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STEREOCHEMISTRY OF TETRAHEDRAL COMPLEXES OF GROUP VIII METALS

CRYSTAL AND MOLECULAR STRUCTURES OF $Co(CO)_2(NO)(PPh_3)$ AND OF $Co(CO)(NO)(PPh_3)_2$

VINCENZO G. ALBANO, PIER L. BELLON and GIANFRANCO CIANI
Istituto di Chimica Generale ed Inorganica, Università degli Studi, Via Venezian 21, 20133 Milano (Italy)

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SUMMARY

The crystal structures of $Co(CO)_2(NO)(PPh_3)$ (I) and of $Co(CO)(NO)(PPh_3)_2$ (II) have been determined, by counter data, in order to provide further information on the stereochemistry of tetrahedral complexes of Group VIII metals. Compound (I) crystallizes in the triclinic space group $P\bar{1}$ with cell dimensions: $a=11.057(15)$, $b=10.251(15)$, $c=10.495(15)$ Å, $\alpha=115.77(7)°$, $\beta=117.60(7)°$, $\gamma=79.04(7)°$ and $Z=2$. Compound (II) crystallizes in the monoclinic space group $P2/c$. The unit cell has dimensions: $a=11.734(15)$, $b=8.235(12)$, $c=17.236(18)$ Å, $\beta=106.33(7)°$, $Z=2$. The structures were refined by full matrix least squares using 2516 reflections for compound (I) and 1352 reflections for compound (II). The final values of the reliability index R were 0.060 and 0.059, respectively. The crystals consist of packings of discrete monomeric molecules. In both species the cobalt atoms display distorted tetrahedral geometries and the carbonyl and nitrosyl groups are indistinguishable because of disorder. The Co–P and Co–C/N distances are 2.224(3) and 1.738(5), 1.762(7), 1.720(7) Å in $Co(CO)_2(NO)(PPh_3)$ and 2.230(3) and 1.718(8) Å in $Co(CO)(NO)(PPh_3)_2$. The angles at the metals deviate from the ideal tetrahedral value, the larger deviation being that of the (C/N)–Co–(C/N) angle, which has a value of 120.0(4)° in $Co(CO)(NO)(PPh_3)_2$. The enlargment of the (C/N)–Co–(C/N) angles is explained in terms of π repulsions between ligand orbitals, whereas the co-ordination geometry of the phosphine ligands is shown to be dominated by interactions with phenyl hydrogens.

INTRODUCTION

A systematic investigation on the stereochemistry of tetrahedral co-ordination in Group VIII metal complexes, with the metal atoms in their lower oxidation states, is in progress in our laboratory. We have recently reported the structures of some tetrahedral Pt and Ir complexes of general formula $ML_nL'_{4-n}$ ($L=CO$, NO and $L'=$ tertiary phosphine)[1–4]. In these the angles at the metal significantly depart from the ideal value of 109.48°. An interpretation of the distortions in terms of π bonding effects has been put forward by Ibers[5]. We have independently presented the same ideas in discussing the structures of tetrahedral compounds containing two phosphine groups: in ref. 6 we state that, when ligands with different accepting abilities are present, the angular distortions can mainly depend on non-bonding repulsions between the ligand orbitals which receive electron density from the metal via π back-donation. If one considers that the π accepting abilities of the aforementioned ligands are in the order $NO^+ > CO > PR_3$, the angular distortions are expected to follow the trend: (ON)–M–(NO) > (ON)–M–(CO) > (OC)–M–(CO) > (ON)–M–P > (OC)–M–P > P–M–P. However, the angles involving one or two phosphine groups very often exhibit distortions which can, in part at least, be accounted for by steric hindrance between bulky ligands; Lippard and Palenik, in reviewing a number of P–Cu–P angles, have pointed out the existence of this effect[7].

In this article we report the crystal structures of two tetrahedral complexes containing L and L′ ligands: $Co(CO)_2(NO)(PPh_3)$, compound (I), and $Co(CO)(NO)(PPh_3)_2$, compound (II). The purpose of this work is to collect more data on the deformation of the molecular geometry as a function of the non-bonding repulsions. Another point of interest lies in the Co–(NO) interactions. A variety of M–N–O angles can be found in the literature; some of the experimental results, such as the N–Ir–N and Ir–N–O angles of 154° and 164°, respectively, in $[Ir(NO)_2(PPh_3)_2]^+$ still remain unexplained[8]. Further structural data on nitrosyl complexes are therefore useful in order to complete the knowledge of the peculiar properties of nitric oxide as a co-ordinating species.

EXPERIMENTAL

Crystal data

Compound (I) $Co(CO)_2(NO)(PPh_3)$, $M = 406.9$, gives deep orange triclinic crystals. The reduced cell has dimensions: $a = 11.057(15)$, $b = 10.251(15)$, $c = 10.495(15)$ Å, $\alpha = 115.77(7)°$, $\beta = 117.60(7)°$, $\gamma = 79.04(7)°$, $U = 949.2$ Å^3, space group $P1$ (*N*.2), $d_{measd.} = 1.41(1)$ g·cm^{-3} (by flotation), $d_{calcd.} = 1.43$ g·cm^{-3}, $Z = 2$, F(000) = 416.

Compound (II) $Co(CO)(NO)(PPh_3)_2$, $M = 640.9$, gives orange monoclinic crystals. The cell dimensions are: $a = 11.734(15)$, $b = 8.235(12)$, $c = 17.236(18)$ Å, $\beta = 106.33(7)°$, $U = 1598.7$ Å^3, $d_{measd.} = 1.33(1)$ g·cm^{-3} (by flotation), $d_{calcd.} = 1.33$ g·cm^{-3} for $Z = 2$, F(000) = 664. Systematic absences ($h0l$ for $l = 2n+1$) indicate two possible space groups, Pc (*N*.7) and $P2/c$ (*N*.13).

For both crystals the cell dimensions were obtained from precession photographs and refined with the "ω-lag" method[9] on the Pailred diffractometer with Mo–K_α radiation ($\lambda = 0.7107$ Å).

Intensity measurements

The intensities were measured on the linear equi-inclination Pailred diffractometer with Mo–K_α radiation, using a graphite monochromator in the case of compound (I) and a silicon monochromator in the case of compound (II).

The crystal of compound (I) was an irregular polyhedron of dimensions 0.67 × 0.36 × 0.31 mm, mounted along the direction of intermediate elongation (c axis). 3420 reflections were collected, belonging to eleven layers from $hk0$ to $hk10$, within the limit $2\theta = 56°$.

The crystal of compound (II) was a parallelopiped of dimensions 0.46 × 0.21 × 0.18 mm, mounted along the direction of shortest elongation (b axis). A set of nine lattice layers from $h0l$ to $h8l$ (2204 reflections) was measured within the sphere $2\theta = 52°$.

No decay occurred during the intensity measurements in both crystals so that the same scale factor was given to all the reflections belonging to the various levels. The integrated intensities were corrected for Lorentz, polarization, and absorption effects. The transmission factors ranged from 0.66 to 0.87 for compound (I) ($\mu = 10.47$ cm^{-1}) and from 0.76 to 0.88 for compound (II) ($\mu = 6.92$ cm^{-1}). The latter corrections were performed by the Busing and Levy method[10], the X-ray path within both samples being computed in 6^3 points.

2516 and 1352 independent reflections, all having a relative statistical error $\sigma(I)/I$ less than 0.25, were used in the solution and refinements of the structures of compounds (I) and (II) respectively.

Determination and refinement of the structures

Preliminary structures for both compounds were obtained from Patterson and Fourier maps. In compound (II) the whole molecule appeared to possess C_2 symmetry, with the metal atom lying at $(0, y, \frac{1}{4})$, so that space group $P2/c$ was chosen as the appropriate one.

The refinements were carried out by full matrix least squares. The phenyl rings were treated as rigid C_6 groups of D_{6h} symmetry (C–C equal to 1.392 Å). The phenyl carbon atoms were assigned individual isotropic thermal factors whereas all the other atoms were treated anisotropically.

The weighting schemes in both structures were of the type $w = 1/(A + B \cdot F_0 + C \cdot F_0^2)$, with the coefficients chosen so as to obtain an approximately constant value of the mean $(w\Delta F^2)$ over the entire range of F and of $\sin \theta/\lambda$. The atomic scattering factors were those reported by Cromer and Mann for Co, P, O, N and C[11], corrected for the real part of the anomalous dispersion[12]; the hydrogen scattering factor (see below) was that given by Forsyth and Wells[13].

For compound (I) no attempts were made to distinguish nitrogen from carbon in the XO ligands at the beginning of the refinement; the three atoms were all assigned the scattering factor $(\frac{2}{3} f_C + \frac{1}{3} f_N)$. In the case of compound (II) with the assumption of space group $P2/c$, which implies a disorder in the carbon and nitrogen distribution, the average scattering factor $(\frac{1}{2} f_C + \frac{1}{2} f_N)$ was adopted.

After a few least squares cycles the difference-Fourier maps of both compounds revealed the presence of all the hydrogen atoms of the phosphine ligands. The coordinates of these atoms (C–H distance equal to 1.08 Å) were computed at the end of each cycle, and their contributions to the structure factors were taken into account. After complete convergence of the disordered model of compound (I), three ordered models, corresponding to each of the three possible positions of the nitrogen atom, were refined and tested.

The final values of the reliability indices $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ were: for compound (I), disordered model, $R = 0.060$ and $R_w = 0.077$ (the ordered models gave $R_w = 0.078$, 0.079 and 0.078), for compound (II) $R = 0.059$ and $R_w = 0.071$. The final difference syntheses for both crystals were rather flat, no signal exceeding 0.6 and 0.4 $e^-/\text{Å}^3$ respectively.

TABLE 1[a,b]

POSITIONAL AND THERMAL PARAMETERS OF THE ATOMS OF COMPOUND (I), $Co(CO)_2(NO)(PPh_3)$

Non-group atoms[c]

Atom	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Co	−2850(0)	−2723(0)	1738(0)	129(1)	−36(1)	171(1)	155(1)	169(2)	203(1
P	−1827(1)	−1622(1)	1072(1)	85(1)	− 5(1)	96(2)	87(1)	77(2)	116(1
C/N(1)	−3733(4)	−4173(5)	8(6)	110(5)	− 3(9)	163(11)	120(6)	133(12)	206(8)
O(1)	−4321(4)	−5101(4)	−1140(5)	166(5)	−65(9)	210(11)	141(5)	52(11)	265(8)
C/N(2)	−3977(5)	−1449(6)	2378(6)	118(6)	−54(11)	155(12)	174(7)	93(13)	193(9)
O(2)	−4707(4)	− 645(6)	2810(6)	156(6)	24(11)	286(13)	260(9)	102(15)	323(10
C/N(3)	−1550(5)	−3165(6)	3208(7)	130(6)	−65(13)	124(13)	256(10)	261(16)	196(9)
O(3)	− 694(5)	−3492(8)	4138(7)	168(7)	−80(17)	57(14)	533(16)	625(24)	319(11)

Phenyl group atoms[d]

Atom	x/a	y/b	z/c	B, Å^2	Atom	x/a	y/b	z/c	B, Å^2
C(1)	−2145(7)	311(2)	1554(4)	3.3(0)	H(2)	−2018	691	3796	4.2
C(2)	−2175(5)	1172(3)	2994(3)	4.2(0)	H(3)	−2427	3322	4526	5.1
C(3)	−2404(4)	2651(3)	3404(2)	5.1(1)	H(4)	−2783	4424	2698	5.3
C(4)	−2604(7)	3271(2)	2377(4)	5.3(1)	H(5)	−2728	2893	137	5.6
C(5)	−2573(5)	2410(3)	938(3)	5.6(1)	H(6)	−2320	262	− 593	4.6
C(6)	−2344(4)	931(3)	526(2)	4.6(1)	H(8)	− 269	−2654	− 870	4.5
C(7)	−2304(3)	−2371(4)	−1027(2)	3.5(0)	H(9)	−1048	−3638	−3745	6.0
C(8)	−1351(2)	−2772(4)	−1646(3)	4.5(1)	H(10)	−3516	−3902	−5514	6.0
C(9)	−1789(2)	−3324(4)	−3262(3)	6.0(1)	H(11)	−5211	−3192	−4413	5.6
C(10)	−3177(3)	−3474(4)	−4257(2)	6.0(1)	H(12)	−4433	−2208	−1539	4.6
C(11)	−4130(2)	−3074(4)	−3638(3)	5.6(1)	H(14)	− 31	−3992	1425	4.2
C(12)	−3692(2)	−2521(4)	−2022(3)	4.6(1)	H(15)	2479	−4243	2502	5.0
C(13)	33(2)	−1728(3)	1939(4)	3.4(0)	H(16)	3956	−2123	3628	5.2
C(14)	614(2)	−3062(2)	1915(4)	4.2(0)	H(17)	2922	253	3670	5.0
C(15)	2026(3)	−3204(2)	2522(4)	5.0(1)	H(18)	412	506	2589	4.0
C(16)	2856(2)	−2012(3)	3154(4)	5.2(1)					
C(17)	2275(2)	− 676(2)	3177(4)	5.0(1)					
C(18)	863(3)	− 534(2)	2570(4)	4.0(0)					

[a] All values × 10^4 except for isotropic thermal parameters.

[b] The numbers in parentheses here and in the succeeding Tables are the esd's on last significant digits.

[c] The β_{ij} are the coefficients of the form: $h^2 \cdot \beta_{11} + k^2 \cdot \beta_{22} + l^2 \cdot \beta_{33} + h \cdot k \cdot \beta_{12} + h \cdot l \cdot \beta_{13} + k \cdot l \cdot \beta_{23}$.

[d] Hydrogen atoms have the same numbers and the same thermal parameters of the carbon atoms to which they are bonded.

Lists of computed and observed structure factor moduli can be obtained on application to the authors. The positional and thermal parameters of all the atoms of the two structures are reported in Tables 1 and 2, respectively.

Computations

All computations were carried out on an IBM 7040 computer. For absorption correction our own programme was used, in which the directions of primary and diffracted beams are evaluated as recently described[14]. Counter data reduction and statistical analysis for weighting schemes were also based upon Fortran programmes

TABLE 2[a]

POSITIONAL AND THERMAL PARAMETERS OF THE ATOMS OF COMPOUND (II), $Co(CO)(NO)(PPh_3)_2$

Nongroup atoms

Atom	*x/a*	*y/b*	*z/c*	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Co	0	1974(1)	2500	43(1)	0(0)	18(1)	96(2)	0(0)	54(0)
P	1658(1)	501(2)	2884(1)	45(1)	−7(3)	14(1)	105(3)	−6(2)	32(0)
C/N	10(5)	3017(8)	1638(4)	69(6)	38(13)	37(7)	127(12)	41(11)	51(3)
O	4(5)	3764(8)	3929(4)	161(8)	−43(16)	90(8)	254(14)	−116(12)	71(3)

Phenyl group atoms

Atom	*x/a*	*y/b*	*z/c*	*B*, Å^2	*Atom*	*x/a*	*y/b*	*z/c*	*B*, Å^2
C(1)	−2937(5)	1853(8)	1715(3)	3.3(1)	H(2)	−3777	378	684	5.2
C(2)	−3834(5)	1476(5)	1017(3)	5.2(1)	H(3)	−5500	2217	204	6.8
C(3)	−4803(3)	2510(7)	747(2)	6.8(2)	H(4)	−5630	4726	967	6.2
C(4)	−4876(5)	3921(8)	1176(3)	6.2(2)	H(5)	−4035	5398	2205	5.6
C(5)	−3979(5)	4298(5)	1873(3)	5.6(1)	H(6)	−2313	3557	2687	4.2
C(6)	−3010(3)	3264(7)	2143(2)	4.2(1)	H(8)	−1200	841	572	4.0
C(7)	−1793(5)	−954(5)	1277(2)	3.0(1)	H(9)	−1294	−1028	−568	4.7
C(8)	−1483(4)	−405(4)	599(2)	4.0(1)	H(10)	−1945	−3875	−504	4.6
C(9)	−1537(3)	−1455(5)	−41(2)	4.7(1)	H(11)	−2495	−4850	696	4.9
C(10)	−1902(5)	−3055(5)	−5(2)	4.6(1)	H(12)	−2398	−2981	1840	4.0
C(11)	−2212(4)	−3604(4)	670(2)	4.9(1)	H(14)	−3897	301	2621	4.1
C(12)	−2157(3)	−2554(5)	1312(2)	4.0(1)	H(15)	−4443	−1339	3665	5.0
C(13)	−2139(4)	−700(6)	2875(2)	3.1(1)	H(16)	−2991	−3262	4509	4.7
C(14)	−3261(3)	−541(5)	2989(2)	4.1(1)	H(17)	−994	−3546	4306	4.5
C(15)	−3568(3)	−1464(6)	3576(3)	5.0(1)	H(18)	−448	−1906	3259	3.9
C(16)	−2752(4)	−2545(6)	4050(2)	4.7(1)					
C(17)	−1630(3)	−2705(5)	3936(2)	4.5(1)					
C(18)	−1323(3)	−1782(6)	3348(3)	3.9(1)					

[a] See footnotes in Table 1.

written in our laboratory. In addition, local versions of entries Nos. 7528, 7531, 7532 and 7535 in the 1966 "International World List of Crystallographic Programs" were used for Fourier analysis, structure factor and least squares calculations; Johnson's ORTEP was used for thermal ellipsoid plotting, and a programme by Domenicano and Vaciago for computation of the molecular parameters.

DESCRIPTION OF THE STRUCTURES AND DISCUSSION

The crystal structures of compounds (I) and (II) consist of well separated monomeric units possessing distorted tetrahedral geometries; the packings, which are shown in Figs. 1 and 2, do not reveal any peculiar features.

In compound (I) the molecule does not possess crystallographic symmetry. Yet the hypothesis that the nitrogen atom occupies one of the three possible positions can be rejected on the basis of the R_w values, which are significantly higher for the ordered models (see Experimental). Moreover, the equivalence of the Co–(C/N) and (C/N)–O distances and the fact that the dimensions and orientations of the three thermal ellipsoids of the C/N atoms are similar, as can be seen in Fig. 3, support the disordered model.

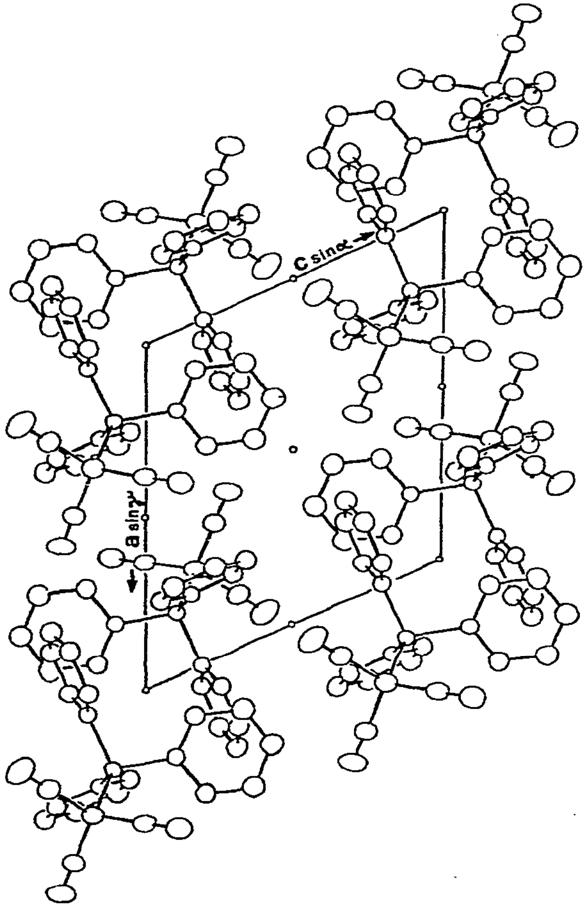

Fig. 1. Projection of the structure of $Co(CO)_2(NO)(PPh_3)$ down the *b* axis.

The molecule of compound (II) simulates a crystallographic C_2 symmetry, the CO and NO ligands being indistinguishable because of the disorder.

A selection of the most important bonding and non-bonding interactions for both structures is reported in Table 3. As can be seen, the Co–P bonds are 2.224(3) and 2.230(3) Å long in compounds (I) and (II) respectively. These values are consistent with a number of Co–P distances which are in the range 2.17–2.23 Å[15,16]. The larger value of 2.27(1) Å found in $(C_2F_4H)Co(CO)_3(PPh_3)$[17] is the result of a strong *trans*-effect of the organic ligand on the phosphine[18].

The Co–(C/N)–O moieties are strictly linear in both compounds. The Co–(C/N) and (C/N)–O distances, 1.74(1), 1.13(1) Å in (I), and 1.72(1), 1.15(1) Å in (II), can be

(*continued on p.* 163)

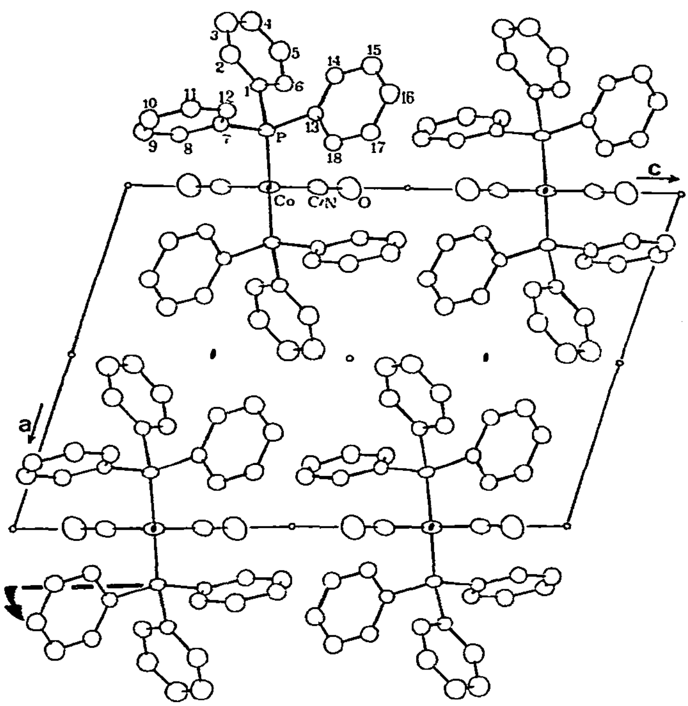

Fig. 2. Projection of the structure of $Co(CO)(NO)(PPh_3)_2$ down the *b* axis. An axis is shown around which the triphenylphosphine group is rotated as a whole, in the direction indicated by the arrow, due to the phenyl hydrogen contacts (see text).

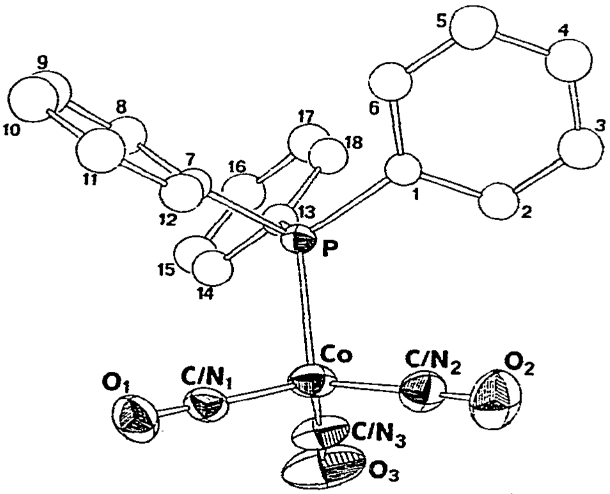

Fig. 3. Overall view by ORTEP of the molecule $Co(CO)_2(NO)(PPh_3)$. Thermal ellipsoids at 40% probability.

TABLE 3

SELECTED BONDING AND NON-BONDING DISTANCES (Å) AND ANGLES (DEGREES) IN THE TWO STRUCTURES

$Co(CO)_2(NO)(PPh_3)$		$Co(CO)(NO)(PPh_3)_2$	
Distances		*Distances*	
Co–P	2.224(3)	Co–P	2.230(3)
Co–C/N(1)	1.738(5)	Co–C/N	1.718(8)
Co–C/N(2)	1.762(7)	C/N–O	1.153(11)
Co–C/N(3)	1.720(7)	P–C(1)	1.840(7)
C/N(1)–O(1)	1.138(6)	P–C(7)	1.850(5)
C/N(2)–O(2)	1.139(8)	P–C(13)	1.851(6)
C/N(3)–O(3)	1.127(9)		
P–C(1)	1.827(3)	P...P′	3.743(3)
P–C(7)	1.825(3)	C/N...C/N′	2.976(11)
P–C(13)	1.827(2)	P...C/N	3.211(7)
		P...C/N′	3.116(8)
P...C/N(1)	3.146(6)		
P...C/N(2)	3.196(8)	*Angles*	
P...C/N(3)	3.144(9)	P–Co–C/N	108.1(2)
C/N(1)...C/N(2)	2.890(7)	P–Co–C/N′	103.5(2)
C/N(1)...C/N(3)	2.931(7)	P–Co–P′	114.1(2)
C/N(2)...C/N(3)	2.903(8)	C/N–Co–C/N′	120.0(4)
		Co–C/N–O	177.4(7)
Angles		Co–P–C(1)	109.5(2)
P–Co–C/N(1)	104.5(3)	Co–P–C(7)	117.4(2)
P–Co–C/N(2)	106.0(3)	Co–P–C(13)	119.7(2)
P–Co–C/N(3)	105.0(3)	P–C(1)–C(4)	177.6(4)
C/N(1)–Co–C/N(2)	111.3(2)	P–C(7)–C(10)	177.0(4)
C/N(1)–Co–C/N(3)	115.9(3)	P–C(13)–C(16)	177.4(4)
C/N(2)–Co–C/N(3)	113.0(3)	C(1)–P–C(7)	102.6(2)
Co–C/N(1)–O(1)	178.5(6)	C(1)–P–C(13)	102.1(3)
Co–C/N(2)–O(2)	178.3(8)	C(7)–P–C(13)	103.3(2)
Co–C/N(3)–O(3)	177.9(6)		
Co–P–C(1)	116.5(3)	*Phenyl hydrogen contacts*	
Co–P–C(7)	113.7(1)	H(6)...C/N	2.66
Co–P–C(13)	114.7(2)	H(6)...O	2.96
P–C(1)–C(4)	178.3(4)	H(8)′...C/N	2.67
P–C(7)–C(10)	176.9(4)	H(8)′...O	2.80
P–C(13)–C(16)	177.4(4)	H(18)′...C(7)	2.64
C(1)–P–C(7)	103.3(3)	H(18)′...C(8)	2.83
C(1)–P–C(13)	103.7(3)	H(6)...Co	3.11
C(7)–P–C(13)	103.4(3)		
Phenyl hydrogen contacts			
H(2)...C/N(2)	2.77		
H(12)...C/N(1)	2.89		
H(14)...C/N(3)	2.83		
H(2)...Co	3.25		
H(12)...Co	3.29		
H(14)...Co	3.25		

compared with those found in $Co(CO)_3(NO)$, 1.83(2), 1.14(3) Å for the Co–(CO) interactions and 1.76(3), 1.10(4) Å for the Co–(NO) interactions[19]. Other examples of Co–(CO) interactions are reported in ref. 16, 17 and 20. The linearity of the Co–N–O moieties in the present compounds is not surprising, although markedly bent linkages have been reported for a number of nitrosyl complexes. Some examples of Co–N–O bonding parameters are reported in Table 4.

TABLE 4

BONDING PARAMETERS IN SOME NITROSYL COBALT COMPLEXES

Compound	*Co–N (Å)*	*N–O (Å)*	*Co–N–O (deg.)*
$Co(NO)(S_2CN(CH_3)_2)_2$[a]	1.70	1.1	127
$[CoCl(NO)(en)_2][ClO_4]$[b]	1.813(2)	1.14(2)	121.3(1.2)
$[Co(NO)_2I]_n$[c]	1.60(4), 1.61(4)	1.16(5), 1.19(5)	168(4), 173(4)
$[Co(NO)_2(NO_2)]_n$[d]	1.67, 1.67	1.11, 1.13	166[e]
$[Co(NO)(NH_3)_5]Cl_2$[f]	1.871(6)	1.154(7)	119.0(9)

[a] Ref. 25. [b] Ref. 26. [c] Ref. 27. [d] Ref. 28. [e] Ref. 23. [f] Ref. 29.

The bond angles around the cobalt atoms are of particular interest. In compound (I) the (C/N)–Co–(C/N) angles are greater (mean 113.4°) and the P–Co–(C/N) angles are smaller (mean 105.2°) than the ideal value. These differences are expected on the basis of the considerations reported in the introduction, and fall into line when compared with the values found in $Pt(CO)(PPh_3)_3$[2] and $Ir(NO)(PPh_3)_3$[3]. In the two latter species, in spite of the higher number of bulky phosphines, the mean P–M–P angles, 105.7(7)° and 101.3(6)° respectively, are smaller than the mean (C/N)–M–P ones, 113.0(1.0)° and 116.8(5)° respectively.

The steric hindrance of the triphenylphosphine has no significant influence on the bond angles in compound (I), the H...(C/N) contacts being almost normal. The bonding parameters in the phosphine are very regular (see Table 3), and are strictly comparable with those found in the free molecule[21].

A significant difference exists between the (C/N)–Co–(C/N) angles in compounds (I) and (II): 113.4° (mean value) *vs.* 120.0(4)°; correspondingly the (C/N)...(C/N) distances vary from 2.91 Å (mean value) to 2.98(1) Å. The variation can be understood in terms of different π electron repulsions. The following sequence of (C/N)–M–(C/N) values in similar compounds, 117.3(1.3)° in $Pt(CO)_2(PPh_2Et)_2$[4], 120.0(4)° in $Co(CO)(NO)(PPh_3)_2$, 125.4(4)° in $Fe(NO)_2(Ph_2PC_5F_6PPh_2)$[22], 128.8(3)° in $Ni(N_3)(NO)(PPh_3)_2$[23], can be taken as an indication of the greater Van der Waals radius of nitrogen in co-ordinated NO with respect to carbon in co-ordinated CO. This result is contrasting with the smaller covalent radius of nitrogen[24] and can only be explained in terms of π^* orbitals population.

The P–Co–P′ angle in compound (II), 114.1(2)°, is very probably determined by the phenyl ring interactions among them and with the CO and NO groups. One short contact between C(7) and H(18)′ pushes the two phosphine ligands away, but other contacts, such as H(6)...(C/N) and H(8)′...(C/N), prevent an excessive enlargment of the P–Co–P′ angle. A compromise among these contrasting interactions is reached by further distortions: (*i*) the planes defined by Co, C/N, C/N′ and Co, P, P′

are no longer perpendicular, the dihedral angle being 86.9(3)° (see Fig. 4); (*ii*) the Co–P–C angles are not equivalent as they are in compound (I). The strict equivalence of the C(*i*)–P–C(*j*) angles in the two structures implies that in compound (II) the latter distortion corresponds to a rotation of PPh_3 as a whole around an axis orthogonal to the Co–P bond and passing through the P atom. This axis lies approximately in the plane of Fig. 2, and the rotation is of about 5° downward.

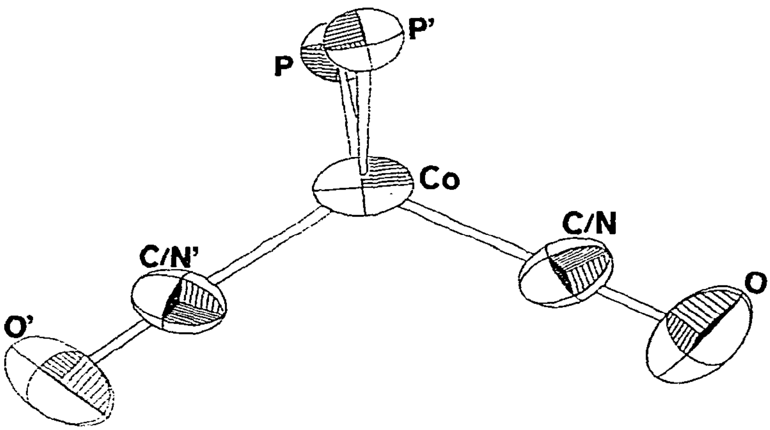

Fig. 4. An ORTEP drawing of the Co(CO)(NO) P_2 moiety of compound (II). The plane of the Figure is that passing through the Co, C/N and C/N' atoms. The ellipsoids are at 40% probability.

The values of the P–M–P angles in $Pt(CO)_2(PPh_2Et)_2$, $[Ir(NO)_2(PPh_3)_2]^+$ and $Ni(N_3)(NO)(PPh_3)_2$ are 97.9(2)°, 116.3(2)° and 120.5(1)° respectively. However, a simple inspection of the molecular drawings of these compounds shows that the orientations of their phenyl rings are essentially equivalent to those found in compound (II); furthermore the dihedral angles between the (M, C/N, C/N') and (M, P, P') planes exhibit similar deviations from orthogonality (86.0(3)°, 85.7(3)° and 85.1(2)° respectively). These facts can be taken as an indication that the same H...(C/N) interactions occur in all these structures, in spite of the differences in the P–M–P angles. Probably this means that the angles (C/N)–M–(C/N) essentially depend from the M–(C/N)–O and (C/N)...(C/N) interactions; once these angles are fixed, the P–M–P angles are determined by a number of phenyl hydrogen interactions.

Lastly, a comparison between the P–Cu–P angles tabulated by Lippard and Palenik[7] and all the P–M–P angles reported above for complexes containing CO and NO ligands, shows the former to be systematically greater than the latter. This difference could be connected to the absence, in the copper complexes, of π accepting ligands other than the PR_3 groups; this might lead to stronger P...P repulsions because of the increased electron population on the phosphorus atoms.

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