fitted with Teflon valves and purified by passing fluorine at atmospheric pressure through the liquid until all the Br_2 and BrF_3 had reacted. After degassing several times, the BrF_5 was vacuum distilled and stored over dry sodium fluoride in a Kel-F storage trap.

Chlorine pentafluoride was prepared according to the method of Pilipovich, *et al.*,[43] by reaction of excess fluorine with cesium chlorotetrafluoride and stored in a previously passivated stainless steel container. The purity of both ClF_5 and BrF_5 was checked by recording their ^{19}F nmr spectra at 26°.

Preparation of $XeF_5^+SbF_6^-$, $XeF_5^+Sb_2F_{11}^-$, $XeF_5^+AsF_6^-$, and $XeF_5^+BF_4^-$. The adduct $XeF_5^+SbF_6^-$ was prepared by addition of an excess of XeF_6 to SbF_5 in HF solution. *Anal.* Calcd: F, 45.23; Sb, 26.35; Xe, 28.42. Found: F, 45.34; Sb, 26.13; Xe, 28.26. The $XeF_5^+Sb_2F_{11}^-$ and $XeF_5^+AsF_6^-$ adducts were prepared by addition of an excess of SbF_5 or AsF_5 to an HF solution of XeF_6. *Anal.* Calcd: F, 50.33; As, 18.04; Xe, 31.64. Found: F, 50.48; As, 18.20; Xe, 31.36. The solutions were pumped on, first at −60° and then at room temperature, until constant weight was achieved. The $XeF_5^+BF_4^-$ adduct was prepared by direct combination of XeF_6 with excess BF_3 in a Kel-F trap at room temperature and pumped to constant weight at −78°.

Preparation and Analysis of F_5XeSO_3F. In a typical preparation 1.293 g (5.27 mmol) of XeF_6 was transferred to a Kel-F reaction vessel and dissolved in 3.642 g (36.39 mmol) of HSO_3F, and excess HSO_3F was removed under vacuum at 40°. The resulting white crystalline solid was volatile and slowly pumped off at room temperature. Analytical results are consistent with the formulation F_5XeSO_3F. *Anal.* Calcd: F, 35.04; S, 9.85; Xe, 40.35. Found: F, 34.23; S, 9.56; Xe, 39.92.

Sample Preparation. Stoichiometric samples were prepared by transferring some of the solid adduct from a Kel-F storage trap to a preweighed Kel-F or glass sample tube in a drybox. Fluorosulfuric acid and antimony pentafluoride were syringed into preweighed Kel-F or glass nmr tubes in a drybox. Sample tubes were attached *via* a Kel-F adapter and Teflon valve to a vacuum line with standard 0.25-in. Teflon Swagelok fittings, frozen at liquid nitrogen temperature and evacuated. Xenon hexafluoride, HF, BrF_5, and ClF_5 were distilled directly from their storage vessels into preweighed Kel-F sample tubes through an all Kel-F and Teflon system. Kel-F sample tubes were sealed by immersing in liquid nitrogen, evacuating, and allowing the tube to collapse by heating with a small electrical heating coil.

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Registry No. XeF_6, 13693-09-9; $XeF_5^+SbF_6^-$, 49756-75-4; $XeF_5^+AsF_6^-$, 49756-76-5; $XeF_5^+BF_4^-$, 49756-77-6; $XeF_5^+Sb_2F_{11}^-$, 50432-33-2; F_5XeSO_3F, 38962-10-6; XeF_5^+, 49756-78-7; ^{129}Xe, 13965-99-6.

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Axial *vs.* Equatorial Bonding in Trigonal-Bipyramidal Complexes. Crystal and Molecular Structure of [Bis(triphenylphosphine)imminium]tetracarbonylcyanoiron(0), $[((C_6H_5)_3P)_2N][Fe(CO)_4CN]$

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The crystal and molecular structure of [bis(triphenylphosphine)imminium]tetracarbonylcyanoiron(0), $[PPN][Fe(CO)_4CN]$, has been determined from three-dimensional X-ray data collected by counter methods. The gold-colored salt crystallizes in space group $P2_1/c$ of the monoclinic system with 4 formula units per unit cell of dimensions $a = 10.749$ (4), $b = 12.909$ (6), $c = 26.801$ (9) Å, and $\beta = 97.98$ (5)°; $\rho_{obsd} = 1.31$ (1), $\rho_{calcd} = 1.32$ g/cm³. The structure has been refined by full-matrix least-squares methods to a weighted R factor on F of 4.55% for the 2314 independent reflections with $F^2 > 3\sigma(F^2)$. The thermal motion of all nonhydrogen atoms has been treated as anisotropic. The phenyl carbon atoms have been treated as rigid groups with a benzene ring geometry. The $[Fe(CO)_4CN]^-$ ion is a distorted trigonal bipyramid (C_{3v} molecular symmetry), isoelectronic with $Fe(CO)_5$, with the cyanide in an axial position as predicted from a simple π-bonding model which is proposed. The three equatorial iron–carbon bond lengths are 1.769 (8), 1.754 (8), and 1.781 (8) Å. The bond length from the iron to the carbon of the axial carbonyl is 1.723 (8) Å and to the cyanide carbon is 1.928 (8) Å. The axial-equatorial difference in the Fe–C carbonyl bond lengths is 0.045 (12) Å, which agrees well with the latest $Fe(CO)_5$ structural data. The difference between axial cyanide and carbonyl Fe–C bond lengths, 0.205 (12) Å, is largely due to the difference in covalent radii of CN^- and CO. The ions pack in layers with parallel close approach (3.50 Å) of one equatorial carbonyl oxygen and the inversion-related oxygen. The PPN cation has a cisoid conformation with a PNP bond angle of 134.6 (3)°.

Introduction

Although the stereochemical lability of five-coordinate complexes is of interest for several reasons, our interest has remained focused on the use of the high sensitivity of the geometry of these complexes to changes in the bonding. The change in structure of a series of complexes as individual ligands are changed allows a systematic investigation of the various components of the bonding. We have used this technique previously in studying the relative importance of the metal d-electron configuration in determining the geometry of a complex.[2,3] Often the difference in energy between two geometries for a five-coordinate complex is very small and in some cases can be determined by changes as small as crystal or solution environments.[4-7]

The observation of a C_{2v} geometry in $Mn(NO)(CO)_4$, in which the nitrosyl occupies an equatorial coordination site

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of the trigonal-bipyramidal complex,[8] raised the question of what factors determine the equatorial *vs.* axial preference for such closely related ligands. The greater availability of metal d orbitals of the proper symmetry to form π bonds with the ligands in equatorial *vs.* axial sites would lead to the expectation that the more strongly π-bonding ligand should preferentially occupy equatorial positions. To test this hypothesis we have prepared and determined the structure for the title compound, a salt of another member of the series of complexes isoelectronic with iron pentacarbonyl.

Experimental Section

Preparation of Crystals. Although the $[Fe(CO)_4CN]^-$ anion was first prepared by Ruff in a reaction which also produced the PPN cation,[9] the reaction gave more than one product and in our hands did not yield crystals suitable for structural studies. The following procedure was used in the synthesis of the crystals used here. The salt [PPN]Cl was prepared by the reaction

$$3Ph_3P + 2Cl_2 + NH_2OH{\cdot}HCl \rightarrow (Ph_3P)_2NCl + Ph_3P{=}O + 4HCl$$

A solution of $[Fe(CO)_4CN]^-$ was prepared by combining, under nitrogen, 0.536 g (1.47 mmol) of $Fe_2(CO)_9$ with 50 ml of CH_3CN and 5 g of KCN. The solution was stirred and heated to 50–60°. After filtering off the excess KCN under nitrogen 0.852 g (1.48 mmol) of [PPN]Cl was added. This was filtered again to remove KCl and placed under vacuum to remove the solvent. The product was extracted with 10 ml of CH_2Cl_2 and 75 ml of diethyl ether. After filtering and washing with pentane, 0.49 g of $[PPN][Fe(CO)_4CN]$ was collected. *Anal.* Calcd for $[((C_6H_5)_3P)_2N][Fe(CO)_4CN]$: C, 67.2; H, 4.14; N, 3.82; P, 8.46; Fe, 7.62. Found: C, 65.9; H, 4.33; N, 3.94; P, 8.40; Fe, 7.69. The density measured by flotation in a carbon tetrachloride–pentane solution is 1.31 g/cm^3.

Determination of the Unit Cell and Collection of Intensity Data. A series of precession photographs (Mo Kα, Zr-filtered radiation) for a large crystal exhibited Laue symmetry $2/m$ and the systematic absences $0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$. These absences are consistent only with space group $C_{2h}{}^5$-$P2_1/c$.

The four lattice constants and the data crystal orientation angles were determined by least-squares refinement using the setting angles of 11 reflections carefully centered at a takeoff angle of 1.0° with monochromatic radiation from a highly oriented graphite crystal.[10] The lattice constants (Mo Kα_1, λ 0.70926 Å) were found to be a = 10.749 (4), b = 12.909 (6), c = 26.801 (9) Å, and cos β = −0.1388 (4) at 22°. For 4 formula units per unit cell the calculated density is 1.32 g/cm^3, which agrees closely with the observed density of 1.31 g/cm^3.

Intensities were collected in the θ-2θ scan mode as previously described.[11] The takeoff angle was changed to 2.0° for data collection. The crystal was intentionally not oriented along a symmetry axis in order to minimize the effects of multiple diffraction.[12] The scan rate was 2°/min and the scan was from 0.6° below the Kα_1 peak to 0.6° above the Kα_2 peak. Backgrounds were counted for 10 sec at both ends of the scan. No filters were used. Copper foil attenuators were used when the count rate exceeded 10,000 cps. Two mirror-related equivalent forms ($\pm h,+k,+l$ and $\pm h,-k,+l$) were collected. The first set was collected to a Bragg 2θ angle of 50°; the second, to 40°. The full width at half-height of ω scans of reflections on each of the three axes averaged about 0.12°, which indicates an acceptable mosaic spread. Three standard reflections, the 200, 020, and 006, were measured periodically to check crystal and instrument stability. A total of 10,773 reflections were observed. These were reduced to values of F^2 and $\sigma(F^2)$ as described previously.[11,13] A value of 0.04 was assigned to the parameter p as a lower bound for $\sigma(F^2)/F^2$.[11] The standards showed a total loss of intensity of 1.7% in the a^* direction, 6.4% in the b^* direction, and 4.8% in the c^* direction. The intensities were corrected for this anisotropic decay based on the projection of the diffraction vector on the three standards.[14] No absorption correction was applied, since for the absorption coefficient of 5.5 cm^{-1} maximum absorption effects are no larger than a few per cent. The two equivalent forms were averaged resulting in 6525 independent reflections of which 2313 had $F^2 > 3\sigma(F^2)$. These data were described as being above background and were used in the refinement of the structure. The standard deviation of the average was chosen as the maximum of that estimated from the range or by averaging individual standard deviations. The R factor for averaging is 9.1% based on F^2.

Solution of the Structure

The position of the iron atom was easily determined from a Patterson synthesis, but the phosphorus atoms did not stand out clearly. Since the structure was not well phased by just the iron atom, direct methods were used to determine the remaining structure.

Structure factors for the 1187 reflections with highest normalized structure factors were normalized according to the equation

$$E_{hkl} = F_{hkl}/\epsilon\left[\left(\sum_{j=1}^{N} f_{j,\theta}{}^2\right)\right]^{1/2}$$

in which F_{hkl} is the observed structure factor and has been corrected for thermal motion. The factor ϵ adjusts for the degeneracy of F_{hkl} for reflections at symmetry locations in reciprocal space, N is the number of atoms in the unit cell, and the atomic scattering factor for the jth atom at the scattering angle θ is $f_{j,\theta}$. Scattering factors for neutral Fe, C, O, N, and P were those tabulated by Cromer and Mann.[15] Those of Stewart, *et al.*,[16] were used for H. Real and imaginary anomalous dispersion factors for Fe and P were those of Cromer.[17] Phases were determined for 233 reflections by iterative use of Sayre's equation.[13,18] The initial sign set consisted of seven reflections of which three were necessary to fix the origin. In the iterative process newly calculated phases with probability greater than 0.95 were used in the next cycle to determine phases of the unphased reflections. Of the 16 solutions the correctly phased solution had the highest consistency index (0.960) and required the least number of cycles (6) to phase all reflections. The consistency index is given by

$$C = \frac{\langle |E_h \sum_{h=h_1+h_2} E_{h_1} E_{h_2}| \rangle}{\langle |E_h| \sum_{h=h_1+h_2} |E_{h_1}||E_{h_2}| \rangle}$$

where the summations are over all pairs of reflections h_1 and h_2 for which $h = h_1 + h_2$ and where the angular brackets indicate an average over all values of h. The last parts of the structure were determined by standard difference Fourier and least-squares techniques. The function minimized is $\Sigma w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factors. The weighting factor, w, is $4F_o{}^2/\sigma^2(F_o{}^2)$. During the final refinements the phenyl rings were refined as rigid groups of D_{6h} ($6/mmm$) symmetry with C–C and C–H bond lengths of 1.392 and 1.084 Å, respectively.

Several least-squares refinements were carried out for various models of the $[Fe(CO)_4CN]^-$ anion in order to determine which one of the atoms bonded to carbon was a nitrogen atom. A combination of thermal parameters and observed bond lengths clearly indicated the axial cyanide location and implied little if any disorder, since, for example, disorder between the two axial ligands would tend to give apparently equal Fe–C bond lengths in contrast to what is observed.

A difference Fourier showed the largest 15 peaks to be in the plane of the phenyl carbons and on lines which bisect carbon-carbon bonds which are across the ring from the phosphorus.

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Table I. Atomic Positional and Thermal Parameters for [PPN][Fe(CO)$_4$CN]

Atom	x	y	z	$10^5\beta_{11}$[a] or B[b]	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Fe	.27884(9)	-.28415(7)	.47516(3)	1480(12)	945(8)	182(2)	67(9)	140(4)	14(3)
P_1	.24063(13)	.15094(11)	.28323(5)	811(15)	581(10)	151(3)	36(12)	70(5)	- 22(5)
P_2	.04041(12)	.15720(11)	.34212(5)	684(14)	566(10)	171(3)	21(11)	57(5)	- 27(5)
NP	.1105(3)	.1180(3)	.29988(14)	715(46)	627(33)	159(8)	34(33)	82(16)	- 60(13)
N_1	.1660(7)	-.3141(6)	.36429(24)	2514(107)	2251(89)	223(12)	959(78)	6(32)	-116(29)
O_2	.4818(5)	-.4153(4)	.44842(19)	1487(67)	1983(63)	337(12)	245(55)	196(24)	- 85(22)
O_3	.2654(8)	-.0618(4)	.46004(25)	6059(171)	889(45)	513(17)	435(83)	845(43)	34(26)
O_4	.0544(7)	-.3756(6)	.5052(3)	3287(135)	3086(102)	719(23)	-1368(92)	1101(47)	-395(38)
O_5	.4026(6)	-.2550(7)	.57634(21)	2606(96)	4852(132)	221(11)	498(99)	- 22(28)	-192(37)
C_1	.2068(7)	-.3013(6)	.4057(3)	1887(102)	1185(67)	216(14)	476(69)	132(33)	16(28)
C_2	.4017(6)	-.3629(6)	.4589(3)	1106(84)	1422(77)	242(14)	- 72(70)	74(29)	- 98(27)
C_3	.2710(9)	-.1405(6)	.4664(3)	3256(152)	929(62)	303(17)	112(101)	438(41)	- 30(34)
C_4	.1406(8)	-.3405(7)	.4932(3)	2198(125)	1706(87)	328(18)	-590(92)	502(40)	-174(32)
C_5	.3537(7)	-.2687(8)	.5358(3)	1436(88)	2699(113)	194(14)	470(92)	91(31)	0(38)
$P_{11}C_1$	.3768(4)	.0743(3)	.31406(15)	824(78)	567(48)	160(12)	- 49(49)	85(23)	- 45(20)
$P_{11}C_2$	.5009(5)	.0933(3)	.30743(16)	893(77)	792(54)	287(16)	6(61)	100(30)	11(24)
$P_{11}C_3$	.5964(3)	.0293(5)	.33038(20)	755(80)	1042(68)	362(19)	79(68)	100(33)	- 69(30)
$P_{11}C_4$	.5678(5)	-.0536(4)	.35996(18)	1222(107)	988(69)	325(19)	428(72)	- 18(35)	24(30)
$P_{11}C_5$	.4437(6)	-.0726(3)	.36650(15)	1307(97)	1059(69)	297(17)	254(73)	47(36)	143(27)
$P_{11}C_6$	.3482(3)	-.0086(4)	.34364(17)	794(68)	915(59)	201(13)	133(59)	1(26)	13(24)
$P_{12}C_1$	.2403(5)	.1299(3)	.21694(12)	1177(77)	562(48)	168(12)	114(54)	126(28)	- 32(21)
$P_{12}C_2$	.1357(4)	.0827(3)	.18979(20)	1619(99)	661(53)	161(13)	- 54(62)	68(30)	- 1(21)
$P_{12}C_3$	.1303(5)	.0678(3)	.13809(20)	2508(141)	828(61)	174(15)	-207(76)	11(37)	- 45(24)
$P_{12}C_4$	.2294(6)	.1001(4)	.11355(13)	2877(161)	938(70)	155(14)	174(89)	161(43)	- 8(25)
$P_{12}C_5$	.3340(5)	.1472(4)	.14070(21)	1957(121)	1426(82)	226(17)	56(87)	268(38)	15(32)
$P_{12}C_6$	.3394(4)	.1621(4)	.19239(21)	574(102)	1370(72)	166(14)	- 1(74)	208(31)	- 34(26)
$P_{13}C_1$	.2887(4)	.2848(3)	.29306(17)	789(64)	577(46)	156(11)	- 73(51)	126(23)	- 14(22)
$P_{13}C_2$	.3784(4)	.3186(4)	.33212(16)	926(75)	646(56)	232(14)	14(50)	132(28)	- 86(21)
$P_{13}C_3$	.3956(4)	.4241(4)	.34127(16)	1083(88)	874(63)	311(18)	-157(65)	219(32)	-233(29)
$P_{13}C_4$	.3229(5)	.4958(3)	.31135(22)	1623(110)	578(54)	342(19)	-118(67)	387(38)	- 60(28)
$P_{13}C_5$	.2332(5)	.4621(4)	.27229(19)	2225(133)	647(64)	280(17)	22(72)	200(40)	83(26)
$P_{13}C_6$	.2161(4)	.3565(4)	.26315(14)	1650(98)	601(52)	201(13)	- 29(63)	66(30)	19(24)
$P_{21}C_1$	-.0152(3)	.0460(3)	.37267(16)	577(60)	657(51)	159(12)	- 11(46)	47(23)	- 12(20)
$P_{21}C_2$	-.0643(4)	.0572(3)	.41776(17)	1084(80)	731(55)	219(14)	- 7(55)	150(28)	- 25(24)
$P_{21}C_3$	-.1072(4)	-.0293(5)	.44129(14)	1363(92)	1104(69)	202(14)	-127(72)	189(30)	40(28)
$P_{21}C_4$	-.1011(4)	-.1260(3)	.41974(20)	1258(90)	801(67)	256(17)	-167(61)	46(32)	128(26)
$P_{21}C_5$	-.0520(4)	-.1381(3)	.37465(20)	1114(83)	606(55)	282(16)	- 13(56)	6(31)	- 24(25)
$P_{21}C_6$	-.0090(4)	-.0516(4)	.35112(13)	985(73)	634(49)	178(12)	16(54)	87(24)	3(22)
$P_{22}C_1$	.1237(4)	.2374(4)	.39044(16)	766(66)	630(55)	171(12)	- 89(52)	140(25)	- 47(21)
$P_{22}C_2$	.1132(4)	.3437(4)	.38815(16)	871(73)	806(61)	219(14)	-132(61)	135(27)	-103(26)
$P_{22}C_3$	.1839(5)	.4051(3)	.42399(22)	1208(88)	868(61)	281(17)	-246(67)	231(32)	-199(29)
$P_{22}C_4$	.2668(4)	.3502(5)	.46211(17)	1492(105)	1414(89)	184(15)	-442(84)	134(33)	-138(30)
$P_{22}C_5$	.2781(4)	.2519(5)	.46440(15)	1422(94)	1289(77)	181(15)	-281(82)	- 9(31)	13(28)
$P_{22}C_6$	.2066(5)	.1905(3)	.42856(21)	1132(81)	900(63)	183(13)	-176(62)	30(28)	8(24)
$P_{23}C_1$	.0959(3)	-.2719(3)	.18586(19)	738(65)	464(44)	219(13)	16(47)	63(27)	10(22)
$P_{23}C_2$	.1234(4)	-.2656(3)	.23806(18)	1036(76)	588(50)	216(14)	- 55(54)	- 8(28)	- 22(22)
$P_{23}C_3$	.2209(5)	-.2126(4)	.25999(14)	1255(91)	747(56)	299(16)	- 82(63)	- 20(36)	-120(27)
$P_{23}C_4$	.3090(4)	-.1659(3)	.22971(24)	931(82)	858(65)	430(22)	- 15(63)	- 48(40)	-235(34)
$P_{23}C_5$	.2815(4)	-.1722(3)	.17751(23)	826(82)	748(57)	401(20)	-205(58)	213(34)	-101(29)
$P_{23}C_6$	.1750(5)	-.2252(4)	.15559(14)	745(69)	843(56)	280(15)	-127(57)	84(29)	- 38(26)
$P_{11}H_2$	.52294	.15772	.28449	7.0					
$P_{11}H_3$	.69279	.04401	.32531	7.0					
$P_{11}H_4$	.64214	-.10334	.37787	7.0					
$P_{11}H_5$	.42163	-.13698	.38962	7.0					
$P_{11}H_6$	.25179	-.02326	.34879	7.0					
$P_{12}H_2$	.05880	.05775	.20887	7.0					
$P_{12}H_3$	.04913	.03125	.11691	7.0					
$P_{12}H_4$	.22519	.08851	.07325	7.0					
$P_{12}H_5$	.41093	.17226	.12153	7.0					
$P_{12}H_6$	.42060	.19875	.21349	7.0					
$P_{13}H_2$	.43479	.26277	.35536	7.0					
$P_{13}H_3$	.46525	.45049	.37162	7.0					
$P_{13}H_4$	.33629	.57807	.31851	7.0					
$P_{13}H_5$	.17686	.51701	.24913	7.0					
$P_{13}H_6$	.14640	.33019	.23287	7.0					
$P_{21}H_2$	-.06901	.13301	.43448	7.0					
$P_{21}H_3$	-.14538	-.02080	.47634	7.0					
$P_{21}H_4$	-.13451	-.10487	.43810	7.0					
$P_{21}H_5$	-.04726	-.21394	.35799	7.0					
$P_{21}H_6$	.02911	-.06014	.31613	7.0					
$P_{22}H_2$	.04790	.37926	.35848	7.0					
$P_{22}H_3$	.17515	.48854	.42222	7.0					
$P_{22}H_4$	.32240	.40711	.48098	7.0					
$P_{22}H_5$	.34257	.21641	.49399	7.0					
$P_{22}H_6$	.21533	.10713	.43025	7.0					
$P_{23}H_2$	.06180	-.30193	.26156	7.0					
$P_{23}H_3$	.25126	-.20765	.30057	7.0					
$P_{23}H_4$	.39188	-.12461	.24683	7.0					
$P_{23}H_5$	.34303	-.13585	.15409	7.0					
$P_{23}H_6$	.15357	-.23014	.11509	7.0					

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

[b] Isotropic temperature factor in Å^2.

This was interpreted as anisotropic thermal motion. The phenyl carbons were allowed anisotropic thermal motion in the final refinements, although positional parameters were still constrained to a rigid group.

Table II. Calculated Bond Lengths and Angles

Bond	Distance (Å)^{b}	Atoms	Angles (°)
$Fe-C_1$	1.928(8)	C_1-Fe-C_2	84.8(3)
$Fe-C_2$	1.769(8)	C_1-Fe-C_3	88.8(3)
$Fe-C_3$	1.754(8)	C_1-Fe-C_4	88.7(3)
$Fe-C_4$	1.781(8)	C_1-Fe-C_5	175.9(3)
$Fe-C_5$	1.723(8)	C_2-Fe-C_3	124.1(4)
C_1-N_1	1.147(7)	C_2-Fe-C_4	120.8(4)
C_2-O_2	1.158(7)	C_3-Fe-C_4	114.5(4)
C_3-O_3	1.145(7)	C_4-Fe-C_5	95.1 (4)
C_4-O_4	1.117(8)	P_1-NP-P_2	134.60(25)
C_5-O_5	1.152(7)	N_1-C_1-Fe	178.0(7)
P_1-P_2	2.923(2)	O_2-C_2-Fe	179.4(7)
P_1-NP	1.581(4)	O_3-C_3-Fe	179.2(8)
P_2-NP	1.587(4)	O_4-C_4-Fe	179.1(9)
O_2-O_2	3.504(11)	O_5-C_5-Fe	177.7(10)
$P_1-P_{11}C_1$	1.794	C_2-Fe-C_5	91.8(3)
$P_1-P_{12}C_1$	1.787	C_3-Fe-C_5	91.1(4)
$P_1-P_{13}C_1$	1.790	$NP-P_1-P_{11}C_1$	111.9
$P_2-P_{21}C_1$	1.797	$NP-P_1-P_{12}C_1$	108.1
$P_2-P_{22}C_1$	1.788	$NP-P_1-P_{13}C_1$	114.2
$P_2-P_{23}C_1$	1.800	$NP-P_2-P_{21}C_1$	108.7
		$NP-P_2-P_{22}C_1$	115.5
		$NP-P_2-P_{23}C_1$	110.3
		$P_{11}C_1-P_1-P_{12}C_1$^{c}	108.0
		$P_{11}C_1-P_1-P_{13}C_1$	108.4
		$P_{12}C_1-P_1-P_{13}C_1$	105.9
		$P_{21}C_1-P_2-P_{22}C_1$	106.9
		$P_{21}C_1-P_2-P_{23}C_1$	107.0
		$P_{22}C_1-P_2-P_{23}C_1$	108.0
		$P_1-P_{11}C_1-P_{11}C_2$	121.8
		$P_1-P_{11}C_1-P_{11}C_6$	118.2
		$P_1-P_{12}C_1-P_{12}C_2$	121.1
		$P_1-P_{12}C_1-P_{12}C_6$	118.9
		$P_1-P_{13}C_1-P_{13}C_2$	122.5
		$P_1-P_{13}C_1-P_{13}C_6$	117.2
		$P_2-P_{21}C_1-P_{21}C_2$	120.2
		$P_2-P_{21}C_1-P_{21}C_6$	119.8
		$P_2-P_{22}C_1-P_{22}C_2$	120.3
		$P_2-P_{22}C_1-P_{22}C_6$	119.6
		$P_2-P_{23}C_1-P_{23}C_2$	119.7
		$P_2-P_{23}C_1-P_{23}C_6$	120.3

average of 4 non-cyanides = 1.757(12) Å^{a}
average of equatorial carbonyls = 1.768(8) Å
C-P-C ave. = 107.4(4)°
P-C-C ave. = 120.0(4)°

[a] The standard deviation of the average is defined as $\left(\frac{\Sigma(x_i-\bar{x})^2}{n(n-1)}\right)^{1/2}$ where n is the number of observations

[b] The standard deviations for the P-C bond lengths are approximately .005 Å as estimated from the variance of the atomic coordinates.

[c] The standard deviations for the C-P-C and P-C-C angles are approximately .3° as estimated from the variance of the atomic coordinates.

Table III. Rms Amplitudes of Vibration (Å) along Principal Axes

Atom	Axis 1	Axis 2	Axis 3
Fe	0.244 (1)	0.278 (1)	0.300 (1)
P_1	0.205 (2)	0.244 (2)	0.237 (2)
P_2	0.197 (2)	0.215 (2)	0.250 (2)
NP	0.189 (7)	0.219 (6)	0.255 (6)
N_1	0.275 (8)	0.311 (8)	0.496 (9)
O_2	0.269 (7)	0.349 (6)	0.418 (6)
O_3	0.266 (7)	0.368 (7)	0.613 (8)
O_4	0.252 (9)	0.440 (8)	0.643 (9)
O_5	0.272 (7)	0.387 (7)	0.648 (9)
C_1	0.260 (10)	0.280 (9)	0.372 (9)
C_2	0.252 (10)	0.282 (9)	0.357 (9)
C_3	0.268 (12)	0.299 (12)	0.447 (10)
C_4	0.238 (11)	0.330 (10)	0.453 (10)
C_5	0.261 (10)	0.277 (10)	0.483 (10)

The final values for the agreement factors R_1 and R_2 are 4.28 and 4.55% in which

$$R_1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$$

$$R_2 = [[\Sigma w(|F_o| - |F_c|)^2]/\Sigma w|F_o|^2]^{1/2}$$

The standard deviation of an observation of unit weight defined as

$$\left[\frac{(\Sigma[|F_o|-|F_c|]^2/\sigma^2(F_o)}{N_o - N_v}\right]^{1/2}$$

is 1.30, indicating the assigned standard deviations are slightly small. The final difference Fourier had no peaks larger than 0.23 e/Å^3. The final values of the atomic parameters and their standard deviations estimated from the inverse matrix and the error in the cell constants are given in Table I. Table II lists important bond distances and angles that may be derived from these parameters.[19] Table III gives the rms amplitudes of vibration along principal axes of the individual atom thermal ellipsoids.

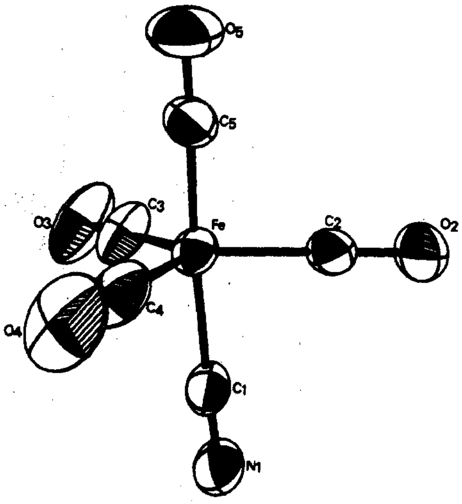

Figure 1. A perspective drawing of $[Fe(CO)_4CN]^-$. The thermal ellipsoids represent 25% probability contours.

Description and Discussion of the Structure

The salt consists of discrete $[((C_6H_5)_3P)_2N]^+$ cations and $[Fe(CO)_4CN]^-$ anions. The $[Fe(CO)_4(CN)]^-$ anion (Figure 1) is a (slightly distorted) trigonal-bipyramidal complex with approximately C_{3v} molecular symmetry. There is a distinct difference in bond lengths to the three types of ligands: axial carbonyl, equatorial carbonyl, and cyanide. The Fe-C bond lengths are 1.768 (8) (average of three), 1.723 (8), and 1.928 (8) Å, respectively. The difference between the equatorial and axial carbonyl Fe-C bond length is 0.045 (12) Å, which agrees with the latest electron diffraction value of 0.027 (7) Å for $Fe(CO)_5$.[20] This kind of contraction of axial *vs.* equatorial bond lengths has been explained at length elsewhere.[2-6,8,21-24]

The 0.205 (12) Å difference for the cyanide and axial carbonyl Fe-C bond lengths is qualitatively consistent with the expected difference in covalent radii of the two ligands. In the tetrahedral d^{10} complex $Ni(CO)_4$, the Ni-C bond length is 1.84 (3) Å.[25] The Ni-C bond length in the isoelectronic $[Ni(CN)_4]^{4-}$ anion may be estimated if we assume

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(19) See paragraph at end of paper regarding supplementary material.

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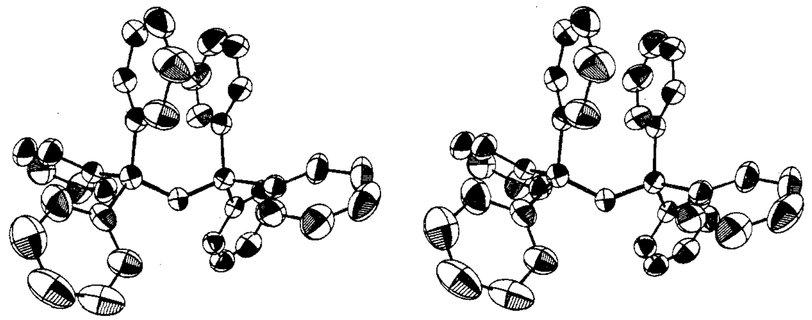

Figure 2. A stereoscopic pair of perspective drawings of $[N(P(C_6H_5)_3)_2]^+$. The thermal ellipsoids represent 25% probability contours. Phosphorus 1 is on the left with ring 1 in the rear, ring 2 in front, and ring 3 pointing up. Ring 1 on phosphorus 2 is also in the rear, ring 2 points up, and ring 3 is in the foreground.

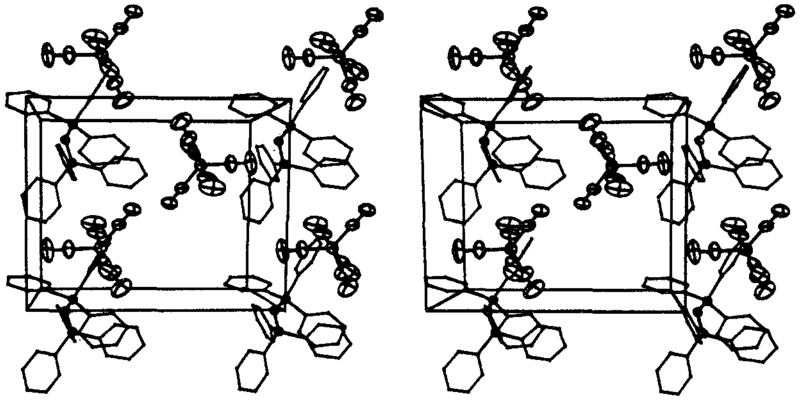

Figure 3. A stereoscopic pair of perspective drawings of the layered packing in the unit cell of $[N(P(C_6H_5)_3)_2][Fe(CO)_4CN]$. The thermal ellipsoids represent 25% probability contours. The phenyl carbons are drawn artificially small for clarity. The vertical line represents a unit translation in the *a* direction. The horizontal line represents a unit translation in the *b* direction. The line which goes into the page runs from $^1/_4$ to $^3/_4$ in *c*.

the metal covalent radius change for the square-planar Ni^{2+} to tetrahedral Ni^0 is the same as the change for square-planar Pt^{2+} to tetrahedral Pt^0. The Pt-P bond length in square-planar Pt^{2+} complexes is about 2.24 Å.[26-32] The Pt-P bond length in the tetrahedral Pt^0 complex $[Pt(P(C_6H_5)_3)_3(CO)]$ is 2.340 (6) Å.[33] If the difference of 0.10 Å is added to the Ni-C bond length of 1.86 Å in $CaNi(CN)_4 \cdot 5H_2O$[34] and $BaNi(CN)_4 \cdot 5H_2O$,[35] a bond length of 1.96 Å is predicted for the $[Ni(CN)_4]^{4-}$ ion. Thus the difference in Ni-C bond lengths between the isoelectronic species $Ni(CO)_4$ and $[Ni(CN)_4]^{4-}$ is expected to be about 0.12 Å, and this can be taken as an estimate of the difference in the covalent radius of CN^- and CO. Of course the actual bond lengths in any given complex depend on the bond order as well as the covalent radii, so the magnitude of this difference will vary. In $[Fe(CO)_4CN]^-$ the difference of 0.205 (12) Å would seem to imply a much higher bond order for the metal bond to CO relative to CN^-. The trans interaction for cyanide relative to carbonyl has been discussed at length elsewhere.[36,37] The iron-axial carbonyl bond length in $[Fe(CO)_4CN]^-$ of 1.723 (8) Å is only slightly less than the average bond length of 1.748 (15) Å in the $[Fe(CO)_4H]^-$ anion.[38]

The PPN cation (Figure 2) shows the same cisoid conformation as that observed in another salt and the P-N bond lengths are similar.[39] The P-N-P angle is somewhat smaller than that observed previously; for this salt the angle is 134.6 (31)° as compared with previous values from 137 (2) to 142 (1)°. The average P-C bond length of 1.79 Å and the average C-P-C angle of 107.4° are similar to those reported.

A packing diagram of the structure is shown in Figure 3. The ions pack in layers perpendicular to the c^* axis. The iron atom lies approximately at $^1/_4$, $^1/_4$, $^1/_2$ with the threefold axis of the trigonal bipyramid nearly perpendicular to *b*. Thus all of the $[Fe(CO)_4(CN)]^-$ groups are oriented with their molecular threefold axis oriented in the same way but with the cyanide group pointing up for half the anions and down for the other half. The result is the face-centered array in the plane with $z = {}^1/_2$ (which is diagramed in Figure 3) in which each $[Fe(CO)_4(CN)]^-$ is surrounded by four nearest

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(26) Some individual bond distances in the square-planar Pt^{2+} complexes *trans*-$[Pt_2Cl_4(P(C_3H_7)_3)_2]$,[27] $[Pt_2Cl_2(BCN)_2(P(C_3H_7)_3)_2]$,[28] *cis*-$[Pt(P(CH_3)_3Cl_2]$,[29] *trans*-$[Pt(P(C_2H_5)_3)_2Br_2]$,[30] *trans*-$[Pt(P(C_2H_5)_3)_2Cl_2]$,[30] *trans*-$[Pt(P(C_6H_5)_2(C_2H_5))_2HCl]$,[31] and $[Pt(P(C_6H_5)_3)_2(CO_3)]$[32] are 2.230 (9), 2.244 (8), 2.248 (8), 2135 (4), 2.300 (19), 2.267 (8), and 2.240 (10) Å, respectively.

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neighbors with opposite orientations of their dipoles. This strong dipolar coupling explains the high degree of order in the structure.

The thermal motion of the anion atoms is relatively large; two equatorial oxygens and the axial oxygen have extremely large rms amplitudes of vibration. The other oxygen, O_2, is involved in a very close-packing interaction with O_2 of the inversion-related anion at 3.504 (11) Å. Presumably this interaction constrains this oxygen somewhat while the other oxygens are able to vibrate freely in the holes created by the bulky cation. Large isotropic thermal motion for carbonyl oxygens has also been reported in a structure of the PPN cation with $Cr_2(CO)_{10}I^-$.[39]

In a trigonal-bipyramidal complex of symmetry D_{3h} the d orbitals split into the irreducible representations $a_1'(d_{z^2})$, $e'(d_{x^2-y^2}, d_{xy})$, and $e''(d_{xz}, d_{yz})$. Only the e′ and e″ orbitals are of the proper symmetry to participate in metal-to-ligand π bonding. For the axial ligands only the e″ oribtals are available for π bonding. For the equatorial ligands both the e′ and e″ sets are available. This simple analysis leads to the expectation that (in the absence of overwhelming countereffects such as strong steric repulsion) the more strongly π-bonding ligands should preferentially occupy equatorial positions. The isoelectronic series of which $Fe(CO)_5$ is the parent compound is an especially good test of this hypothesis. Since NO^+ is a stronger π-bonding ligand than CO, $Mn(NO)(CO)_4$ should have the nitrosyl in the equatorial position, as observed.[8] Since CN^- is a weaker π-bonding ligand than CO, $[Fe(CO)_4CN]^-$ should have the cyanide in the axial position, as this structure establishes. Other complexes which are not strictly isoelectronic are also expected to show this trend. Thus $[Fe(CO)_4H]^-$ would be expected to have the hydride in the axial position, as has been observed.[38]

Acknowledgment. We thank Mr. Richard F. Trecartin for preparing the crystalline materials used in this study. We gratefully acknowledge the financial support of the National Science Foundation (through Grant GP-29764). We thank the University of California Computing Center for the use of subsidized computer time.

Registry No. $[PPN][Fe(CO)_4CN]$, 49792-33-8.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-770.

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Crystal Structure of $Xe_2F_{11}^+AuF_6^-$ and the Raman Spectrum of $Xe_2F_{11}^+$

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Crystals of $Xe_2F_{11}^+AuF_6^-$ are orthorhombic with $a = 9.115$ (6) Å, $b = 8.542$ (25) Å, $c = 15.726$ (20) Å, $V = 1224$ Å^3, $Z = 4$, $d_c = 4.24$ g cm^{-3}, and space group *Pnma*. A structure determination using three-dimensional Mo Kα X-ray data resulted in a conventional R factor of 0.036 for 862 independent reflections for which $I \geq 3\sigma(I)$ ($R = 0.052$ for the 1140 independent data, including zero weight data). The anion is essentially octahedral, with an average Au–F bond distance of 1.86 (1) Å. The $Xe_2F_{11}^+$ consists of two crystallographically independent XeF_5 groups bridged by a common fluorine atom, with a bridge angle of 169.2 (2)°; the bridge bond lengths are 2.23 Å (average) *vs.* 1.84 Å (average) for the other Xe–F distances. Each XeF_5 group departs significantly from the ideal C_{4v} symmetry of the XeF_5^+ cation. However, the F_{ax}–Xe–F_{eq} angles are ~80° for both XeF_5^+ and the XeF_5 groups in $Xe_2F_{11}^+$. The cis angle furthest from the bridging fluorine atom is larger than the others indicating that the bridging F atom may be deflecting the nonbonding Xe(VI) valence electron pair from its ideal position in each pseudooctahedral, XeF_5^+-like component of $Xe_2F_{11}^+$. Raman data indicate that the complex cation behaves vibrationally like two weakly coupled XeF_5^+ species with a "bridge stretch" at ~360 cm^{-1}. This and the structural data indicate that $F_5Xe^+F^-XeF_5^+$ must be a major canonical form in the resonance hybrid description of the cation.

Introduction

Recently we set out to synthesize AuF_6^- and obtained[1] our first salt of this anion in the form of the complex cation salt $Xe_2F_{11}^+AuF_6^-$. Since both ions were novel and of structural interest, we were fortunate that our synthetic method yielded suitable single crystals for an X-ray structural analysis.

Bartlett and his coworkers[2] had prepared a salt of empirical formula $F_{17}PtXe_2$, at the time they characterized the salt $XeF_5^+PtF_6^-$, and considered it likely to be $Xe_2F_{11}^+PtF_6^-$. The composition of the latter, which can also be expressed as $2XeF_6 \cdot PtF_5$ adduct, suggested that the compound $2XeF_6 \cdot SbF_5$, described even earlier[3] by Gard and Cady, was also probably an $Xe_2F_{11}^+$ salt.

On the basis of Raman data[4] for $2XeF_6 \cdot AsF_5$ and $XeF_6 \cdot AsF_5$ and the crystal structure of $XeF_5^+AsF_6^-$,[5] Bartlett and Wechsberg[4] concluded that the former complex was $Xe_2F_{11}^+AsF_6^-$. Although Bartlett and Wechsberg were able to obtain single crystals of the arsenic complex,[4] all showed

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