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METAL COMPLEXES OF FLUOROPHOSPHINES

XIV *. STRUCTURES OF FIVE ZEROVALENT METAL COMPLEXES OF METHYLAMINOBIS(DIFLUOROPHOSPHINE) **

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Summary

Details are presented of single crystal X-ray diffraction determinations of the structures of the five zerovalent metal complexes $Cr[PF_2N(CH_3)_2]_4[(PF_2)_2NCH_3]$, $Fe[(PF_2)_2NCH_3]_4$, and $[CH_3N(PF_2)_2]_3Co_2L_2$ (L = CO, CH_3NHPF_2, and $(CH_3)_2NPF_2$). The chromium atom in $Cr[PF_2N(CH_3)_2]_4[(PF_2)_2NCH_3]$ has a distorted octahedral coordination with four monodentate $(CH_3)_2NPF_2$ ligands and one bidentate $CH_3N(PF_2)_2$ ligand; the small bite of the latter ligand distorts one of the idealized 90° angles of the CrP_6 octahedron to 67°. The iron atom in $Fe[(PF_2)_2NCH_3]_4$ has a distorted trigonal bipyramidal coordination with three monodentate $CH_3N(PF_2)_2$ ligands and one bidentate $CH_3N(PF_2)_2$ ligand. The bidentate $CH_3N(PF_2)_2$ ligand in $Fe[(PF_2)_2NCH_3]_4$ is coordinated to an axial and an equatorial position of the FeP_5 trigonal bipyramid and because of its small bite squeezes the relevant P_{ax}–Fe–P_{eq} angle from the ideal value of 90° down to 69°. The structures of the binuclear cobalt complexes $[CH_3N(PF_2)_2]_3Co_2L_2$ (L = CO, $(CH_3)_2NPF_2$, and CH_3NHPF_2) may be regarded as consisting of two $CoCoLP_3$ trigonal bipyramids linked through a cobalt–cobalt bond. Further linking of the two trigonal bipyramids occurs through the three biligate bimetallic $CH_3N(PF_2)_2$ ligands, each of which bridges an equatorial position of one trigonal bipyramid with an equatorial position of the other trigonal bipyramid thereby leading to a [3.3.3]propellane structure in which the edge shared by the three five-membered chelate rings is the cobalt–cobalt bond. Significant deviations from three-fold symmetry occur in

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* For part XIII of this series see R.B. King, M. Shimura, and G.M. Brown, Inorg. Chem., 23 (1984) 1398. This work was taken from the Ph.D. dissertation of M. Chang, University of Georgia, 1978.

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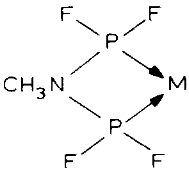
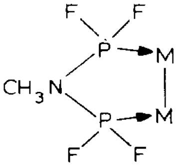
these trigonal bipyramids and in a given binuclear cobalt complex the two trigonal bipyramids are twisted by about 30° relative to each other.

Introduction

During the past several years transition metal complexes of the small bite chelating π-acceptor ligand $CH_3N(PF_2)_2$ have been of considerable interest [1]. This ligand can function as a small bite bidentate ligand forming either four-membered chelate rings (I) in mononuclear complexes or five-membered chelate rings (II) in binuclear complexes. This paper presents full details on single crystal X-ray diffraction studies on five zerovalent metal complexes of $CH_3N(PF_2)_2$ including examples of both the monometallic (I) and bimetallic (II) chelate rings. Preliminary communications have appeared on the structures of the five complexes discussed in detail in this paper [2–5] as well as other complexes of $CH_3N(PF_2)_2$ [6–11]. Other metal complexes of $CH_3N(PF_2)_2$ which have been characterized structurally include $[CH_3N(PF_2)_2]_4Mo_2Cl_2$ [12] and rather complicated products from the reactions of $CH_3N(PF_2)_2$ with benzalacetonetricarbonyliron [13] and with *fac*-$(CH_3CN)_3$-$Mo(CO)_3$ in the presence of small amounts of hydrogen chloride [14].



(I)



(II)

Experimental

The compounds $Cr[PF_2N(CH_3)_2]_4[(PF_2)_2NCH_3]$, $Fe[(PF_2)_2NCH_3]_4$, and $[CH_3N(PF_2)_2]_3Co_2[PF_2N(CH_3)_2]_2$were prepared by the reported procedures which involve metal vapor reactions [15]. The compounds $[CH_3N(PF_2)_2]_3Co_2L_2$ ($L = CH_3NHPF_2$ and CO) were prepared by reactions of $CH_3N(PF_2)_2$ with $Co_2(CO)_8$ under the reported conditions [16]. Suitable single crystals for X-ray diffraction were grown from the solvents indicated in Table 1. The single crystals were mounted on the top of a glass fiber and examined on an Enraf–Nonius CAD-4 automated diffractometer. The orientation matrix and cell dimensions were calculated using 25 accurately centered reflections. Diffraction data were then collected at 20°C using Mo-K_α radiation (λ 0.71068 Å) monochromatized by a graphite crystal. The ω–2θ scan technique was used to record the intensities for all reflections for which $4° \leq 2\theta \leq 50°$. Three intensity control reflections, monitored for every 10000 second interval, showed no greater than 15% fluctuations during the data collection. The raw intensity data were corrected for Lorentz-polarization effects using crystallographic program number 2A from the NRC crystallographic program system by F.R. Ahmed, S.R. Hall, M.E. Pippy, and C.P. Huber of the National Research Council of Canada, Ottawa, Canada, as modified by W.H. DeCamp, University of Georgia, Athens, Georgia, for the Enraf–Nonius CAD-4 diffractometer. However,

TABLE 1

SUMMARY OF CRYSTAL DATA, DATA COLLECTION PARAMETERS, AND LEAST-SQUARES RESIDUALS FOR THE FIVE ZEROVALENT METAL COMPLEXES OF METHYLAMINOBIS(DIFLUOROPHOSPHINE)

	$Cr(PF_2NMe_2)_4(PF_2)_2NMe$	$Fe[(PF_2)_2NMe]_4$	$[MeN(PF_2)_2]_3Co_2L_2$		
			L = PF_2NHMe	L = PF_2NMe_2	L = CO
Crystallization solvent	CH_2Cl_2	hexane	CH_2Cl_2/hexane	CH_2Cl_2/hexane	CH_2Cl_2/hexane
Formula weight	671	724	817	845	675
Space group	$P2_1/n$	$P2_1/n$	$Aba2$	$P4_12_12$	$P2_1/n$
a, Å	17.653(3)	16.777(3)	14.049(3)	10.578(2)	15.657(3)
b, Å	15.436(3)	10.486(2)	16.999(3)	10.578(2)	13.962(3)
c, Å	9.270(2)	15.538(3)	10.616(2)	24.846(4)	9.377(2)
β, deg	91.79(2)	117.05(2)	90.00(2)	90.00(2)	96.59(2)
V, Å^3	2530	2434	2535	2780	2036
Z	4	4	4	4	4
$d_{\text{calcd.}}$ g/cm^3	1.76	1.98	2.14	2.02	2.20
μ(Mo-K_α), cm^{-1}	9.56	12.92	19.96	18.24	22.98
reflections observed	1879	2656	1017	777	2250
R_1	0.0519	0.0391	0.0288	0.0471	0.0314
R_2	0.0523	0.0373	0.0274	0.0482	0.0318

TABLE 2

POSITIONAL PARAMETERS FOR $Cr[PF_2N(CH_3)_2]_4[(PF_2)_2NCH_3]$

Atom	x	y	z	Atom	x	y	z
Cr	0.87974(10)	0.25106(14)	0.74221(20)	F(11)	0.8488(4)	0.2907(5)	1.0939(8)
P(1)	0.9515(2)	0.1681(2)	0.8938(4)	F(12)	0.7877(4)	0.3947(5)	0.9623(8)
P(2)	0.9791(2)	0.3401(2)	0.7115(4)	N(1)	1.0055(6)	0.2002(7)	1.0270(11)
P(3)	0.8105(2)	0.3377(2)	0.5944(4)	N(2)	0.9906(6)	0.4401(7)	0.7721(12)
P(4)	0.9191(2)	0.1743(2)	0.5529(4)	N(3)	0.7535(7)	0.3121(9)	0.4590(13)
P(5)	0.7745(2)	0.1807(2)	0.7896(4)	N(4)	0.8866(6)	0.0781(7)	0.5060(13)
P(6)	0.8214(2)	0.3032(2)	0.9310(4)	N(5)	0.7442(5)	0.2432(8)	0.9211(10)
F(1)	1.0071(5)	0.1023(5)	0.8237(8)	C(1)	1.0504(8)	0.1361(10)	1.1155(15)
F(2)	0.9072(4)	0.0936(5)	0.9711(8)	C(2)	1.0159(8)	0.2912(9)	1.0748(15)
F(3)	1.0028(4)	0.3503(5)	0.5490(8)	C(3)	1.0614(9)	0.5876(10)	0.7421(18)
F(4)	1.0594(4)	0.3026(4)	0.7571(8)	C(4)	0.9284(9)	0.4969(9)	0.8093(18)
F(5)	0.7552(4)	0.3994(5)	0.6744(9)	C(5)	0.7434(8)	0.2257(11)	0.4005(15)
F(6)	0.8545(5)	0.4163(6)	0.5261(11)	C(6)	0.7161(9)	0.3801(13)	0.3718(16)
F(7)	1.0074(4)	0.1617(5)	0.5425(8)	C(7)	0.8667(9)	0.0137(9)	0.6055(16)
F(8)	0.9123(4)	0.2206(5)	0.4019(7)	C(8)	0.8935(11)	0.0448(11)	0.3514(17)
F(9)	0.7645(4)	0.0888(5)	0.8511(10)	C(9)	0.6731(7)	0.2402(13)	1.0021(15)
F(10)	0.7018(4)	0.1736(6)	0.6907(8)				

absorption corrections were not made since they were relatively small (Table 1).

Table 1 indicates the numbers of observed reflections ($I > 3\sigma(I)$) used for structure solution and refinement of the five compounds as well as the final values for R_1 and R_2 which were obtained by least squares anisotropic refinement. Positional parameters, bond distances, and bond angles for the five compounds are given in Tables 2–16. Specific details of the structure solutions are indicated below:

(1) $Cr[PF_2N(CH_3)_2]_4[(PF_2)_2NCH_3]$ *(Fig. 1).* The positions of the chromium

(*Continued on p. 21*)

TABLE 3

BOND DISTANCES (Å) FOR $Cr[PF_2N(CH_3)_2]_4[(PF_2)_2NCH_3]$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Cr	P(1)	2.261(4)	P(4)	N(4)	1.645(12)
Cr	P(2)	2.253(4)	P(5)	F(9)	1.542(9)
Cr	P(3)	2.248(4)	P(5)	F(10)	1.556(8)
Cr	P(4)	2.246(4)	P(5)	N(5)	1.656(11)
Cr	P(5)	2.207(4)	P(6)	F(11)	1.582(8)
Cr	P(6)	2.210(4)	P(6)	F(12)	1.564(9)
P(1)	F(1)	1.568(8)	P(6)	N(5)	1.647(11)
P(1)	F(2)	1.575(8)	N(1)	C(1)	1.495(18)
P(1)	N(1)	1.613(11)	N(1)	C(2)	1.484(18)
P(2)	F(3)	1.584(8)	N(2)	C(3)	1.483(18)
P(2)	F(4)	1.577(7)	N(2)	C(4)	1.455(18)
P(2)	N(2)	1.652(11)	N(3)	C(5)	1.449(21)
P(3)	F(5)	1.568(9)	N(3)	C(6)	1.469(22)
P(3)	F(6)	1.582(10)	N(4)	C(7)	1.408(19)
P(3)	N(3)	1.633(12)	N(4)	C(8)	1.531(20)
P(4)	F(7)	1.576(7)	N(5)	C(9)	1.484(16)
P(4)	F(8)	1.573(8)			

TABLE 4. BOND ANGLES (deg) FOR $Cr[PF_2N(CH_3)_2]_4[(PF_2)_2NCH_3]$

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
P(1)	Cr	P(2)	90.0(1)	Cr	P(1)	F(2)	114.8(3)
P(1)	Cr	P(3)	178.0(2)	Cr	P(1)	N(1)	127.5(4)
P(1)	Cr	P(4)	90.3(1)	F(1)	P(1)	F(2)	92.4(4)
P(1)	Cr	P(5)	93.3(1)	F(1)	P(1)	N(1)	98.8(5)
P(1)	Cr	P(6)	88.8(1)	F(2)	P(1)	N(1)	99.5(5)
P(2)	Cr	P(3)	88.3(1)	Cr	P(2)	F(3)	114.3(3)
P(2)	Cr	P(4)	87.8(1)	Cr	P(2)	F(4)	116.0(3)
P(2)	Cr	P(5)	171.2(2)	Cr	P(2)	N(2)	127.9(4)
P(2)	Cr	P(6)	105.2(1)	F(3)	P(2)	F(4)	91.6(4)
P(3)	Cr	P(4)	90.8(1)	F(3)	P(2)	N(2)	101.3(5)
P(3)	Cr	P(5)	88.2(1)	F(4)	P(2)	N(2)	98.7(5)
P(3)	Cr	P(6)	90.5(1)	Cr	P(3)	F(5)	114.1(3)
P(4)	Cr	P(5)	100.3(1)	Cr	P(3)	F(6)	115.8(4)
P(4)	Cr	P(6)	167.0(2)	Cr	P(3)	N(3)	129.4(5)
P(5)	Cr	P(6)	66.8(1)	F(5)	P(3)	F(6)	92.5(5)
Cr	P(1)	F(1)	117.1(3)	F(5)	P(3)	N(3)	97.6(5)
F(6)	P(3)	N(3)	100.2(6)	F(11)	P(6)	N(5)	102.3(5)
Cr	P(4)	F(7)	116.3(3)	F(12)	P(6)	N(5)	101.5(5)
Cr	P(4)	F(8)	116.0(3)	P(1)	N(1)	C(1)	120.5(9)
Cr	P(4)	N(4)	124.6(4)	P(1)	N(1)	C(2)	125.6(9)
F(7)	P(4)	F(8)	92.8(4)	C(1)	N(1)	C(2)	113.9(10)
F(7)	P(4)	N(4)	102.1(5)	P(2)	N(2)	C(3)	119.6(9)
F(8)	P(4)	N(4)	99.1(5)	P(2)	N(2)	C(4)	123.9(9)
Cr	P(5)	F(9)	129.3(3)	C(3)	N(2)	C(4)	113.1(11)
Cr	P(5)	F(10)	126.9(3)	P(3)	N(3)	C(5)	125.1(10)
Cr	P(5)	N(5)	98.8(4)	P(3)	N(3)	C(6)	120.3(11)
F(9)	P(5)	F(10)	92.9(5)	C(5)	N(3)	C(6)	113.9(12)
F(9)	P(5)	N(5)	102.7(5)	P(4)	N(4)	C(7)	123.8(10)
F(10)	P(5)	N(5)	101.3(5)	P(4)	N(4)	C(8)	120.9(10)
Cr	P(6)	F(11)	125.1(3)	C(7)	N(4)	C(8)	113.9(11)
Cr	P(6)	F(12)	131.7(3)	P(5)	N(5)	P(6)	94.8(5)
Cr	P(6)	N(5)	99.0(4)	P(5)	N(5)	C(9)	130.6(10)
F(11)	P(6)	F(12)	92.3(4)	P(6)	N(5)	C(9)	134.5(10)

TABLE 5. POSITIONAL PARAMETERS FOR $Fe[(PF_2)_2NCH_3]_4$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe	0.49184(6)	0.77975(9)	0.73644(7)	F(9)	0.5426(3)	0.5193(4)	0.6774(4)
P(1)	0.4381(1)	0.8205(2)	0.5873(1)	F(10)	0.5303(3)	0.4988(4)	0.8186(3)
P(2)	0.3821(1)	0.9057(2)	0.6924(1)	F(11)	0.2385(3)	0.4836(5)	0.6482(4)
P(3)	0.5224(1)	0.7909(2)	0.8839(1)	F(12)	0.2546(3)	0.5042(6)	0.5093(3)
P(4)	0.3689(1)	0.6444(2)	0.8640(2)	F(13)	0.7019(2)	0.7554(4)	0.8481(3)
P(5)	0.4854(1)	0.5811(2)	0.7234(1)	F(14)	0.6500(3)	0.7755(4)	0.6834(3)
P(6)	0.2934(1)	0.5703(2)	0.6112(2)	F(15)	0.6208(4)	1.1703(5)	0.6859(4)
P(7)	0.6224(1)	0.8238(2)	0.7623(1)	F(16)	0.6671(4)	1.1806(5)	0.8482(4)
P(8)	0.6015(2)	1.0960(2)	0.7624(2)	N(1)	0.3575(4)	0.9193(5)	0.5757(4)
F(1)	0.3934(3)	0.7209(4)	0.5046(3)	N(2)	0.4566(4)	0.7377(5)	0.9304(4)
F(2)	0.4890(3)	0.8900(4)	0.5391(3)	N(3)	0.3928(4)	0.4952(5)	0.6644(4)
F(3)	0.2904(3)	0.8776(4)	0.6911(3)	N(4)	0.6662(3)	0.9689(5)	0.7783(4)
F(4)	0.3864(3)	1.0465(4)	0.7275(3)	C(1)	0.2923(5)	0.9959(8)	0.4929(6)
F(5)	0.6142(3)	0.7349(5)	0.9602(3)	C(2)	0.4835(7)	0.7602(8)	1.0362(6)
F(6)	0.5399(3)	0.9283(4)	0.9284(3)	C(3)	0.3976(6)	0.3521(7)	0.6566(8)
F(7)	0.3928(3)	0.5256(4)	0.9323(4)	C(4)	0.7640(5)	0.9844(8)	0.7982(6)
F(8)	0.3018(3)	0.6999(5)	0.8983(4)				

TABLE 6

BOND DISTANCES (Å) FOR $Fe[(PF_2)_2NCH_3]_4$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Fe	P(1)	2.114(2)	P(5)	F(9)	1.574(3)
Fe	P(2)	2.111(2)	P(5)	F(10)	1.576(5)
Fe	P(3)	2.111(2)	P(5)	N(3)	1.664(5)
Fe	P(5)	2.090(2)	P(6)	F(11)	1.577(4)
Fe	P(7)	2.091(1)	P(6)	F(12)	1.572(6)
P(1)	F(1)	1.558(4)	P(6)	N(3)	1.683(5)
P(1)	F(2)	1.549(4)	P(7)	F(13)	1.566(5)
P(1)	N(1)	1.647(5)	P(7)	F(14)	1.577(4)
P(2)	F(3)	1.558(3)	P(7)	N(4)	1.628(5)
P(2)	F(4)	1.564(4)	P(8)	F(15)	1.574(5)
P(2)	N(1)	1.673(6)	P(8)	F(16)	1.562(6)
P(3)	F(5)	1.569(4)	P(8)	N(4)	1.665(5)
P(3)	F(6)	1.567(5)	N(1)	C(1)	1.509(9)
P(3)	N(2)	1.667(4)	N(2)	C(2)	1.512(10)
P(4)	F(7)	1.566(5)	N(3)	C(3)	1.534(5)
P(4)	F(8)	1.560(4)	N(4)	C(4)	1.489(10)
P(4)	N(2)	1.675(5)			

TABLE 7

BOND ANGLES (deg) FOR $Fe[(PF_2)_2NCH_3]_4$

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
P(1)	Fe	P(2)	69.1(1)	Fe	P(2)	F(3)	126.6(2)
P(1)	Fe	P(3)	161.9(1)	Fe	P(2)	F(4)	125.6(1)
P(1)	Fe	P(5)	96.8(1)	Fe	P(2)	N(2)	98.9(2)
P(1)	Fe	P(7)	93.1(1)	F(3)	P(2)	F(4)	94.1(2)
P(2)	Fe	P(3)	93.6(1)	F(3)	P(2)	N(1)	104.2(2)
P(2)	Fe	P(5)	126.3(1)	F(4)	P(2)	N(1)	104.3(3)
P(2)	Fe	P(7)	127.4(1)	Fe	P(3)	F(5)	118.1(1)
P(3)	Fe	P(5)	97.8(1)	Fe	P(3)	F(6)	115.7(2)
P(3)	Fe	P(7)	93.6(1)	Fe	P(3)	N(3)	124.7(2)
P(5)	Fe	P(7)	104.0(1)	F(5)	P(3)	F(6)	95.1(2)
Fe	P(1)	F(1)	125.0(2)	F(5)	P(3)	N(2)	99.3(2)
Fe	P(1)	F(2)	124.8(2)	F(6)	P(3)	N(2)	98.3(2)
Fe	P(1)	N(1)	99.6(2)	F(7)	P(4)	F(8)	93.9(3)
F(1)	P(1)	F(2)	94.7(2)	F(7)	P(4)	N(2)	99.5(3)
F(1)	P(1)	N(1)	105.5(2)	F(8)	P(4)	N(2)	98.0(3)
F(2)	P(1)	N(1)	104.9(2)	Fe	P(5)	F(9)	116.0(2)
Fe	P(5)	F(10)	118.2(2)	F(15)	P(8)	N(4)	99.4(2)
Fe	P(5)	N(3)	126.0(2)	F(16)	P(8)	N(4)	99.7(3)
F(9)	P(5)	F(10)	94.0(2)	P(1)	N(1)	P(2)	92.4(3)
F(9)	P(5)	N(3)	97.8(2)	P(1)	N(1)	C(1)	132.6(4)
F(10)	P(5)	N(3)	98.5(2)	P(2)	N(1)	C(1)	134.9(4)
F(11)	P(6)	F(12)	94.0(3)	P(3)	N(2)	P(4)	119.9(3)
F(11)	P(6)	N(3)	99.4(2)	P(3)	N(2)	C(2)	119.3(4)
F(12)	P(6)	N(3)	98.7(3)	P(4)	N(2)	P(2)	120.3(4)
Fe	P(7)	F(13)	118.4(1)	P(5)	N(3)	P(6)	119.0(3)
Fe	P(7)	F(14)	115.5(2)	P(5)	N(3)	C(3)	120.8(4)
Fe	P(7)	N(4)	125.8(1)	P(6)	N(3)	C(3)	120.2(4)
F(13)	P(7)	F(14)	94.4(2)	P(7)	N(4)	P(8)	119.8(2)
F(13)	P(7)	N(4)	98.3(2)	P(7)	N(4)	C(4)	119.2(4)
F(14)	P(7)	N(4)	98.3(2)	P(8)	N(4)	C(4)	120.7(4)
F(15)	P(8)	F(16)	93.2(3)				

TABLE 8

POSITIONAL PARAMETERS FOR $Co_2[(PF_2)_2NCH_3]_3[PF_2NHCH_3]_2$

Atom	*x*	*y*	*z*
Co	0.06412(7)	0.06169(6)	0.00000(0)
P(1)	0.0219(2)	0.0778(1)	−0.1883(2)
P(2)	−0.0201(2)	0.1106(1)	0.1389(3)
P(3)	0.1674(2)	−0.0154(1)	0.0634(3)
P(4)	0.1591(2)	0.1552(1)	−0.0053(3)
F(1)	0.0908(4)	0.1219(3)	−0.2801(5)
F(2)	−0.0658(4)	0.1313(3)	−0.2185(6)
F(3)	0.0046(5)	0.0938(4)	0.2806(5)
F(4)	−0.0199(4)	0.2014(3)	0.1552(7)
F(5)	0.2490(5)	−0.0468(3)	−0.0240(6)
F(6)	0.2392(4)	0.0180(3)	0.1633(6)
F(7)	0.1186(4)	0.2358(3)	−0.0474(6)
F(8)	0.1940(4)	0.1854(3)	0.1259(5)
N(1)	0.0000(0)	0.0000(0)	−0.2779(10)
N(2)	−0.1371(5)	0.0965(4)	0.1373(8)
N(4)	0.2589(6)	0.1489(4)	−0.0804(7)
C(1)	0.0000(0)	0.0000(0)	−0.4205(13)
C(2)	−0.2053(7)	0.1448(6)	0.2130(11)
C(4)	0.3362(7)	0.2092(6)	−0.0726(11)

and all six phosphorus atoms were located by the direct method. The remaining non-hydrogen atoms were located in succeeding Fourier syntheses using a program FORDAP written by Z. Zalkin, Lawrence Radiation Laboratory, Livemore, California.

(2) $Fe[(PF_2)_2NCH_3]_4$ *(Fig. 2).* The positions of the iron and five phosphorus atoms were located by the direct method. The remaining non-hydrogen atoms were located in succeeding Fourier syntheses.

(3) $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$ *and* $[CH_3N(PF_2)_2]_3Co_2[PF_2N(CH_3)_2]_2$ *(Fig. 3 and 4, respectively).* The position of the cobalt atom was located from a three-dimensional Patterson map. A Fourier synthesis using the cobalt position indicated the position of all phosphorus atoms. The remaining non-hydrogen atoms

TABLE 9

BOND DISTANCES (Å) FOR $Co_2[(PF_2)_2NCH_3]_3[PF_2NHCH_3]_2$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Co	Co′	2.769(1)	P(2)	N(2)	1.674(7)
Co	P(1)	2.103(3)	P(3)	F(5)	1.571(7)
Co	P(2)	2.068(3)	P(3)	F(6)	1.571(7)
Co	P(3)	2.070(2)	P(3)	N(2′)	1.605(8)
Co	P(4)	2.079(2)	P(4)	F(7)	1.550(6)
P(1)	F(1)	1.567(6)	P(4)	F(8)	1.565(7)
P(1)	F(2)	1.568(7)	P(4)	N(4)	1.620(9)
P(1)	N(1)	1.658(6)	N(1)	C(1)	1.514(17)
P(2)	F(3)	1.571(7)	N(2)	C(2)	1.523(13)
P(2)	F(4)	1.553(5)	N(4)	C(4)	1.499(13)

TABLE 10

BOND ANGLES (deg) FOR $Co_2[(PF_2)_2NCH_3]_3[PF_2NHCH_3]_2$

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Co′	Co	P(1)	85.0(1)	Co	P(2)	F(3)	118.8(3)
Co′	Co	P(2)	86.0(1)	Co	P(2)	F(4)	118.5(3)
Co′	Co	P(3)	88.8(1)	Co	P(2)	N(2)	119.3(3)
Co′	Co	P(4)	178.3(1)	F(3)	P(2)	F(4)	94.2(4)
P(1)	Co	P(2)	117.6(1)	F(3)	P(2)	N(2)	101.4(4)
P(1)	Co	P(3)	126.1(1)	F(4)	P(2)	N(2)	100.0(3)
P(2)	Co	P(3)	115.2(1)	Co	P(3)	F(5)	122.5(3)
P(1)	Co	P(4)	93.2(1)	Co	P(3)	F(6)	116.3(2)
P(2)	Co	P(4)	94.7(1)	Co	P(3)	N(2′)	119.8(3)
P(3)	Co	P(4)	92.3(1)	F(5)	P(3)	F(6)	92.9(3)
Co	P(1)	F(1)	118.6(2)	F(5)	P(3)	N(2′)	101.5(4)
Co	P(1)	F(2)	119.5(3)	F(6)	P(3)	N(2′)	98.1(4)
Co	P(1)	N(1)	119.6(3)	Co	P(4)	F(7)	116.5(2)
F(1)	P(1)	F(2)	94.7(3)	Co	P(4)	F(8)	115.4(2)
F(1)	P(1)	N(1)	98.0(3)	Co	P(4)	N(4)	121.5(3)
F(2)	P(1)	N(1)	101.4(3)	F(7)	P(4)	F(8)	94.7(3)
F(7)	P(4)	N(4)	103.6(4)	P(2)	N(2)	C(2)	121.2(6)
F(8)	P(4)	N(4)	100.7(4)	P(3)	N(2′)	P(2′)	114.1(4)
P(1)	N(1)	P(1′)	109.9(6)	P(3)	N(2′)	C(2′)	124.2(6)
P(1)	N(1)	C(1)	125.0(3)	P(4)	N(4)	C(4)	124.0(6)
P(2)	N(2)	P(3′)	114.1(4)				

TABLE 11

POSITIONAL PARAMETERS FOR $Co_2[PF_2N(CH_3)_2]_2[(PF_2)_2NCH_3]_3$

Atom	x	y	z
Co	0.45931(20)	0.50608(23)	0.94668(8)
P(1)	0.6531(5)	0.5187(5)	0.9334(2)
P(2)	0.3864(5)	0.3242(5)	0.9498(2)
P(3)	0.3868(5)	0.6801(5)	0.9709(2)
P(4)	0.4049(5)	0.5289(5)	0.8665(2)
F(1)	0.7076(10)	0.4740(12)	0.8787(4)
F(2)	0.7204(11)	0.6493(12)	0.9329(5)
F(3)	0.3031(12)	0.2763(10)	0.9027(4)
F(4)	0.4764(12)	0.2052(10)	0.9486(5)
F(5)	0.4086(14)	0.7932(10)	0.9311(4)
F(6)	0.2426(11)	0.7045(11)	0.9771(5)
F(7)	0.4675(11)	0.6417(11)	0.8360(4)
F(8)	0.4608(11)	0.4269(10)	0.8264(4)
N(1)	0.7515(14)	0.4395(15)	0.9742(5)
N(2)	0.2896(52)	0.2896(52)	1.0000(0)
N(3)	0.2584(14)	0.5393(15)	0.8472(5)
C(1)	0.8887(17)	0.4112(21)	0.9624(8)
C(2)	0.1857(41)	0.1857(41)	1.0000(0)
C(3)	0.2307(20)	0.5470(19)	0.7871(7)
C(4)	0.1472(18)	0.5302(23)	0.8830(8)

TABLE 12

BOND DISTANCES (Å) FOR $Co_2[PF_2N(CH_3)_2]_2[(PF_2)_2NCH_3]_3$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Co	Co′	2.740(3)	P(3)	F(5)	1.569(12)
Co	P(1)	2.081(5)	P(3)	F(6)	1.555(15)
Co	P(2)	2.047(6)	P(3)	N(1′)	1.655(15)
Co	P(3)	2.083(6)	P(4)	F(7)	1.561(12)
Co	P(4)	2.087(5)	P(4)	F(8)	1.584(12)
P(1)	F(1)	1.550(12)	P(4)	N(3)	1.625(16)
P(1)	F(2)	1.554(13)	N(1)	C(1)	1.511(23)
P(1)	N(1)	1.677(15)	N(2)	C(2)	1.544(93)
P(2)	F(3)	1.550(12)	N(3)	C(3)	1.526(22)
P(2)	F(4)	1.597(3)	N(3)	C(4)	1.478(24)
P(2)	N(2)	1.655(57)			

were located in succeeding Fourier syntheses. Both of these $[CH_3N(PF_2)_2]_3Co_2L_2$ derivatives have crystallographically imposed C_2 molecular symmetry.

(4) $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ *(Fig. 5).* The positions of two cobalt and all phosphorus atoms were located by the direct method. The remaining non-hydrogen atoms were located in succeeding Fourier syntheses.

Further details of these structure determinations including tables of thermal parameters and observed and calculated structure factors are given in the doctoral dissertation of one of the authors (M. Chang, University of Georgia, 1978) which is available from University Microfilms, Inc., Ann Arbor, Michigan.

TABLE 13

BOND ANGLES (deg) FOR $Co_2[PF_2N(CH_3)_2]_2[(PF_2)_2NCH_3]_3$

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Co′	Co	P(1)	89.2(1)	Co	P(2)	F(3)	119.1(5)
Co′	Co	P(2)	82.2(2)	Co	P(2)	F(4)	121.0(5)
Co′	Co	P(3)	86.9(2)	Co	P(2)	N(2)	117.6(18)
Co′	Co	P(4)	173.4(2)	F(2)	P(2)	F(4)	93.8(7)
P(1)	Co	P(3)	115.6(2)	F(3)	P(2)	N(2)	98.3(22)
P(1)	Co	P(3)	110.6(2)	F(4)	P(2)	N(2)	102.2(23)
P(2)	Co	P(3)	132.2(2)	Co	P(3)	F(5)	115.9(5)
P(1)	Co	P(4)	96.5(2)	Co	P(3)	F(6)	112.4(5)
P(2)	Co	P(4)	92.3(2)	Co	P(3)	N(1′)	121.1(6)
P(3)	Co	P(4)	94.1(2)	F(5)	P(3)	F(6)	94.6(7)
Co	P(1)	F(1)	119.0(5)	F(5)	P(3)	N(1′)	96.9(7)
Co	P(1)	F(2)	120.7(5)	F(6)	P(3)	N(1′)	100.0(7)
Co	P(1)	N(1)	118.9(6)	Co	P(4)	F(7)	115.7(5)
F(1)	P(1)	F(2)	95.4(7)	Co	P(4)	F(8)	114.7(5)
F(1)	P(1)	N(1)	98.4(7)	Co	P(4)	N(3)	123.5(6)
F(2)	P(1)	N(1)	99.5(7)	F(7)	P(4)	F(8)	93.3(6)
F(7)	P(4)	N(3)	102.1(7)	P(2)	N(2)	P(2′)	107.1(41)
F(8)	P(4)	F(3)	81.0(6)	P(2)	N(2)	C(2)	126.4(20)
P(1)	N(1)	P(3′)	112.5(9)	P(4)	N(3)	C(3)	118.4(12)
P(1)	N(1)	C(1)	125.3(12)	P(4)	N(3)	C(4)	125.2(12)
P(3)	N(1′)	P(1′)	112.5(9)	C(3)	N(3)	C(4)	116.1(15)
P(3)	N(1′)	C(1′)	122.2(12)				

TABLE 14

POSITIONAL PARAMETERS FOR $Co_2[(PF_2)_2NCH_3]_3(CO)_2$

Atom	x	y	z	Atom	x	y	z
Co	0.52615(5)	0.23922(6)	0.39738(9)	F(4′)	0.2578(2)	0.1002(3)	0.2179(5)
Co′	0.41741(5)	0.21810(6)	0.15217(9)	F(5)	0.5836(3)	0.4534(3)	0.4439(4)
P(1)	0.5947(1)	0.1264(1)	0.3182(2)	F(5′)	0.3169(2)	0.4065(3)	0.2299(6)
P(1′)	0.5218(1)	0.1737(1)	0.0479(2)	F(6)	0.6293(2)	0.3975(3)	0.2351(5)
P(2)	0.4169(1)	0.2305(1)	0.5050(2)	F(6′)	0.3722(3)	0.4174(3)	0.0150(5)
P(2′)	0.3523(1)	0.1236(1)	0.2755(2)	O	0.6396(4)	0.2370(5)	0.6622(6)
P(3)	0.5533(1)	0.3774(1)	0.3261(2)	O′	0.2937(4)	0.1927(4)	−0.0974(6)
P(3′)	0.3959(1)	0.3659(1)	0.1630(2)	N(1)	0.6040(3)	0.1206(4)	0.1432(6)
F(1)	0.5747(3)	0.0203(3)	0.3635(5)	N(2)	0.3382(3)	0.1568(4)	0.4411(6)
F(1′)	0.5026(2)	0.0993(3)	−0.0771(4)	N(3)	0.4741(3)	0.4377(3)	0.2344(6)
F(2)	0.6925(2)	0.1201(3)	0.3767(5)	C(1)	0.6737(5)	0.0675(6)	0.0787(9)
F(2′)	0.5691(3)	0.2462(3)	−0.0443(5)	C(2)	0.2655(4)	0.2032(5)	0.5222(8)
F(3)	0.3654(3)	0.3230(3)	0.5357(5)	C(3)	0.4719(5)	0.5451(4)	0.2125(9)
F(3′)	0.3792(3)	0.0163(2)	0.2965(5)	C(4)	0.5953(5)	0.2392(5)	0.5578(8)
F(4)	0.4298(3)	0.1985(3)	0.6652(4)	C(4′)	0.3425(5)	0.2032(5)	0.0007(8)

TABLE 15

BOND DISTANCES (Å) FOR $Co_2[(PF_2)_2NCH_3]_3(CO)_2$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Co	Co′	2.716(1)	P(2′)	F(4′)	1.565(4)
Co	P(1)	2.090(2)	P(3)	F(5)	1.566(4)
Co′	P(1′)	2.093(2)	P(3′)	F(5′)	1.556(4)
Co	P(2)	2.087(2)	P(3)	F(6)	1.568(4)
Co′	P(2′)	2.095(2)	P(3′)	F(6′)	1.570(5)
Co	P(3)	2.100(2)	P(1)	N(1)	1.665(6)
Co′	P(3′)	2.095(2)	P(1′)	N(1)	1.655(5)
Co	C(4)	1.749(7)	P(2)	N(2)	1.663(5)
Co′	C(4′)	1.747(7)	P(2′)	N(2)	1.660(6)
P(1)	F(1)	1.557(4)	P(3)	N(3)	1.655(5)
P(1′)	F(1′)	1.569(4)	P(3′)	N(3′)	1.663(5)
P(1)	F(2)	1.569(4)	N(1)	C(1)	1.502(9)
P(1′)	F(2′)	1.570(5)	N(2)	C(2)	1.496(8)
P(2)	F(3)	1.567(4)	N(3)	C(3)	1.514(8)
P(2′)	F(3′)	1.562(4)	C(4)	O	1.134(9)
P(2)	F(4)	1.558(4)	C(4′)	O′	1.136(9)

Results and discussion

(A) Mononuclear complexes

The structure of $Cr[PF_2N(CH_3)_2]_4[(PF_2)_2NCH_3]$ has the expected octahedral coordination for the central chromium(0) with four monodentate $(CH_3)_2NPF_2$ ligands and one bidentate $CH_3N(PF_2)_2$ ligand (Fig. 1 and 6). Because of the small bite of the bidentate $CH_3N(PF_2)_2$ ligand (i.e., P(5) and P(6) in Fig. 1), the P(5)–Cr–P(6) angle is reduced from the idealized value of 90° to 67°. Because of this distortion the two monodentate $(CH_3)_2NPF_2$ ligands (P(2) and P(4)) which are coplanar with P(5) and P(6) of the $CH_3N(PF_2)_2$ ligand can put their bulky

TABLE 16

BOND ANGLES (deg) FOR $Co_2[(PF_2)_2NCH_3]_3(CO)_2$

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Co′	Co	P(1)	85.1(1)	P(2′)	Co′	P(3′)	120.2(1)
Co′	Co	P(2)	86.2(1)	P(1′)	Co′	C(4′)	94.1(2)
Co′	Co	P(3)	87.7(1)	P(2′)	Co′	C(4′)	92.9(2)
Co′	Co	C(4)	173.7(2)	P(3′)	Co′	C(4′)	93.4(2)
P(1)	Co	P(2)	127.6(1)	Co	P(1)	F(1)	121.2(2)
P(1)	Co	P(3)	116.6(1)	Co	P(1)	F(2)	116.0(2)
P(2)	Co	P(3)	114.5(1)	Co	P(1)	N(1)	119.5(2)
P(1)	Co	C(4)	90.8(2)	F(1)	P(1)	F(2)	94.8(2)
P(2)	Co	C(4)	92.6(2)	F(1)	P(1)	N(1)	101.9(3)
P(3)	Co	C(4)	98.4(2)	F(2)	P(1)	N(1)	98.6(2)
Co	Co′	P(1′)	88.9(1)	Co	P(2)	F(3)	120.5(2)
Co	Co′	P(2′)	84.2(1)	Co	P(2)	F(4)	117.4(2)
Co	Co′	P(3′)	86.6(1)	Co	P(2)	N(2)	118.4(2)
Co	Co′	C(4′)	176.6(2)	F(3)	P(2)	F(4)	94.1(2)
P(1′)	Co′	P(2′)	121.8(1)	F(3)	P(2)	N(2)	101.6(2)
P(1′)	Co′	P(3′)	116.9(1)	F(4)	P(2)	N(2)	100.3(2)
Co	P(3)	F(5)	117.0(2)	Co′	P(3′)	F(5′)	121.2(2)
Co	P(3)	F(6)	122.1(2)	Co′	P(3′)	F(6′)	115.6(2)
Co	P(3)	N(3)	117.8(2)	Co′	P(3′)	N(3)	119.9(2)
F(5)	P(3)	F(6)	94.2(2)	F(5′)	P(3′)	F(6′)	94.1(2)
F(5)	P(3)	N(3)	99.8(2)	F(5′)	P(3′)	N(3)	101.6(2)
F(6)	P(3)	N(3)	101.3(2)	F(6′)	P(3′)	N(3)	99.7(2)
Co′	P(1′)	F(1′)	116.8(2)	P(1)	N(1)	P(1′)	111.1(3)
Co′	P(1′)	F(2′)	120.6(2)	P(1)	N(1)	C(1)	124.8(5)
Co′	P(1′)	N(1)	118.7(2)	P(1′)	N(1)	C(1)	123.9(5)
F(1′)	P(1′)	F(2′)	94.5(2)	P(2)	N(2)	P(2′)	109.7(3)
F(1′)	P(1′)	N(1)	100.2(2)	P(2)	N(2)	C(2)	124.0(4)
F(2′)	P(1′)	N(1)	101.5(2)	P(2′)	N(2)	C(2)	126.2(4)
Co′	P(2′)	F(3′)	122.2(2)	P(3)	N(3)	P(3′)	112.1(3)
Co′	P(2′)	F(4′)	116.5(2)	P(3)	N(3)	C(3)	125.3(4)
Co′	P(2′)	N(2)	117.8(2)	P(3′)	N(3)	C(3)	122.6(4)
F(3′)	P(2′)	F(4′)	94.4(2)	Co	C(4)	O	178.4(7)
F(3′)	P(2′)	N(2)	102.3(2)	Co′	C(4′)	O′	179.3(7)
F(4′)	P(2′)	N(2)	99.0(2)				

dimethylamino groups in to the larger spaces between P(2) and P(6) (P(2)–Cr–P(6) 105°) and between P(4) and P(5) (P(4)–Cr–P(5) 100°) (Fig. 1). The small bite of $CH_3N(PF_2)_2$ thus releases the steric strain explaining why $Cr[PF_2N(CH_3)_2]_4[(PF_2)_2NCH_3]$ is much more stable than $Cr[PF_2N(CH_3)_2]_6$ [15]. Also the chromium–phosphorus distances to the four monodentate $(CH_3)_2NPF_2$ ligands (P(1), P(2), P(3), and P(4)) are significantly longer (average 2.252 Å) than the two chromium–phosphorus distances to the bidentate $CH_3N(PF_2)_2$ ligand (average 2.208 Å) thereby also providing further relief of the steric strain from interactions of the dimethylamino groups of the $(CH_3)_2NPF_2$ ligands.

The structure of $Fe[(PF_2)_2NCH_3]_4$ has the expected trigonal bipyramidal coordination of the central iron(0) with three monodentate $CH_3N(PF_2)_2$ ligands and one bidentate $CH_3N(PF_2)_2$ ligand (Fig. 2 and 6). Because of the small bite of the bidentate $CH_3N(PF_2)_2$ ligand (i.e., (P(1) and P(2) in Fig. 2), the P_{ax}–Fe–P_{eq} angle spanned by this ligand is reduced from the idealized value of 90° to 69°. Part of this

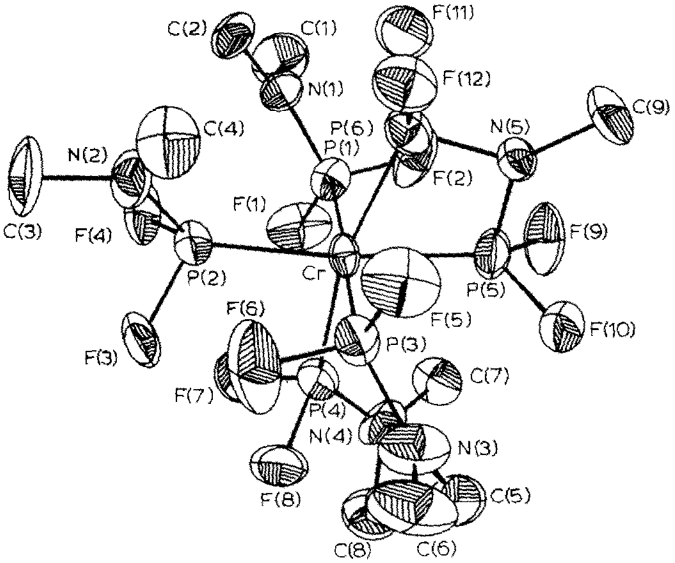


Fig. 1. ORTEP drawing of the structure of $Cr[PF_2N(CH_3)_2]_4[(PF_2)_2NCH_3]$.

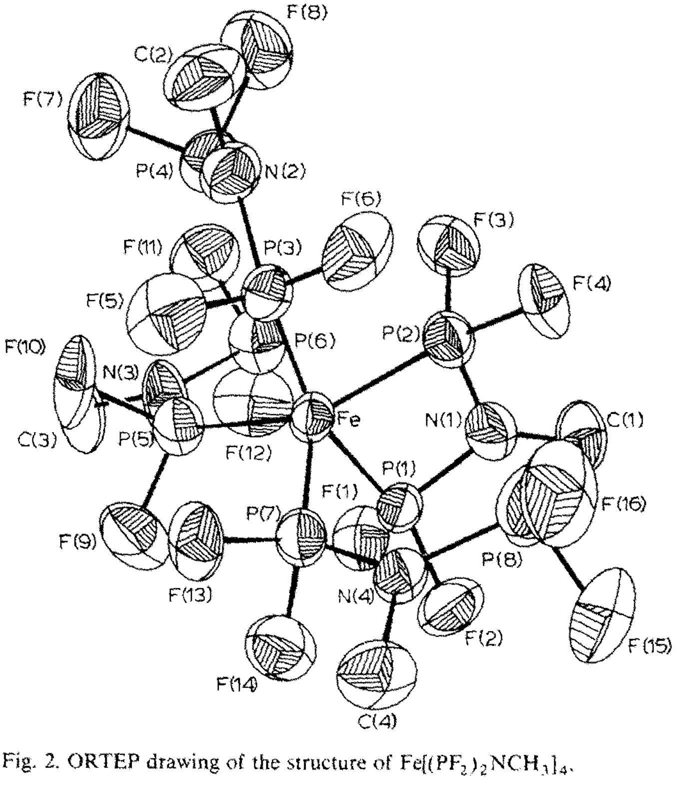


Fig. 2. ORTEP drawing of the structure of $Fe[(PF_2)_2NCH_3]_4$.

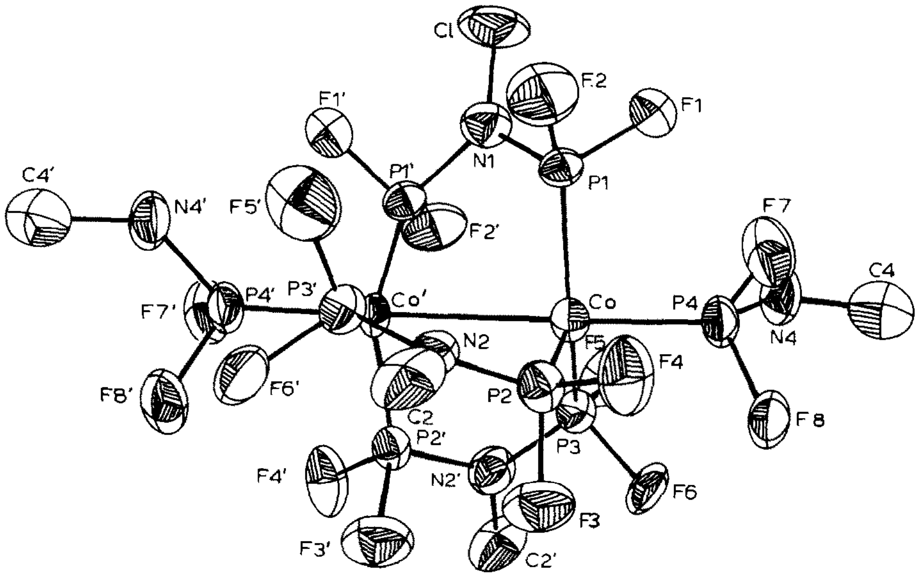


Fig. 3. ORTEP drawing of the structure of $Co_2[(PF_2)_2NCH_3]_3[PF_2NHCH_3]_2$.

distortion involves bending the relevant Fe–P_{ax} bond so that the P_{ax}–Fe–P_{ax} angle is no longer the ideal value of 180° but instead 162°. In all three monodentate $CH_3N(PF_2)_2$ ligands the bonds from the central nitrogen atoms to the coordinated phosphorus atoms are significantly shorter than the bonds from the central nitrogen

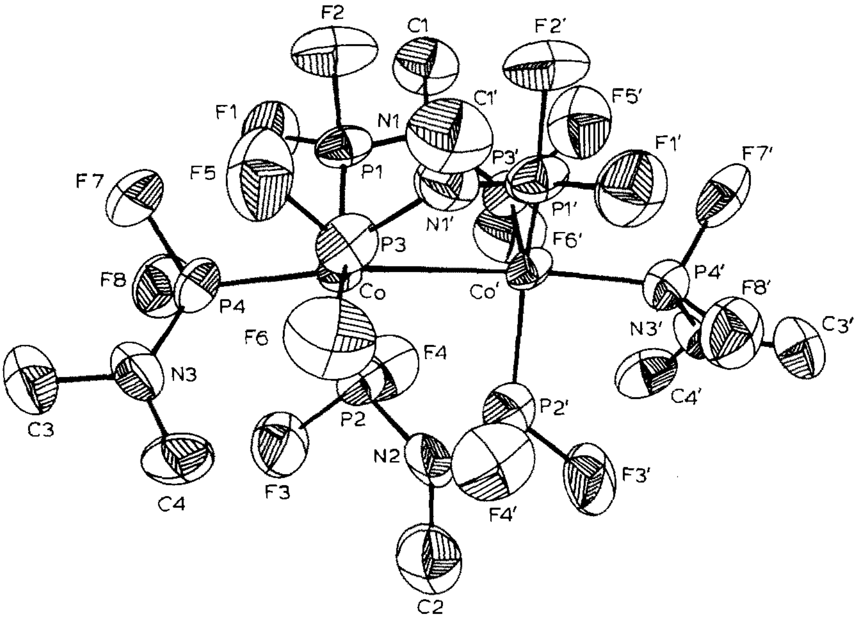


Fig. 4. ORTEP drawing of the structure of $Co_2[PF_2N(CH_3)_2]_2[(PF_2)_2NCH_3]_3$.

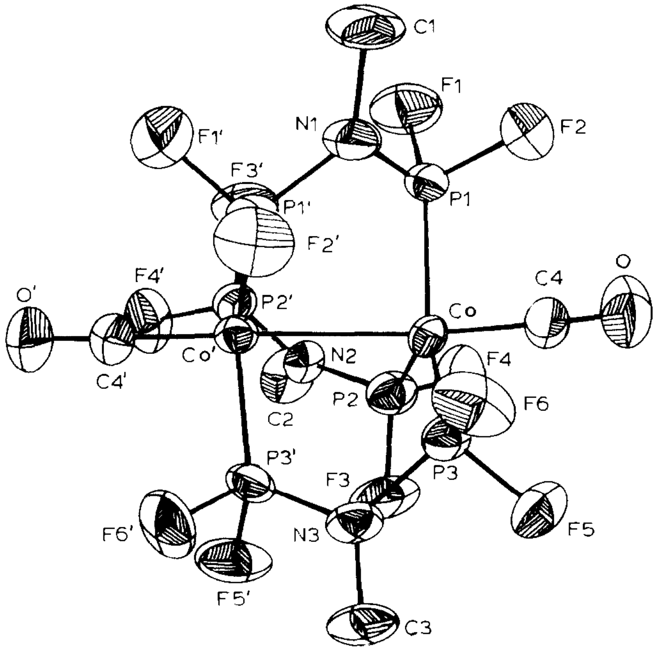
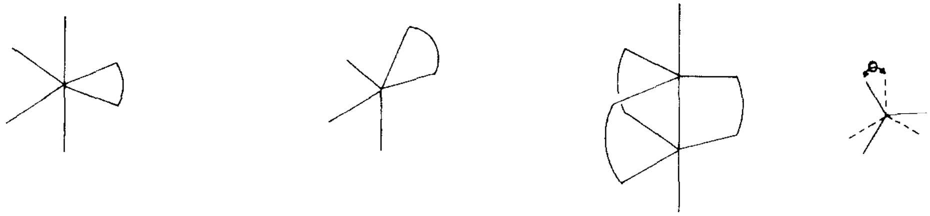


Fig. 5. ORTEP drawing of the structure of $Co_2[(PF_2)_2NCH_3]_3(CO)_2$.

atoms to the uncoordinated phosphorus atoms. This is a natural consequence of the considerable iron–phosphorus $d\pi$–$d\pi^*$ back-bonding in this complex which provides additional electron density for the coordinated phosphorus atom to participate in increased $d\pi$–$p\pi$ multiple bonding with the nitrogen atom relative to the uncoordinated phosphorus atom.

(B) Binuclear complexes

The structures of the binuclear cobalt complexes $[CH_3N(PF_2)_2]_3Co_2L_2$ (L = CO,



$Cr(PF_2NMe_2)_4(PF_2)_2NMe$ $Fe[(PF_2)_2NMe]_4$ (a) (b) $[MeN(PF_2)_2]_3Co_2L_2$ (L = PF_2NHMe, PF_2NMe_2 and CO)

Fig. 6. Idealized coordination polyhedra for the five zerovalent metal complexes of $MeN(PF_2)_2$ discussed in this paper. "Bridges" between coordination positions represent chelating $MeN(PF_2)_2$ ligands (biligate monometallic in the cases of the iron and chromium complexes and biligate bimetallic in the case of the cobalt complexes).

$(CH_3)_2NPF_2$, and CH_3NHPF_2) may be regarded as consisting of two $CoCoLP_3$ trigonal bipyramids linked through a cobalt–cobalt bond with a length ranging from 2.716 Å in $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ to 2.769 Å in $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$ (see Fig. 6). Further linking of the two trigonal bipyramids occurs through the three biligate bimetallic $CH_3N(PF_2)_2$ ligands (structure II), each of which bridges an equatorial position of one trigonal bipyramid with an equatorial position of the other bipyramid thereby leading to a [3.3.3]propellane structure in which the edge shared by the three five-membered chelate rings is the cobalt–cobalt bond. The idealized three-fold symmetry of the trigonal bipyramids is distorted considerably so that rather than having three P_{eq}–Co–P_{eq} angles of the idealized 120° one of these angles is opened to values ranging from 126.1° in $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$ to 132.2° in $[CH_3N(PF_2)_2]_3Co_2[PF_2N(CH_3)_2]_2$ and the other two angles are correspondingly close to values ranging from 110.6° to 117.6°. This distortion is very

TABLE 17

SELECTED DIHEDRAL ANGLES [a]

Atom 1	Atom 2	Atom 3	Atom 4	Angle (deg)
(1) For $Co_2[(PF_2)_2NCH_3]_3[PF_2NHCH_3]_2$				
P(1)	Co	Co′	P(1′)	34.9(1)
P(1)	Co	Co′	P(2′)	−153.1(1)
P(1)	Co	Co′	P(3′)	−91.5(1)
P(2)	Co	Co′	P(1′)	153.1(1)
P(2)	Co	Co′	P(2′)	−88.7(1)
P(2)	Co	Co′	P(3′)	26.6(1)
P(3)	Co	Co′	P(1′)	−91.5(1)
P(3)	Co	Co′	P(2′)	26.6(1)
P(3)	Co	Co′	P(3′)	142.0(1)
(2) For $Co_2[PF_2N(CH_3)_2]_2[(PF_2)_2NCH_3]_3$				
P(1)	Co	Co′	P(1′)	84.1(2)
P(1)	Co	Co′	P(2′)	−159.9(2)
P(1)	Co	Co′	P(3′)	−26.5(2)
P(2)	Co	Co′	P(1′)	−159.9(2)
P(2)	Co	Co′	P(2′)	−43.9(2)
P(2)	Co	Co′	P(3′)	89.5(2)
P(3)	Co	Co′	P(1′)	−26.5(2)
P(3)	Co	Co′	P(2′)	89.5(2)
P(3)	Co	Co′	P(3′)	−137.2(2)
(3) For $Co_2[(PF_2)_2NCH_3]_3(CO)_2$				
P(1)	Co	Co′	P(1′)	−31.3(1)
P(1)	Co	Co′	P(2′)	90.8(1)
P(1)	Co	Co′	P(3′)	−148.3(1)
P(2)	Co	Co′	P(1′)	−159.6(1)
P(2)	Co	Co′	P(2′)	−37.4(1)
P(2)	Co	Co′	P(3′)	83.4(1)
P(3)	Co	Co′	P(1′)	85.7(1)
P(3)	Co	Co′	P(2′)	−152.1(1)
P(3)	Co	Co′	P(3′)	−31.3(1)

[a] The dihedral angle 1–2–3–4 is considered positive in sign if the vector 3–4 is clockwise from vector 1–2 when viewed down 2–3 and negative if counterclockwise.

different from that previously found [17] for the binuclear complex $[CH_3N[P(OCH_3)_2]_2]_2Co_2(CO)_4$ having two small bite bidentate ligand bridges rather than three. In $[CH_3N[P(OCH_3)_2]_2]_2Co_2(CO)_4$ the coordination polyhedron of one of the cobalt atoms is a much less distorted trigonal bipyramid and that of the other cobalt can be more nearly approximated by a square pyramid [17]. The distortions of the axial bonds in the $[CH_3N(PF_2)_2]_3Co_2L_2$ derivatives are much less than those of the equatorial bonds noted above since the Co–Co–P_{ax} angles are 178.3° and 173.4° in $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$ and $[CH_3N(PF_2)_2]_3Co_2[PF_2N(CH_3)_2]_2$, respectively, and the Co–Co–CO angle is 173.7° as compared with an idealized value of 180°. The dihedral angles in Table 17 indicate that in the $[CH_3N(PF_2)_2]_3Co_2L_2$ complexes (L = CO, $(CH_3)_2NPF_2$, and CH_3NHPF_2) the two trigonal bipyramids in a given complex are twisted by an average of about 30° (i.e., angle θ in Fig. 6b) about the Co–Co axis relative to each other although because of the deviations from three-fold symmetry noted above an exact figure for this twist is not readily determined. This twist is presumably a method of minimizing strain in the [3.3.3]-propellane structure of these complexes.

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