Inorganica Chimica Acta, *187* (1991) 31–38

Preparation and properties of cobalt(II) phosphine complexes containing nitro and nitrosyl ligands

Omar Alnaji, Michèle Dartiguenave*, Yves Dartiguenave
Laboratoire de Chimie Inorganique, Université P. Sabatier, 118 route de Narbonne, 31062 Toulouse-Cédex (France)

Michel Simard and André L. Beauchamp*
Département de Chimie, Université de Montréal, C.P. 6128, Succ. A, Montreal, H3C 3J7 (Canada)

(Received February 13, 1991)

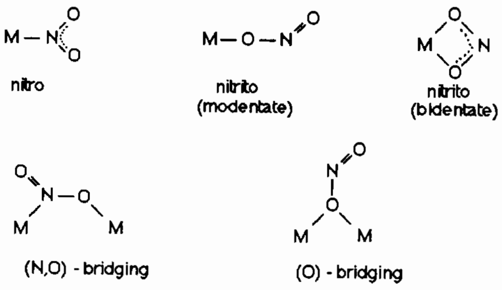
Abstract

Reactions of the tertiary phosphines PMe_3, PEt_3, PMe_2Ph, $PMePh_2$ and PPh_3 with $Co(NO_2)_2$ are described. For PMe_3 and PMe_2Ph, five-coordinate $Co(NO_2)_2(PR_3)_3$ complexes (**1**, **2**) are isolated. With PEt_3, only $Co(NO)(NO_2)_2(PEt_3)_2$ (**3**) is obtained, whereas the $Co(NO)(NO_2)_2(PMe_3)_2$ (**4**) and $Co(NO)(NO_2)_2(PMe_2Ph)_2$ (**5**) analogs result from the reaction of **1** and **2** with NO gas. From EPR measurements, the electronic structures of **1** and **2** are found to correspond to low-spin d^7 square-pyramidal complexes in the solid state. Compounds **3**, **4** and **5** are pseudo-octahedral Co(III) species containing three different nitrogen oxide ligands, namely NO, O-bonded NO_2 and N-bonded NO_2. The reactions of **1** and **2** with CO are solvent dependent: in methanol $Co(NO)(CO)(PMe_3)_2$ is obtained, but in toluene a mixture of **5** and $Co(NO)_2(NO_2)(PMe_2Ph)$ precipitates. $Co(NO)(NO_2)_2(PEt_3)_2$ reacts with O_2 to form the cobalt(II) complex $Co(NO_3)_2(OPEt_3)_2$ shown by X-ray diffraction to be a distorted octahedron with bidentate nitrate ligands and two $OPEt_3$ ligands in *cis* positions.

Introduction

Molecular cobalt(II) complexes are usually prepared with chloride, bromide, iodide or thiocyanate as anionic ligands [1–3]. Cyanide compounds, synthesized to evaluate the electronic influence of a strong-field ligand, show other interesting properties: $[Co(CN)_5]^{3-}$ is a hydrogenation catalyst, whereas $Co(CN)_2(PR_3)_3$ activates molecular oxygen [4–6]. On the other hand, sulfate, nitrate and perchlorate are present most of the time as simple counter-ions, although examples of metal-coordinated species are found [7, 8: NO_3^- [8a], SO_4^- [8b, c], ClO_4^- [8d, e]].

The nitrite anion, in addition to acting as counter-ion, can coordinate to a metal centre in a variety of ways. Scheme 1 shows five different modes of coordination, which have all been experimentally illustrated [9, 10]. The first cobalt–NO_2 complexes to be synthesized were Co(III) species, some of which showed an equilibrium between the nitro and nitrito isomers [9]. Various other compounds have also been reported [11], but only a few species containing phosphine ligands are known: $Co(NO_2)(acac)_2(PMe_2Ph)$, $Co(NO_2)_2(acac)(PMe_2Ph)_2$ [12] and $[Co(NO_2)_2(NH_2CH_2CH_2PPh_2)_2]^+$ [13]. Surprisingly, no four- or five-coordinated cobalt complexes of compositions $Co(NO_2)_2(PR_3)_n$ ($n=2$, 3) have been isolated so far, in spite of the fact that the nickel analogs are well known [14] and $Ni(NO_2)_2(PPh_2CH_2CH_2PPh_2)$ has been crystallographically characterized [15].



Scheme 1.

An attractive feature of the metal-coordinated NO_2 group is its ability to act as an oxygen atom transfer reagent in the metal coordination sphere**,

---

*Authors to whom correspondence should be addressed.

**Observed for NO_2^- complexes with different metals: Ni [16a–e], Pd [16f–h], Re and Mn [16i], Ru [16j–l].

0020-1693/91/$3.50

being oxidized into NO_3^- or reduced into NO. Nitro–cobalt(II) complexes have been shown to be particularly effective in these processes [17]. For these reasons, during the course of our work on the synthesis and reactivity of tertiary phosphine complexes $CoX_2(PR_3)n$ ($n=2$, 3), we became interested in investigating more thoroughly the influence of tertiary phosphines on the stability and reactivity of the $Co(NO_2)_2$ entity. We wish to describe here the reaction of $Co(NO_2)_2$, prepared *in situ* by reaction of $NaNO_2$ on $Co(NO_3)_2$ in methanol, with PMe_3, PEt_3, PMe_2Ph, $PMePh_2$ and PPh_3. For PMe_3 and PMe_2Ph, the five-coordinate compounds $Co(NO_2)_2(PMe_3)_3$ (**1**) and $Co(NO_2)_2(PMe_2Ph)_3$ (**2**) were isolated as solids. With PEt_3, only $Co(NO)(NO_2)_2(PEt_3)_2$ was obtained. It reacted with molecular oxygen to give $Co(NO_3)_2(OPEt_3)_2$ (**9**) which was structurally characterized. Reductive nitrosylation of these complexes was found to take place with NO gas, whereas reductive nitrosylation or carbonylation occurred with CO.

Experimental

Physical measurements

IR spectra were recorded as Nujol mulls on Perkin-Elmer 577 or 983 spectrophotometers. UV–Vis spectra were obtained on a Cary 14 spectrophotometer. EPR spectra were measured on a Bruker ER 200TT spectrometer operating at X band frequency between 100 and 300 K. Magnetic susceptibilities were determined by the Faraday method, using a Cahn microbalance coupled with a Drusch electromagnet. Measurements were performed at 298 K. $HgCo(NCS)_4$ was used as standard ($Xg=16.44\times10^{-6}$ cgs emu). The experimental values were corrected for the diamagnetism of the ligands.

Crystal data for $Co(NO_3)_2(OPEt_3)_2$

Formula $C_{12}H_{30}CoN_2O_8P_2$, formula weight = 451.26, monoclinic, $C2/c$, $a=16.795(4)$, $b=7.863(3)$, $c=15.752(6)$ Å, $\beta=94.07(2)°$, $V=2074.9$ Å^3, $D_{calc}=1.444$ g cm^{-3}, $Z=4$, λ(Cu Kα) = 1.54178 Å (graphite monochromator), μ(Cu Kα) = 86.3 cm^{-1}, $T=170$ K.

Crystallographic measurements and structure determination

The crystals were isolated directly from the reaction mixture. Beside a brown solid, which was shown to be amorphous, the sample contained some violet crystals of the title compound. Most of the crystals were of poor quality, but a plate of dimensions $0.08\times0.36\times0.40$ mm was found to be acceptable for X-ray work.

The crystal was mounted in a Lindemann capillary and centered on an Enraf-Nonius CAD-4 diffractometer. A set of 25 reflections ($20\leqslant\theta\leqslant25°$) randomly distributed in the Laue sphere was generated and the reduced cell ($a=7.832(6)$, $b=9.238(9)$, $c=15.74(2)$ Å, $\alpha=85.95(9)$, $\beta=89.85(8)$, $\gamma=64.90(7)°$) was obtained by the autoindexing procedure. Oscillation photographs taken along the three axes showed the expected layer-line separations and a Laue mirror perpendicular to the shortest axis. The Niggli parameters indicated that the reduced cell could be transformed into a monoclinic C-centered cell, whose unique axis is the one for which mirror symmetry had already been observed. Beside the absences due to C-centering (hkl, $h+k\neq2n$), a fast precollection revealed only one condition of absence ($h0l$, $l\neq2n$), which identified Cc and $C2/c$ as the possible space groups.

A total of 1972 independent reflections was collected as previously described [18] using Cu Kα radiation. Two octants of reflections ($0\leqslant h\leqslant20$, $0\leqslant k\leqslant9$, $-19\leqslant l\leqslant19$) were measured in the reciprocal sphere limited by $2\theta=140°$. A set of 1445 reflections with $I\geqslant3\sigma(I)$ was retained for structure determination and refinement. Seven standard reflections checked every hour showed random fluctuations within ±1.9%. Crystal orientation was also checked every 100 reflections. These intensities were corrected for the effects of Lorentz, polarization and absorption (grid $10\times10\times10$, transmission range = 0.08–0.55).

The structure was solved and refined in the centrosymmetric space group $C2/c$ by using the SHELX package [19]. This choice of the space group was confirmed by successful refinement. As the unit cell has an eight-fold general equipoint, but contains only four molecules, only one half of the molecule needs to be defined. The SHELX direct methods revealed the position of the cobalt atom on equipoint e (two-fold axis) and those of nearly all non-hydrogen atoms in the asymmetric unit. Those missing were located from a subsequent ΔF map. Isotropic refinement of all non-hydrogen atoms converged to $R=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|=0.140$ and $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}=0.164$. The hydrogen atoms were fixed at idealized positions with a constant isotropic temperature factor $U=0.073$ Å^2. Their positions were recalculated after each cycle. In the latest stage, the non-hydrogen atoms were refined anisotropically. At convergence, the residuals were $R=0.082$ and $R_w=0.090$. In the final ΔF map, the highest electron density peaks (0.70–0.85 e/Å^3) were within 1.2 Å from Co or P. The general background was below ±0.5 e/Å^3. The refined parameters are listed in Table 1.

TABLE 1. Refined coordinates ($\times 10^4$) and equivalent temperature factors ($\times 10^3$)

Atom	x	y	z	U_{eq}
Co	0	5720(3)	2500	30
P	1104(1)	2933(3)	1555(1)	31
O(1)	835(3)	4060(7)	2265(3)	36
O(2)	−386(3)	6664(8)	1313(3)	40
O(3)	−946(4)	7828(8)	2359(4)	43
O(4)	−1308(4)	8591(8)	1055(4)	56
N	−900(5)	7719(9)	1552(5)	41
C(11)	1349(6)	4172(11)	652(5)	43
C(12)	1910(5)	5683(12)	887(5)	45
C(13)	1957(5)	1744(11)	1941(5)	37
C(14)	2305(6)	500(11)	1334(6)	52
C(15)	347(5)	1423(11)	1187(5)	45
C(16)	−399(5)	2223(13)	757(5)	47

The scattering factors used were from standard sources [20]. Anomalous dispersion was taken into account for Co and P [21].

Materials and methods

Solvent distillation and all other manipulations were performed under an argon atmosphere by using standard Schlenk techniques. Tetrahydrofurane, toluene and ether were distilled over Na/benzophenone just before use. Methylene chloride was distilled over Na_2CO_3 and stored on 4 Å molecular sieves. Methanol and acetonitrile were distilled over molecular sieves. All solvents were degassed by three freeze–thaw cycles before use. Trimethylphosphine was synthesized by a modification of the literature method [22]. Other tertiary phosphines (Aldrich) were checked by NMR and purified by distillation when needed. $Co(NO_2)_2$ was prepared *in situ* by reacting $Co(NO_3)_2 \cdot 6H_2O$ (0.5 g; 1.7 mmol) on $NaNO_2$ (0.24 g; 3.5 mmol) in methanol (15 ml). The solution was stirred overnight. The orange–red solution of $Co(NO_2)_2$, obtained after elimination of $NaNO_3$ by filtration, was used directly.

Elemental analyses were performed by the Service Central de Microanalyse du CNRS, Lyon, France.

Synthetic work

$Co(NO_2)_2(PMe_3)_3$ (1)

To a stirred solution of $Co(NO_2)_2$ (1.7 mmol) in methanol (15 ml) was added PMe_3 in excess (5.2 mmol) at room temperature. The solution turned green immediately. Methanol was removed *in vacuo* and the crude complex recrystallized from an ethanol/ether mixture at 0 °C overnight. The green crystals of $Co(NO_2)_2(PMe_3)_3$ were filtered and dried under argon. Yield: 75%. *Anal.* Calc. for $C_9H_{27}N_2O_4P_3Co$: C, 28.51; H, 7.18; N, 7.39; P, 24.51; Co, 15.54. Found: C, 27.83; H, 7.07; N, 7.84; P, 24.46; Co, 15.69%.

$Co(NO_2)_2(PMe_2Ph)_3$ (2)

0.71 g (5.2 mmol) of PMe_2Ph were added slowly to a stirred solution of $Co(NO_2)_2$ (1.7 mmol) in 15 ml of methanol. The resulting green solution was kept at 5 °C for 5 h. Adding ether gave rise to a mixture of green and red crystals, which were filtered and dried under argon. Mixing with acetone allowed the separation by filtration of the insoluble green crystals of $Co(NO_2)_2(PMe_2Ph)_3$ in 50% yield. *Anal.* Calc. for $C_{24}H_{33}N_2O_4P_3Co$: C, 50.98; H, 5.88; N, 4.95; Co, 10.42. Found: C, 50.66; H, 5.88; N, 5.14; Co, 10.22%. The red filtrate kept at −5 °C for 10 h gave a few red crystals of $Co(NO)(PMe_2Ph)_3$, which were filtered and dried under argon.

$Co(NO)(NO_2)_2(PEt_3)_2$ (3)

When 0.6 g (5.2 mmol) of PEt_3 was added to $Co(NO_2)_2$ (1.7 mmol) dissolved in 15 ml of methanol, the solution turned green immediately. Gradually, the color changed and, after 0.5 h, it had turned brown. Methanol was removed *in vacuo* and the crude complex recrystallized from 20 ml of methanol. Brown crystals precipitated when the solution was kept at 0 °C overnight. Yield: 40%. *Anal.* Calc. for $C_{12}H_{30}N_3O_5P_2Co$: C, 34.54; H, 7.25; N, 10.07; P, 14.85; Co, 14.12. Found: C, 34.56; H, 7.05; N, 9.95; P, 15.04; Co, 14.40%.

$Co(NO)(NO_2)_2(PR_3)_2$ ($PR_3=PMe_3$ (4), PMe_2Ph (5))

These complexes were obtained by bubbling NO through a toluene solution of $Co(NO_2)_2(PR_3)_3$ (3.0 mmol). The green solution turned brown immediately, but stirring was maintained for 0.5 h. Brown crystals precipitated when the solution was left at −20 °C. They were filtered and dried under argon. *Anal.* Calc. for $C_6H_{18}N_3O_5P_2Co$ (4): C, 21.63; H, 5.45; N, 12.61. Found: C, 21.10; H, 5.42; N, 12.40%. *Anal.* Calc. for $C_{16}H_{22}N_3O_5P_2Co$ (5): C, 42.03; H, 4.85; N, 9.19; Co, 12.89. Found: C, 42.30; H, 5.10; N, 9.80; Co, 12.63%.

4 was also prepared by reacting $Ag(NO_2)$ (0.4 g; 2.6 mmol) with $CoBr_2(PMe_3)_3$ (0.15 g; 1.1 mmol) dissolved in 10 ml of CH_2Cl_2. The color of the solution changed from violet to green after 5 min, then to brown 2 min later. AgBr was eliminated by filtration. CH_2Cl_2 was removed *in vacuo* and the brown oily solid recrystallized from 15 ml of ether. Brown crystals of 4 were obtained after leaving the solution at −20 °C overnight (40% yield).

$Co(NO)_2(NO_2)(PMe_3)$ (6) and $Co(NO)_2(NO_2)(PMe_2Ph)$ (7)

These complexes were obtained by the method used for $Co(NO)(NO_2)_2(PR_3)_2$, but methanol or THF was used as solvent. *Anal.* Calc. for $C_3H_9N_3O_4PCo$, **6**: C, 14.95; H, 3.76; N, 17.43. Found: C, 14.75; H, 3.70; N, 16.85%. Calc. for $C_8H_{11}N_3O_4PCo$ (**7**): C, 31.70; H, 3.66; N, 13.86. Found: C, 31.05; H, 3.51; N, 13.12%.

$Co(NO)(CO)(PMe_3)_2$ (8)

$Co(NO_2)_2(PMe_3)_3$ (1 g; 3.72 mmol) was dissolved in methanol (15 ml). The solution was stirred for 0.5 h in the presence of CO (2.64 mmol). The green solution turned brown immediately. Evaporation of methanol under vacuum gave rise to a brown solid. Recrystallization in 20 ml of ether gave red crystals which precipitated overnight at −70 °C. *Anal.* Calc. for $C_7H_{18}NO_2P_2Co$: C, 31.24; H, 6.74: N, 5.20. Found: C, 31.39; H, 7.15; N, 5.37%.

$Co(NO_3)_2(OPEt_3)_2$ (9)

O_2 gas was bubbled through a brown solution of $Co(NO)(NO_2)_2(PEt_3)_2$ (0.5 g; 0.9 mmol) in ether. No color change occurred. Violet crystals precipitated when the solution was kept overnight at −20 °C. They were filtered, washed with ether, and dried in vacuum. *Anal.* Calc. for $C_{12}H_{30}N_2O_8P_2Co$: C, 31.94; H, 6.70; N, 6.21; P, 13.73; Co, 13.06. Found: C, 32.21; H, 6.57; N, 5.95; P, 14.01; Co, 13.32%.

Results and discussion

Adding PR_3 (=PMe_3, PEt_3, PMe_2Ph, $PMePh_2$) to the orange–red solution of $Co(NO_2)_2$ in methanol gave rise to green solutions from which green precipitates were obtained after work up. With PPh_3, no color change occurred and a white compound, which was not characterized, precipitated slowly.

The green PMe_3 and PMe_2Ph solutions were stable enough to give, at 0 °C and after adding ether, dark green crystals of $Co(NO_2)_2(PMe_3)_3$ (**1**) and $Co(NO_2)_2(PMe_2Ph)_3$ (**2**), respectively. These solids could be kept indefinitely at low temperature, but they decomposed slowly at room temperature into brown oily powders. The latter materials proved to be difficult to characterize, but the presence of phosphine oxide, NO and NO_2 groups was demonstrated by IR. In the case of PMe_2Ph, a few red crystals of $Co(NO)(PMe_2Ph)_3$, soluble in acetone ($\nu(NO) = 1620$ cm^{-1}), coprecipitated with **2**. $Co(NO)(PR_3)_3$ complexes were previously obtained when tertiary phosphines were reacted with $Co(NO_2)_2$ in alcohol [23, 24]. Their formation can be related to the stabilization of the electron-rich cobalt centre by NO^+, a strong π-acceptor, as indicated by the low value of the NO stretch (1620 cm^{-1}). $Co(NO_2)_2(PR_3)_3$ ($PR_3 = PEt_3$, $PMePh_2$) could not be isolated as stable green materials. With $PMePh_2$, a green compound precipitated first, but it rapidly turned brown even at −5 °C. Recrystallization in toluene gave a mixture of the brown solid $Co(NO)_2(NO_2)(PMePh_2)$ ($\nu(NO) = 1770$, 1835 cm^{-1} and $\delta(NO_2) = 814$ cm^{-1}), and a white powder containing dimethylphenylphosphine oxide. With PEt_3, the green oil obtained following solvent elimination turned brown after 0.5 h. Recrystallization from ether at 0 °C gave brown crystals of $Co(NO)(NO_2)_2(PEt_3)_2$ (**3**) ($\nu(NO) = 1640$ cm^{-1}; $\nu(NO_2) = 1295$, 1185 cm^{-1}; $\delta(NO_2) = 804$ cm^{-1}). Formation of this complex results from the known capability of the nitrosyl compounds $Co(NO)(PR_3)_3$ present in the solution to act as NO transfer reagents [25].

$Co(NO_2)_2(PMe_3)_3$ (1) and $Co(NO_2)_2(PMe_2Ph)_3$ (2)

The dinitrotris(tertiary phosphine)cobalt(II) compounds are low spin. In the solid state at room temperature and at 120 K, axially symmetric spectra with $g_\perp > g_\parallel$ are observed. The spectrum of $Co(NO_2)_2(PMe_3)_3$ is illustrated in Fig. 1. The experimental g values are: $g_\parallel = 2.04$ and $g_\perp = 2.17$ at 293 K, $g_\parallel = 2.05$ and $g_\perp = 2.16$ at 120 K. Elemental analysis, magnetic moments (2.08 BM for **1** and 2.16 BM for **2**) and EPR spectra indicate five-coordination about the cobalt(II) centre. The two limiting geometries, trigonal bipyramid (TBP) and square pyramid (SP), can be distinguished from their EPR g values because of the difference in d orbital occupancies [2, 3, 5, 26]. The values observed here ($g_\perp > g_\parallel > 2.002$) support the square-pyramidal geometry in the solid state. Consequently, **1** and **2**

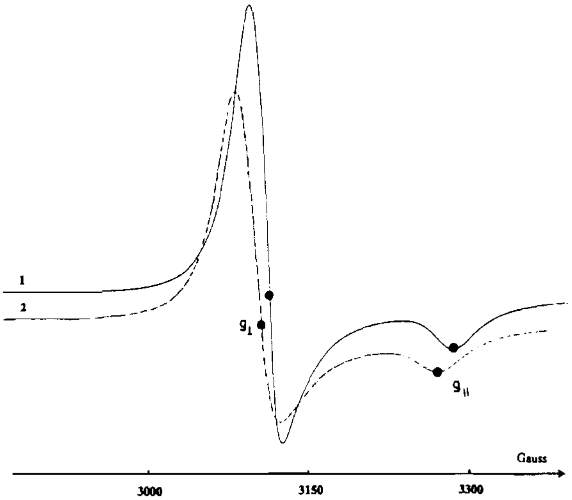


Fig. 1. Solid-state EPR spectra of $Co(NO_2)_2(PMe_3)_3$: **1**, 293 K; **2**, 120 K.

differ from $CoCl_2(PMe_3)_3$ and $[CoCl(PMe_3)_4]^+$ [27] for which a TBP ground state was observed in the solid state.

On the other hand, when **1** and **2** are dissolved in methanol, the broad featureless EPR signal at $\langle g \rangle = 2.13$ observed at low temperature is reminiscent of the spectra of the halide compounds $CoX_2(PMe_3)_3$ (X = Cl, Br, I). Thus, a distorted structure intermediate between TBP and SP, as proposed for the halide systems, could also be present for **1** and **2** in solution.

IR spectroscopy indicates N-coordination for the two nitro groups, because of the presence of the $\delta(NO_2)$ vibration at 812 cm^{-1} and of the two stretching bands characteristic of N coordination [28] at 1340 and 1290 cm^{-1}.

Reactivity of the complexes toward NO and CO

1 and **2** reacted immediately with NO in toluene to give $Co(NO)(NO_2)_2(PR_3)_2$ (**4** and **5**) as brown crystals. Surprisingly, the triethylphosphine analog **3** was obtained in a one-step reaction when attempting to synthesize $Co(NO_2)_2(PEt_3)_3$.

$$Co(NO_2)_2(PR_3)_3 + NO \longrightarrow Co(NO)(NO_2)_2(PR_3)_2 + PR_3$$

$PR_3 = PMe_3$ (**4**), PMe_2Ph (**5**)

NO acts as a nitrosylating agent toward **1** and **2**, as previously observed with $CoX_2(PR_3)_2$ (X = halide) [29, 30]. Complexes **3**, **4** and **5** can be described as low-spin cobalt(III) complexes, with bent Co–NO entities ($\nu(NO) = 1640$ cm^{-1} for **4** and **5**, 1650 cm^{-1} for **3**). The band at 805 cm^{-1}, characteristic of the $\delta(NO_2)$ vibration for a N-bonded nitro group, is also apparent for the three complexes. It is difficult to ascertain the binding mode (N- or O-coordination) of the nitro group from the 1500–1000 cm^{-1} range, because of the presence of phosphine vibrations. However, in **5**, a weak band at 1185 cm^{-1} could be related to an O-bonded $\nu(NO_2)$ vibration. The similar spectroscopic data for the three complexes indicate similar structures. Since **5** has been shown by X-ray diffraction [31] to be a pseudo-octahedral Co(III) complex including a bent NO group, two *trans* phosphines, a N-bonded nitro group and an O-bonded nitrito group, complexes **3** and **4** likely possess both N-bonded and O-bonded groups as well. Moreover, the CoNO unit is bent, in contrast with the case of $Co(NO)I_2(PMe_3)_2$, where a linear CoNO entity is present [30].

Reduction of **1** with CO occurred at room temperature in methanol. Work up of the solution yielded red crystals of the ether-soluble $Co(NO)(CO)(PMe_3)_2$ compound ($\nu(NO) = 1710$ cm^{-1}; $\nu(CO) = 1945$ cm^{-1}) and to an intractable brown solid, which we were unable to characterize. This process implies reduction of the cobalt compound, since $Co(NO)(CO)(PMe_3)_2$ has also been obtained by reaction of $NaNO_2$ with $CoBr(CO)_2(PMe_3)_2$ or by reacting CO with $Co(NO)(PMe_3)_3$ [32]. It is also solvent-dependent: when the reaction was run in toluene, no carbonyl complexes were isolated. **2** gave a mixture of $Co(NO)(NO_2)_2(PMe_2Ph)_2$ (**5**) and $Co(NO)_2(NO_2)(PMe_2Ph)$ (**7**)* ($\nu(NO) = 1825$ and 1775 cm^{-1}) via a complex pattern of reactions that is not understood. **7** was also obtained when CO was bubbled through a toluene solution of **5** for several hours. The reaction implies oxygen transfer from NO_2 to CO, since the loss of CO_2 is observed by IR. With PEt_3 as ligand, an oily intractable mixture of compounds was obtained, but not characterized.

Reactivity with O_2

Previous work indicated that O_2 reacts with coordinated NO to give NO_2^-, NO_3^- or mixed NO_2^-/NO_3^- species, depending on the binding mode of NO [34]. It has been assumed that oxygenation proceeds by electrophilic attack of O_2 on the NO ligand, followed by rearrangement of the N-coordinated ONO_2 moiety. We have reacted O_2 with complexes **3**–**5**. Only oily, intractable mixtures of species including OPR_3 ligands were obtained, except with $Co(NO)(NO_2)_2(PEt_3)_2$.

Bubbling O_2 through an ether solution of $Co(NO)(NO_2)_2(PEt_3)_2$ (**3**) produced no obvious color change in the brown solution. However, when the solution was kept at −20 °C overnight, precipitation of violet crystals of $Co(NO_3)_2(OPEt_3)_2$ (**9**) occurred. A brown oily solid, different from the starting material, co-precipitated with **9**, but it could not be characterized.

$Co(NO_3)_2(OPEt_3)_2$ (9)

This complex (and its $OPMe_3$ analog) can be prepared directly by reacting the phosphine oxide on $Co(NO_3)_2$ [35]. Its magnetic moment (4.8 BM at r.t.) is as expected for a high-spin octahedral cobalt(II) complex. In agreement with this is the violet color of the solution, resulting from two electronic transitions at 17 850 ($\epsilon = 110$) and 47 650 ($\epsilon = 1950$) cm^{-1}, respectively. Two vibrations at 1015 and 1290 cm^{-1} could be identified in the IR spectrum for the coordinated NO_3^- ligand. These bands are found at the same places for $Co(NO_3)_2(OPMe_3)_2$. However, the presence of the PEt_3 unit [36] makes it difficult to identify the bands observed between 1520 and 1470 cm^{-1} for the latter complex.

---

*The iodo analog $Co(NO)_2I(PPh_3)$ has been structurally characterized [33].

The crystal structure of **9** was determined by X-ray diffraction. The molecular geometry and atom numbering scheme are presented in Fig. 2. The unit cell shown in Fig. 3 contains four such molecular entities.

The inner coordination sphere around the cobalt atom corresponds to a distorted octahedron. The Co atom lies on a crystallographic two-fold axis relating the two halves of the molecule. Interatomic distances and angles are listed in Table 2. The arrangement of phosphine oxide and bidentate nitrate ligands around the metal is similar to that of $Co(NO_3)_2(OPMe_3)_2$ [37]. The chelating nitrate imposing a small O–Co–O angle of 59.0(2)° in the ring, the remaining angles around the metal exhibit large deviations from the ideal octahedral values: 138.1(2) and 163.2(2)° (twice) between *trans* pairs of donor atoms, 87.6(2)–104.4(2)° range between *cis* pairs. The Co–O–P angle observed here (140.9(4)°) is appreciably greater than in the $OPMe_3$ analog, but this angle has been shown to vary over a wide range in phosphine oxide complexes [38].

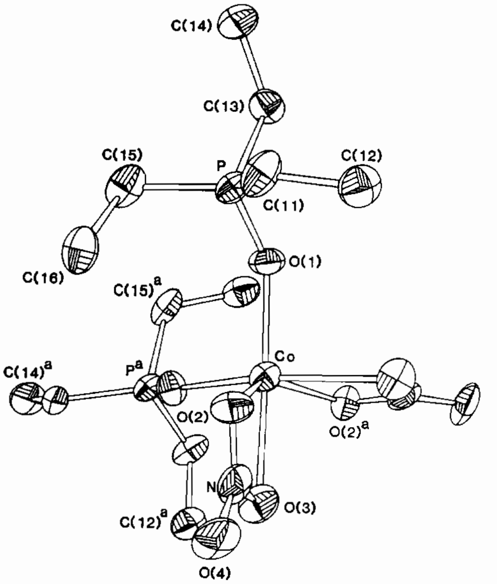


Fig. 2. ORTEP drawing of the $Co(NO_3)_2(OPEt_3)_2$ molecule. Ellipsoids correspond to 50% probability. H atoms are omitted for simplicity. The Co atom occupies a crystallographic two-fold axis relating the two halves of the molecule (a = $-x$, y, $\frac{1}{2}-z$).

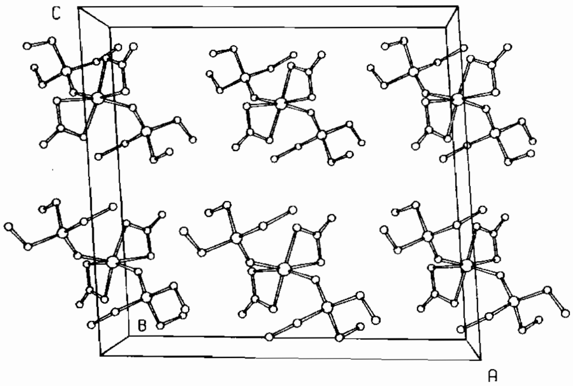


Fig. 3. View of the unit cell of $Co(NO_3)_2(OPEt_3)_2$ down the *b* axis. Atoms can be identified by comparison with Fig. 2. Hydrogens are omitted.

TABLE 2. Interatomic distances and bond angles

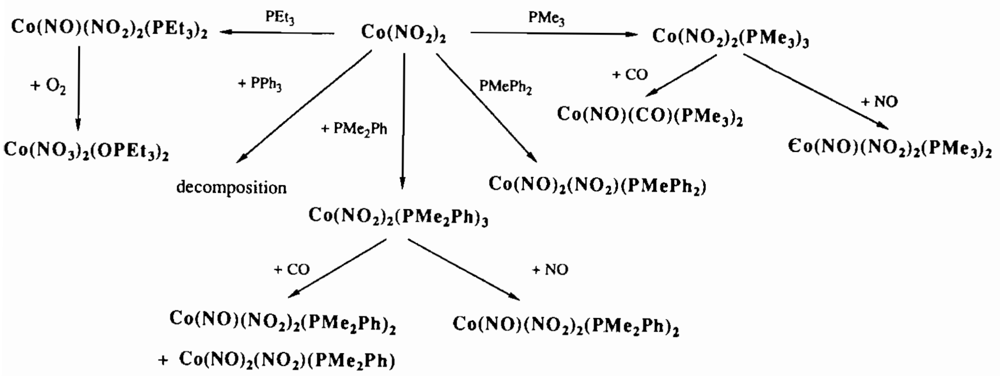
Distances (Å)			
Co–O(1)	1.970(6)	Co–O(2)	2.073(5)
Co–O(3)	2.295(6)	P–O(1)	1.522(6)
P–C(11)	1.795(9)	P–C(13)	1.782(8)
P–C(15)	1.805(9)	C(11)–C(12)	1.545(13)
C(13)–C(14)	1.513(12)	C(15)–C(16)	1.518(12)
N–O(2)	1.274(10)	N–O(3)	1.281(10)
N–O(4)	1.216(10)		
Angles (°)			
O(1)–Co–O(1)^a	97.0(2)	O(1)–Co–O(2)	104.4(2)
O(1)–Co–O(2)^a	103.0(2)	O(1)–Co–O(3)	163.2(2)
O(1)–Co–O(3)^a	90.0(2)	O(2)–Co–O(2)^a	138.1(2)
O(2)–Co–O(3)	59.0(2)	O(2)–Co–O(3)^a	90.0(2)
O(3)–Co–O(3)^a	87.6(2)	Co–O(1)–P	140.9(4)
Co–O(2)–N	98.1(5)	Co–O(3)–N	87.6(4)
O(1)–P–C(11)	111.3(4)	O(1)–P–C(13)	109.1(4)
O(1)–P–C(15)	112.4(4)	C(11)–P–C(13)	109.4(4)
C(11)–P–C(15)	107.4(4)	C(13)–P–C(15)	107.2(4)
P–C(11)–C(12)	113.4(6)	P–C(13)–C(14)	117.4(6)
P–C(15)–C(16)	114.2(6)	O(2)–N–O(3)	115.3(7)
O(2)–N–O(4)	122.6(7)	O(3)–N–O(4)	122.0(7)

^{a} $-x$, y, $\frac{1}{2}-z$.

Asymmetric bidentate binding is not uncommon for the NO_3^- ligand, but no satisfactory explanation for this effect has yet been proposed [39]. Our nitrate group definitely binds asymmetrically, with Co–O distances of 2.073(5) and 2.295(6) Å. The geometry of the coordinated ligand clearly reflects its bidentate character: the coordinated N–O distances (1.274(10) and 1.281(10) Å) are definitely longer than the free N–O bond (1.216(10) Å). Both the change in bond orders and the steric effect of chelate formation could explain the intra-ring O–N–O angle (115.3(7)°) being smaller than the other two (122.6(7) and 122.0(7)°). The group is planar within 1σ (0.008 Å) and the metal lies 0.073(2) Å from this plane.

Conclusions

The series of experiments described above indicates that $Co(NO_2)_2$ can behave like CoX_2 (X = Cl, Br, I), leading to similar complexes with tertiary phosphines (Scheme 2). However, two differences are observed:



Scheme 2.

(a) five-coordinate complexes $Co(NO_2)_2(PR_3)_3$ can be stabilized, but they adopt a square-pyramidal ground state geometry, in contrast with the trigonal-bipyramidal geometry found for their halide analogues;

(b) no stable four-coordinate species could be isolated: they behave as reactive intermediates, since they present an unsaturation in the metal coordination sphere, allowing oxygen atom transfer to occur.

With CO, no adducts are observed in toluene, where reductive nitrosylation occurs, but in methanol, reductive carbonylation takes place. With O_2, a nitrato Co(II) complex of phosphine oxide has been isolated with PEt_3.

NO adducts are formed only by PMe_3, PEt_3 and PMe_2Ph, a behavior possibly related to the phosphine cone angles, which suggests that steric factors could contribute to the stability of the complexes. These adducts are among the rare examples of molecules in which coexist three different types of nitrogen oxides, that is, NO, O-bonded NO_2 and N-bonded NO_2.

Supplementary material

Temperature factors, hydrogen coordinates, distances to least-squares plane, and structure factor amplitudes (12 pages) are available upon request from A. L. B.

Acknowledgements

Support from the Centre National de la Recherche Scientifique, the Université P. Sabatier, the Natural Science and Engineering Research Council of Canada, and the Ministère de l'Education du Québec, is gratefully acknowledged. This work was made possible by travel grants (no. 85/0245) in the framework of the NATO Research Program for International Cooperation.

References

1 F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc., 83* (1961) 4690; F. A. Cotton, D. M. L. Goodgame, M. Goodgame and A. Sacco, *J. Am. Chem. Soc., 83* (1961) 4157; F. A. Cotton; O. D. Faut, D. M. L. Goodgame and R. H. Holm, *J. Am. Chem. Soc., 83* (1961) 1780; W. E. Hatfield and J. T. Yoke III, *Inorg. Chem., 1* (1962) 470, 475; A. Turco, C. Pecile, M. Nicolini and M. Martelli, *J. Am. Chem. Soc., 85* (1963) 3510; M. Nicolini, C. Pecile and A. Turco, *J. Am. Chem. Soc., 87* (1965) 2379; P. Rigo, M. Bressan and A. Turco, *Inorg. Chem. 7* (1968) 1460; J. F. White and M. F. Farona, *Inorg. Chem., 10* (1971) 1080; J. A. Bertrand and D. L. Plymale, *Inorg. Chem., 5* (1966) 879; A. Bertacco, U. Mazzi and A. A. Orio, *Inorg. Chem., 11* (1972) 2547; M. Bressan and P. Rigo, *Inorg. Chem., 14* (1975) 38; I. B. Joedicke, H. V. Studer and J. T. Yoke III, *Inorg. Chem., 15* (1976) 1352; J. J. Sznadjer, A. Jablonski and W. Wojciechowski, *J. Inorg. Nucl. Chem., 41* (1979) 305.

2 O. Stelzer, W. S. Sheldrick and J. Subramanian, *J. Chem. Soc., Dalton Trans.,* (1977) 966.

3 T. Nowlin and K. Cohn, *Inorg. Chem., 10* (1971) 2801; T. Nowlin, S. Subramanian and K. Cohn, *Inorg. Chem., 11* (1972) 2907; T. Nowlin and K. Cohn, *Inorg. Chem., 11* (1972) 560.

4 D. A. White, A. J. Solodar and M. M. Baizer, *Inorg. Chem., 11* (1972) 2160; P. Rigo and A. Turco, *Coord. Chem. Rev., 8* (1972) 175; J. Halpern, B. L. Goodall, G. P. Khare, H. S. Lim and J. J. Pluth, *J. Am. Chem. Soc., 97* (1975) 2301.

5 J. J. Alexander and H. B. Gray, *J. Am. Chem. Soc., 89* (1967) 3356.

6 L. D. Brown and K. N. Raymond, *Inorg. Chem., 14* (1975) 2595; R. S. Drago, J. R. Stahlbush, D. J. Kitko and J. Breese, *J. Am. Chem. Soc., 102* (1980) 1884.

7 Y. Nishida and H. Shimohori, *Bull. Chem. Soc. Jpn, 46* (1973) 2406.

8 (a) K. J. Coskran, T. J. Huttemann and J. G. Verkade, *Adv. Chem. Ser., 62* (1967) 590; (b) A. M. Brodie, S. H. Hunter, G. A. Rodley and C. J. Wilkins, *Inorg.*

Chim. Acta, 2 (1968) 195; (c) C. Benelli, M. Di Vaira, G. Noccioli and L. Sacconi, *Inorg. Chem., 16* (1977) 182; (d) P. L. Johnson, J. H. Enemark, R. D. Feltham and K. Bizot-Swedo, *Inorg. Chem., 15* (1976) 2989; (e) R. D. Feltham and R. S. Nyholm, *Inorg. Chem., 4* (1965) 1334.

9 M. A. Hitchman and G. L. Rowbottom, *Coord. Chem. Rev., 42* (1982) 55.

10 S. M. Jorgensen, *Z. Anorg. Chem., 5* (1983) 147; 19, 109; E. Billman, *Z. Anal. Chem., 39* (1900) 284; F. Basolo and G. S. Hammaker, *J. Am. Chem. Soc., 82* (1960) 1001; J. Chatt, L. A. Duncanson, B. M. Gatehouse, J. Lewis, R. S. Nyholm, M. L. Tobe, P. F. Todd and L. M. Venanzi, *J. Chem. Soc.,* (1959) 4073.

11 D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem., 3* (1964) 1389; L. El-Sayed and R. O. Ragsdale, *Inorg. Chem., 6* (1967) 1644; I. Grenthe and E. Nordin, *Inorg. Chem., 18* (1979) 1109.

12 S. Hayakawa, H. Nishikawa, K. Kashiwabara and M. Shibata, *Bull. Chem. Soc. Jpn., 54* (1981) 3593.

13 M. Atoh, K. Kashiwabara, H. Ito, T. Ito and J. Fujita, *Bull. Chem. Soc. Jpn., 57* (1984) 3139.

14 A. Merle, M. Dartiguenave and Y. Dartiguenave, *Bull. Soc. Chim. Fr.,* (1972) 87; G. Booth and J. Chatt, *J. Chem. Soc.,* (1962) 2099.

15 J. Kriege-Simondsen and R. D. Feltham, *Inorg. Chim. Acta, 71* (1983) 185.

16 (a) R. Ugo, S. Bhaduri, B. F. G. Johnson, A. Khair, A. Pickard and Y. Benn-Taarit, *J. Chem. Soc., Chem. Commun.,* (1976) 694; (b) R. D. Feltham and J. C. Kriege, *J. Am. Chem. Soc., 101* (1979) 5064; (c) D. T. Doughty, G. Gordon and R. P. Stewart, Jr., *J. Am. Chem. Soc., 101* (1979) 2645; (d) J. Kriege-Simondsen, G. Elbaze, M. Dartiguenave, R. D. Feltham and Y. Dartiguenave, *Inorg. Chem., 21* (1982) 230; (e) R. S. Berman and J. K. Kochi, *Inorg. Chem., 19* (1980) 248; (f) M. A. Andrews and K. P. Kelly, *J. Am. Chem. Soc., 103* (1981) 2894; (g) D. A. Muccigrosso, F. Mares, S. E. Diamond and J. Solar, *Inorg. Chem., 22* (1983) 960; (h) R. A. Clement, U. Klabunde and G. W. Parshall, *J. Mol. Catal., 4* (1978) 87; (i) J. B. Sheridan, G. L. Geoffroy and A. L. Rheingold, *J. Am. Chem. Soc., 109* (1987) 1584; (j) F. R. Keene, D. J. Salmon and T. J. Meyer, *J. Am. Chem. Soc., 99* (1977) 4821; (k) F. R. Keene, D. J. Salmon, J. L. Walsh, H. D. Abruna and T. J. Meyer, *Inorg. Chem., 19* (1980) 1896; (l) D. T. Doughty, G. Gordon and R. P. Stewart, Jr., *J. Am. Chem. Soc., 103* (1981) 3388.

17 B. S. Tovrog, S. E. Diamond and F. Mares, *J. Am. Chem. Soc., 101* (1979) 270; B. S. Tovrog, F. Mares and S. E. Diamond, *J. Am. Chem. Soc., 102* (1980) 6616; B. S. Tovrog, S. E. Diamond, F. Mares and A. Szalkiewicz, *J. Am. Chem. Soc., 103* (1981) 3522.

18 F. Bélanger-Gariépy and A. L. Beauchamp, *J. Am. Chem. Soc., 102* (1980) 3461.

19 G. Sheldrick, *SHELX76,* crystallographic program system, University of Cambridge, U.K., 1976.

20 D. T. Cromer and J. T. Waber, *Acta Crystallogr., 18* (1965) 104; R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys., 42* (1965) 3175.

21 D. T. Cromer, *Acta Crystallogr., 18* (1965) 17.

22 W. Wolfsberger and H. Schmidbaur, *Synth. Inorg. Met.-Org. Chem., 4* (1974) 149.

23 M. Bressan and P. Rigo, *J. Chem. Soc., Chem. Commun.,* (1974) 553.

24 J. O. Albright, J. C. Clardy and J. G. Verkade, *Inorg. Chem., 16* (1977) 1575.

25 A. Sacco, G. Vasapollo and P. Giannoccaro, *Inorg. Chim. Acta, 32* (1979) 171; C. B. Ungermann and K. G. Caulton, *J. Am. Chem. Soc., 98* (1976) 3862.

26 A. Pezeshk, F. T. Greenaway and G. Vincow, *Inorg. Chem., 17* (1978) 3421; Y. Nishida and S. Kida, *Inorg. Nucl. Chem. Lett., 7* (1971) 325; W. De W. Horrocks Jr., G. R. van Hecke and D. De W. Hall, *Inorg. Chem., 6* (1967) 694; O. Stelzer, W. S. Sheldrick and J. Subramanian, *J. Chem. Soc., Dalton Trans.,* (1977) 966; J. M. Assour and W. K. Kahn, *J. Am. Chem. Soc., 87* (1965) 207.

27 O. Alnaji, M. Zinoune, A. Gleizes, M. Dartiguenave and Y. Dartiguenave, *Nouv. J. Chim., 4* (1980) 707.

28 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* Wiley, New York, 4th edn., 1986, p. 221; K. Nakamoto, J. Fujita and H. Murata, *J. Am. Chem. Soc., 80* (1958) 4817; G. Blyholder and A. Kittila, *J. Phys. Chem., 67* (1963) 2147; F. Basolo and G. S. Hammaker, *Inorg. Chem., 1* (1962) 1.

29 C. Pratt-Brock, J. P. Collman, G. Dolcetti, P. H. Farnham, J. A. Ibers, J. E. Lester and C. A. Reed, *Inorg. Chem., 12* (1973) 1304.

30 O. Alnaji, Y. Pérès, M. Dartiguenave, F. Dahan and Y. Dartiguenave, *Inorg. Chim. Acta, 114* (1986) 151.

31 R. D. Feltham, *ACS Annual Meet., Las Vegas, 1982,* and personal communication.

32 Y. Pérès, *Thèse de 3e cycle,* Université P. Sabatier, Toulouse, 1985.

33 B. L. Haymore, J. C. Huffman and N. E. Butler, *Inorg. Chem., 22* (1983) 168.

34 S. G. Clarkson and F. Basolo, *Inorg. Chem., 12* (1973) 1528; W. C. Trogler and L. G. Marzilli, *Inorg. Chem., 13* (1974) 1008; K. R. Laing and W. R. Roper, *J. Chem. Soc., Chem. Commun.,* (1968) 1568; K. R. Grundy, K. R. Laing and W. R. Roper, *J. Chem. Soc., Chem. Commun.,* (1970) 1500; M. Kubota and D. A. Philips, *J. Am. Chem. Soc., 97* (1975) 5637.

35 M. W. G. De Bolster, C. Boutkan, T. A. Van der Knaap, L. Van Zweeden, I. E. Kortram and W. L. Groeneveld, *Z. Anorg. Allg. Chem., 443* (1978) 269; F. A. Cotton, D. M. L. Goodgame and R. H. Soderberg, *Inorg. Chem., 2* (1963) 1162.

36 J. Sznajder, A. Jablonski and W. Wojciechowski, *J. Inorg. Nucl. Chem., 41* (1974) 305. P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc. A,* (1966) 1462.

37 F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc., 85* (1963) 2402.

38 M. Dartiguenave, Y. Dartiguenave, M. J. Olivier and A. L. Beauchamp, *J. Coord. Chem., A21* (1990) 275.

39 C. C. Addison, N. Logan, S. C. Wallwork and C. D. Garner, *Q. Rev., 25* (1971) 289.