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Five-coordinate Diphosphine Complexes of the $\{CoNO\}^8$ Group, and their Disproportionation Reactions to Cobalt(III) and $\{Co(NO)_2\}^{10}$ Derivatives

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Abstract

The syntheses and characterization of some new five-coordinate, mononitrosyl $\{CoNO\}^8$ complexes of the type $[Co(NO)(P\text{-}P)_2](BF_4)_2$ (P-P = alkyl- or phenyl-substituted ditertiary phosphine) are described, and their stereochemistry and dynamic behaviour studied by $^{31}P\{^1H\}$ NMR. The mononitrosyl complexes, which contain linearly coordinated Co–NO groups, disproportionate in solution in the presence of anionic ligands (X^- = halide or pseudohalide), giving dinitrosyl derivatives $[Co(NO)_2(P\text{-}P)]^+$ and cobalt(III) complexes *trans*-$[CoX_2(P\text{-}P)_2]^+$, which were isolated in the solid state as the tetraphenyl- or tetrafluoroborate salts. The reaction provides a useful synthetic route, especially for pseudohalide cobalt(III) complexes. The IR, electronic and ^{31}P NMR spectroscopic properties of the cobalt(III) complexes are consistent with a *trans* stereochemistry, while those of the $\{Co(NO)_2\}^{10}$ derivatives suggest a pseudotetrahedral structure with linearly-coordinated NO groups. The stoichiometry of the dismutation reactions was examined in dichloromethane solution by NMR and IR techniques. A possible mechanism is presented, which involves the formation of a six-coordinate *trans*-$[CoX(NO)(P\text{-}P)_2]^+$ intermediate containing a strongly bent Co–NO moiety.

Introduction

A large number of phosphino–nitrosyl complexes of the $\{Co(NO)\}^8$ and $\{Co(NO)_2\}^{10}$** groups has been reported, and their structures and reactivity extensively studied [1–3]. The major work has been done with unidentate phosphorus ligands, which form a variety of complexes of types $Co(NO)L_3$ [4], $CoX(NO)_2L$ [4b, 5], $[Co(NO)_2L_2]^+$ [4b, 5], $[CoX(NO)L_3]^+$ [5–7], $CoX_2(NO)L_2$ [8] (X = halide or pseudohalide), and $[Co(NO)L_4]^{2+}$ [7], where L is PR_3, $P(OR)_2Ph$ or $P(OR)_3$. This contrasts with the paucity of cobalt–nitrosyl derivatives containing diphosphines (P-P), which are essentially restricted to some compounds with 1,2-bis(diphenylphosphino)ethane and *cis*-1,2-bis(diphenylphosphino)ethylene [3], such as the tetrahedral cations $[Co(NO)_2(P\text{-}P)]^+$ [4b, 9, 10]. No five-coordinate $\{CoNO\}^8$ complexes of type $[Co(NO)(P\text{-}P)_2]^{2+}$ have been reported, even if analogous $[Co(NO)(L\text{-}L)_2]^{n+}$ derivatives with bidentate ligands containing nitrogen, oxygen, sulfur or arsenic as donor atoms have been known for a number of years [11]. We now find that some compounds of type $[Co(NO)(P\text{-}P)_2]Y_2$ (I) (Y = non-coordinating anion) can be simply obtained in acetonitrile solution either by reacting nitric oxide with cobalt(II) complexes $[Co(P\text{-}P)_2]Y_2$, or from $[Co(H_2O)_6]Y_2$ salts in the presence of diphosphine. By this route we have prepared, and report here, a series of five-coordinate, stereochemically non-rigid $[Co(NO)(P\text{-}P)_2]^{2+}$ cations, isolated in the solid state as tetrafluoroborate salts, which contain the diphosphine ligands reported in Scheme 1.

Moreover, the conversion of $\{CoNO\}^8$ nitrosyl derivatives into the reported cobalt(III) and cobalt(–I) species, according to eqn. (1), has been studied

$$\underset{\mathbf{I}}{2[Co(NO)(P\text{-}P)_2]^{2+}} + 2X^- \longrightarrow \underset{\mathbf{II}}{[Co(NO)_2(P\text{-}P)]^+} + \underset{\mathbf{III}}{trans\text{-}[CoX_2(P\text{-}P)_2]^+} + P\text{-}P \qquad (1)$$

by IR and ^{31}P NMR spectroscopy. A number of $[Co(NO)_2(P\text{-}P)]BPh_4$ (II) and *trans*-$[CoX_2(P\text{-}P)_2]BF_4$ (III) complexes has been obtained and characterized by IR, ^{31}P NMR, and UV–Vis spectroscopy.

Analogous redox reactions have been previously observed for complexes $[Co(NO)(Ph_2PCH_2CH_2SEt)_2](BF_4)_2$ [12] in the presence of thiocyanate ions, and for mononitrosyl derivatives $Co(NCS)_2(NO)(PMe_3)_2$ [13] and $[Co(NCS)(NO)L_3]^+$ [L = $P(OEt)_3$ or $P(OEt)_2Ph$] [6]. This synthetic procedure offers an alternative to the usual preparation methods of cobalt(III)–diphosphine complexes, which generally imply air- or halogen-oxidation of the appropriate

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**In order to avoid ambiguities that can arise from the NO^+–NO^- formalism, Enemark and Feltham's notation is used.

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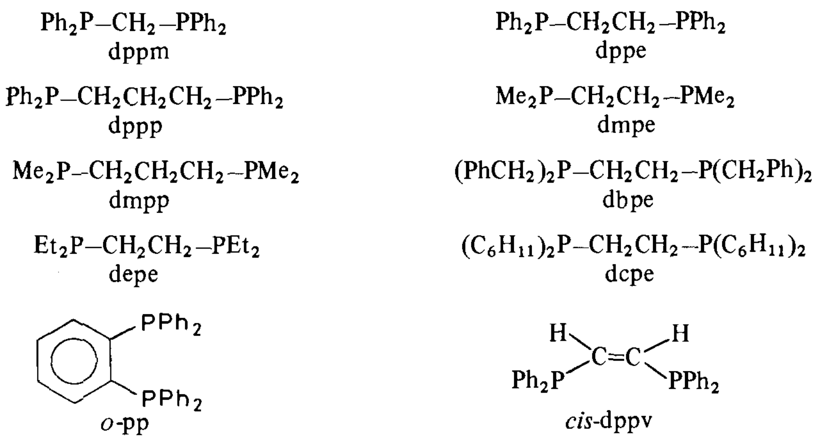

Scheme 1.

cobalt(II) compound [3]. In particular, this reaction is a valuable route to pseudohalide complexes of cobalt(III) when, owing to the instability of the corresponding halide derivatives [13, 14], these cannot be prepared by metathesis. Finally, a possible mechanism for the dismutation reaction (1) is presented and discussed.

Experimental

Chemicals

The diphosphine ligands were purchased from Strem Chemicals, except dmpp which was prepared according to the method of Cloyd and Meek [15], $[Co(H_2O)_6](BF_4)_2$ was from Ventron; NaOCN, NEt_4OCN, KSCN, NEt_4SCN, NaN_3, NEt_4Cl and $NaBPh_4$ from Fluka AG. Nitric oxide (Matheson-Union Carbide) was purified by passing through a cold trap. The $[Co(P\text{-}P)_2](BF_4)_2$ complexes used as starting materials were prepared by reacting $[Co(H_2O)_6](BF_4)_2$ and the appropriate diphosphine in 2-propanol-dichloromethane solution. All solvents were distilled and degassed before use.

Characterization Methods

Infrared spectra were obtained in Nujol mulls (CsI plates) with a Jasco DS 702 G spectrophotometer, and calibrated against the absorption of a polystyrene film at 2850.7, 1601.4 and 1028.0 cm^{-1}. Visible and UV spectra were recorded with a Varian Cary 2300 spectrophotometer. Conductance data were obtained for 10^{-3} M nitromethane solutions using a Metrohm 518 conductivity bridge. $^{31}P\{^1H\}$ NMR spectra were recorded at 32.44 MHz with a Bruker WP 80 SY FT spectrometer equipped with a variable-temperature probe. Chemical shifts are given in ppm downfield from external aqueous 85% H_3PO_4. At room temperature, the $^{31}P\{^1H\}$ NMR spectra of **II** and **III** show rather broad signals due to the interaction with the quadrupolar ^{59}Co nucleus. In comparison, the linewidths for signals of species **I** are relatively small, probably because ^{59}Co relaxation times are much faster in the trigonal bipyramidal complexes [16]. To avoid broadening of the signals, the ^{31}P NMR spectra of all complexes were run at low temperature in dichloromethane (213–183 K), acetonitrile (228 K) or $CHF_2Cl–CD_2Cl_2$ (1:1) (183–133 K) solutions. Elemental analyses were performed in the Microanalytical Laboratory of the Istituto di Chimica, Università di Udine. Analytical and physical data are summarized in Table 1, IR and ^{31}P NMR data are reported in Table 2, UV–Vis data for complexes **III** are listed in Table 3.

Syntheses

All preparations were performed under argon by using standard Schlenk techniques.

$[Co(NO)(P\text{-}P)_2](BF_4)_2$ (P-P = dmpe, depe, dppe, dbpe, o-pp, cis-dppv, dmpp)

(a) $[Co(H_2O)_6](BF_4)_2$ (1 mmol) and P-P (P-P = dmpe, depe, dppe, dbpe, *o*-pp, dmpp) (2 mmol) were dissolved in acetonitrile (20 cm^3). The resulting red–orange or green (depe) solutions became more intensely coloured upon saturation with NO (1 atm.). After 10 min NO was removed, 2-propanol (30 cm^3) was added, and the solution volume was reduced *in vacuo* to precipitate the products.

(b) Complexes $[Co(P\text{-}P)_2](BF_4)_2$ (P-P = depe, dppe, dbpe, *o*-pp, *cis*-dppv) (1 mmol) were dissolved in acetonitrile (20 cm^3) and treated with NO (1 atm.). After 10 min, 2-propanol (20 cm^3) was added, and the volume of the solution was halved *in vacuo*. The solid which had separated was filtered off, washed with ethanol, and dried *in vacuo*. The crude products were recrystallized from dichloromethane/2-propanol (P-P = depe, dppe, dbpe, *o*-pp, *cis*-dppv) or from acetonitrile/2-propanol (dmpe, dmpp). Yields in the range 84–93%.

TABLE 1. Physical and analytical data

Complex	Colour	Λ_M^{a} (cm^2 ohm^{-1} mol^{-1})	Analysis: found (calc.) (%)		
			C	H	N
[Co(NO)(dmpe)$_2$](BF$_4$)$_2$	red–brown	186	25.28(25.61)	5.73(5.73)	2.42(2.49)
[Co(NO)(depe)$_2$](BF$_4$)$_2$	brown	190	35.46(35.59)	7.14(7.17)	2.04(2.07)
[Co(NO)(dppe)$_2$](BF$_4$)$_2$	ochre	172	58.89(58.96)	4.61(4.57)	1.30(1.32)
[Co(NO)(dbpe)$_2$](BF$_4$)$_2$	olive green	165	61.56(61.51)	5.56(5.51)	1.20(1.20)
[Co(NO)(*o*-pp)$_2$](BF$_4$)$_2$	red–brown	166	61.83(62.37)	4.15(4.19)	1.23(1.21)
[Co(NO)(*cis*-dppv)$_2$](BF$_4$)$_2$	red–brown	171	58.87(59.18)	4.13(4.20)	1.34(1.33)
[Co(NO)(dmpp)$_2$](BF$_4$)$_2$	brown	184	27.96(28.46)	6.09(6.14)	2.31(2.37)
[Co(NO)$_2$(dppe)]BPh$_4$	red–brown	52	71.62(71.78)	5.34(5.30)	3.28(3.35)
[Co(NO)$_2$(dcpe)]BPh$_4$	orange–brown	50	69.22(69.77)	7.99(7.96)	3.19(3.25)
[Co(NO)$_2$(dbpe)]BPh$_4$	orange–brown	47	72.66(72.65)	5.86(5.87)	3.08(3.14)
[Co(NO)$_2$(*o*-pp)]BPh$_4$	red–brown	49	73.46(73.32)	5.02(5.01)	3.09(3.17)
[Co(NO)$_2$(*cis*-dppv)]BPh$_4$	red–brown	51	72.32(71.96)	5.14(5.07)	3.31(3.36)
[Co(NO)$_2$(dppp)]BPh$_4$	red–brown	52	71.88(72.01)	5.51(5.45)	3.26(3.29)
trans-[Co(NCS)$_2$(dppm)$_2$]BF$_4$	red	83	60.41(60.60)	4.28(4.30)	2.71(2.72)
trans-[Co(NCS)$_2$(dmpe)$_2$]BF$_4$	orange–red	94	29.48(29.91)	5.75(5.74)	4.92(4.98)
trans-[Co(NCS)$_2$(depe)$_2$]BF$_4$	orange–red	86	38.99(39.18)	7.19(7.17)	4.11(4.15)
trans-[Co(NCS)$_2$(dppe)$_2$]BF$_4$	ochre	83	61.17(61.26)	4.60(4.57)	2.62(2.65)
trans-[Co(NCS)$_2$(dbpe)$_2$]BF$_4$	orange	93	63.04(63.59)	5.48(5.51)	2.31(2.39)
trans-[Co(NCS)$_2$(*o*-pp)$_2$]BF$_4$	brown	88	64.29(64.48)	4.18(4.19)	2.48(2.43)
trans-[Co(NCS)$_2$(*cis*-dppv)$_2$]BF$_4$	red–brown	84	61.26(61.49)	4.22(4.21)	2.63(2.66)
trans-[Co(NCS)$_2$(dmpp)$_2$]BF$_4$	red	90	32.42(32.56)	6.16(6.15)	4.72(4.74)
trans-[Co(NCO)$_2$(dmpe)$_2$]BF$_4$	orange	91	31.44(31.72)	6.08(6.06)	5.26(5.29)
trans-[Co(NCO)$_2$(depe)$_2$]BF$_4$	pink–red	92	40.97(41.14)	7.55(7.53)	4.37(4.36)
trans-[Co(NCO)$_2$(dppe)$_2$]BF$_4$	red	88	63.06(63.18)	4.74(4.71)	2.69(2.73)
trans-[Co(NCO)$_2$(*o*-pp)$_2$]BF$_4$	red–brown	85	66.51(66.33)	4.24(4.31)	2.45(2.50)
trans-[Co(NCO)$_2$(*cis*-dppv)$_2$]BF$_4$	brown	83	63.17(63.43)	4.32(4.34)	2.70(2.74)
trans-[Co(NCO)$_2$(dmpp)$_2$]BF$_4$	orange–red	89	34.51(34.43)	6.59(6.50)	4.98(5.02)
trans-[Co(N$_3$)$_2$(depe)$_2$]BF$_4$	red–brown	94	37.74(37.40)	7.64(7.53)	12.98(13.09)
trans-[Co(N$_3$)$_2$(*o*-pp)$_2$]BF$_4$	red–brown	86	64.63(64.19)	4.28(4.31)	7.42(7.49)
trans-[Co(N$_3$)$_2$(*cis*-dppv)$_2$]BF$_4$	red–brown	89	60.83(61.08)	4.38(4.34)	8.29(8.22)

[a] In nitromethane at 22 °C, for 10^{-3} M solutions.

TABLE 2. IR and ^{31}P NMR data

Complex	IR^{a} (cm^{-1})	^{31}P{^{1}H} NMR^{b}	
		δ (ppm)	*T* (K)
[Co(NO)(dmpe)$_2$](BF$_4$)$_2$	1785	57.7(s)	228^{c}
[Co(NO)(depe)$_2$](BF$_4$)$_2$	1808	72(m), 82(m)	133^{d}
[Co(NO)(dppe)$_2$](BF$_4$)$_2$	1807	73.8(t), 80.6(t)^{e}	183
[Co(NO)(dbpe)$_2$](BF$_4$)$_2$	1806	62(m), 78(m)	133^{d}
[Co(NO)(*o*-pp)$_2$](BF$_4$)$_2$	1808	49.9(t), 72.7(t)^{f}	173
[Co(NO)(*cis*-dppv)$_2$](BF$_4$)$_2$	1824	66(m), 73(m)	133^{d}
[Co(NO)(dmpp)$_2$](BF$_4$)$_2$	1795	6.7(t), −14.4(t)^{g}	228^{c}
[Co(NO)$_2$(dppe)]BPh$_4$	1841, 1789	65.6(s)	213
[Co(NO)$_2$(dcpe)]BPh$_4$	1848, 1776	87.3(s)	213
[Co(NO)$_2$(dbpe)]BPh$_4$	1838, 1786	69.2(s)	213
[Co(NO)$_2$(*o*-pp)]BPh$_4$	1847, 1792	63.6(s)	213
[Co(NO)$_2$(*cis*-dppv)]BPh$_4$	1864, 1803	73.8(s)	213

(continued)

TABLE 2. *(continued)*

Complex	IR[a] (cm^{-1})	^{31}P{^{1}H} NMR[b]	
		δ (ppm)	*T* (K)
[Co(NO)$_2$(dppp)]BPh$_4$	1840, 1787	27.2(s)	213
trans-[Co(NCS)$_2$(dppm)$_2$]BF$_4$	2094	−14.2(s)	213
trans-[Co(NCS)$_2$(dmpe)$_2$]BF$_4$	2109	60.4(s)	228[c]
trans-[Co(NCS)$_2$(depe)$_2$]BF$_4$	2101	66.3(s)	213
trans-[Co(NCS)$_2$(dppe)$_2$]BF$_4$	2105	45.1(s)	213
trans-[Co(NCS)$_2$(dbpe)$_2$]BF$_4$	2102	61.4(s)	228[c]
trans-[Co(NCS)$_2$(*o*-pp)$_2$]BF$_4$	2092	44.8(s)	213
trans-[Co(NCS)$_2$(*cis*-dppv)$_2$]BF$_4$	2089	49.0(s)	213
trans-[Co(NCS)$_2$(dmpp)$_2$]BF$_4$	2102	9.5(s)	228[c]
trans-[Co(NCO)$_2$(dmpe)$_2$]BF$_4$	2243	57.1(s)	228[c]
trans-[Co(NCO)$_2$(depe)$_2$]BF$_4$	2253	62.6(s)	213
trans-[Co(NCO)$_2$(dppe)$_2$]BF$_4$	2267	41.8(s)	213
trans-[Co(NCO)$_2$(*o*-pp)$_2$]BF$_4$	2262, 2229	43.3(s)	213
trans-[Co(NCO)$_2$(*cis*-dppv)$_2$]BF$_4$	2261	48.1(s)	213
trans-[Co(NCO)$_2$(dmpp)$_2$]BF$_4$	2237	5.6(s)	228[c]
trans-[Co(N$_3$)$_2$(depe)$_2$]BF$_4$	2039	62.7(s)	213
trans-[Co(N$_3$)$_2$(*o*-pp)$_2$]BF$_4$	2049, 2028	41.1(s)	213
trans-[Co(N$_3$)$_2$(*cis*-dppv)$_2$]BF$_4$	2054	44.9(s)	213

[a] In Nujol mull. [b] In CH$_2$Cl$_2$ solution, unless otherwise stated. Multiplicity given in parentheses by s = singlet, t = triplet, m = broad multiplet. [c] In CH$_3$CN solution. [d] In CD$_2$Cl$_2$–CHF$_2$Cl solution. [e] *J*(P–P′) = 23.5 Hz. [f] *J*(P–P′) = 32.0 Hz, [g] *J*(P–P′) = 49.1 Hz.

TABLE 3. UV-Vis data for complexes **III**[a]

Complex	λ_{max} (nm) (ε (M^{-1} cm^{-1}))
trans-[Co(NCS)$_2$(dppm)$_2$]BF$_4$	580(sh), 435(19000), 345(28500)
trans-[Co(NCS)$_2$(dmpe)$_2$]BF$_4$	485(480), 380(4700), 310(10800)[b]
trans-[Co(NCS)$_2$(depe)$_2$]BF$_4$	505(540), 390(5900), 335(10900)
trans-[Co(NCS)$_2$(dppe)$_2$]BF$_4$	570(sh), 425(18300), 350(24200)
trans-[Co(NCS)$_2$(dbpe)$_2$]BF$_4$	535(sh), 350(23100), 305(22500)
trans-[Co(NCS)$_2$(*o*-pp)$_2$]BF$_4$	580(sh), 440(19000), 360(25500)
trans-[Co(NCS)$_2$(*cis*-dppv)$_2$]BF$_4$	590(sh), 450(13400), 360(25200)
trans-[Co(NCS)$_2$(dmpp)$_2$]BF$_4$	500(480), 380(5200), 325(10400)[b]
trans-[Co(NCO)$_2$(dmpe)$_2$]BF$_4$	485(210), 335(6400), 285(22500)[b]
trans-[Co(NCO)$_2$(depe)$_2$]BF$_4$	505(270), 345(sh), 305(28600)
trans-[Co(NCO)$_2$(dppe)$_2$]BF$_4$	555(sh), 380(32500), 295(sh)
trans-[Co(NCO)$_2$(*o*-pp)$_2$]BF$_4$	550(sh), 390(31600), 305(sh)
trans-[Co(NCO)$_2$(*cis*-dppv)$_2$]BF$_4$	550(320), 385(33700), 305(9700)
trans-[Co(NCO)$_2$(dmpp)$_2$]BF$_4$	500(310), 345(sh), 300(23700)[b]
trans-[Co(N$_3$)$_2$(depe)$_2$]BF$_4$	545(620), 380(sh), 330(12700)
trans-[Co(N$_3$)$_2$(*o*-pp)$_2$]BF$_4$	620(sh), 435(sh), 325(16400)
trans-[Co(N$_3$)$_2$(*cis*-dppv)$_2$]BF$_4$	625(sh), 445(sh), 345(20300)

[a] In dichloromethane solution, unless otherwise stated. [b] In acetonitrile solution.

[Co(NO)$_2$(dcpe)]BPh$_4$

[Co(dcpe)$_2$](BF$_4$)$_2$ (1 mmol) was stirred in acetonitrile (30 cm^3), and the reaction vessel was saturated with NO. An immediate colour change from orange to red–brown was observed. After 10 min, NaBPh$_4$ (1.5 mmol) in 2-propanol (20 cm^3) was added, and the solution was concentrated. The red–brown precipitate was filtered off, dried *in vacuo*, and recrystallized from dichloromethane/2-propanol. This complex was also obtained using $[Co(H_2O)_6](BF_4)_2$ (1 mmol) and dcpe (2 mmol) as starting materials, by following the same procedure. Yield 75%.

$[Co(NO)_2(dppp)]BPh_4$

$[Co(H_2O)_6](BF_4)_2$ (1 mmol) and dppp (2 mmol) were dissolved in acetonitrile (20 cm^3), and the reaction vessel was saturated with NO. After stirring for 10 min, a solution of $NaBPh_4$ (1.5 mmol) in 2-propanol (30 cm^3) was slowly added, and the solution volume was reduced *in vacuo*. The red–brown solid which had separated was filtered off and recrystallized from dichloromethane/2-propanol. Yield 72%.

trans-$[Co(NCS)_2(P\text{-}P)_2]BF_4$ (P-P = dmpe, depe, dppe, dbpe, o-pp, cis-dppv, dmpp) and $[Co(NO)_2(P\text{-}P)]BPh_4$ (P-P = dppe, dbpe, o-pp, cis-dppv)

Complexes $[Co(NO)(P\text{-}P)_2](BF_4)_2$ (0.5 mmol) and KSCN (0.5 mmol) were stirred in acetone–ethanol (30 cm^3, 1:5 ratio). For complete conversion, the following reaction times were necessary: dppe, *o*-pp, *cis*-dppv, 1 h; depe and dbpe, 24 h; dmpe and dmpp, 72 h. Complexes *trans*-$[Co(NCS)_2(P\text{-}P)_2]BF_4$ precipitated and were filtered off, washed with ethanol, and dried *in vacuo*. The crude products were recrystallized from dichloromethane/2-propanol (P-P = depe, dppe, dbpe, *o*-pp), dichloromethane–acetonitrile (2:1)/2-propanol (*cis*-dppv) or from acetonitrile/2-propanol (dmpe, dmpp). Yields in the range 72–81%. Upon dropwise addition of $NaBPh_4$ (0.4 mmol) dissolved in ethanol (15 cm^3) to the filtered solutions, complexes $[Co(NO)_2(P\text{-}P)]BPh_4$ precipitated, which were filtered off, dried *in vacuo*, and recrystallized from dichloromethane/2-propanol (P-P = dppe, dbpe, *o*-pp, *cis*-dppv). Yields in the range 71–78%.

trans-$[Co(NCS)_2(dppm)_2]BF_4$

Complex $[Co(H_2O)_6](BF_4)_2$ (1 mmol), KSCN (1 mmol), and dppm (2 mmol) were stirred in acetonitrile (20 cm^3) in an NO atmosphere. Red microcrystals separated immediately, which were filtered off, washed with ethanol, and recrystallized from dichloromethane/ethanol. Yield 90%.

trans-$[Co(NCO)_2(P\text{-}P)_2]BF_4$ (P-P = dmpe, depe, dppe, cis-dppv, o-pp, dmpp)

Complexes $[Co(NO)(P\text{-}P)_2](BF_4)_2$ (0.5 mmol) and NaOCN (0.5 mmol) were stirred in acetone/2-propanol (30 cm^3, 1:2 ratio). After 24 h (72 h for dmpe and dmpp) the solutions were concentrated, and the solids formed were filtered off, washed with 2-propanol, and dried under vacuum. The products were recrystallized from dichloromethane/2-propanol (P-P = depe, *o*-pp, *cis*-dppv) or from acetone/2-propanol (P-P = dmpe, dmpp). In the case of dppe complex, the crude product was a greenish powder, which gave red needles by slow evaporation of dichloromethane solutions. Yields in the range 67–81%.

trans-$[CoCl_2(P\text{-}P)_2]BF_4$ (P-P = o-pp, cis-dppv)

Dichloromethane solutions (20 cm^3) of $[Co(NO)(P\text{-}P)_2](BF_4)_2$ (0.5 mmol) and NEt_4Cl (0.5 mmol) were stirred for 1 h. After adding 2-propanol (20 cm^3), the solutions were concentrated. The solids formed thereby were filtered off, washed with 2-propanol and ether, and recrystallized from dichloromethane/2-propanol. Yields: 85 (*o*-pp), 76% (*cis*-dppv). The properties of these complexes are identical to those reported by Gray *et al.* [10] and by Levason *et al.* [14].

trans-$[Co(N_3)_2(P\text{-}P)_2]BF_4$ (P-P = depe, o-pp, cis-dppv)

Complexes $[Co(NO)(P\text{-}P)_2(BF_4)_2$ (0.1 mmol) and NaN_3 (0.1 mmol) were stirred in acetone/2-propanol (10 cm^3, 1:5 ratio) for 24 h, during which time the suspensions turned darker. The solids were filtered off, washed with 2-propanol, dried *in vacuo* and recrystallized from dichloromethane/2-propanol. Yields: 68 (depe), 63 (*o*-pp), 66% (*o*-dppv). **Caution**: Apparently these cobalt(III) derivatives are safe, but azido metal complexes are potentially explosive.

Results and Discussion

Synthesis of $\{CoNO\}^8$ Derivatives

Passage of NO through a solution containing $[Co(H_2O)_6](BF_4)_2$ and the diphosphine (1:2 molar ratio) in anhydrous acetonitrile gives orange–brown solutions (or dark green when P-P is depe) wherefrom compounds having the composition $[Co(NO)(P\text{-}P)_2](BF_4)_2$ (P-P = dppe, dmpe, depe, dbpe, *o*-pp, *cis*-dppv and dmpp) precipitate by addition of 2-propanol. By contrast, reaction of $[Co(H_2O)_6](BF_4)_2$ with the ligands dppm, dppp (which do not form stable square-planar complexes) and dcpe leads to dinitrosyl derivatives. These were isolated in a pure form only with the ligands dppp and dcpe. Complexes **I** are easily prepared also by using the corresponding square-planar cobalt(II) complexes $[Co(P\text{-}P)_2](BF_4)_2$ as starting material. However, when square-planar $[Co(dcpe)_2](BF_4)_2$ is reacted with NO at ambient conditions, only the dinitrosyl derivative **II** is obtained. The complexes $[Co(NO)(P\text{-}P)_2](BF_4)_2$ are diamagnetic, and are found to be 1:2 electrolytes in nitromethane. Their IR spectra show a strong ν(NO) band in the 1785–1825 cm^{-1} region, in agreement with the presence of linear Co–NO groups [17]. At room temperature, the proton decoupled ^{31}P NMR spectra of mononitrosyl derivatives **I** show a single resonance which separates into two broad signals of intensity ratio 1:1 by lowering the temperature. On further cooling, these signals sharpen up into two triplets in the case of the complexes which contain dppe, *o*-pp and dmpp (Table 2), while with the *cis*-dppv, depe and dbpe derivatives the low-limiting spectra are not reached even at 133 K (CD_2Cl_2–CHF_2Cl solution), the lowest available temperature. The spectral behaviour is entirely reversible with temperature. The dmpe derivative is sufficiently soluble only in acetonitrile, and this prevents studies at lower temperatures.

The spectroscopic data are clear evidence in favour of a trigonal-bipyramidal structure, with a linear Co–NO group involving an equatorial site, and the diphosphine ligands spanning axial and equatorial positions. These results agree with the empirical generalization that all linear $\{MNO\}^8$ groups exist in TBP complexes [1]. An intramolecular exchange process between axial and equatorial phosphorus atoms, which appears to be rapid at room temperature on the NMR scale, accounts for the temperature dependence shown by ^{31}P NMR spectra of $[Co(NO)(P\text{-}P)_2]^{2+}$ cations. A fluxional behaviour for TBP complexes with bidentate phosphines [18, 19] is quite common, as in the case of $[M(NO)(dppe)_2]^+$ (M = Fe, Ru), which are known to be TBP with an equatorial NO ligand [20].

It is clear that both the chelate ring size and the nature of organic substituents at phosphorus are important in determining the dynamic of the intramolecular rearrangement. The mononitrosyl derivative with dmpp, which is the only one forming a six-membered chelate ring, gives a static spectrum already at 228 K, while all complexes containing five-membered chelate rings are still non-rigid at 190 K. A similar effect of the chain length on the rearrangement barrier has been observed for the stereochemically non-rigid $[Ir(CO)(P\text{-}P)_2]^+$ species, in which the activation energy of exchange process decreases with the bite of chelate in the order dppp > dppe > dppm [21]. Considering the ligands with $-PPh_2$ groups which form five-membered chelate rings, it can be seen that the chelate backbone exerts a considerable effect on the temperature at which static spectra are obtained, as shown by the sequence dppe > *o*-pp > *cis*-dppv, i.e. $-CH_2-CH_2- > o\text{-}(C_6H_4) > cis\text{-}(-CH{=}CH-)$. Probably, the large difference between the dppe and *cis*-dppv complexes arises both from the shorter C–C bond length and from the greater steric hindrance produced by the vinylidene bridge. It should also be noted that the alkyl-substituted ligands seem to have lower barriers, as judged by our inability to achieve static spectra.

Disproportionation Reaction of $[Co(NO)(P\text{-}P)_2]^{2+}$ Complexes

When the $[Co(NO)(P\text{-}P)_2](BF_4)_2$ derivatives are stirred in alcohol–acetone with an equivalent amount of X^- (halide or pseudohalide), they disproportionate to produce $\{Co(NO)_2\}^{10}$ and cobalt(III) compounds, according to eqn. (1). This reaction is of interest as a general synthetic method, even if complications can arise from the instability of either reaction product. Disproportionation (1) occurs also in dichloromethane solution; its stoichiometry in this solvent has been established by quantitative IR analysis, using standard solutions of the complexes $[Co(NCS)_2(P\text{-}P)_2]BF_4$ and $[Co(NO)_2(P\text{-}P)]BPh_4$ (P-P = dppe, *o*-pp and *cis*-dppv). Moreover, ^{31}P NMR measurements show that one mole of free diphosphine is formed per mole of **II** and **III**. The rate of reaction (1) appears to depend on the nature of the diphosphine (phenyl- > alkyl-substituted ligands) and of the anionic ligand ($NCS^- > NCO^- \geqslant$ halide). In particular, we have examined the reactions of **I** with one equivalent amount of SCN^- by following the typical $\nu(NO)$ and $\nu(CN)$ bands in the 1550–1865 and 2090–2110 cm^{-1} regions of the IR spectra. At room temperature, fast reactions are observed with the mononitrosyls which contain dppe, *o*-pp and *cis*-dppv: IR spectra of the reaction mixtures show that **I** is quantitatively transformed into the corresponding **II** and **III** derivatives within 3 min.

With ethyl-substituted depe, this reaction is slow enough to be conveniently followed by IR. Just after mixing, the IR spectrum of a solution of $[Co(NO)(depe)_2](BF_4)_2$ and NEt_4SCN (1:1 molar ratio, 2.5×10^{-2} M) shows $\nu(NO)$ absorptions at 1828, 1796 and 1560 cm^{-1}, and two sharp bands in the $\nu(CN)$ region at 2060 and 2105 cm^{-1}. No detectable amounts of starting mononitrosyl compound **I** are present. With time, the absorptions at 2060 and 1560 cm^{-1} fade, while the typical bands of $[Co(NO)_2(P\text{-}P)]^+$ and $[Co(NCS)_2(depe)_2]^+$ at 1828 and 1796 cm^{-1} [$\nu(NO)$] and at 2105 cm^{-1} [$\nu(CN)$] gain in intensity, in agreement with eqn. (1). The broad NO band at 1560 cm^{-1} and the NCS one at 2060 cm^{-1} can be reasonably attributed to a six-coordinate, bent-nitrosyl intermediate* of type $[Co(NCS)(NO)(P\text{-}P)_2]^+$ (**IV**), formed according to equilibrium (2), in which addition of a thiocyanate ion to cobalt results in the

$$\underset{\textbf{I}}{[Co(NO)(P\text{-}P)_2]^{2+}} + X^- \rightleftharpoons \underset{\textbf{IV}}{trans\text{-}[CoX(NO)(P\text{-}P)_2]^+} \qquad (2)$$

bending of the Co–NO moiety. Conversion of the linear $\{CoNO\}^8$ group of **I** into the bent one of **IV** implies a two-electron transfer from an orbital which is mainly localized on the metal to a π^* antibonding NO orbital, with the formally Co(I) becoming Co(III). A similar change of NO coordination mode from

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*Assignment of the CN band of the $[Co(NCS)(NO)(depe)_2]^+$ intermediate is not straightforward, since it apparently falls nearly at the same frequency as in the free SCN^- ion.

linear to strongly bent has been reported for analogous five-coordinate species $[Co(NO)(L\text{-}L)_2]^{2+}$ [L-L = *o*-phenylenebis(dimethylarsine) (das) or ethylenediamine (en)], which adds an anion (X^-) to give *trans*-$[CoX(NO)(L\text{-}L)_2]^{2+}$ derivatives. X-ray studies of *trans*-$[Co(NCS)(NO)(das)_2]ClO_4$ [11k] and *trans*-$[CoX(NO)(en)_2]ClO_4$ (X = Cl [11g], ClO_4 [11h]), which exhibit ν(NO) absorptions in the 1550–1670 cm^{-1} region, have confirmed the presence of bent Co–NO groups.

Intermediates $[CoX(NO)(P\text{-}P)_2]^+$ have been observed also in the reactions of $[Co(NO)(depe)_2]^{2+}$ with NCO^- [ν(CN) = 2199 cm^{-1}, ν(NO) = 1550 cm^{-1}], Cl^- [ν(NO) = 1565 cm^{-1}], Br^- [ν(NO) = 1572 cm^{-1}] and I^- [ν(NO) = 1578 cm^{-1}]. When the diphosphine is phenyl-substituted, complexes **IV** are more reactive, and can be detected only when X is Cl; their NO absorptions appear in the range 1670–1685 cm^{-1}. Apparently, the position of the NO band is strongly dependent on the diphosphine basicity, but is relatively insensitive of X^-. In all cases the absorptions attributed to bent NO groups gradually decrease in intensity with progress of reaction, while the typical bands of the corresponding dinitrosyl increase. There are no evidences for nitric oxide dissociation. The initial position of equilibrium (2) depends on the nature of P-P. Thus, in the case of depe, at room temperature, equilibrium (2) appears to be shifted to the right for Co:Cl^- ratio of 1:1, while under the same experimental conditions (2.5×10^{-2} M solution) addition of Cl^- to $[Co(NO)(dppe)_2]^{2+}$ converts only half of mononitrosyl **I** into six-coordinate intermediate **IV**. These results are in agreement with the observation that the stabilities of cobalt(III) complexes containing various phenyl-substituted phosphines are much lower than those of the corresponding alkyl-substituted phosphine compounds, possibly due to steric reasons [10, 14, 22, 23]. Furthermore, the position of equilibrium (2) depends on the nature of X^-, and is shifted to the right in the order NCS $\approx$ NCO > Cl. Several attempts to isolate complexes **IV** in the solid state have been unsuccessful, since only impure samples containing variable amounts of **II** and **III** were isolated.

The *trans* structure of intermediate **IV** can be inferred from low-temperature ^{31}P NMR experiments. A dichloromethane solution of **I** (P-P = *cis*-dppv, depe) and NEt_4SCN (1:1 molar ratio) was prepared and kept at –80 °C in an NMR tube. After shaking to ensure mixing, the ^{31}P NMR spectrum of the samples showed a single signal at 61.5 (depe) or 54.1 (*cis*-dppv) ppm, in agreement with the formation of a *trans* adduct, in which the phosphorus atoms of the diphosphines occupy equivalent positions. The sample temperature was then raised to 30 °C, and again lowered to –80 °C. In the case of *cis*-dppv, the ^{31}P NMR spectrum revealed that dismutation (1) had occurred, with quantitative formation of **II**, **III** and free ligand in a 1:1:1 molar ratio. In the case of depe, the ^{31}P NMR spectrum showed that reaction (1) had occurred to the extent of 20%, and that 80% of intermediate **IV** was still present in solution.

The dismutation of $\{CoNO\}^8$ complexes **I** to cobalt(III) and $\{Co(NO)_2\}^{10}$ derivatives formally implicates the net transfer of a NO^- group between two $\{CoNO\}^8$ units. It is likely that this reaction occurs via a μ-bridged nitrosyl, formed by association of **IV** with coordinatively-unsaturated, +2-charged complex **I**, which can react with X^- to give **II**, **III** and free diphosphine. This hypothesis readily accounts for the change in oxidation state of cobalt, and is in agreement with the nucleophilic character of the nitrosyl nitrogen in bent-nitrosyl **IV**. Similar μ-bridged nitrosyl intermediates have been proposed for other intermolecular transfers of a metal-bound NO [11j, 12, 24, 25] even if a nitric oxide dissociative mechanism, as reported for the formation of nitrosylhemoglobine, cannot be excluded [26].

These results show that formation of Co(–I) and Co(III) complexes via disproportionation reactions is a fairly common feature of $\{CoNO\}^8$ derivatives, since it occurs not only in the presence of thiocyanate, as previously reported [7, 12, 13] but also of other coordinating anions such as N_3^-, NCO^-, or halide. However, it should be noted that the five-coordinate species $[Co(NO)(L\text{-}L)_2]^{2+}$ (L-L = das, en) add halide or pseudohalide to give six-coordinate complexes of type **IV**, wich are stable both in the solid state and in solution [11k, g].

$\{Co(NO)_2\}^{10}$ and Cobalt(III) Derivatives

Cationic complexes **II** are best prepared by addition of equimolar KSCN to an ethanol–acetone suspension of **I**. After elimination of the insoluble cobalt(III) derivatives, complexes **II** can be precipitated as the tetraphenylborate salts. By this route, analytically pure samples were obtained with dppe, *cis*-dppv or dbpe. Complexes **II** containing the two former ligands have been previously reported [4b, 9, 10]. With depe, dmpe and dmpp the dinitrosyl derivatives are formed, as shown by IR measurements, but are not obtained pure in the solid state, since they undergo some decomposition in solution. Moreover, with dcpe and dppp, which do not form species **I**, the dinitrosyls **II** can be obtained by direct reaction of NO with acetonitrile solutions of $[Co(H_2O)_6](BF_4)_2$ and diphosphine (1:2 molar ratio). The IR spectra of these reaction mixtures, even after short times (1 min), show only the presence of dinitrosyl **II**. Reaction yields are always high [*c*. 75%, based on starting Co(II)], thus indicating that the $\{Co(NO)_2\}^{10}$ derivatives with these ligands are not formed according to eqn. (1). By operating with P-P:Co(II) ratios lower than 2, the yields drastically decrease, thus suggesting that probably the diphosphine and not NO is the reducing agent.

The air-stable $\{Co(NO)_2\}^{10}$ complexes behave as 1:1 electrolytes in nitromethane solution, and show two strong NO absorptions in the 1775–1865 cm^{-1} region of the IR spectrum, suggesting the presence of linear Co–NO moieties (Table 2). Furthermore, the ^{31}P NMR spectra of **II** show a single signal, indicating the presence of magnetically equivalent phosphorus atoms. These data are in agreement with a pseudo-tetrahedral structure, with a chelating diphosphine and two linearly-coordinated NO groups. In the case of $[Co(NO)_2(dppe)]^+$, this geometry has been established by X-ray diffractometry [9b].

Cobalt(III) species **III** can be obtained from mononitrosyl derivatives **I** via disproportionation reaction (1), or more directly by bubbling NO gas through a stirred solution of $[Co(H_2O)_6](BF_4)_2$, NaX and diphosphine in a 1:1:2 molar ratio. In all cases only the *trans* isomer has been obtained. When X = NCS or NCO, complexes **III** are sparingly soluble, and easily separate from the reaction mixture. When azide ion is used, the separation of **II** and **III** is more difficult, since the two products have similar solubilities. Repeated recrystallizations are necessary, thus giving poorer yields. Because of the potential hazard of azido derivatives, we have restricted the syntheses to a few diphosphine derivatives. In the case of X = Cl, we have isolated in the solid state the already known cobalt(III) complexes with *o*-pp and *cis*-dppv [10, 14]. With the ligands dppe and dppm, apparently the dichloro derivatives quickly decompose in solution, and were not obtained in the solid state. It is probable that the steric interactions in **III** are larger with halide than with pseudohalide, and the resulting weakening of Co–X bonds may promote a redox decomposition process [10, 14]. Other cobalt(III) complexes with some diphosphines reported in Scheme 1 have been previously prepared by different procedures [10, 15, 23, 27].

Complexes **III** are air-stable, diamagnetic solids, which are soluble in solvents such as dichloromethane, acetonitrile, acetone or nitromethane. The pseudohalide derivatives are stable also in solution, while halide complexes undergo slow decomposition; all of them behave as 1:1 electrolytes in freshly prepared nitromethane solutions. On the basis of ^{31}P NMR spectra, which contain a single resonance, a *trans* stereochemistry can be assigned to $[CoX_2(P\text{-}P)_2]^+$ cations (Table 2). In the case of pseudohalide derivatives, the *trans* arrangement is additionally supported by IR spectra, which show a single stretching mode for the coordinated anion (Table 2). Compounds *trans*-$[Co(NCS)_2(P\text{-}P)_2]BF_4$ show a single strong band in the 2090–2110 cm^{-1} region, together with absorptions at 840–860 cm^{-1}, attributable to ν(CN) and ν(CS) stretchings, respectively. These data indicate N-coordinated thiocyanate groups [28], as found for analogous cobalt(III) complexes with phosphorus ligands, though the δ(NCS) bands (which are generally observed below 500 cm^{-1}) cannot be assigned unambiguously [6, 13].

The cyanato complexes show absorptions in three different regions: 2235–2270, 1330–1360 and 570–590 cm^{-1}, which correspond to CN and CO stretchings, and to the NCO bending frequencies, respectively. In these compounds, a decision between N- and O-bonding is not possible. Finally, the azido complexes exhibit strong absorptions in the range 2025–2055 cm^{-1}. Probably due to solid state effects, the X stretching modes of *trans*-$[Co(X)_2(o\text{-}pp)_2]BF_4$ ($X = NCO, N_3$), which are single in dichloromethane solution, appear splitted in Nujol mull.

The electronic spectra of cobalt(III) diphosphine complexes show a three-band system (Table 3); the two more intense absorptions on the high energy side are probably due to ligand-to-metal charge-transfer transitions, while the weak band in the visible region can be assigned as $^1A_{1g} \rightarrow {}^1E_g$. These spectral features agree well with the *trans* disposition of the X ligands [10, 29]. A rough spectrochemical ordering of the diphosphine ligands can be based on the energy of the first spin-allowed d–d transition of $[Co(NCS)_2(P\text{-}P)_2]^+$, and is dmpe > dmpp > depe > dbpe > dppe ≈ dppm ≈ *cis*-dppv ≈ *o*-pp.

Conclusions

Five-coordinate, stereochemically non-rigid $\{CoNO\}^8$ complexes **I**, containing a linearly coordinated nitrosyl group, are easily prepared in acetonitrile solution by reacting NO with cobalt(II) complexes of diphosphines containing non-coordinating anions. In the presence of coordinating anions, trigonal-bipyramidal cations **I** disproportionate according to eqn. (1). This provides a useful synthetic route to complexes **II** and **III**, which is noteworthy especially for pseudohalide derivatives *trans*-$[CoX_2(P\text{-}P)_2]Y$. The dismutation process apparently implies a first step in which five-coordinate **I** is converted into six-coordinate intermediate **IV**, containing a strongly bent Co–NO group. In the second step, intermolecular transfer of a nitrosyl ligand as NO^- probably occurs via a bridged Co(μ-NO)Co intermediate, which can be formed by electrophylic attack of **I** to the nitrogen of the bent NO group of **IV**.

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