PMePh_2)_2$: 0.250 g. of the complex was dissolved in 40ml of acetone and stirred for two days under an atmosphere of CO. The solvent was removed by flowing nitrogen very slowly through the reaction vessel. The dark brown oil was dissolved in 30 ml of toluene, and 30 ml of hexane was added to this solution. After one day at -10 °C, abundant precipitation of the red compound $Co(NO)(CO)(PMePh_2)_2$ was observed. A light brown solid also formed. This brown compound dissolved after shaking the mixture several times at room temperature. The remaining red crystals of $Co(NO)(CO)(PMePh_2)_2$ were washed with methanol and vacuum dried. [ν_{CO}: 1934(s) cm^{-1}; ν_{NO}: 1699(s) cm^{-1}; Anal. calcd. for $CoNO_2P_2C_{27}H_{26}$: C, 62.68; H, 5.07; N, 2.70. Found: C, 62.62.; H, 5.02; N, 2.88.]. Yield 0.144 g (64%).

C. $Co(NO)(NO_2)_2(PPh_3)_2$ and MX [M = Na, K; X = Cl, Br]: 0.250 mmoles of the complex were mixed in 40 ml of acetone with the same number of moles of MX. The light brown solutions formed were stirred under positive pressure of CO for two days. A change to black occurred. The black solutions were filtered to remove light yellow insoluble materials. The solvent was removed and the dark oil obtained was dissolved in 10 ml of toluene. 10 ml of hexane were added to each of the toluene solutions and then cooled at -10 °C for two days. Black crystalline $Co(NO)_2Cl(PPh_3)$ and $Co(NO)_2Br(PPh_3)$ were isolated from these solutions.(86)

Reactions with acyl halides:

A. $Co(NO)(NO_2)_2L_2$ (L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, PEt_2Ph, $PEtPh_2$) react with acyl halides RCOX (R = $C_6H_5^-$, CH_3^-, $CH_3(CH_2)_4^-$, adipoyl$^-$ and X = Cl, Br) to form the corresponding bisnitrosyl, monophosphine, monohalide cobalt complexes. The other products of these reactions are gaseous NO, phosphine oxides and the corresponding carboxylic acid. The process is represented by equation 4.2.

$$Co(NO)(NO_2)_2L_2 + RCOX \longrightarrow Co(NO)_2XL + OL + NO + RCOOH \qquad (4.2)$$

Reactions performed by mixing stoichiometric amounts of the reagents were completed in approximately five minutes. The processes were followed by observing the appearance of the characteristic pattern of the nitrosyl bands for the bisnitrosyl complexes and the disappearance of the NO peaks of the starting materials using liquid infrared spectroscopy in THF. A summary of the infrared stretching frequencies for the bis-nitrosyl complexes prepared is shown in Table 4.1. NO gas was detected by infrared spectroscopy. The carboxylic acid was detected by GC-Mass Spectroscopy using a computer controlled HP 5930A quadrupole mass spectrometer. In control reactions, $Co(NO)(NO_2)_2L_2$ in pure THF was converted into $Co(NO)_2(ONO)L$ after stirring for one day under carfully controlled nitrogen atmosphere. Reactions of these $Co(NO)_2(ONO)L$ complexes with RCOX produced the corresponding $Co(NO)_2XL$ complexes by substitution of the ONO^- ligand for the halogen. Reactions performed with excess of the acyl halides resulted in the formation of the corresponding bischloro or bisbromo bisphosphine oxide cobalt complexes. To prove the authenticity of some of the products, $Co(NO)_2XL$ (X = Cl, Br; L = PPh_3 and $PMePh_2$) were prepared by alternative routes shown in the appropriate section of Figure 1.1.

Reactions with Nitric Oxide:

A. $Co(NO)(NO_2)_2(PPh_3)_2$: 0.250 g. of the complex was dissolved in 40 ml of acetone and stirred under an atmosphere of purified nitric oxide After 10 minutes the solution turned black. The solvent was removed and the black oil obtained was dissolved in 20 ml of toluene. 10 ml of hexane were added and the mixture was stored at -10° C for one day. Black crystalline $Co(NO)_2(ONO)(PPh_3)$ precipitated. The compound was washed with cold n-pentane and vacuum dried. This compound could also be prepared by alternative routes: Method 2: Dissolving $Co(NO)(NO_2)_2(PPh_3)_2$ in CH_2Cl_2 produces $Co(NO)_2(ONO)(PPh_3)$ and triphenylphosphineoxide. An acetone or a THF solution of the same starting material produces the bis-nitrosyl after stirring for one day. The product is isolated as indicated before. $OPPh_3$ crystals can be also obtained if 1:3 toluene:hexane solutions are used to precipitate the products. The process can be represented by:

$$Co(NO)(NO_2)_2(PPh_3)_2 \xrightarrow[\text{Acetone, THF}]{CH_2Cl_2,\ CH_3CN} Co(NO)_2(ONO)(PPh_3) + OPPh_3 \quad (4.3)$$

0.2500 g of $Co(NO)(NO_2)_2(PPh_3)_2$ was dissolved in 15.0 ml of CH_2Cl_2 and the resulting black solution that formed after 15 min of stirring was used for ^{14}N NMR studies after being filtrated in a

glove bag filled with dry nitrogen. A nitrosyl resonance was obtained at 56 ppm from nitromethane and confirmed the presence of linear nitrosyls in this compound.

Method 3:(87)

$Co(NO)_2(ONO)(PPh_3)$ was prepared from the reaction of 0.50 mmoles of $[Co(NO)_2(PPh_3)_2]ClO_4$ with 2.50 mmoles of KNO_2 in 15 ml of ethanol.

B. $Co(NO)(NO_2)_2(PMe_2Ph)_2$ and $Co(NO)(NO_2)_2(PMePh_2)_2$:

These complexes produce the corresponding bis-nitrosyls when dichloromethane solutions are exposed to purified nitric oxide. Only oils could be obtained from these preparations, however Table 4.1 shows the ν_{NO} frequencies for $Co(NO)_2(ONO)(PMePh_2)$ and $Co(NO)_2(ONO)(PMe_2Ph)$.

TABLE 4.1 INFRARED DATA FOR $Co(NO)_2XL$.[a]

Complex	υ_{NO}	Additional nonphosphine bands		
$Co(NO)_2Cl(PPh_3)$	1819(s),1765(s), 1737(s)	Co-Cl		303[b]
	1829(s),1764(vs)[c]			
	1817(s),1753(vs)[d]			
$Co(NO)_2Cl(PMePh_2)$	1844(s),1788(vs)			
	1818(s),1755(vs)[d]			
$Co(NO)_2Cl(PMe_2Ph)$	1820(s),1770(vs)[d]			
$Co(NO)_2Cl(PMe_3)$	1826(s),1753(vs)[d]			
$Co(NO)_2Br(PPh_3)$	1823(s),1771(s), 1742(s)			
	1883(m),1770(vs)[c]			
	1824(m),1760(s)[d]			
$Co(NO)_2Br(PMePh_2)$	1822(s),1759(s)[d]			
$Co(NO)_2Br(PMe_2Ph)$	1818(m),1760(s)[d]			
$Co(NO)_2I(PPh_3)$	1826(s),1781(s), 1750(s)			
	1834(m),1778(vs)[e]			
$Co(NO)_2(ONO)(PPh_3)$	1830(s),1761(vs)	-ONO	$\upsilon_{NO_{as}}$	1401
	1831(s),1766(vs)[c]		$\upsilon_{NO_{sym}}$	1095
	1830(s),1769(s)[d]		δ_{ONO}	757
$Co(NO)_2(ONO)(PMePh_2)_2$	1844(m),1790(s)[c]			
$Co(NO)_2(ONO)(PMe_2Ph)_2$	1840(m),1785(s)[c]			
$Co(NO)_2(NCS)(PPh_3)$	1849(m),1797(s)	-NCS	υ_{NC} 2066(vs)	
			υ_{CS} 834(m)	

[a]All frequencies are reported in cm^{-1} using the polystyrene band at 1601 cm^{-1} as standard.
[b]Determined using parafin oil mull and CsI windows.
[c]CH_2Cl_2, [d]THF, [e]$CHCl_3$.

Collection and Reduction of X-Ray Intensity Data:

Crystals of $Co(NO)_2(ONO)(PPh_3)$ prepared by method 2 were grown from a toluene-hexane solution. The compound crystallizes as black rectangular parallelopipeds. One of the crystals was mounted on a glass fiber using a coating of cyanoacrylate adhesive and used for data collection.

Several well-formed crystals of $Co(NO)_2Cl(PPh_3)$ obtained from the reaction of $Co(NO)(NO_2)_2(PPh_3)_2$ with NaCl and CO in acetone were crystallized from a toluene-pentane solution and examined under a microscope. One well-defined, rectangular crystal was selected for data collection.

The determination of the Bravais lattices, cell dimensions and the collection of intensity data were carried out with a Syntex $P2_1$ diffractometer equipped with a scintillation counter and a graphite monochromator. The cell constants were determined using the centering of 25 reflections with $13° < 2\theta\ (MoK\alpha) < 26°$. After least squares refinement[46] of the setting angles, the crystal system and axis lengths were checked using axial photographs. Several omega-scans showed sharp Bragg peaks with a width at half height of 0.31°. The crystallographic data is shown in Table 4.2. Data collections were carried out at room temperature with $MoK\alpha$ radiation using $\theta - 2\theta$ scan technique. The intensities of two standard reflections, measured every 98 reflections, showed no decay during data collection. The data revealed systematic absences characteristic of the monoclinic space group C2/C for both compounds. The data was corrected for Lorentz and polarization effects.

Solution and Refinement of the Structures:

The structure of $Co(NO)_2(ONO)(PPh_3)$ was solved by the heavy-atom Patterson method. MULTAN gave the positions of all nonhydrogen atoms. The final cycles of least-squares refinement were carried out with anisotropic nonhydrogen atoms, and isotropic hydrogen atoms.(45) These conditions gave final residual indices R = 0.053 and Rw = 0.063 where refinement was based on minimization of $\Sigma w = (|Fo| - |Fc|)^2$ with $w = 4Fo^2/\sigma^2(Fo^2)$ and $\sigma^2(F_o^2) = \sigma^2(I) + (PF_o^2)^2$ where $\sigma^2(I)$ is the standard deviation of the F_o^2 due to counting statistics, F_o and F_c are the observed and calculated structure amplitudes and "P", the factor to prevent overweighting of strong reflection set to 0.03. The "Goodness of Fit" was 2.61. The highest peak from the final diference map was 1.088 e.$Å^{-3}$ at 0.905 Å from the cobalt atom of $Co(NO)_2(ONO)(PPh_3)$.

The structure of $Co(NO)_2Cl(PPh_3)$ was solved using standard MULTAN packages. All the hydrogen and the non-hydrogen atoms were located by succesive refinements and difference electron density maps with the use of full-matrix, least-squares techniques. Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms with isotropic thermal parameters.(45) All data with $F_o > 3\sigma(F_o)$ were included in least squares calculations. Final refinement of the model by using 2295 independent reflections converged with R = 0.034 and Rw = 0.039. the "Goodness of Fit", defined by $[\Sigma w(|Fo| - |Fc|)^2/(n - m)]^{1/2}$ where n is the number of reflections used in the refinement of m is

TABLE 4.2 SUMMARY OF CRYSTALLOGRAPHIC DATA FOR $Co(NO)_2Cl(PPh_3)$[a] and $Co(NO)_2(ONO)(PPh_3)$[a]

Compound	$Co(NO)_2Cl(PPh_3)$	$Co(NO)_2(ONO)(PPh_3)$
Formula	$CoN_2O_2ClPC_{18}H_{15}$	$CoN_3O_4C_{10}H_{15}$
Formula weight	416.66	427.25
Crystal shape	Parallelpipeds	Rectangular
Crystal dimensions, mm	0.25 x 0.12 x 0.42	0.20 x 0.15 x 0.30
Crystal color	Black	Black
Crystal system	Monoclinic	Monoclinic
Space group	C2/c (No. 15)	C2/c (No. 15)
Cell dimensions[b]		
a, Å	16.955(5)	15.963(4)
b, Å	10.430(4)	13.201(3)
c, Å	21.239(2)	18.676(3)
β, deg.	95.96(2)	103.92(2)
V, $Å^3$	3771(2)	3820(1)
Z	8	8
Temperature, °C	25	24
$d_{obs.}$[c], $g \cdot cm^{-3}$	1.461(5)	1.471(5)
$d_{calc.}$, $g \cdot cm^{-3}$	1.461(5)	1.481(5)
Radiation, Å	MoKα, = 0.71069	MoKα, = 0.71069
Monochromator	Graphite crystal	Graphite Crystal
Data collection method	θ - 2θ scan	θ - 2θ scan

TABLE 4.2 continued

Portion of the sphere collected	h k $\pm$ ℓ	h k $\pm$ ℓ
Scan speed, deg./min	Variable (3 - 20)	Variable (3 - 20)
Scan range, deg. (2θ)	1.2 below $K\alpha_1$ to 1.4 above $K\alpha_2$	1.2 below $K\alpha_1$ to 1.4 above $K\alpha_2$
Scan to background time	2.0	2.0
Decomposition	Not significant	None
Max. shift during least squares (Δ/σ)	0.35	0.71
Number of unique data	3331	3559
Number of data used in calculations	2295	2147
Number of variables	271	244
Absorption coefficient (μ), cm^{-1}	11.46	10.04
$R(F) = \sum\|\|Fo\| - \|Fc\|\|/\sum Fo$	0.034	0.053
$Rw(F) = (\sum w(\|Fo\| - \|Fc\|)^2/\sum wFo^2)^{1/2}$	0.039	0.063

[a]The standard deviation of the least significant figure is given in parenthesis in this and the following tables.

[b]Cell dimemsions were obtained from a least-squares refinement of setting angles of 25 reflections in the 2θ range 13-26.

[c]Density was determined by flotation using a solution of hexane and carbon tetrachloride.

the number of refined parameters, was 1.53. The largest peak in the final electron density map was 0.374 e.$Å^{-3}$ located at 1.05 Å from the cobalt atom. The calculations were made on a Digital PDP 11/34a Computer at the X-ray Laboratory of the Chemistry Department of the University of Arizona.

Results and Discussion

Reactions of $Co(NO)(NO_2)_2L_2$ complexes (L = PPh_3, $PMePh_2$ and PMe_2Ph with carbon monoxide produce bisnitrosyls, nitrosyl-carbonyls and nitrosyl-dicarbonyl complexes. $Ni(NO_2)_2L_2$ complexes (L = PMe_2Ph, PCy_3, PEt_3, PMe_3, ½ of DPPE and DPPP) are known to react with CO to form $Ni(NO_2)(NO)L_2$ complexes and CO_2.[12,13] These reactions occur via the transfer of an oxygen atom from a nitro group to a coordinated CO ligand as indicated on Figure 4.1.

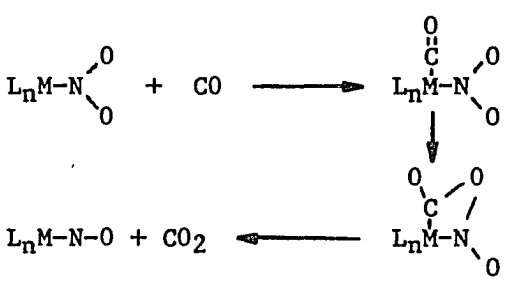
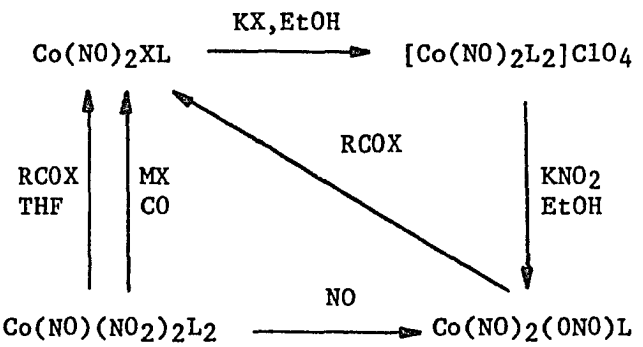


Figure 4.1 Mechanism proposed for oxygen atom transfer from NO_2 to CO

$Co(NO)(NO_2)_2L_2$ complexes were not observed to produce the expected $Co(NO)_2(NO_2)L$ products when exposed to an atmosphere of CO for different periods of time, even at high pressures of 3100 psi. Reactions at one atmosphere of CO produced $Co(NO)(CO)L_2$ complexes. At high pressures of CO the products were $Co(NO)(CO)_2L$ complexes. Bisnitrosyl complexes were obtained by reacting $Co(NO)(NO_2)_2L_2$ complexes with CO in the presence of

MX (M = Na, K; X = Cl, Br). By these reactions $Co(NO)_2Br(PPh_3)$ and $Co(NO)_2Cl(PPh_3)$ were prepared. Figure 4.2 shows a scheme for preparation of these bisnitrosyl complexes.



L = PPh_3, $PMePh_2$, PMe_2Ph

X = Cl, Br

R = CH_3^-, $CH_3(CH_2)_2CH_2^-$, $CH_3(CH_2)_3CH_2^-$, $C_6H_5^-$

Figure 4.2 Preparation of $Co(NO)_2XL$ complexes.

Reactions of $Co(NO)(NO_2)_2L_2$ with acyl halides were observed to produce $Co(NO)_2XL$ complexes and the corresponding carboxylic acids as final products. Formation of carbonyl complexes was observed from the reaction of $Co(NO)L_3$ (L = PPh_3, PMe_2Ph) with benzoyl chloride,[84] but cobalt carbonyl complexes did not form from the reaction of $Co(NO)(NO_2)_2L_2$ and RCOX. Instead, the instantaneous formation of black and dark green bisnitrosyl halide phosphine complexes took place. Reactions with NO gave $Co(NO)_2(ONO)L$ complexes as products. These nitrito complexes could be transformed into $Co(NO)_2XL$ by reacting them with the appropriate acyl halide (Figure 4.2).

Structure of $Co(NO)_2Cl(PPh_3)$:

The unit cell of $Co(NO)_2Cl(PPh_3)$ contains well-separated molecules. A perspective view of the complex with the N(1)-Co-N(2) plane normal to the paper is shown in Figure 4.4. Tables 4.3 and 4.4, contain bond distances, angles and positional parameters for $Co(NO)_2Cl(PPh_3)$. The cobalt atom has pseudotetrahedral geometry. The angle between the planes formed by N(1)-Co-N(2) and P-Co-Cl ia 88.6(0)°. The smallest interligand angle about the cobalt is Cl-Co-P (98.89(3)°), and the largest is N(1)-Co-N(2) (116.8(3)°). The Co-P distance of 2.248(1)Å, the Co-N distances of 1.663(3) and 1.661(3)Å, and the N-O distances of 1.148(3) and 1.151(3)Å compare favorably with similar distances in other bisnitrosyl-cobalt complexes and especially well with $Co(NO)_2I(PPh_3)$ whose structure was recently reported.[88] The chloride and iodine complexes are isomorphous and share the same structural features. Both of them have pseudotetrahedral geometry at the Co atom and the absence of strongly bent NO ligands. In $Co(NO)_2Cl(PPh_3)$ the two nitrosyl ligands are bent with Co-N(1)-O(1) = 161.8(3)° and Co-N(2)-O(2) = 158.7(3)°. These angles are smaller than those reported for other cobalt dinitrosyl complexes. The geometry of the $Co(NO)_2$ fragment is also in good agreement with the Martin and Taylor[89] correlation of the O-M-O and N-M-N angles for $\{M(NO)_2\}^{10}$ complexes.

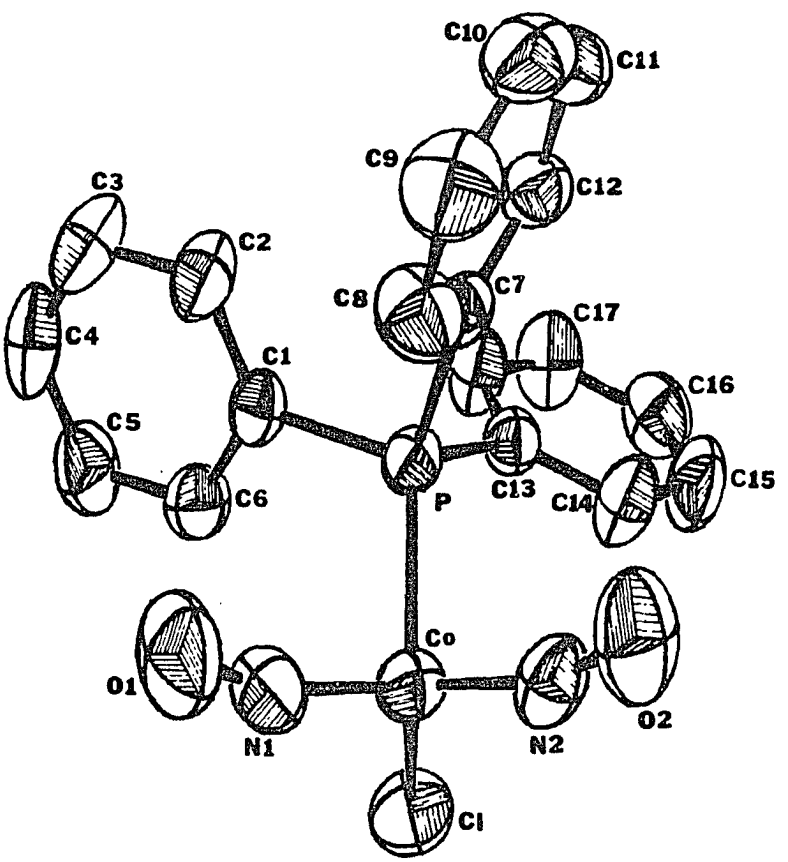


Figure 4.3. ORTEP drawing of $Co(NO)_2Cl(PPh_3)$. Vibrational ellipsoids are drawn at the 50% probability level.

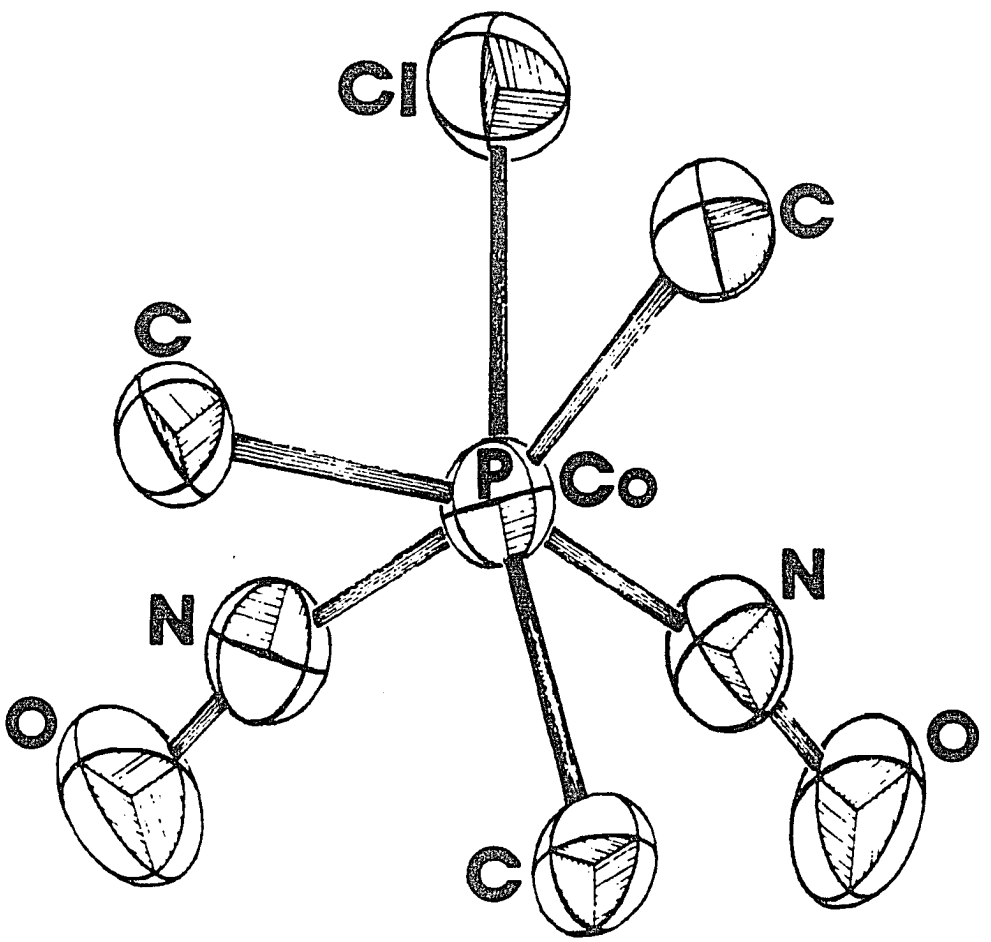


Figure 4.4 Perspective view of $Co(NO)_2Cl(PPh_3)$ along the P-Co bond. Phenyl groups have been omitted for clarity.

TABLE 4.3 SELECTED INTERATOMIC DISTANCES AND ANGLES FOR $Co(NO)_2Cl(PPh_3)$.

		Distances	
Co-Cl	2.246(1)	O(1)-N(1)	1.148(3)
Co-P	2.248(1)	O(2)-N(2)	1.151(3)
Co-N(1)	1.661(3)	C(1)-C(2)	1.372(4)
Co-N(2)	1.663(3)	C(1)-C(6)	1.382(4)
P-C(1)	1.823(3)	C(2)-C(3)	1.394(5)
P-C(7)	1.816(3)	C(3)-C(4)	1.364(5)
P-C(13)	1.816(3)	C(4)-C(5)	1.374(5)
		Angles	
Cl-Co-P	98.80(3)	N(1)-Co-N(2)	116.9(1)
Cl-Co-N(1)	115.85(9)	Co-P-C(1)	112.47(9)
Cl-Co-N(2)	116.73(9)	Co-P-C(7)	110.87(9)
P-Co-N(1)	103.19(9)	Co-P-C(13)	116.32(9)
P-Co-N(2)	100.73(9)	Co-N(1)-O(1)	161.8(3)

Numbers in parenthesis are estimated standard deviations in the least significant digits.

TABLE 4.4 POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Co(NO)_2Cl(PPh_3)$

Atom	x	y	z	$B_{eq}(Å^2)$[a]
Co	0.26376(3)	0.09199(4)	-0.20454(2)	3.735(9)
Cl	0.17437(6)	-0.0626(1)	-0.19549(5)	5.96(2)
P	0.34993(5)	0.04260(8)	-0.12045(4)	3.09(2)
O(1)	0.3690(20	0.0878(3)	-0.2962(1)	7.96(8)
O(2)	0.2446(2)	0.3430(3)	-0.1707(2)	7.62(8)
N(1)	0.3180(2)	0.0784(3)	-0.2950(1)	4.84(7)
N(2)	0.2376(2)	0.2380(3)	-0.1853(1)	4.81(7)
C(1)	0.4149(2)	-0.0888(3)	-0.1366(1)	3.34(6)
C(2)	0.4959(2)	-0.0776(3)	-0.1263(2)	4.81(8)
C(3)	0.5431(2)	-0.1806(4)	-0.1397(2)	6.2(1)
C(4)	0.5094(2)	-0.2907(4)	-0.1632(2)	6.01(9)
C(5)	0.4284(2)	-0.3016(4)	-0.1739(2)	5.35(9)
C(6)	0.3817(2)	-0.2006(3)	-0.1609(2)	4.40(8)
C(7)	0.4155(2)	0.1753(3)	-0.0985(2)	3.57(7)
C(8)	0.4415(2)	0.2491(4)	-0.1464(2)	5.46(9)
C(9)	0.4940(3)	0.3463(4)	-0.1318(2)	6.7(1)
C(10)	0.5203(2)	0.3731(4)	-0.0707(2)	6.4(1)
C(11)	0.4938(2)	0.3041(4)	-0.0232(2)	5.58(9)
C(12)	0.4417(2)	0.2043(3)	-0.0368(2)	4.39(8)
C(13)	0.3072(2)	-0.0013(3)	-0.0486(1)	3.28(7)
C(14)	0.2423(2)	0.0647(4)	-0.0319(2)	4.89(8)
C(15)	0.2108(2)	0.0345(4)	0.0233(2)	6.1(1)
C(16)	0.2409(2)	-0.0602(4)	0.0617(2)	5.20(9)
C(17)	0.3047(3)	-0.1268(4)	0.0452(2)	5.5(1)
C(18)	0.3372(2)	-0.0978(3)	-0.0096(2)	4.54(8)
H(2)	0.523(2)	0.007(3)	0.390(1)	
H(3)	0.597(2)	0.177(3)	0.372(1)	
H(4)	0.541(2)	0.357(3)	0.328(1)	
H(5)	0.404(2)	0.388(3)	0.310(1)	
H(6)	0.330(2)	0.208(3)	0.331(1)	
H(8)	0.576(2)	0.228(3)	0.687(1)	
H(9)	0.488(2)	0.384(3)	0.664(1)	
H(10)	0.446(2)	0.440(3)	0.562(2)	
H(11)	0.489(2)	0.317(3)	0.484(1)	
H(12)	0.579(2)	0.155(3)	0.505(2)	
H(14)	0.725(2)	0.369(3)	0.445(2)	
H(15)	0.676(2)	0.422(3)	0.534(2)	
H(16)	0.285(2)	0.415(3)	0.399(1)	
H(17)	0.320(2)	0.195(3)	0.568(1)	
H(18)	0.379(2)	0.143(3)	0.479(1)	

[a]Isotropic equivalent thermal parameter defined as: $8Pl^2(U_{11} + U_{22} + U_{33})/3$.
Hydrogen thermal values were fixed at a value of B = 5.0Å2.

Structure of $Co(NO)_2(ONO)(PPh_3)$:

The unit cell of $Co(NO)_2(ONO)(PPh_3)$ contains well-separated molecules. A perspective view of the complex with the N(1)-Co-N(2) plane perpendicular to the paper is shown in Figure 4.6. Bond distances and positional parameters for $Co(NO)_2(ONO)(PPh_3)$ are listed in Tables 4.5-4.6. The cobalt atom has pseudotetrahedral coordination geometry. The angle between the N(1)-Co-N(2) and P-Co-O(31) planes is 84.8(3)° degrees. The smallest interligand angle about the cobalt is the P-Co-O(31) angle at 101.6(1)°, and the largest is the N(1)-Co-N(2) angle at 122.9(2)°. O(31) is displaced 9.8(3)° degrees toward N(2) or 0.324(4) Å apart from the idealized position. The Co-P distance (2.276(1) Å), Co-N distances (1.647(3) Å and 1.713(4) Å) and N-O distances (1.143(4) and 1.139(7) Å) compare favorably with similar distances in other bisnitrosyl-cobalt complexes.[88,90,91] In $Co(NO)_2(ONO)(PPh_3)$ the two NO ligands are in the range of linear nitrosyls with Co-N(1)-O(1) = 168.7(3)° and Co-N(2)-O(2) = 158.0(4)°. The two nitrosyls are geniculated in an "attracto" conformation[89] which is characteristic of the first-row transition metal dinitrosyls. The angle O(1)-Co-O(2) is 116.7° in agreement with the Martin and Taylor correlation of the O-M-O and N-M-N angles for $\{M(NO)_2\}^{10}$ complexes. The N(3)-O(31) distance in the nitrito group is 1.282(7) Å and the distance of the exo-oxygen [O(32)] to the nitrogen atom [N(3)] is 0.997(9) Å. The angle O(31)-N(3)-O(32) is 121.6(8)° which is very close to 120° for sp^2 hybridization. Interestingly, the exo-oxygen of the -ONO group is directed toward the cobalt atom. The Co-O(32) distance is 2.782(5) Å

which is much longer than an oxygen-cobalt bond distance (1.98 Å) but shorter than the normal Van der Waals contacts (3.537Å).

Comparison of the crystal structure of $Co(NO)_2(ONO)(PPh_3)$ with $Co(NO)_2Cl(PPh_3)$, $Co(NO)_2I(PPh_3)$ and other $M(NO)_2L_2$ complexes.

The structures of a number of four-coordinate dinitrosyl complexes are known including $M(NO)_2(PPh_3)_2$ (M = Fe, Ru, Os), $[M'(NO)_2(PPh_3)_2]^+$ (M' = Co, Rh, Ir), and $Co(NO)_2X(PPh_3)$ ($X = Cl^-$, I^-, ONO^-).[88,90-94] All have distorted tetrahedral geometry with nearly linear NO ligands. The greatest distortion about the metal occurs in $[Rh(NO)_2(PPh_3)_2]^+$. The smallest dihedral angle between the planes N(1)-M-N(2) and P-M-X [84.8(4)°] and the greatest bending of the nitrosyl ligands, occur in $Co(NO)_2(ONO)(PPh_3)$ [Co-N(2)-O(2) = 158.0(4)°]. This bending found in the nitrosyl ligands for the neutral bis-nitrosyl species does not fit in the trend of M-N-O angles proposed by J. A. Ibers for the isoelectronic $M(NO)_2(PPh_3)_2^+$ complexes (Rh > Ir > Co). It also indicates the existence of greater amount of NO^- character in these complexes as compared with the $[Co(NO)_2(PPh_3)_2]^+$ species.

The N-Co-N angles for the $Co(NO)_2X(PPh_3)$ complexes of 122.9(2)°, 121.7(1)° and 116.8(3)° for $X = ONO^-$, I^-, and Cl^- respectively are in the range of N-M-N angles (110°-124°) found for other first-row $\{M(NO)_2\}^{10}$ complexes. Much larger values for the N-M-N angles are found for the heavier transition metals Rh, Ir, Ru and Os. Figure 4.7 shows

the Martin and Taylor correlation of O-M-O angle with the N-M-N angle for $\{M(NO)_2\}_{10}$ complexes including the new values for the ONO^-, I^- and Cl^- cobalt complexes.

A unique structural feature of the molecule $Co(NO)_2(ONO)(PPh_3)$ is the eclipsed configuration of the fragment O(31)N(1)N(2)Co-PC(1)C(7)C(13). A perspective vew of this molecule with the P-Co bond normal to the paper is shown in Figure 4.6. The corresponding view for $Co(NO)_2Cl(PPh_3)$ is shown in Figure 4.4. The chloro compound shows the staggered configuration which is a general characteristic of the structures reported for other $M(NO)_2L_2$ complexes.[85,88]

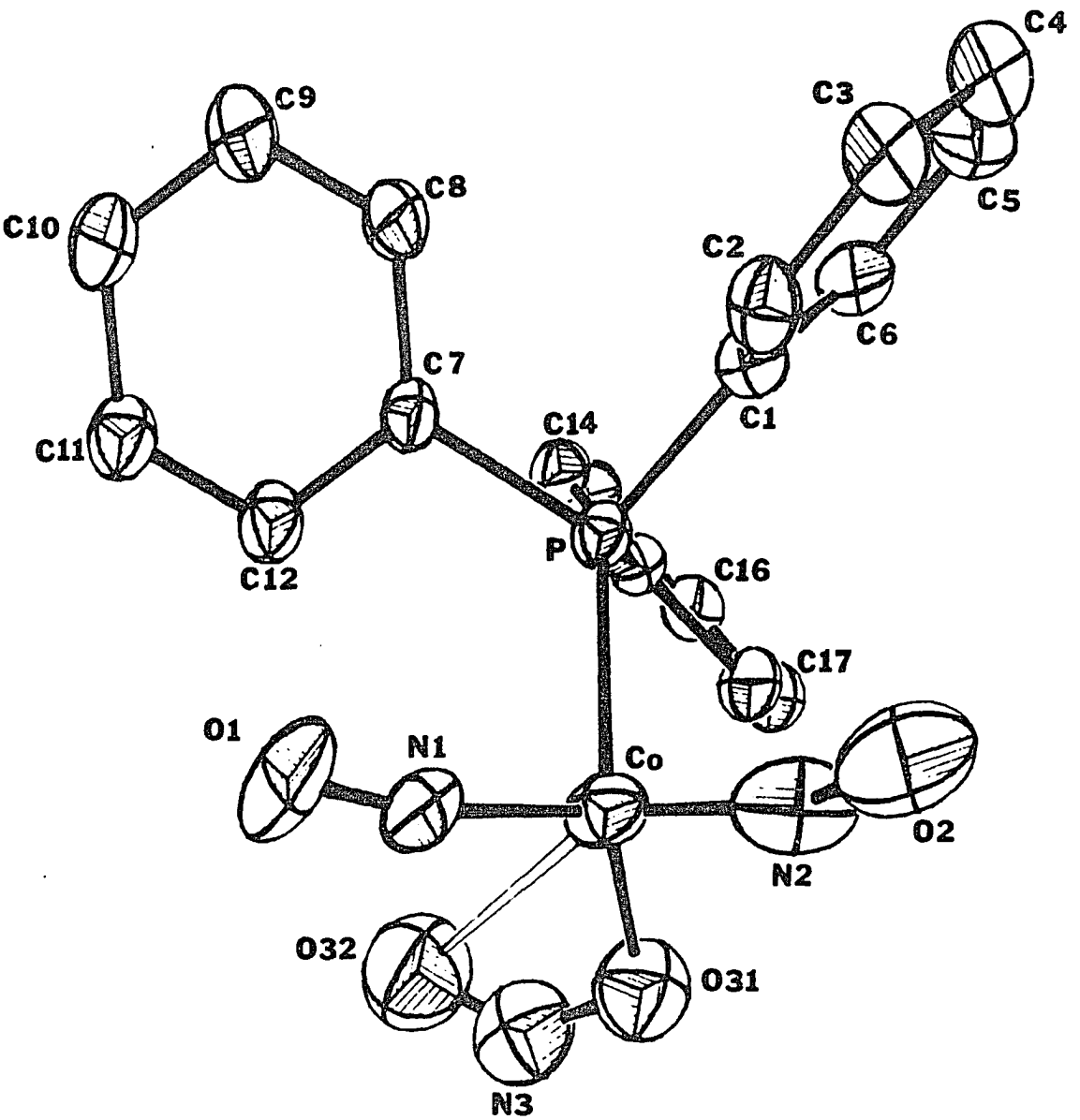


Figure 4.5. ORTEP drawing of $Co(NO)_2(ONO)(PPh_3)$. Vibrational ellipsoids are drawn at the 50% probability level.

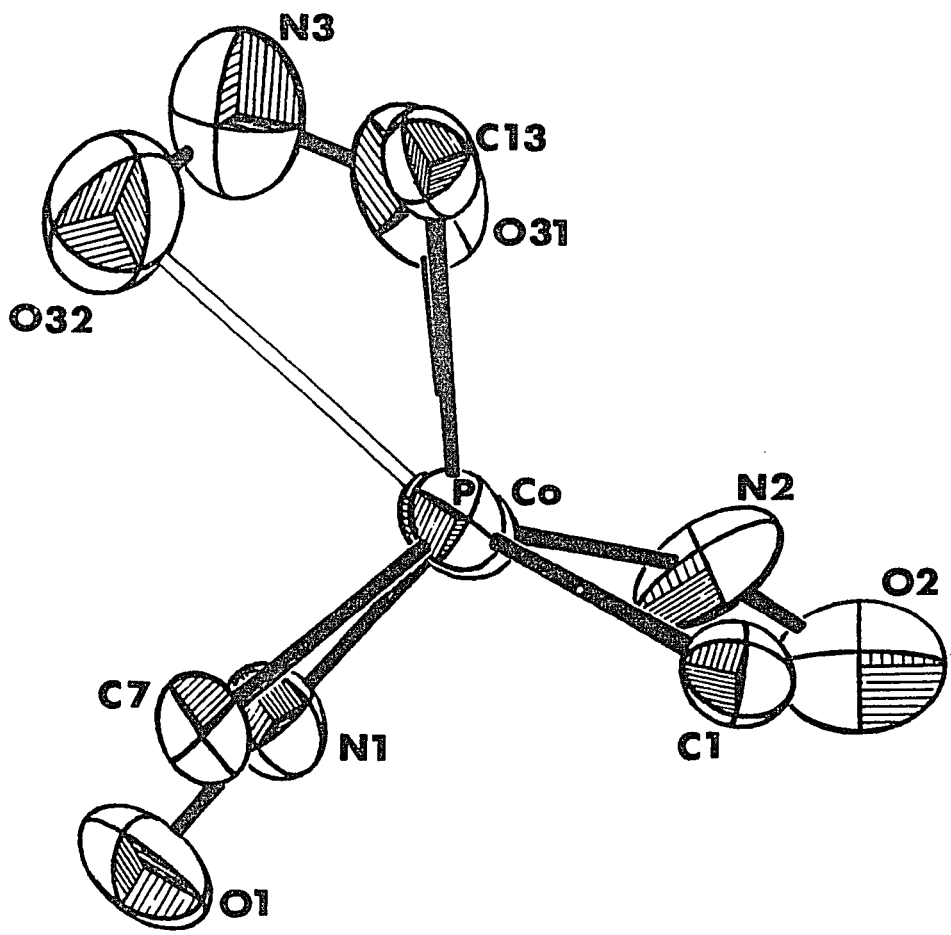


Figure 4.6. Perspective view of $Co(NO)_2(ONO)(PPh_3)$ with the P-Co bond normal to the paper. Phenyl rings have been omitted for clarity.

TABLE 4.5 SELECTED INTERATOMIC DISTANCES AND ANGLES FOR $Co(NO)_2(ONO)(PPh_3)$.

		Distances	
Co-P	2.276(1)	P-C7	1.819(3)
Co-O31	1.945(5)	P-C13	1.818(3)
Co-N1	1.647(3)	O1-N1	1.143(4)
Co-N2	1.713(4)	O2-N2	1.139(7)
P-C1	1.819(3)	O31-N3	1.282(7)
		Angles	
P-Co-O31	101.6(1)	Co-P-C7	112.72(9)
P-Co-N1	103.3(1)	Co-P-C13	116.32(9)
P-Co-N2	103.7(1)	C1-P-C7	105.4(1)
O31-Co-N1	119.2(2)	C1-P-C13	105.5(1)
O31-Co-N2	103.0(2)	C7-P-C13	104.3(1)
N1-Co-N2	122.9(2)	Co-O31-N3	114.8(4)
Co-P-C1	111.6(1)	Co-N1-O1	168.7(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

TABLE 4.6 POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Co(NO)_2(ONO)PPh_3$.

Atom	x	y	z	B(A2)
Co	0.86684(4)	0.01485(5)	0.09073(5)	5.46(2)
P	0.72042(7)	0.00122(8)	0.05840(7)	3.54(2)
O1	0.8794(3)	0.2191(3)	0.1272(3)	9.3(1)
O2	0.9102(3)	-0.0419(4)	-0.0403(3)	10.5(2)
O31	0.8978(3)	-0.0892(4)	0.1663(3)	10.3(2)
O32	0.8646(4)	0.0043(4)	0.2387(3)	12.7(2)
N1	0.8827(3)	0.1348(3)	0.1144(3)	5.7(1)
N2	0.8983(3)	-0.0371(5)	0.0173(3)	8.3(1)
N3	0.8889(4)	-0.0630(6)	0.2301(3)	10.8(2)
C1	0.6804(3)	-0.0200(3)	-0.0402(3)	3.8(1)
C2	0.7093(3)	0.0436(4)	-0.0896(3)	4.8(1)
C3	0.6792(4)	0.0321(4)	-0.1643(3)	5.6(1)
C4	0.6220(4)	-0.0446(4)	-0.1917(3)	5.7(1)
C5	0.5937(3)	-0.1084(4)	-0.1447(3)	5.5(1)
C6	0.6228(3)	-0.0956(4)	-0.0691(3)	4.6(1)
C7	0.6665(3)	0.1155(3)	0.0783(2)	3.6(1)
C8	0.6025(3)	0.1631(4)	0.0264(3)	4.3(1)
C9	0.5634(3)	0.2495(4)	0.0449(3)	5.1(1)
C10	0.5875(3)	0.2893(4)	0.1145(3)	5.3(1)
C11	0.6518(3)	0.2424(4)	0.1668(3)	5.0(1)
C12	0.6919(3)	0.1576(4)	0.1491(3)	4.4(1)
C13	0.6739(3)	-0.0994(3)	0.1029(2)	3.6(1)
C14	0.5996(3)	-0.0864(4)	0.1262(3)	4.2(1)
C15	0.5655(3)	-0.1648(4)	0.1600(3)	5.4(1)
C16	0.6060(4)	-0.2585(4)	0.1689(3)	6.2(1)
C17	0.6798(4)	-0.2720(4)	0.1453(4)	6.5(2)
C18	0.7148(3)	-0.1943(4)	0.1131(3)	5.1(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)-
*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)].

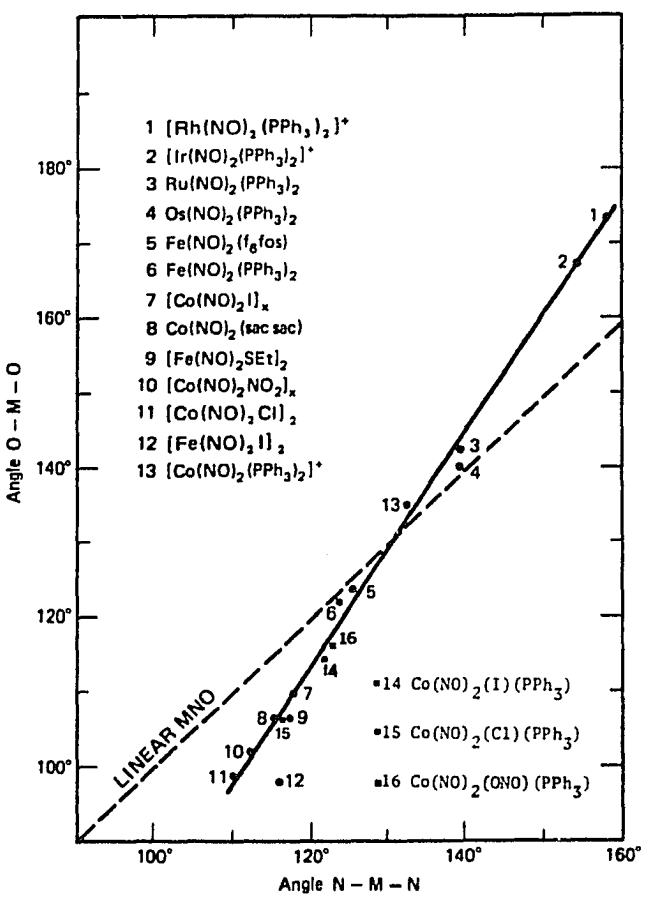


Figure 4.7. Correlation of O-M-O angle with the N-M-N angle for $\{M(NO)_2\}^{10}$ complexes. (Modification of Figure 4 from Reference 89).

CHAPTER 5

REACTIONS OF $CoNO_x$ COMPLEXES WITH OXYGEN: THE CRYSTAL STRUCTURES OF $Co(NO_3)_2(OPMePh_2)_2$ AND $Co(NO_2)_2(OPMePh_2)_2$

Introduction

The study of reactions in which dioxygen can be activated by a metal center is important for understanding both biological and commercial systems.[6,95,96] Recently, the study of metal complexes and dioxygen interactions has received considerable attention.[26,27,97,98] In particular, those complexes with nitro and nitrosyl ligands have been the subject of many recent studies.[7,8,16,17,29] Reaction of coordinated nitrosyls with molecular oxygen have been observed to produce coordinated nitro groups.[7,15,24,29,99] Formation of coordinated nitrate has been observed only in a few ruthenium compounds and one cobaloxime complex.[18-20]

Reactions of $Co(NO)(NO_2)_2L_2$ and $Co(NO)_2(ONO)L + OL$ with molecular oxygen produce cobalt bisnitrate complexes as the only Co containing products. The formation of $Co(NO_3)_2(OL)_2$ from the reaction of $Co(NO)(NO_2)_2L_2$ and O_2 is inhibited by the presence of a tenfold excess of olefin. Instead, $Co(NO_2)_2(OL)_2$ and the corresponding olefin oxide are formed. These reactions are discussed in this final chapter together with the crystal structures of $Co(NO_3)_2(OPMePh_2)_2$ and $Co(NO_2)_2(OPMePh_2)_2$.

Experimental

Since the cobalt nitrito and nitrate complexes are hygroscopic, the reactions were performed in dry, conventionally purified solvents.[35] Oxygen from Mattheson Co. was dried by passage through a silica gel column. Solid state infrared spectra were obtained from KBr pellets using a Perkin-Elmer Model 983 controlled by remote Data Station. ^{13}C NMR spectra were obtained from a Bruker 250 spectrometer. G.C.-Mass spectroscopy studies were made in a computer controlled HP 5930 A quadrupole mass spectrometer. Microanalyses were carried out by Atlantic MicroLabs, Atlanta, Georgia and The University of Arizona Analytical Center.

Collection and Reduction of X-Ray Intensity Data:

Crystals of $Co(NO_3)_2(OPMePh_2)_2$ suitable for X-Ray work were obtained from the reaction of a toluene solution of $Co(NO)(NO_2)_2(PMePh_2)_2$ with dry oxygen at room temperature. Violet needles formed after one day. A well defined rectangular needle was enclosed in a 0.5 mm glass capillary and mounted in a syntex $P2_1$ auto-diffractometer.

Crystals of $Co(NO_2)_2(OPMePh_2)_2$ suitable for diffraction were obtained by slowly removing the solvent from an acetone solution of this compound. Preliminary photographic data of a crystal mounted in air revealed that the material belongs to the monoclinic system (Laue symmetry 2/m).[45] Systematic absences characteristic of the space group $P2_1/n$ were observed for both $Co(NO_3)_2(OPMePh_2)_2$ and $Co(NO_2)_2(OPMePh_2)_2$.

Cell constants were obtained by the least squares refinement of 24 reflections centered and indexed by a Nova 1200 computer that controlled the Syntex $P2_1$ autodiffractometer where the intensity data were collected.(46) These cell dimensions and other crystallographic data are compiled in Table 5.1. Intensity data for the hk $\pm$ ℓ octant were collected in one shell of 2θ by using the $\theta - 2\theta$ technique. The intensities of two standard reflections were measured every 98 reflections. The intensity of these standards did not vary significantly during the course of the data collections. The data were reduced to F_o^2 and $\sigma(F_o^2)$ by published procedures.(45,46) Lorentz and Polarization factors were calculated on the assumption of 50% mosaicity and 50% perfection of the monochromator crystal. The factor to prevent overweighting of strong reflections, P, was set equal to 0.03 in both cases.

Solution and Refinement of the Structures:

The structure of $Co(NO_2)_2(OPMePh_2)_2$ was solved by the heavy-atom method in which the position of the cobalt atom was readily determined from a three-dimensional Patterson map. The remaining non-hydrogen atoms were located by succesive refinements and difference electron density maps. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = \sigma^2(I) + (PF_o^2)^2$ where $\sigma^2(I)$ is the standard deviation of F_o^2 due to counting statistics, F_o and F_c are the observed and calculated structure amplitudes respectively. The agreement indices for the F_o refinement are $R = \sum/|F_o| - |F_c|/\sum|F_o|$ and $Rw = (\sum w(|F_o| =$

$|F_c|)^2/\sum wF_o^2)^{1/2}$. Atomic scattering factors were taken from the tabulation of Cromer and Waber.(45) Anomolous dispersion terms were included in F_c. The hydrogen atoms of the phenyl rings were calculated and included in the refinement after the third cycle of least squares. At this point, three new cycles of refinements produced the positions of the hydrogen atoms of the methyl groups. All of the 37 non-hydrogen atoms were refined anisotropically and the final model refined to convergence with R = 4.1 and Rw = 4.4. All parameter shifts during the final cycle of refinement were less than 0.01σ. No peaks greater than 0.200 $e.A^{-3}$ were found after the final difference map. The "Goodness of Fit" for the structure was 1.42.

The structure of $Co(NO_3)_2(OPMePh_2)_2$ was also solved by the heavy-atom method in which the position of the cobalt atom was readily determined from a three-dimensional Patterson map.(45) The remaining nonhydrogen atoms were located by successive refinements and difference electron density maps. Isotropic refinement of the 39 nonhydrogen atoms in the molecule converged with R = 0.084 and Rw = 0.090. The discrepancy indices R and Rw were defined in the usual manner. At this point, the phenyl rings C(21) to C(26) and C(51) to C(56) were refined isotropically and the remaining 27 nonhydrogen atoms were refined anisotropically. The hydrogen atom positions were calculated and the final model was refined to convergence with R = 0.050 and Rw = 0.048. All parameter shifts during the final cycle of refinement were less than 0.01σ. Two peaks were located after the final difference map. Their size and location were: 0.369 $e.Å^{-3}$ at 1.004 Å from C(53) and 0.560 Å from C(54);

0.368 e.$Å^{-3}$ at 1.505 Å from C(21) and 0.761 Å from C(26). The calculations were carried out in a digital PDP 11/34a computer at the X-ray Laboratory of the Chemistry Department of the University of Arizona.

TABLE 5.1 SUMMARY OF CRYSTALLOGRAPHIC DATA FOR $Co(NO_3)_2(OPMePh_2)_2$[a] AND $Co(NO_2)_2(OPMePh_2)_2$.[a]

Compound	$Co(NO_3)_2(OPMePh_2)_2$	$Co(NO_2)_2(OPMePh_2)_2$
Formula	$CoN_2O_8P_2C_{26}H_{26}$	$CoN_2O_6P_2C_{26}H_{26}$
Formula weight	615.373	583.373
Crystal shape	Rectangular needle	Rectangular plates
Crystal color	Violet	Violet
Crystal system	Monoclinic	Monoclinic
Crystal dimensions, mm	0.20 x 0.25 x 0.33	0.5 x 0.5 x 0.05
Space group	$P2_1/n$	$P2_1/n$
Cell dimensions[b]		
a, Å	10.943(4)	12.814(6)
b, Å	12.868(3)	11.985(4)
c, Å	20.514(6)	18.411(6)
β, deg	94.02(3)	98.87(3)
V, $Å^3$	2888.6(6)	2794(2)
Z	8	8
Temperature °C	24	21
$d_{obs.}$[c], $g \cdot cm^{-3}$	1.401(5)	1.381(5)
$d_{calc.}$, $g \cdot cm^{-3}$	1.411(5)	1.387(5)
Radiation, Å	MoKα, = 0.71069	MoKα, = 0.71069
Monochromator	Graphite crystal	Graphite crystal
Data collection method	θ - 2θ scan	θ - 2θ scan

TABLE 5.1 continued

Portion of the sphere collected	h k $\pm$ ℓ	h k $\pm$ ℓ
Scan speed, deg./min	Variable	Variable
Scan range, deg.	1.1 below K_{α_1} and 1.3 above K_{α_2}	1.2 below $K\alpha_1$ and 1.4 above $K\alpha_2$
Scan to background time	2.0	2.0
Decomposition of standards	0.5%	none
Max. Shift during last least squares (Δ/σ)	0.01	0.01
Number of unique data	5118	4950
Number of data used in calculations	2237	2664
Number of variables	292	335
$R(F) = \sum\|\|Fo\| - \|Fc\|\|/\sum Fo$	0.050	0.041
$Rw(F) = (\sum w(\|Fo\| - \|Fc\|)^2/-$ $\sum wFo^2)^{1/2}$	0.048	0.044

[a]The standard deviation of the least significant figure is given in parenthesis in this and the following tables.

[b]Cell dimensions were obtained from a least-squares refinement of setting angles of 20 reflections.

[c]Densities were determined by flotation using solutions of toluene and carbon tetrachloride.

Results and Discussion

$Co(NO)(NO_2)_2(L)_2$ [L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, PEt_3, PEt_2Ph, $PEtPh_2$, PBu_3, $PPrPh_2$, and 1/2DPPPr] react with dry oxygen in aromatic hydrocarbons, CH_3CN and THF to produce the corresponding cis-bis-(phosphine-oxide)cobalt(II)dinitrates. The best results (100% yields and purest products) are obtained in toluene. All of these nitrates have an intense violet color, very similar electronic spectra[100] and about the same infrared stretching frequencies for the nitrate groups.[34,100-105] The presence of two bands separated by 50-56 cm^{-1} in the 1700-1800 cm^{-1} region of the infrared spectrum indicated a bidentate coordination of the NO_3^- ligands in these complexes.[101]

The reaction of $Co(NO)(NO_2)_2(PMePh_2)_2$ with O_2 in toluene first produces a light brown insoluble intermediate that slowly changes to well-formed rectangular needles of the violet colored $Co(NO_3)_2(OPMePh_2)_2$. This reaction occurs with a 100% yield with complete precipitation of the product from the transparent mother liquor that does not show the presence of dissolved phosphine after the crystallization is complete. The crystal structure of one of these needles was determined by X-ray diffraction. The nitrate groups were found to be bidentate, in agreement with the infrared results. The nitrate groups have a cis configuration around the cobalt atom. In this respect, this structure is similar to that reported for $Co(NO_3)_2(OPMe_3)_2$.[105] This type of coordination is expected to be

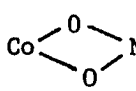
present in all of the $Co(NO_3)_2(OL)_2$ obtained by this method since the imfrared (KBr) spectra for the NO_3 groups are very similar. The oxidations of $Co(NO)(NO_2)_2L_2$ complexes also occur in CH_3CN and THF where the bisnitrates bisphosphine oxide complexes of Co(II) are more soluble and precipitate cleanly after one day at -10°C.

The reactions of $Co(NO)(NO_2)_2(L)_2$ complexes with molecular oxygen to form the $Co(NO_3)_2(OL)_2$ complexes imply the breakage (or activation) of the oxygen molecule in some intermediate step of the reaction. Activation of oxygen molecules by nitrosyl and nitro groups in transition metal complexes is observed by reaction with a variety of substrates[15,19-21] including olefins which form epoxides, alcohols and ketones.[7,8,16,17] Based on these facts, oxidations of $Co(NO)(NO_2)_2(PPh_3)_2$ and $Co(NO)(NO_2)_2(PMePh_2)_2$ were performed in the presence of excess olefin. It was found that each of the olefins (norbornylene, cyclohexene, cyclopentene, and 2-methyl-2-pentene) inhibit the formation of the Co(II)-bisnitrate complexes and instead grey-violet $Co(NO_2)_2(OL)_2$ complexes are formed. The elemental analysis of $Co(NO_2)_2(OPMePh_2)_2$ obtained from the reaction of $Co(NO)(NO_2)_2(PMePh_2)_2$ and O_2 in toluene in the presence of a tenfold excess of cyclohexene is shown in Table 2.1. The filtrate of this reaction was distilled under reduced pressure and the material collected in a trap cooled with liquid nitrogen. GC-Mass spectroscopy analysis of this sample showed the presence of another material with a molecular weight corresponding to $C_6H_{10}O$. The ^{13}C NMR spectrum of this compound showed it to be cyclohexene oxide. The process can be represented by:

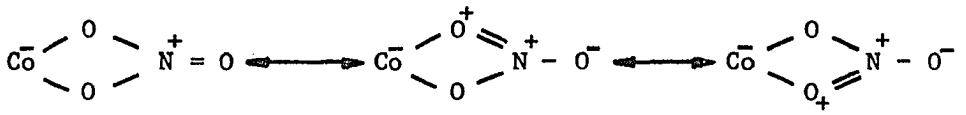
$$Co(NO)(NO_2)_2(PMePh_2)_2 + O_2 + C_6H_{10} \longrightarrow Co(NO_2)_2(OPMePh_2)_2 + C_6H_{10}O \text{ (Cyclohexene oxide).} \qquad (5.1)$$

Similar results were obtained for cyclopentene and norbornylene.

Discussion of the Structures:

$Co(NO_3)_2(OPMePh_2)_2$ crystallizes in the monoclinic system $P2_1/n$. Well separated molecules are contained in the unit cell. This structure was found to be similar to that of $Co(NO_3)_2(OPMe_3)_2$.[105] The cobalt atom is surrounded by six oxygen atoms, with the nitrates acting as bidentate ligands and arranged in a cis-configuration. A perspective view of the molecule is given in Figure 5.1. The coordination sphere is shown in Figure 5.2. Tables 5.2-5.3 show bond distances, angles and atomic positions for $Co(NO_3)_2(OPMePh_2)_2$. The bite angles of the NO_3 ligands [O(11)-Co-O(12) and O(21)-Co-O(22)] are 59.1(2)° and 59.5(2)°. These angles are smaller than those found for $Co(NO_3)_3$[106] which has three equivalent nitrate groups with bite angles of 68°. Better agreement exists with the bite angles of the nitrate groups in $Co(NO_3)_2(OPMe_3)_2$ [57(1)°]. The planar $Co(NO_3)$ groups in $Co(NO_3)_2(OPMePh_2)_2$ are slightly distorted from C_{2v} symmetry. The Co-O distances are between 2.073(4) and 2.223(4) Å. The distortion found is of the type[107]  . The angles Co-O-N range from 89.0(4)° to 95.8(3)° to fit the distortion imposed. The exo-oxygen atoms are approximately 0.033Å closer to the nitrogens than the oxygens bonded to the cobalt atom. The distances O(13)-N(1) and O(23)-N(2) are

1.221(5) and 1.211(6) Å respectively, and are equal to the most probable values of the N-O bond length for the uncoordinated nitrate ion.[108] The distances and angles found in $Co(NO_3)_2(OPMePh_2)_2$ agree with a covalent interaction of the nitrate ligands with the cobalt atom that can be represented by the following valence bond structures:



The phosphine-oxide oxygens are at 1.983(3) and 1.974(4)Å apart from the cobalt atom, slightly closer than the nitrate oxygens. The P(1)-O(1) and P(2)-O(2) distances are 1.494(3) and 1.497(4) Å and the angles P(1)-O-Co and P(2)-O-Co are 146.2(2)° and 147.9(3)° respectively. The P atoms are in essentially the same pseudotetrahedral environment. The C-P distances with an average of 1.79 Å agree well with equivalent distances found in similar compounds.[87,105] The structure of $Co(NO_3)_2(OPMePh_2)_2$ contain less symmetric nitrate groups than those in $Co(NO_3)_3$[106] and $Co(NO_3)_2(OPMe_3)_2$, and more are symmetric than the nitrate groups in the anion $[Co(NO_3)_4]^{2-}$.[107] A comparison of these structures is shown in Figure 5.3.

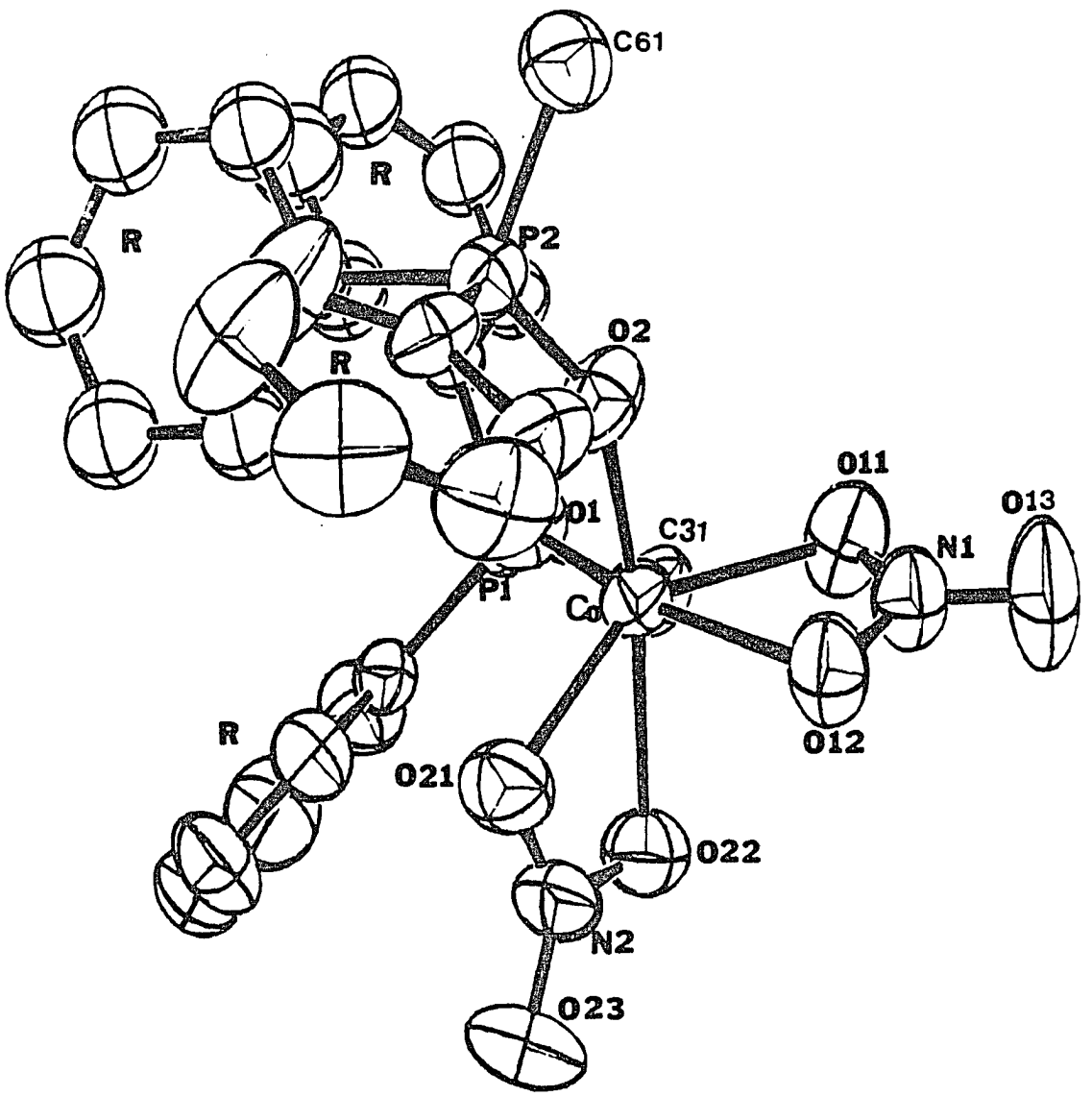


Figure 5.1. ORTEP drawing of $Co(NO_3)_2(OPMePh_2)_2$. Vibrational ellipsoids are drawn at the 50% probability level.

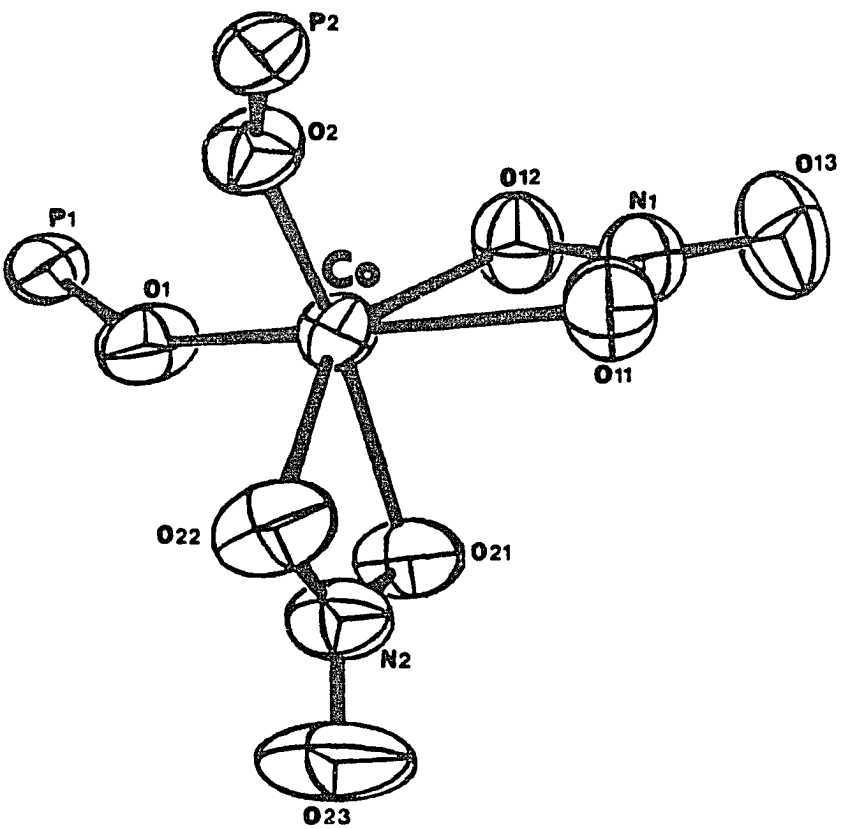


Figure 5.2. Perspective view of the coordination sphere of $Co(NO_3)_2(OPMePh_2)_2$.

TABLE 5.2 SELECTED INTERATOMIC DISTANCES AND ANGLES FOR $Co(NO_3)_2(OPMePh_2)_2$.

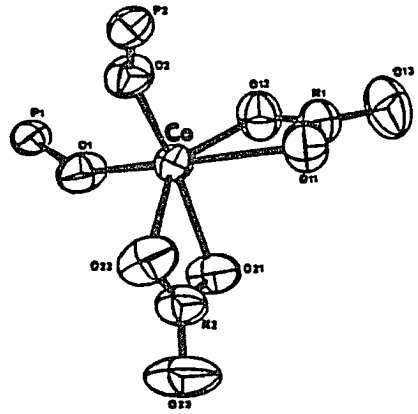
Distances			
Co-O1	1.983(3)	P2-O2	1.497(4)
Co-O2	1.974(4)	P2-C41	1.793(6)
Co-O11	2.115(4)	P2-C51	1.786(5)
Co-O12	2.200(4)	P2-C61	1.785(6)
Co-O21	2.073(4)	O11-N1	1.266(6)
Co-O22	2.223(4)	O12-N1	1.243(5)
P1-O1	1.494(3)	O13-N1	1.221(5)
P1-C11	1.792(6)	O22-N2	1.258(6)
P1-C21	1.793(5)	O21-N2	1.265(6)
P1-C31	1.778(5)	O23-N2	1.211(6)
Angles			
O1-Co-O2	97.5(2)	O21-Co-O22	59.5(2)
O1-Co-O11	102.1(2)	Co-O1-P1	146.2(2)
O1-Co-O12	160.8(2)	Co-O2-P2	147.9(3)
O1-Co-O21	104.1(2)	Co-O11-N1	94.0(3)
O1-Co-O22	92.8(2)	Co-O12-N1	90.6(3)
O2-Co-O11	98.4(2)	Co-O21-N2	95.8(3)
O2-Co-O12	89.9(2)	Co-O22-N2	89.0(4)
O2-Co-O21	102.8(2)	O11-N1-O12	116.2(5)
O2-Co-O22	161.4(2)	O11-N1-O13	122.5(6)
O11-Co-O12	59.1(2)	O12-N1-O13	121.3(6)
O11-Co-O21	143.4(2)	O21-N2-O22	115.6(5)
O11-Co-O22	94.4(2)	O21-N2-O23	122.8(6)
O12-Co-O21	91.3(2)	O22-N2-O23	121.6(7)
O12-Co-O22	85.3(2)		

Numbers in parentheses are estimated standard deviations in the least significant digits.

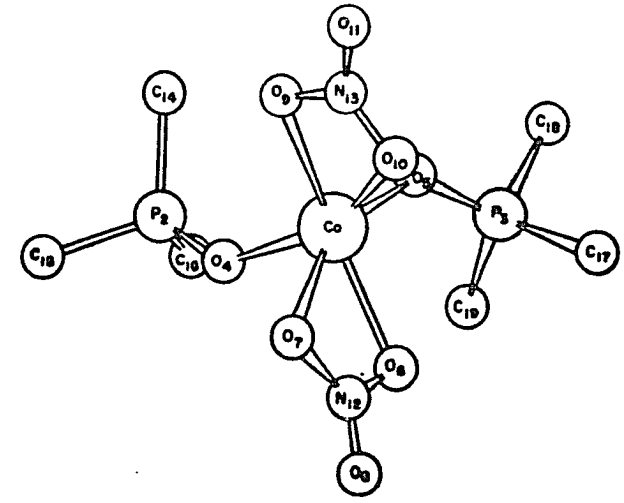
TABLE 5.3 POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Co(NO_3)_2(OPMePh_2)_2$.

Atom	x	y	z	B(A2)
Co	0.49090(8)	0.10392(7)	0.21728(4)	3.23(2)
P1	0.6401(2)	0.2936(1)	0.14655(9)	3.37(4)
P2	0.1999(2)	0.1778(1)	0.19425(9)	3.68(4)
O1	0.5382(4)	0.2256(3)	0.1655(2)	4.2(1)
O2	0.3198(4)	0.1444(4)	0.2267(2)	5.1(1)
O11	0.5634(4)	0.1431(3)	0.3123(2)	5.4(1)
O12	0.4811(4)	-0.0059(3)	0.2989(2)	5.2(1)
O13	0.5479(5)	0.0397(5)	0.3956(2)	8.1(2)
O21	0.4742(4)	-0.0160(4)	0.1498(2)	5.3(1)
O22	0.6535(4)	0.0131(4)	0.1927(2)	5.3(1)
O23	0.6232(6)	-0.1197(4)	0.1297(3)	8.6(2)
N1	0.5302(5)	0.0587(4)	0.3374(3)	4.6(1)
N2	0.5850(6)	-0.0432(4)	0.1559(3)	5.2(2)
C11	0.6956(6)	0.2509(5)	0.0710(3)	3.5(1)
C12	0.6399(7)	0.1685(6)	0.0385(4)	5.5(2)
C13	0.6810(8)	0.1348(7)	-0.0192(4)	8.2(3)
C14	0.7772(8)	0.1815(8)	-0.0445(4)	9.5(3)
C15	0.8362(8)	0.2628(8)	-0.0122(4)	8.2(3)
C16	0.7939(6)	0.2993(6)	0.0450(4)	5.8(2)
C21	0.5884(5)	0.4247(5)	0.1339(3)	3.2(1)*
C22	0.6467(6)	0.5091(5)	0.1618(3)	4.4(2)*
C23	0.6017(7)	0.6083(6)	0.1481(4)	5.7(2)*
C24	0.5024(7)	0.6228(6)	0.1091(4)	5.4(2)*
C25	0.4415(7)	0.5413(7)	0.0811(4)	6.8(2)*
C26	0.4840(7)	0.4398(6)	0.0937(4)	5.9(2)*
C31	0.7658(6)	0.2929(5)	0.2060(3)	4.7(2)
C41	0.0995(5)	0.0694(5)	0.1788(3)	3.8(2)
C42	0.1170(7)	-0.0193(5)	0.2162(4)	5.4(2)
C43	0.0430(7)	-0.1050(5)	0.2033(4)	6.1(2)
C44	-0.0479(7)	-0.1019(6)	0.1552(4)	6.6(2)
C45	-0.0666(7)	-0.0137(6)	0.1195(4)	7.5(2)
C46	0.0083(7)	0.0711(6)	0.1303(4)	6.2(2)
C51	0.2123(5)	0.2373(5)	0.1163(3)	3.3(1)*
C52	0.2697(6)	0.1821(6)	0.0701(3)	4.8(2)*
C53	0.2760(7)	0.2207(6)	0.0070(4)	5.8(2)*
C54	0.2230(7)	0.3126(6)	-0.0079(4)	6.3(2)*
C55	0.1648(7)	0.3696(6)	0.0368(4)	5.9(2)*
C56	0.1587(6)	0.3312(5)	0.0993(3)	4.7(2)*
C61	0.1266(6)	0.2651(6)	0.2466(3)	5.0(2)

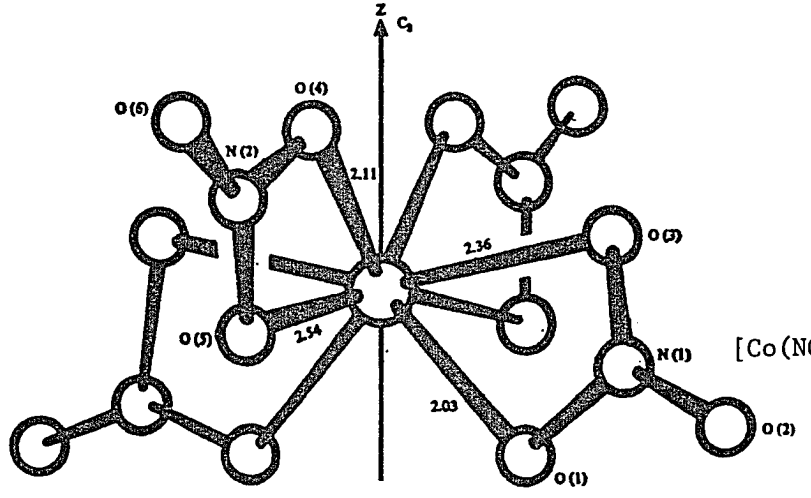
Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)-*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)].



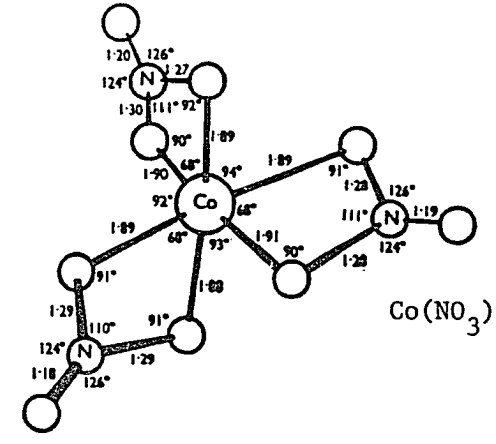
$Co(NO_3)_2(OPMePPh_2)_2$



$Co(NO_3)_2(OPMe_3)_2$



$[Co(NO_3)_3]^{2-}$



$Co(NO_3)_3$

Figure 5.3. Comparison of the coordination spheres of $Co(NO_3)_x$

$Co(NO_2)_2(OPMePh_2)_2$ also crystallizes in the monoclinic system $P2_1/n$. Well separated molecules are contained in the unit cell. This structure was found to be similar to that of $Co(NO_3)_2(OPMePh_2)_2$. The cobalt atom is surrounded by six oxygen atoms, with the nitrito groups acting as bidentate ligands and arranged in a cis-configuration. A perspective view of this molecule is given in Figure 5.4. The coordination sphere is shown on Figure 5.5. Tables 5.4-5.5 show bond distances, angles and atomic positions for this molecule. The bite angle of the NO_2^- groups [O(11)-Co-O(12) and O(21)-Co-O(22)] are 56.4 and 57.4° that is, about 2.8° smaller than the corresponding angles in $Co(NO_3)_2(OPMePh_2)_2$. The $Co(NO_2)$ groups are planar and show essentially C_{2v} symmetry. The Co-O distances range from 2.106(4) to 2.221(4) Å. The ONO angles are 113.2(6) and 111.1(4) degrees, which are significantly smaller than the corresponding angles in $Co(NO_3)_2(OPMePh_2)_2$ which are 116.2(5)° and 115.6(5)°. The N(1)-O(11)-[1.224(6)], N(1)-O(12)[1.229(7)], N(2)-O(21)[1.255(5)] and N(2)-O(22)[1.238(5)] distances, of the NO_2 groups resemble those of other NO_2 complexes of cobalt, especially the chelating NO_2 ligands of $Co(NO)(NO_2)_2L_2$ (L = $PMePh_2$ and PMe_2Ph).

The phosphine oxide oxygens are at 1.993(2) and 2.006(2) Å from the cobalt atom, slightly closer than the nitrito oxygens. The P-O distances are 1.499(2) Å and the P-O-Co angles are 135.7(2) and 136.7(2) degrees, which are ten degrees smaller than the P-O-Co angles in the corresponding nitrato complex. The P atoms are in essentially the same pseudotetrahedral environment. The C-P distances with an average of

1.79 Å agree well with equivalent distances in similar compounds.(31,87,105) The phenyl rings are well behaved and show more of thermal vibrations than those of $Co(NO_3)_2(OPMePh_2)_2$.

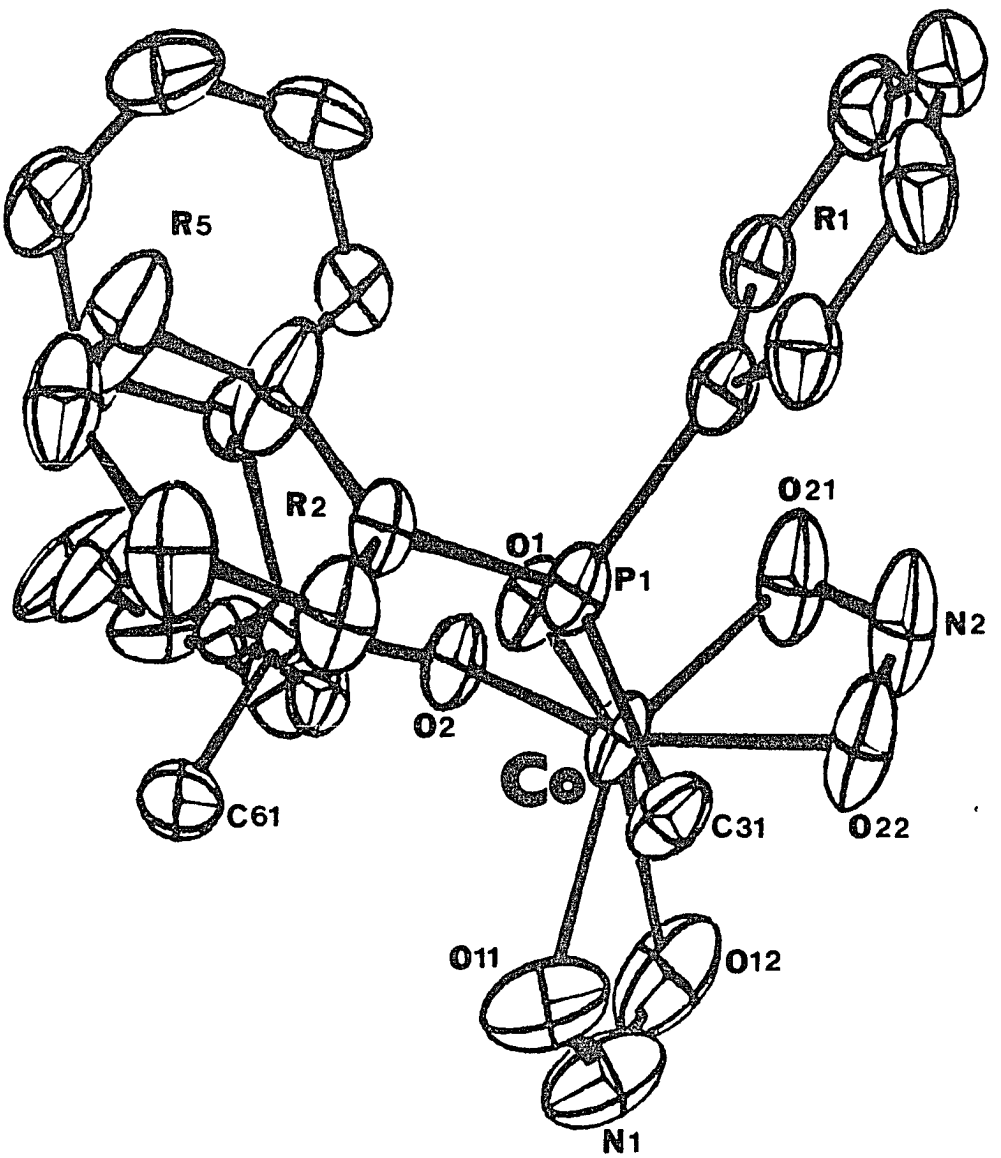


Figure 5.4. ORTEP drawing of $Co(NO_2)_2(OPMePh_2)_2$. Vibrational ellipsoids are drawn at the 50% probability level.

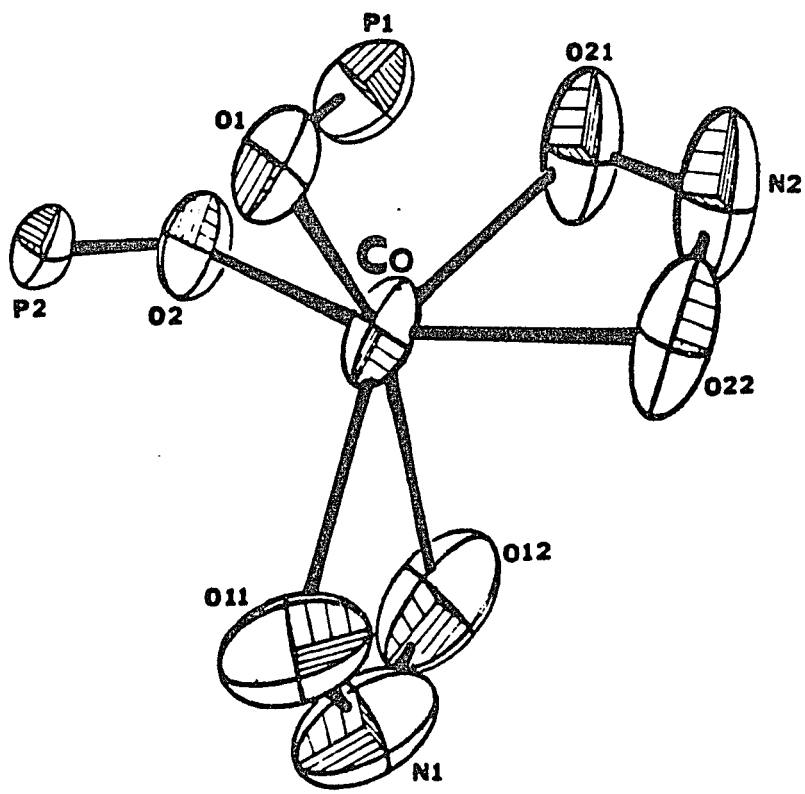


Figure 5.5. Perspective view of the coordination sphere of $Co(NO_2)_2(OPMePh_2)_2$.

TABLE 5.4 SELECTED INTERATOMIC DISTANCES AND ANGLES FOR $Co(NO_2)_2(OPMePh_2)_2$.

Distances			
Co-O1	2.006(2)	P1-C21	1.795(4)
Co-O2	1.993(2)	P1-C31	1.778(4)
Co-O11	2.106(4)	P2-O2	1.499(2)
Co-O12	2.221(4)	P2-C41	1.792(4)
Co-O21	2.083(3)	P2-C51	1.793(4)
Co-O22	2.191(3)	P2-C61	1.779(4)
Co-N1	2.581(6)	O11-N1	1.224(6)
Co-N2	2.579(5)	O12-N1	1.229(7)
P1-O1	1.499(2)	O21-N2	1.255(5)
P1-C11	1.791(4)	O22-N2	1.238(5)
Angles			
O1-Co-O2	95.4(1)	O12-Co-N1	28.4(2)
O1-Co-O11	97.1(1)	O12-Co-N2	94.8(2)
O1-Co-O12	153.4(2)	O21-Co-O22	57.4(1)
O1-Co-O21	105.0(1)	O21-Co-N1	124.3(2)
O1-Co-O22	92.3(1)	O21-Co-N2	28.8(1)
O1-Co-N1	125.1(2)	O22-Co-N1	94.8(2)
O1-Co-N2	99.7(1)	O22-Co-N2	28.6(1)
O2-Co-O11	103.2(1)	N1-Co-N2	111.7(2)
O2-Co-O12	93.5(1)	Co-O1-P1	135.7(2)
O2-Co-O21	98.2(1)	Co-O2-P2	136.7(2)
O2-Co-O22	155.6(1)	Co-O11-N1	98.1(4)
O2-Co-N1	99.6(2)	Co-O12-N1	92.3(4)
O2-Co-N2	127.0(2)	Co-O21-N2	98.1(3)
O11-Co-O12	56.4(2)	Co-O22-N2	93.4(3)
O11-Co-O21	147.5(2)	Co-N1-O11	53.9(3)
O11-Co-O22	98.8(2)	Co-N1-O12	59.3(3)
O11-Co-N1	28.0(2)	O11-N1-O12	113.2(6)
O11-Co-N2	124.6(2)	Co-N2-O21	53.1(2)
O12-Co-O21	98.5(2)	Co-N2-O22	58.0(2)
O12-Co-O22	89.9(2)	O21-N2-O22	111.1(4)

Numbers in parentheses are estimated standard deviations in the least significant digits.

TABLE 5.5 POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Co(NO)_2(OPMePh_2)_2$.

Atom	x	y	z	$B_{eq}(Å^2)$
Co	0.47943(4)	0.04273(5)	0.19636(4)	4.72(1)
P1	0.59486(8)	0.27916(9)	0.17412(7)	3.97(2)
P2	0.23604(8)	0.1216(1)	0.14764(7)	4.03(2)
O1	0.5044(2)	0.1986(2)	0.1632(2)	4.51(7)
O2	0.3260(2)	0.0403(2)	0.1558(2)	5.01(7)
O11	0.4807(4)	0.0797(4)	0.3083(2)	9.7(1)
O12	0.4634(4)	-0.0855(3)	0.2810(3)	10.5(1)
O21	0.5327(3)	-0.0603(3)	0.1186(2)	8.6(1)
O22	0.6461(3)	-0.0020(3)	0.2011(2)	8.4(1)
N1	0.4704(5)	-0.0155(5)	0.3302(3)	10.6(2)
N2	0.6291(4)	-0.0595(4)	0.1446(3)	9.6(2)
C11	0.6749(3)	0.2668(3)	0.1029(2)	4.3(1)
C12	0.6420(3)	0.2008(4)	0.0411(3)	4.9(1)
C13	0.7030(4)	0.1950(4)	-0.0143(3)	6.4(1)
C14	0.7941(4)	0.2562(5)	-0.0092(3)	6.9(1)
C15	0.8280(4)	0.3205(4)	0.0519(3)	6.7(1)
C16	0.7690(3)	0.3263(4)	0.1066(3)	5.2(1)
C21	0.5474(3)	0.4203(3)	0.1685(2)	4.1(1)
C22	0.5902(4)	0.5039(4)	0.2142(3)	5.6(1)
C23	0.5496(4)	0.6115(4)	0.2043(3)	6.4(1)
C24	0.4703(4)	0.6358(4)	0.1498(3)	6.6(1)
C25	0.4282(5)	0.5537(5)	0.1049(4)	8.9(2)
C26	0.4663(5)	0.4465(4)	0.1139(3)	7.8(1)
C31	0.6789(3)	0.2596(4)	0.2594(3)	5.2(1)
C41	0.1153(3)	0.0438(4)	0.1302(2)	4.3(1)
C42	0.1171(3)	-0.0681(4)	0.1440(3)	5.6(1)
C43	0.0265(4)	-0.1325(4)	0.1298(3)	6.8(1)
C44	-0.0651(4)	-0.0840(5)	0.1002(3)	7.8(1)
C45	-0.0692(4)	0.0256(6)	0.0876(4)	11.4(2)
C46	0.0205(4)	0.0903(5)	0.1018(4)	9.4(2)
C51	0.2395(3)	0.2160(3)	0.0725(2)	4.13(9)
C52	0.3046(3)	0.1931(4)	0.0209(3)	5.1(1)
C53	0.3086(4)	0.2662(4)	-0.0364(3)	6.7(1)
C54	0.2485(5)	0.3596(5)	-0.0432(3)	7.9(2)
C55	0.1840(5)	0.3823(4)	0.0069(4)	8.1(2)
C56	0.1800(4)	0.3124(4)	0.0647(3)	6.0(1)
C61	0.2354(4)	0.2022(4)	0.2287(3)	6.2(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $8PI^2(U_{11} + U_{22} + U_{33})/3$.

APPENDIX A

LIST OF ABBREVIATIONS

Me = methyl

Et = ethyl

Pr = propyl

Ph = phenyl

Cy = cyclohexyl

DPPPr = 1,3-Bis(diphenylphosphino)propane

X = a halogen or a pseudohalogen

R = alkyl

Ar = aryl

TMP = trimethylphosphite

THF = tetrahydrofuran

M = metal

L = phosphine ligand

OL = phosphine oxide

s = strong

m = medium

w = weak

vw = very weak

ppm = parts per million

TMS = tetramethylsilane

Hz = Hertz

AT = acquisition time

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