STEREOCHEMISTRY OF TETRAHEDRAL COMPLEXES OF GROUP VIII
METALS. CRYSTAL AND MOLECULAR STRUCTURES OF
DINITROSYLCARBONYLTRIPHENYLPHOSPHINEIRON,
$Fe(NO)_2(CO)(PPh_3)$, AND OF
DINITROSYLBIS(TRIPHENYLPHOSPHINE)IRON, $Fe(NO)_2(PPh_3)_2$

V.G. ALBANO, A. ARANEO, P.L. BELLON, G. CIANI and M. MANASSERO

Istituto di Chimica Generale ed Inorganica, Universita' degli Studi, 21, via Venezian, 20133, Milano (Italy)

Summary

Single crystal X-ray structures of $Fe(NO)_2(CO)(PPh_3)$ (I) and of
$Fe(NO)_2(PPh_3)_2$ (II) have been determined. Compound (I) forms triclinic
crystals of space group $P\bar{1}$, with cell constants a 10.96(1)Å, b 10.20(1)Å, c
10.45(1)Å, α 115.84(8)°, β 117.33(8)°, γ 78.90(8)°, U 933.4Å^3, Z 2. Com-
pound (II) forms monoclinic crystals of space group $P2/c$ with cell constants a
11.70(1) Å, b 8.20(1) Å, c 17.24(2) Å, β 106.60(8)°, U 1584.6 Å^3, Z 2. Both
crystals contain discrete molecules of distorted tetrahedral geometry. In com-
pound (I) the CO and NO ligands are disordered; the principal bonding parame-
ters are: Fe—C/N 1.709 Å, C/N—O 1.148 Å, Fe—C/N—O 177.9°, Fe—P
2.260(3) Å, C/N—Fe—C/N 103.9° and P—Fe—C/N 114.4°. In compound (II),
which possesses C_2 symmetry, the principal bonding parameters are: Fe—N
1.650(7) Å, N—O 1.19(1) Å, Fe—N—O 178.2(7)° N—Fe—N 123.8(4)°, Fe—P
2.267(2) Å, P—Fe—P 111.9(1)°. These values are compared with those found in
other tetrahedral complexes of Group VIII metals and discussed in terms of π
metal—ligand interactions.

Introduction

Several structures of tetrahedral complexes of the Group VIII metals in
low oxidation states have been determined. These complexes contain π accept-
ing ligands of differing acidities, mainly phosphines, carbon monoxide and
nitric oxide, e.g. $Fe(NO)_2(P_2Ph_4C_5F_6)$ [1], $Fe_2(NO)_4I_2$ [2], $[Co(NO)_2I]_n$
[2], $Co(NO)(CO)(PPh_3)_2$ and $Co(NO)(CO)_2(PPh_3)$ [3], $Ni(N_3)(NO)(PPh_3)_2$
[4], $Ru(NO)_2(PPh_3)_2$ [5], $[Ir(NO)_2(PPh_3)_2]^+$ [6], $Ir_2(NO)_4(PPh_3)_2$ [7], Ir-
$(NO)(CO)(PPh_3)_2$ [8], $Ir(NO)(PPh_3)_3$ [9], $Pt(CO)_2(PPh_2Et)_2$ [10], and Pt-

$(CO)(PPh_3)_3$ [11,12]. All these complexes attain the closed configuration of eighteen electrons in the valence shell and exhibit a more or less distorted tetrahedral geometry. In some of the NO derivatives significant bending of the M—N—O angles has been observed.

Deviations from the ideal geometry are generally expected when non-equivalent ligands are bound to the central atom but the type and the extent of these distortions have been explained [3,9] by assuming that the non-bonded radius of a π-acid ligand is an increasing function of the degree of population of its accepting orbitals, and so depends not only on the intrinsic acidity of that ligand but also on the competing effects of the other groups bound to the central atom. The generally accepted scale of π accepting ability, $PR_3 < CO < NO$, allows the prediction that the L—M—L angles will increase in the order: P—M—P < P—M—(CO) < P—M—(NO) < (CO)—M—(CO) < (CO)—M—(NO) < (NO)—M—(NO). The known structures qualitatively fit this trend (packing forces play a role; see, for instance, refs. 11 and 12), but the non-rigidity of the phosphine ligand makes it difficult to distinguish between phosphorus hindrance and conformational hindrance of the attached groups.

Moreover there are considerable differences among the nitrosyl complexes of ruthenium and iridium and the corresponding iron and cobalt species; thus the elements of the second and third transition series exhibit substantially wider angles at the metal and often a significant bending of the nitrosyl group. Some bending in M—C—O interactions in C_{2v} and in C_{3v} symmetries has been predicted by Kettle [13,14] on the basis of non-equivalent d_π—π^* interactions. However, the bending so far observed for carbonyl complexes is never very significant. This rationalisation can obviously be extended to nitrosyl groups of C_{2v} symmetry, but the reason why the M—N—O bending is not a systematic effect was unclear.

In this paper we report the structures of two further complexes of this family, $Fe(NO)_2(CO)(PPh_3)$ (I) and $Fe(NO)_2(PPh_3)_2$ (II), whose geometries are useful for a more complete description and rationalisation of the behaviour of nitrosyl complexes.

Experimental

Preparation of the compounds

$Fe(NO)_2(CO)(PPh_3)$ (I) was prepared following the method described in ref. 15, which leads to a mixture of (I) and $Fe(NO)_2(PPh_3)_2$ (II). Compound (II), first described by Malatesta and Araneo [16], has been obtained as the only product with the following modification of the procedure described in ref. 15. Dinitrosyldicarbonyliron (2.6 g, 15 mmol) was treated with triphenylphosphine (9.2 g, 35 mmol) in a flask fitted with a Bunsen valve, under nitrogen atmosphere at about 85° for 18 h. The resulting crude dark material was dissolved in methylene chloride (10 ml) and recrystallized by addition of pentane (95%).

Crystal data

Compound (I), $C_{19}H_{15}FeN_2O_3P$, M 405.8, gives brown triclinic crystals. The reduced cell has dimensions: a 10.96(1), b 10.20(1), c 10.45(1) Å, α

115.84(8)°, β 117.33(8)°, γ 78.90(8)°, U 933.4 Å^3, space group $P\bar{1}$ (No. 2), D_m 1.42(2) g·cm^{-3} (by flotation), D_c 1.44 g·cm^{-3}, Z 2, $F(000)$ 416.

Compound (II), $C_{36}H_{30}FeN_2O_2P_2$, M 639.8, gives brown monoclinic crystals. The cell dimensions are: a 11.70(1), b 8.20(1), c 17.24(2) Å, β 106.60(8)°, U 1584.6 Å^3, D_m 1.33(2) g·cm^{-3} (by flotation), D_c 1.34 g·cm^{-3}, Z 2, $F(000)$ 664. Systematic absences ($h0l$ for l odd) indicate two possible space groups Pc (No. 7) or $P2/c$ (No. 13); the structure has been successfully refined in the latter space group.

Compounds (I) and (II) are isomorphous with $Co(NO)(CO)_2(PPh_3)$ and $Co(NO)(CO)(PPh_3)_2$, respectively [3]. For both crystals the cell dimensions were determined from precession photographs using Mo-K_α radiation (λ 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.

The crystal of (I), a multifaced polyhedron of dimensions 0.35 × 0.21 × 0.17 mm, was mounted along the direction of maximum elongation (c axis). 2540 reflections were collected belonging to eleven reciprocal lattice layers, from $hk0$ to $hk10$, within the limit $2\theta \leqslant 48°$.

The crystal of (II), a parallelopiped of dimensions 0.28 × 0.20 × 0.10 mm, was mounted along the direction of maximum elongation (b axis). 2270 reflections were collected belonging to eight reciprocal lattice layers, from $h0l$ to $h7l$, within the limit $2\theta \leqslant 54°$.

No decay was observed during the intensity measurements. The integrated intensities were corrected for Lorentz, polarization, and absorption effects. The transmission factors ranged from 0.84 to 0.95 for (I) ($\mu = 9.36$ cm^{-1}) and from 0.88 to 0.97 for (II) ($\mu = 6.21$ cm^{-1}). The absorption corrections were performed by the Busing and Levy method [17], the X-ray path within both samples being computed in 6^3 points. 1448 and 1198 independent non-zero reflections, all having relative statistical error $\sigma(I)/I$ less than 0.25, were used in the refinements of the structures of (I) and (II), respectively.

Refinement of the structures

Both structures were directly refined using as starting coordinates those determined for the isomorphous cobalt compounds. Preliminary refinements were carried out by block-diagonal least-squares. The phenyl rings were treated as rigid groups of D_{6h} symmetry (C — C distance 1.392 Å), and the carbon atoms in the rings were assigned individual isotropic thermal parameters, whereas the non-group atoms were treated anisotropically. The coordinates of the phenyl hydrogen atoms (C — H distance 1.08 Å) were computed at the end of each refinement cycle and their contributions to structure factors were taken into account.

Weighting schemes in both refinements were of the type: $w = 1/(A + B \cdot |F_o| + C \cdot |F_o|^2)$, with coefficients chosen so as to give approximately constant values of the mean $w \cdot \Delta F^2$ over the entire ranges of F_o and of $\sin^2 \theta / \lambda^2$. The atomic scattering factors were those reported by Cromer and Mann [18] for Fe, P, O, N and C, corrected for the real part of the anomalous scattering [19]. The hydrogen scattering factor was that given by Forsyth and Wells [20].

TABLE 1^{a,b}

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

Non-group atoms[c]

Atom	x	y	z	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Fe	−2807(1)	−2756(1)	1741(1)	119(1)	−51(2)	129(3)	169(2)	192(3)	191(2)
P	−1823(1)	−1623(2)	1065(2)	86(2)	−1(3)	94(4)	89(2)	92(4)	121(2)
O(1)	−4351(6)	−5086(6)	−1151(8)	154(8)	−74(13)	162(17)	147(9)	71(18)	241(12)
O(2)	−4689(6)	−628(8)	2842(8)	141(8)	18(17)	263(20)	263(13)	103(24)	333(16)
O(3)	−677(7)	−3544(10)	4102(9)	154(9)	−41(22)	58(20)	526(22)	645(36)	335(17)
C/N(1)	−3742(6)	−4154(7)	14(8)	94(7)	−31(14)	104(16)	131(10)	122(20)	174(12)
C/N(3)	−3949(7)	−1451(9)	2404(9)	105(9)	−58(18)	135(20)	201(13)	125(23)	228(15)
C/N(3)	−1561(7)	−3195(9)	3171(9)	114(9)	−64(18)	89(19)	260(15)	297(25)	207(14)

Phenyl Group Atoms[d]

Atom	x	y	z	$B(Å^2)$	Atom	x	y	z
C(1)	−2146(10)	301(4)	1550(5)	3.3(1)	H(2)	−1975	690	3820
C(2)	−2154(7)	1171(4)	3007(5)	4.1(1)	H(3)	−2396	3337	4557
C(3)	−2390(6)	2659(5)	3421(4)	5.1(1)	H(4)	−2803	4438	2700
C(4)	−2619(10)	3279(4)	2378(5)	5.4(1)	H(5)	−2789	2891	109
C(5)	−2611(7)	2409(4)	920(5)	5.6(1)	H(6)	−2368	242	−627
C(6)	−2375(5)	920(5)	506(4)	4.3(1)	H(8)	−252	−2628	−875
C(7)	−2303(4)	−2370(5)	−1029(4)	3.4(1)	H(9)	−1024	−3601	−3753
C(8)	−1340(3)	−2755(5)	−1651(5)	4.6(1)	H(10)	−3506	−3896	−5525
C(9)	−1774(4)	−3303(5)	−3269(5)	5.9(1)	H(11)	−5219	−3210	−4418
C(10)	−3169(4)	−3468(5)	−4265(4)	5.8(1)	H(12)	−4450	−2237	−1543
C(11)	−4132(3)	−3083(5)	−3643(5)	5.4(1)	H(14)	− 30	−4005	1412
C(12)	−3700(4)	−2535(5)	−2026(5)	4.5(1)	H(15)	2497	−4269	2495
C(13)	36(3)	−1727(4)	1940(5)	3.3(1)	H(16)	3986	−2138	3632
C(14)	620(4)	−3073(4)	1909(5)	4.1(1)	H(17)	2948	256	3689
C(15)	2042(4)	−3221(3)	2518(5)	5.0(1)	H(18)	417	519	2603
C(16)	2879(3)	−2023(4)	3158(5)	4.9(1)				
C(17)	2295(4)	−676(4)	3190(5)	4.6(1)				
C(18)	872(4)	−528(3)	2580(5)	4.0(1)				

^{a}All values × 10^4 except for isotropic thermal parameters. ^{b}The numbers in parentheses here and in the other 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.

Compound (I) was refined with the assumption of complete $(NO) - (CO)$ disorder, adopting the weighted scattering factor $(\frac{1}{3}f_C + \frac{2}{3}f_N)$ for the disordered atoms. After convergence of refinement for this model $(R_w = 0.0707)$, three ordered models (corresponding to three possible locations of the C atom) were refined and rejected on the basis of their R_w indices, which were higher $(R_w = 0.0721$ in all three cases). Three further cycles of full matrix refinement led to the reliability indices $R = \Sigma(\|F_o|-K-|F_c\|)/\Sigma|F_o| = 0.050$ and $R_w = [\Sigma w(|F_o|-K-|F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.065$. For compound (II) the full matrix refinement gave $R = 0.052$ and $R_w = 0.064$.

The final difference syntheses for both structures were rather flat, no peak exceeding 0.6 and 0.5 e·Å^{-3} being observed. Lists of computed and observed structure factor moduli can be obtained on application to the authors.

Positional and thermal parameters of all atoms in structures (I) and (II) are reported in Tables 1 and 2 respectively.

Computations

All computations were carried out on a Univac 1106 computer. For absorption corrections our own programme was used, in which the directions of primary and diffracted beam are evaluated as described in ref. 21; counter data reduction and statistical analysis for weighting schemes were also based upon FORTRAN programmes written in our laboratory. In addition, local versions of entries Nos. 7528, 7531, 7532 and 7535 in the 1966 "World List of Crystallographic Programs" were used for Fourier analyses, structure factor and least squares computations; a programme by Domenicano and Vaciago was used for computations of molecular parameters.

Description of the structures and discussion

The principal bond distances and angles determined in the complexes Fe(NO)$_2$(CO)(PPh$_3$) and Fe(NO)$_2$(PPh$_3$)$_2$ [compounds (I) and (II), respectively] are reported in Tables 3 and 4, together with the corresponding values found in the isomorphous and isoelectronic complexes Co(NO)(CO)$_2$(PPh$_3$) and Co(NO)(CO)(PPh$_3$)$_2$. Drawings of the single molecules and of their packing are omitted here because these are practically the same as those in the cobalt compounds [3].

The crystal structure of (I) consists of discrete monomeric molecules of distorted tetrahedral geometry. The true symmetry of coordination around the iron atom is C_s, but very nearly C_{3v} because the CO and NO ligands are disordered as they are in the corresponding cobalt complex. The experimental bonding parameters for these ligands are, consequently, only weighted averages; these ligands are bound in an essentially linear fashion, the average angle Fe-N/C—O being 177.9°. The Fe—N/C and N/C—O distances have mean lengths 1.709 and 1.148 Å, while the corresponding values for the cobalt analogue are 1.740 and 1.135 Å. These differences indicate the increased contribution of the NO ligand in the iron complex. The Fe—P distance is 0.036 Å longer than the corresponding Co—P value and the difference may be explained in terms of a lower π character of the Fe—P interaction as a consequence of the greater electron withdrawal of the other ligands. The bond angles P—Fe—C/N and

TABLE 2^a

POSITIONAL AND THERMAL PARAMETERS OF THE ATOMS IN COMPOUND (II), Fe(NO)$_2$(PPh$_3$)$_2$

Non-group Atoms

Atom	x	y	z	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Fe	0	2061(1)	2500	45(1)	0(0)	32(1)	105(0)	0(0)	38(0)
P	1672(1)	512(2)	2888(1)	47(1)	−1(3)	21(1)	111(3)	−2(2)	32(0)
O	−8(6)	3727(8)	3942(4)	179(8)	−58(17)	120(9)	262(14)	−141(13)	70(3)
N	16(4)	3009(8)	1659(4)	74(5)	26(12)	57(6)	118(11)	34(11)	52(3)

Phenyl Group Atoms

Atom	x	y	z	$B(Å^2)$	Atom	x	y	z	$B(Å^2)$
C(1)	−2948(5)	1868(8)	1706(3)	3.4(1)	H(2)	−3795	382	676	5.2
C(2)	−3853(5)	1485(6)	1009(3)	5.2(1)	H(3)	−5533	2221	197	6.8
C(3)	−4830(3)	2520(7)	739(2)	6.8(2)	H(4)	−5663	4742	957	6.3
C(4)	−4902(5)	3937(8)	1167(3)	6.3(2)	H(5)	−4054	5424	2199	5.5
C(5)	−3998(5)	4320(6)	1865(3)	5.5(1)	H(6)	−2317	3585	2679	4.4
C(6)	−3021(3)	3286(7)	2135(2)	4.4(1)	H(8)	−1201	872	581	4.0
C(7)	−1787(5)	−943(5)	1283(2)	3.1(1)	H(9)	−1274	−1003	−555	4.6
C(8)	−1476(4)	−384(4)	608(2)	4.0(1)	H(10)	−1898	−3874	−495	4.8
C(9)	−1517(4)	−1439(5)	−30(2)	4.6(1)	H(11)	−2453	−4868	705	4.9
C(10)	−1868(5)	−3053(5)	3(2)	4.8(1)	H(12)	−2379	−2993	1844	3.9
C(11)	−2179(4)	−3612(4)	678(2)	4.9(1)	H(14)	−3894	331	2624	4.0
C(12)	−2138(4)	−2557(5)	1318(2)	3.9(1)	H(15)	−4434	−1322	3669	4.9
C(13)	−2136(4)	−694(6)	2869(2)	3.2(1)	H(16)	−2980	−3276	4502	4.8
C(14)	−3258(3)	−524(5)	2988(2)	4.0(1)	H(17)	−983	−3576	4290	4.6
C(15)	−3561(3)	−1454(6)	3576(3)	4.9(1)	H(18)	−444	−1924	3245	4.0
C(16)	−2743(4)	−2553(6)	4044(2)	4.8(1)					
C(17)	−1621(3)	−2721(5)	3925(2)	4.6(1)					
C(18)	−1318(3)	−1792(6)	3337(3)	4.0(1)					

^{a}See footnotes to Table 1.

TABLE 3

SELECTED BONDING AND NON-BONDING DISTANCES (Å) AND ANGLES (°) IN Fe(NO)$_2$(CO)(PPh$_3$) COMPARED WITH THE CORRESPONDING VALUES IN SQUARE BRACKETS, OF THE ISOMORPHOUS Co(NO)(CO)$_2$(PPh$_3$)

Fe—P	2.260(3)	[2.224(3)]
Fe—C/N(1)	1.704(6)	[1.738(5)]
Fe—C/N(2)	1.732(8)	[1.762(7)]
Fe—C/N(3)	1.690(8)	[1.720(7)]
C/N(1)—O(1)	1.150(8)	[1.138(6)]
C/N(2)—O(2)	1.147(11)	[1.139(7)]
C/N(3)—O(3)	1.147(12)	[1.127(9)]
P—C(1)	1.808(4)	[1.827(3)]
P—C(7)	1.815(4)	[1.825(3)]
P—C(13)	1.814(3)	[1.827(2)]
P...C/N(1)	3.129(9)	[3.146(6)]
P...C/N(2)	3.168(11)	[3.196(8)]
P...C/N(3)	3.133(12)	[3.144(9)]
C/N(1)...C/N(2)	2.858(10)	[2.890(7)]
C/N(1)...C/N(3)	2.899(9)	[2.931(7)]
C/N(2)...C/N(3)	2.860(11)	[2.903(8)]
P—Fe—C/N(1)	103.3(4)	[104.5(3)]
P—Fe—C/N(2)	104.3(4)	[106.0(3)]
P—Fe—C/N(3)	104.0(4)	[105.0(3)]
C/N(1)—Fe—C/N(2)	112.6(3)	[111.3(2)]
C/N(1)—Fe—C/N(3)	117.3(4)	[115.9(3)]
C/N(2)—Fe—C/N(3)	113.4(4)	[113.0(3)]
Fe—C/N(1)—O(1)	178.9(6)	[178.5(6)]
Fe—C/N(2)—O(2)	1.77.3(11)	[178.3(8)]
Fe—C/N(3)—O(3)	177.5(7)	[177.9(6)]
Fe—P—C(1)	116.6(4)	[116.5(3)]
Fe—P—C(7)	113.4(2)	[113.7(1)]
Fe—P—C(13)	114.2(2)	[114.7(2)]
P—C(1)—C(4)	178.5(3)	[178.3(4)]
P—C(7)—C(10)	177.2(3)	[176.9(4)]
P—C(13)—C(16)	177.1(2)	[177.4(4)]
C(1)—P—C(7)	103.4(3)	[103.3(3)]
C(1)—P—C(13)	103.6(4)	[103.7(3)]
C(7)—P—C(13)	104.2(3)	[103.4(3)]

TABLE 4

SELECTED BONDING AND NON-BONDING DISTANCES (Å) AND ANGLES (°) IN Fe(NO)$_2$(PPh$_3$)$_2$ COMPARED WITH THE CORRESPONDING VALUES, IN SQUARE BRACKETS, OF THE ISOMORPHOUS Co(NO)(CO)(PPh$_3$)$_2$

Fe—P	2.267(2)	[2.230(3)]
Fe—N	1.650(7)	[1.718(8)]
N—O	1.190(10)	[1.153(11)]
P—C(1)	1.833(7)	[1.840(7)]
P—C(7)	1.853(5)	[1.850(5)]
P—C(13)	1.841(5)	[1.851(6)]
P...P′	3.755(2)	[3.743(3)]
N...N′	2.910(10)	[2.976(11)]
P...N	3.177(6)	[3.211(7)]
P...N′	3.095(7)	[3.116(8)]
P—Fe—N	107.4(2)	[108.1(2)]
P—Fe—N′	103.3(2)	[103.5(2)]
P—Fe—P′	111.9(1)	[114.2(2)]
N—Fe—N′	123.8(4)	[120.0(4)]
Fe—N—O	178.2(7)	[177.4(7)]
Fe—P—C(1)	108.8(2)	[109.5(2)]
Fe—P—C(7)	117.4(2)	[117.4(2)]
Fe—P—C(13)	119.7(2)	[119.7(2)]
P—C(1)—C(4)	177.2(4)	[177.6(4)]
P—C(7)—C(10)	176.9(3)	[177.0(4)]
P—C(13)—C(16)	177.7(3)	[177.4(4)]
C(1)—P—C(7)	103.2(3)	[102.6(2)]
C(1)—P—C(13)	102.8(3)	[102.1(3)]
C(7)—P—C(13)	103.4(2)	[103.3(2)]

TABLE 5

IRON—NITROSYL INTERACTIONS IN VARIOUS COMPOUNDS

Compound	Fe—N(Å)	N—O(Å)	N—Fe—N(°)	Fe—N—O(°)	Ref. no.
$(NO)_2Fe(SEt)_2Fe(NO)_2$	1.67(1)	1.17(2)	117.4	167	23
$Cs[Fe_4S_3(NO)_7]\cdot H_2O$	1.69	1.20(6)			23
$(NO)_2(FeI)_2(NO)_2$	$\begin{cases}1.69(2)\\1.64(2)\end{cases}$	1.11(3) 1.19(3)	117.8(10) 115.0(10)	161(3) 161(3)	22
$Fe(NO)_2(P_2Ph_4C_5F_6)$	1.65(1)	1.18(1)	125.4(4)	177.4(7)	1
$Fe(NO)_2(CO)_2$	1.77(2)	1.12(3)			24
$Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$	1.63(4)	1.13(2)			25
$Fe(NO)[S_2CN(Me)_2]_2$	1.71(2)	1.02(2)		173(2)	26
$Fe(NO)[S_2CN(Et)_2]_2$	1.69(2)	1.16(5)		174(4)	27

C/N—Fe- C/N have average values of 103.9 and 114.4°, respectively; the corresponding values in the cobalt isomorph are 105.1 and 113.4°. The differences are small, but since the packing forces are practically equal in the two crystals they can be considered significant, and are in agreement with the presence in the iron complex of two nitrosyl groups (see Introduction).

The crystal structure of $Fe(NO)_2(PPh_3)_2$ (II) contains discrete monomeric molecules located on two-fold symmetry axes. The Fe—P distance is 0.037 Å longer than the corresponding value in the cobalt isomorph; the difference is equal to that found for the $Fe(NO)_2(CO)(PPh_3)$- $Co(NO)(CO)_2$-(PPh_3) couple and confirms the explanation reported above. The M—P bond lengths are not significantly different if the comparison is made between the two iron complexes and the two cobalt complexes, respectively, indicating that the distances depend mainly on the number of NO ligands. Other comparable iron- phosphorus interactions are 2.224 Å in $Fe(NO)_2(P_2Ph_4C_5F_6)$ [1] and 2.24—2.25 Å in $Fe_3(CO)_{11}(PPh_3)$ [22]. The P—Fe- P angle is 2.2° lower than the corresponding value in the cobalt isomorph, as expected on the basis of the preceding discussion and the introduction. We cannot exclude the possibility, however, that the variation is caused by nitrosyl—hydrogen contacts.

The nitrosyl ligands are strictly linear and the Fe—N and the N—O distances are in the range of those found in other iron—nitrosyl complexes such as those listed in Table 5. It may be noted that the N—Fe- N angle in (II), essentially the same as in $Fe(NO)_2(P_2Ph_4C_5F_6)$ [1], is 3.8° wider than the corresponding angle in $Co(NO)(CO)(PPh_3)_2$. The difference is particularly noteworthy since the crystal packings in the two isostructural compounds are equal, and this confirms once more that the nitrosylic nitrogen atom is moderately but significantly bulkier than the carbonylic carbon atom in complexes of the first transition series.

Significantly bent iron—nitrosyl interactions have been found in the complexes $(NO)_2Fe(SEt)_2Fe(NO)_2$ [23] and $(NO)_2(FeI)_2(NO)_2$ [2]. This bending has been explained by Dahl et al. [2] in terms of a different degree of usage of the two non-degenerate couples of π and π^* orbitals on each NO interacting with the metal atom, determined by the direct Fe- Fe interaction present in the dimeric species.

A comparison of the N/C—M—N/C angles in the iron and cobalt complexes with those found in $Ru(NO)_2(PPh_3)_2$ (139.2°) [5], $Ir(NO)(CO)(PPh_3)_2$ (128.8°) [8], $[Ir(NO)_2(PPh_3)_2]^+$ (154.2°) [6], $Ir_2(NO)_4(PPh_3)_2$ (156°) [7],

and $Pt(CO)_2(PPh_2Et)_2$ (117°) [10] shows that in the latter compounds the angles in which the nitric oxide is involved are systematically larger than in the iron and cobalt compounds. This indicates that the nitrosylic nitrogen possesses a substantially larger non-bonded radius when coordinated to elements of the second and third transition series. Carbon monoxide, on the other hand, does not exhibit this peculiarity in either case. The best example of the different behaviour of the two ligands is given by the couple $Co(NO)(CO)(PPh_3)_2$ — $Ir(NO)(CO)(PPh_3)_2$; CO and NO are very similar in the cobalt complex, and have practically equal non-bonded interactions with the phenylic hydrogen atoms; consequently the conformations of the two phosphine ligands are equal and the molecule is located on two-fold axes in the crystal, determining the NO—CO disorder. This is not the case for $Ir(NO)(CO)(PPh_3)_2$ in which the two ligands behave so differently that the two-fold molecular symmetry is de-troyed, the crystal packing changes, and NO and CO become distinguishable.

On the basis of all the experimental results the following summary is possible.

(*i*). In the monomeric tetrahedral complexes of iron and cobalt containing one or two NO groups, the M—N—O interactions are linear. When two NO groups are present the N—M—N angle is in the range 124—125°, which may be considered the "normal" angle in the typical NO^+ complexes.

(*ii*). The Fe–N—O interactions are significantly bent in $(NO)_2(FeI)_2$-$(NO)_2$ [2] and $(NO)_2Fe(SEt)_2Fe(NO)_2$ [23]; the N—Fe–N angle in these complexes is some 8° lower than the "normal" value. The ligand bending, as discussed above, derives from particularly asymmetric metal—ligand π interactions and the closure of the angle at the metal indicates that π orbitals are less populated and consequently less bulky than in the monomeric species. Both effects are attributable to direct metal—metal bonding.

(*iii*). In the ruthenium and iridium complexes the N—M—N angles are wider than the "normal" value and the bending of the ligands is again signifi-cant (174° in $Ru(NO)_2(PPh_3)_2$ [5], 174° in $Ir(NO)(CO)(PPh_3)_2$ [8], 163.5° in $[Ir(NO)_2(PPh_3)_2]^+$ [6], and 167° in $Ir_2(NO)_4(PPh_3)_2$ [7]. By analogy with the dimeric iron complexes, the metal—nitrosyl π interactions can be regarded as stronger and more asymmetric than in the "normal" case. The ligand bending accompanying these interactions shows that, in the absence of other perturbing effects, Kettle's prediction [13,14] is experimentally ob-servable only when the π interactions are particularly strong. Simple qualitative MO arguments reported by Gaughan, Corden, Eisenberg and Ibers describe the situation clearly [5].

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