azide whose half-wave potential is 0.19 V is clearly one coordinated to a cobalt, while the larger potential of 0.34 V is well beyond those observed for free azide (normally found in the range 0.21–0.28 V). Together, these two waves correspond to an azide to cobalt molar ratio of 3:1.

The observed spectroscopic and polarographic evidence for this substance is in full agreement with the structural findings. In the polarographic studies, the azide whose half-wave potential is 0.19 V is clearly that of the cation; this potential agrees well with what was observed for *trans*-[Co(NH$_3$)$_4$(N$_3$)](N$_3$)$_2$. The larger wave is then due to the azides coordinated in the anionic complex. (Rather than deduce the infrared and electronic absorption spectra of the complex anion by subtracting the contribution of the known cation from the observed spectra of the polymerization isomer, attempts are being made to isolate the anion as a metallic salt.)

In theory, the PMR spectrum of the isomer might be expected to show two separate peaks. Thus far, it has not been possible to resolve this spectrum because of interference resulting from proton exchange with the DMSO (the only suitable solvent for this complex) and indirect coupling with the cobalt-59 nucleus.

It is obvious from the results of this investigation that there are circumstances when the traditional analytical methods cannot provide conclusive evidence for the structural identification of a coordination complex. In this case, single-crystal X-ray diffraction analysis provided the necessary information: that a hitherto unsuspected anionic complex ion resulted in the formation of the polymerization isomer *trans*-diazidotetraamminecobalt(III) *trans*-tetraazidodiamminecobaltate(III).

Acknowledgment. The authors wish to thank the Computer Center for Information Services of Rutgers University for its financial support as well as the Rutgers Research Council. The assistance of N. R. Nelson, B. Gerdes, and the chemistry staff of Rutgers is gratefully acknowledged.

Registry No. [*trans*-Co(NH$_3$)$_4$(N$_3$)$_2$][*trans*-Co(NH$_3$)$_2$(N$_3$)$_4$], 54689-17-7.

Supplementary Material Available. A table of observed and calculated 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 \$4.00 for photocopy or \$2.50 for microfiche, referring to code number AIC40625K.

References and Notes

(1) R. B. Hagel and L. F. Druding, *Inorg. Chem.*, **9**, 1496 (1970).
(2) W. E. Cooley, C. F. Liu, and J. C. Bailar Jr., *J. Am. Chem. Soc.*, **81**, 4189 (1959).
(3) A. G. Maddock and A. B. J. B. Todesco, *J. Inorg. Nucl. Chem.*, **26**, 1535 (1964).
(4) T. Moeller, "Inorganic Chemistry", Wiley, New York, N.Y., 1952 pp 247–249.
(5) L. F. Druding, H. C. Wang, R. E. Cohen, and F. D. Sancilio, *J. Coord. Chem.*, **3**, 105 (1973).
(6) A small amount of the meridional isomer has been isolated and recrystallized from a saturated solution of NaN$_3$. These crystals are triclinic with a = 5.698 (2) Å, b = 7.509 (2) Å, c = 10.056 (3) Å, α = 97.92 (3)°, β = 87.20 (3)°, γ = 100.25 (4)°, and Z = 2. A structure analysis is in progress and will be reported upon completion.
(7) D. Forster and W. DeW. Horrocks Jr., *Inorg. Chem.*, **5**, 1510 (1966).
(8) L. F. Druding and F. D. Sancilio, *Acta Crystallogr., Sect. B*, **30**, 2386 (1974).
(9) L. F. Druding, D. M. Lukaszewski, and F. D. Sancilio, *Anal. Chem.*, **47**, 176 (1975).
(10) J. I. Bryant and M. D. Kemp, *Anal. Chem.*, **32**, 758 (1960).
(11) The conventional equivalent cell would have a = 6.928 Å, b = 7.661 Å, c = 9.671 Å, α = 107.35°, β = 92.62°, and γ = 116.35° (hkl = new $hk\bar{l}$).
(12) P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Crystallogr.*, **18**, 1035 (1965).
(13) Supplementary material.
(14) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(15) "International Tables for X-Ray Crystallography", Vol. II, Kynoch Press, Birmingham, England, 1959.
(16) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS", Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.
(17) D. W. J. Cruickshank, "Computing Methods and the Phase Problem in X-Ray Crystal Structure Analysis", Pergamon Press, Oxford, 1961.
(18) "X-Ray 73, Program System for X-Ray Crystallography", Computer Science Center, University of Maryland, 1973.
(19) J. F. Blount, "Computer Programs for X-Ray Crystallography", unpublished, 1974.
(20) G. H. Palenik, *Acta Crystallogr., Sect. B*, **24**, 4506 (1964).
(21) G. M. Barrow, R. H. Krueger, and F. Basolo, *J. Inorg. Nucl. Chem.*, **2**, 340 (1956).

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Aryldiazo Complexes. Structure of an Iron–Aryldiazo Complex, $[\mathrm{Fe(CO)_2(N_2C_6H_5)(P(C_6H_5)_3)_2}][\mathrm{BF_4}]$

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The structure of $[\mathrm{Fe(CO)_2(N_2C_6H_5)(P(C_6H_5)_3)_2}][\mathrm{BF_4}]$ has been determined crystallographically. The compound crystallizes from acetone as solvent-free crystals in space group $C_{2h}{}^5$-$P2_1/c$ with a = 13.447 (4) Å, b = 14.260 (4) Å, c = 22.755 (16) Å, β = 113.29 (2)°, Z = 4, ρ_{exptl} = 1.37(1) g/cm^3, and ρ_{calcd} = 1.373 g/cm^3. Based on 3159 unique reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$, the structure was solved and refined by full-matrix, least-squares methods to R = 0.064 and R_w = 0.088. The structure consists of discrete cations and anions; the BF$_4$ anions are partially disordered. The iron cation is five-coordinate with a coordination geometry close to trigonal bipyramidal. Apparently for steric reasons, the two carbonyl groups are nonequivalent. The phenyldiazo ligand in this complex is singly bent with Fe–N = 1.702 (6) Å, N–N = 1.201 (7) Å, N–C = 1.404 (8) Å, Fe–N–N = 179.2 (5)°, and N–N–C = 124.2 (6)°. The short Fe–N and N–N distances, as well as the general ligand geometry, suggest that multiple metal–nitrogen and nitrogen–nitrogen bonding is present and that the complex is best described as a PhN$_2^+$ complex of Fe(0). Structural and spectroscopic data suggest that the aryldiazo ligand is a good π acceptor but a poor σ donor.

Introduction

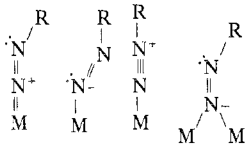
Aryldiazo ligands, as well as others which contain nitrogen–nitrogen multiple bonds, have been of great interest in recent years because of their close relationship to dinitrogen and nitrosyl ligands. Recently, structural and synthetic studies have shown the reaction chemistry of diazo ligands to be varied and interesting.[1–8] Especially noteworthy is the preparation of aroyl- and acyldiazo ligands from coordinated dinitrogen in rhenium, molybdenum, and tungsten complexes. Thus the close relationship between N$_2$ and RN$_2$ ligands, at least for

Table I. Summary of Crystal Data and Intensity Collection

Compd	$[Fe(CO)_2(N_2C_6H_5)(P(C_6H_5)_3)_2][BF_4]$	Radiation	Cu $K\alpha_1$ (λ 1.54056 Å) postfiltered with 1 mil of Ni foil
Formula	$C_{44}H_{35}FeBN_2O_2F_4P_2$	Temp	22.0 (5)°
Formula wt	828.38 amu	μ	41.48 cm^{-1}
a	13.447 (4) Å	Transmission factors	0.186–0.348
b	14.260 (4) Å	Receiving aperture	5.0 mm wide by 4.0 mm high, 32 cm from crystal
c	22.755 (16) Å	Takeoff angle	3.1°
β	113.29 (2)°	Scan speed	2.0° in 2θ/min
V	4008 $Å^3$	Scan range	0.95° below $K\alpha_1$ to 0.85° above $K\alpha_2$
Z	4	Background counting	10 sec for $2\theta < 50°$; 20 sec thereafter
Density	1.373 g/cm^3 (calcd) 1.37 (1) g/cm^3 (exptl)	2θ limits	3.0–95.5°
Space group	$C_{2h}{}^5$-$P2_1/c$	Final no. of variables	212
Crystal dimensions	0.46 × 0.40 × 0.37 mm	Unique data used ($F_o{}^2 > 3\sigma(F_o{}^2)$)	3159
Crystal vol	0.0744 mm^3		
Crystal shape	Parallelepiped along [001] direction; tetragonal cross section with {110} faces	Error in observation of unit wt	3.32 electrons

complexes containing these metals, is firmly established.[3,4]

Of special interest are the varied coordination geometries attainable by aryldiazo ligands. Indeed, three of the four modes of coordination described in A–D have been clearly identified structurally; only the totally linear (C) geometry remains undiscovered.



A B C D

Structural studies of diazo complexes yield valuable insights into the nature of diazo ligands and into new reaction pathways. We now report the molecular and crystal structure of the title compound, $[Fe(CO)_2(N_2Ph)(PPh_3)_2][BF_4]$,[9] which, when it was first reported,[10] was the first structural study of an aryldiazo complex containing a first-row transition metal. Structures of aryldiazo complexes containing Mo[11] and Re[5] had been reported previously. Recently, Rh,[6] Ru,[12] and Mn[13] aryldiazo complexes have also been studied structurally. Preliminary structural results on this iron complex have been discussed before.[6,14,15]

Experimental Section

Crystal Preparation. The title complex was prepared according to the method of Lalor and Carroll[14] by allowing equimolar quantities of $Fe(CO)_3(PPh_3)_2$[16] and $[PhN_2][BF_4]$[17] to react in dichloromethane. The orange product was recrystallized several times from CH_2Cl_2–Et_2O to yield orange crystals of the 1:1 methylene chloride solvate. However, examination of the crystals showed them to be of poor quality. Beautiful red-orange prisms of the solvent-free complex were grown from acetone and proved to be of acceptable quality for structural work. Since the iron–diazo complex is stable in air, a suitable crystal was mounted in air on a glass fiber. Anal. Calcd for $C_{44}H_{35}FeBN_2O_2F_4P_2$: C, 63.80; H, 4.26; Fe, 6.74; N, 3.38; O, 3.86; P, 7.48. Found: C, 63.91; H, 4.30; Fe, 6.69; N, 3.32; O, 3.80; P, 7.36. Elemental analyses were performed by Meade Microanalytical Laboratory, Amherst, Mass. Magnetic measurements using a Faraday balance showed the crude product to be distinctly paramagnetic (about 0.6 BM), but the paramagnetism decreased with successive recrystallizations. An unidentified yellow iron carbonyl compound was the principal impurity. Large single crystals of the iron–diazo complex (~1 mm on edge) were grown from acetone, carefully separated from the mother liquor, and crushed. This powder was diamagnetic. Although Sutton and Fisher[15] reported their material to be paramagnetic, it too probably contained a paramagnetic impurity.

Crystallographic Data. Preliminary film data showed the crystals to belong to the monoclinic system with extinctions ($h0l$, l odd; $0k0$, k odd) characteristic of the centrosymmetric space group $C_{2h}{}^5$-$P2_1/c$. Using a least-squares procedure based on the angular positions of 21 hand-centered reflections in diverse regions of reciprocal space (in the range $32° < 2\theta < 62°$), accurate unit cell dimensions were determined. See Table I for pertinent crystal information and details of data collection. The mosaicity of the crystal was acceptable for the θ–2θ scan technique. The widths at half-height of several strong, low-angle reflections (ω scan, open counter) lay in the range 0.12–0.18°.

Data collection was carried out using a Picker four-circle diffractometer. Background counts were measured at both ends of the scan range with both the counter and crystal stationary. The intensities of six standard reflections were measured every 75 reflections, and five of the six were found to decrease uniformly and linearly by 3–5% during the course of data collection. The very strong 110 reflection increased by 2%, presumably because radiation damage brought about increased mosaicity and decreased secondary extinction. The observed intensities were modified to correct for this apparent isotropic crystal decomposition.

The intensities of 3889 unique reflections were measured (k and $l \geq 0$) out to 2θ(Cu $K\alpha_1$) = 95.5°; past this point very few were above background. The data were processed in the usual way with $\sigma(F_o{}^2)$ calculated using a value of 0.04 for p.[18] Only reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$ were used in subsequent calculations. An absorption correction was applied to the data using gaussian integration.[19] The R index for averaging 161 pairs of symmetry-related reflections was 6.0% before the absorption correction was applied and 1.6% afterward. Fourteen reflections were deleted from the data set because of instrument failure. A total of 719 reflections were considered unobserved ($F_o{}^2 < 3\sigma(F_o{}^2)$).

Structure Refinement. The structure was solved using a Patterson synthesis to locate the iron and two phosphorus atoms. Subsequent refinements and difference Fourier syntheses were used to locate the remaining atoms, including all 35 hydrogen atoms. The structure was refined using full-matrix, least-squares techniques. The isotropic model (seven rigid-body phenyl groups and no hydrogen atoms) converged to R indices of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.106$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2} = 0.150$. During the refinements, the quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights, w, are taken as $4F_o{}^2/\sigma^2(F_o{}^2)$. Atomic scattering factors were taken from Cromer and Waber's tabulation.[20] The anomalous dispersion terms for Fe and P were included in F_c.[21] All seven phenyl groups were refined as rigid, planar bodies with a constant and uniform C–C distance of 1.397 Å and with isotropic thermal parameters. Although all H atoms were located in the difference Fourier syntheses,

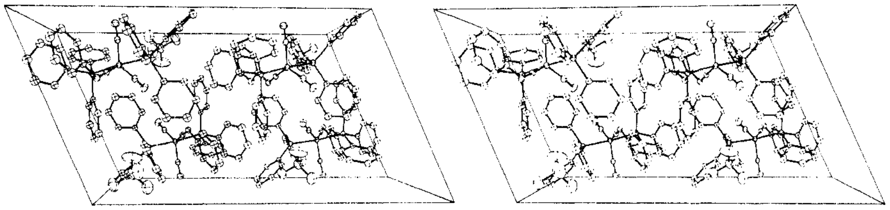


Figure 1. A stereoview of a unit cell of $[Fe(CO)_2(N_2Ph)(PPh_3)_2][BF_4]$. The *x* axis is almost vertical, the *y* axis is perpendicular to the paper coming toward the reader, and the *z* axis is horizontal to the right. Vibrational ellipsoids are drawn at the 20% probability level.

their positions were idealized and they were included as fixed contributions in final anisotropic refinements; the C–H distance was assumed to be 1.00 Å, CCH was assumed to be 120.0°, and *B* of a hydrogen atom was assumed to be equal to *B* of the carbon atom to which it was attached.

In addition to hydrogen atoms, a difference Fourier synthesis revealed four peaks in a pseudotetrahedral array about the boron atom which were related to the refined tetrahedral array of fluorine atoms by a C_4 rotation around its C_2 axis. Two models were chosen for the disordered F_4 group: (1) four anisotropic atoms occupying the most populated tetrahedral site; (2) two rigid tetrahedra (F–F distance = 2.29 Å) whose origins were not constrained at all and which had isotropic thermal parameters. The first model was refined anisotropically, including the hydrogen contributions, to an *R* index of 0.065. Two cycles of anisotropic refinement (isotropic F_4 groups) caused the second model to converge to $R = 0.077$. In the second model, the first F_4 group had an occupancy of 74% with thermal parameters of 10, 11, 11, and 14 Å^2, and the second F_4 group had an occupancy of 26% with *B*'s of 13, 13, 15, and 25 Å^2. The coordinates of the boron atom and of the two centers of the F_4 groups were all the same within 2σ. Thus, the first model was chosen because all of the bond distances and angles about the coordination spheres of Fe, P(1), P(2), C(1), C(2), N(1), and N(2) were the same within 0.7σ for the two models.

A final cycle of refinement, including a variable isotropic extinction parameter, converged to $R = 0.064$ and $R_w = 0.088$. The largest parameter shift in the final cycle of refinement was 0.3σ. The error in observation of unit weight is 3.32 electrons. The extinction parameter is small, $8\ (3) \times 10^{-7}$ electron^{-2}. A final difference Fourier synthesis of residual electron density revealed nothing interesting. Of the strongest ten peaks four belong to the weaker F_4 image (0.4–0.6 e/Å^3) and six belong to residuals near various phenyl groups (0.3–0.6 e/Å^3). A typical phenyl carbon atom had an intensity of 2.2 e/Å^3. All but 15 unobserved reflections obey the relation $|F_c^2 - F_o^2| < 4\sigma(F_o^2)$; 13 fell in the range 4σ–6σ, and 2 fell in the range 6σ–8σ. There were no trends of the quantity $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, diffractometer setting angles, or Miller indices.

The final positional and thermal parameters of atoms and groups appear in Tables II and III, and root-mean-square amplitudes of vibration are given in Table IV.[22] A listing of the observed and calculated structure amplitudes for those data used in the refinement is available.[22]

Discussion

General Description of the Structure. The structure of $[Fe(CO)_2(N_2Ph)(PPh_3)_2][BF_4]$ consists of discrete cations and anions with the geometry of the cation being very close to trigonal bipyramidal. A stereodrawing of the unit cell is shown in Figure 1. The labeling scheme, together with bond distances and angles in the inner coordination sphere, is shown in Figures 2 and 3. The triphenylphosphine ligands are trans to each other with P(1)–Fe–P(2) near 176° (see Table V). The trigonal plane is very well defined; a least-squares plane through Fe, C(1), C(2), and N(1) shows distances of these four atoms and also O(1), O(2), and N(2) from the trigonal plane to be less than the standard deviation of the respective distance. The shortest intermolecular contacts are H(222)–H(223) = 2.28 Å and H(234)–H(15) = 2.37 Å. The shortest C–H intermolecular contact is 2.60 Å.

The carbonyl ligands are essentially linear, as expected, with Fe–C–O about 175° for both. The small but significant bending of the carbonyls is typical of solid-state structures of transition metal carbonyl complexes; however, there are several interesting aspects of this bending. (1) Both carbonyls are bent by about the same amount (~5°). (2) Both oxygen atoms are bent in the same manner, toward the aryldiazo ligand which is the better π acceptor. (3) The torsion angles about the Fe–C(1) and Fe–C(2) bonds are very small, 6 (8) and 2 (7)°, respectively, indicating that the oxygen atoms remain in the trigonal plane upon bending (see Table V).

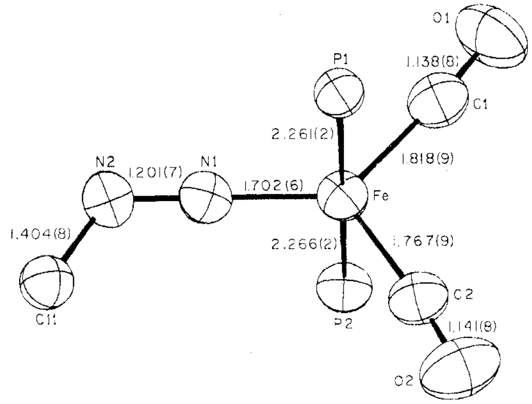


Figure 2. The coordination sphere with some bond distances for $[Fe(CO)_2(N_2Ph)(PPh_3)_2][BF_4]$. Vibrational ellipsoids are drawn at the 50% probability level.

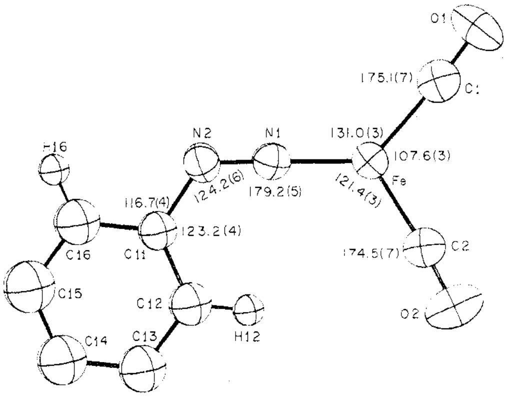


Figure 3. The trigonal plane with some bond angles for $[Fe(CO)_2(N_2Ph)(PPh_3)_2][BF_4]$. The vibrational ellipsoids are drawn at the 50% probability level.

Despite the partial disorder, the refined BF_4 anion has nearly tetrahedral symmetry. Considering the problem of disorder and the asymmetric environment of the anion, the distortions from idealized tetrahedral symmetry are not significant. The F–B–F angles range between 104 and 114°. The thermal ellipsoids of the fluorine atoms have the expected shapes and are not too much larger than those belonging to the carbonyl oxygen atoms. The foregoing suggests that the model chosen for the anion is acceptable. Although the B–F distances range from 1.26 to 1.44 Å, it is hard to attach any significance to this fact. The anion is more or less isolated in the crystal lattice with no obvious interactions with atoms surrounding it. The three shortest intermolecular contacts involving fluorine atoms are with phenyl hydrogen atoms and fall in the range 2.35–2.47 Å.

The distances and the angles in the iron cation are in the

Table II. Final Parameters for $[Fe(CO)_2(N_2C_6H_5)(P(C_6H_5)_3)_2][BF_4]$

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0.722845 (78)	0.186546 (68)	0.227440 (45)	55.99 (89)	36.62 (67)	16.45 (29)	2.54 (55)	12.31 (38)	3.04 (32)
P(1)	0.67891 (13)	0.25843 (12)	0.131879 (77)	54.1 (14)	44.3 (11)	17.16 (47)	4.60 (97)	11.88 (63)	4.08 (56)
P(2)	0.75412 (14)	0.11547 (12)	0.322183 (78)	60.6 (14)	35.9 (10)	17.34 (46)	0.53 (92)	14.24 (63)	2.42 (54)
O(1)	0.60547 (49)	0.33490 (40)	0.26437 (27)	121.1 (56)	62.1 (37)	40.0 (19)	30.9 (38)	41.1 (28)	3.0 (21)
O(2)	0.95004 (49)	0.23336 (44)	0.26568 (26)	67.1 (49)	103.3 (48)	33.6 (18)	−5.7 (38)	16.2 (23)	10.4 (23)
N(1)	0.67555 (41)	0.08297 (43)	0.18951 (25)	53.5 (43)	45.8 (38)	16.9 (15)	2.7 (33)	10.4 (20)	1.0 (20)
N(2)	0.64350 (45)	0.00962 (43)	0.16283 (27)	66.3 (47)	43.1 (37)	21.5 (16)	−0.2 (35)	14.7 (22)	−3.1 (21)
C(1)	0.65454 (63)	0.28023 (55)	0.25101 (34)	75.0 (65)	49.7 (49)	21.8 (21)	0.0 (45)	17.8 (30)	8.3 (25)
C(2)	0.86020 (69)	0.21894 (49)	0.25198 (33)	63.6 (66)	49.4 (46)	21.3 (21)	2.6 (43)	15.7 (30)	6.5 (24)
F(1)	0.17287 (66)	−0.03805 (38)	0.16559 (31)	339. (11)	52.1 (35)	53.5 (22)	31.1 (49)	54.7 (39)	13.2 (23)
F(2)	0.09621 (61)	0.03808 (55)	0.07630 (32)	219.3 (81)	170.6 (67)	42.8 (22)	85.9 (61)	24.6 (34)	8.0 (30)
F(3)	0.07424 (65)	0.08937 (44)	0.16072 (34)	254.2 (92)	96.7 (44)	66.0 (26)	12.3 (53)	58.9 (42)	−10.3 (28)
F(4)	0.23005 (66)	0.10023 (55)	0.15495 (57)	175.5 (83)	110.8 (59)	164.0 (65)	−65.0 (61)	17.8 (57)	−2.0 (49)
B	0.1499 (11)	0.04547 (84)	0.13906 (56)	151. (13)	59.8 (80)	32.0 (38)	8.6 (84)	17.6 (55)	−14.4 (43)

Group	$x_c{}^c$	y_c	z_c	δ	ϵ	η
1	0.7658 (3)	−0.1196 (2)	0.1269 (2)	2.226 (3)	−3.139 (3)	−2.567 (3)
11	0.7978 (2)	0.4533 (2)	0.1306 (1)	2.912 (14)	1.778 (2)	−1.779 (14)
12	0.7184 (3)	0.1215 (2)	0.0314 (2)	1.731 (3)	3.054 (3)	−2.286 (3)
13	0.4265 (3)	0.3111 (2)	0.0719 (1)	−0.229 (3)	2.734 (3)	3.144 (3)
21	0.8239 (3)	−0.0971 (2)	0.3141 (1)	1.961 (3)	−2.734 (3)	−2.896 (3)
22	0.9354 (2)	0.2031 (2)	0.4496 (1)	0.167 (3)	2.725 (3)	0.751 (3)
23	0.5366 (3)	0.1170 (2)	0.3480 (2)	−0.873 (5)	−2.263 (3)	2.157 (5)

[a] Estimated standard deviations of the least significant figure are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The quantities given in the table are the thermal coefficients multiplied by 10^4. [c] x_c, y_c, and z_c are the fractional coordinates of the rigid-group centers; the angles δ, ϵ, and η (radians) have been defined previously: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 793 (1965).

range to be expected for iron–carbonyl–phosphine complexes (Table VI). The P–C and C–O distances and the Fe–C–O and Fe–P–C angles found here are normal. The Fe–P distances, though near the expected values, are distinctly longer than the average. Of special interest is the apparent nonequivalence of the two carbonyl ligands.[23] The Fe–C distances differ by 0.051 (13) Å and Fe–C(1) is the longest distance of those reported in the table. Furthermore, the C(1)–O(1) carbonyl ligand is displaced by about 11° in the trigonal plane away from N(1) and toward C(2). This displacement destroys the otherwise almost perfect trigonal-bipyramidal geometry.

The steric interaction of the bulky phenyl group of the diazo ligand with both triphenylphosphine ligands leads to small, but observable, distortions in the cation. The C(1)–O(1) ligand is displaced in the trigonal plane; the Fe–P bonds are lengthened slightly and are bent away (about 2°) from the diazo phenyl group. The phenyl groups of the phosphine ligands assume the common propeller conformation;[24] however, phenyl groups 21 and 12, which are nearest to the diazo phenyl group, are twisted considerably about the P–C bonds in order to minimize the steric interaction with this group. Consequently, these two phosphine phenyl groups have the largest Fe–P–C–C torsion angles, 66.5 (4) and 73.4 (4)°, respectively. There are no intramolecular H–H interactions less than 2.5 Å. There are three nonbonded intramolecular C–H interactions less than 2.6 Å: C(221)–H(236) = 2.56 Å, C(111)–H(136) = 2.57 Å, and C(1)–H(112) = 2.59 Å.

The Phenyldiazo Ligand. The phenyldiazo ligand in this iron complex assumes the singly bent geometry A. The Fe–N(1)–N(2) angle is essentially linear (179.2 (5)°) and the N(1)–N(2)–C(11) angle is 124.2 (6)°, suggesting sp hybridization about N(1) and sp^2 about N(2). The slight bend in the Fe–N(1)–N(2) angle is caused by a small movement of N(2) in the trigonal plane; the dihedral angle between the N(1)–C(1)–C(2) and N(2)–N(1)–Fe planes is ~3°. In fact, the whole diazo ligand is close to being planar and almost lies in the trigonal plane. The torsion angle about N(1)–N(2) is 5°, and the torsion angle about C(11)–N(1) is 6.2 (9)° (see Table V). Thus the angle between the trigonal and diazo phenyl planes is 7.2 (3)°, and between the trigonal and N(1)–N(2)–C(11) planes it is 2.1 (6)°. The torsion angle about the C–N bond is small (~6°) by comparison with those in *trans*-azobenzene (~17°)[25] and in the molybdenum–phenyldiazo complex (~20°), $Mo(HBPz_3)(CO)_2(N_2Ph)$.[11] Although it is difficult to say which forces cause distortions, it is reasonable that the torsion angle about N(2)–C(11) and the N(2)–C(11)–C(12) angle both increase in order to minimize the nonbonded interaction between N(1) and H(12). Resisting an increase in the torsion angle are the π conjugation of the Ph–N–N–Fe network and the disposition of the two bulky triphenylphosphine ligands.

The Fe–N(1) distance at 1.702 (6) Å is the same as the corresponding distance in the five-coordinate, paramagnetic iron–nitrosyl complex $Fe(NO)(S_2CNMe_2)_2$,[26] and it is somewhat longer than the 1.65-Å distances found in the four-coordinate iron–dinitrosyl complexes $[Fe(NO)_2I]_2$,[27] $Fe(NO)_2(PPh_3)_2$,[28] and $Fe(NO)_2(Ph_2PC{=}C(PPh_2)CF_2CF_2CF_2)$.[29] The metal–nitrogen distance in the iron–diazo complex is shorter than the corresponding distances in $ReCl_2(N_2Ph)P_3$[5] or $RuCl_3(N_2To)P_2$.[12] This may be ascribed to several effects: (1) the reduced coordination number of the iron complex, (2) the smaller effective radius of first-row transition metals, and (3) the positive charge on the complex. From Table VII certain trends are evident. Going from top to bottom, the N–N distance decreases indicating a strengthening of the N–N bond and a probable weakening of the metal–nitrogen bond. The N–C distance decreases and the N–N–C angle increases indicating a change of hybridization of N(2) from approximately sp^2 to something more closely approaching sp. An N–N triple bond in a free ligand is 1.10 Å[30] (from PhN_2^+) and a corresponding N–N double bond is 1.24 Å[25,31] (from PhN_2Ph). Although the diazo complexes of Fe, Mo, and Re may all be loosely described as having geometry A, the data in Table VII can be nicely interpreted as representing a continuum of geometries ranging from those described by formalism A to those approaching formalism C.

It is interesting that the N–N stretching frequencies seem to follow the same trend noted above. The respective values for the Ru, Fe, Mo, and Re complexes are 1881,[7] 1723,[14] ca. 1590,[32] and 1534 cm^{-1}.[33] Perhaps a more representative value for a five-coordinate iron complex is 1640 cm^{-1}, which is the

Table III. Derived Positional and Thermal Parameters for Ring Atoms

	Carbon				Hydrogen		
Atom[a]	*x*	*y*	*z*	*B*[b]	*x*	*y*	*z*
C(111)	0.7504 (4)	0.3665 (2)	0.1319 (2)	3.24 (13)			
C(112)	0.7787 (4)	0.4269 (3)	0.1844 (2)	4.21 (15)	0.765	0.409	0.223
C(113)	0.8261 (4)	0.5136 (3)	0.1831 (2)	5.08 (17)	0.846	0.558	0.221
C(114)	0.8453 (4)	0.5400 (3)	0.1293 (2)	5.14 (17)	0.879	0.603	0.128
C(115)	0.8170 (4)	0.4796 (3)	0.0769 (2)	5.09 (17)	0.831	0.499	0.039
C(116)	0.7695 (4)	0.3929 (3)	0.0782 (2)	4.26 (15)	0.750	0.350	0.041
C(121)	0.6991 (4)	0.1839 (3)	0.0731 (2)	3.85 (14)			
C(122)	0.8051 (3)	0.1662 (3)	0.0794 (2)	4.86 (17)	0.867	0.198	0.114
C(123)	0.8244 (3)	0.1038 (4)	0.0378 (3)	5.84 (19)	0.900	0.092	0.042
C(124)	0.7377 (4)	0.0591 (4)	−0.0103 (2)	6.86 (22)	0.752	0.015	−0.041
C(125)	0.6317 (4)	0.0768 (4)	−0.0166 (2)	6.62 (21)	0.570	0.045	−0.051
C(126)	0.6124 (3)	0.1392 (4)	0.0250 (2)	4.94 (17)	0.537	0.152	0.021
C(131)	0.5366 (3)	0.2889 (3)	0.0978 (2)	3.29 (13)			
C(132)	0.4611 (4)	0.2241 (2)	0.1011 (2)	4.51 (16)	0.486	0.162	0.122
C(133)	0.3510 (3)	0.2463 (3)	0.0752 (2)	5.28 (17)	0.297	0.200	0.078
C(134)	0.3163 (3)	0.3332 (3)	0.0460 (2)	5.53 (18)	0.237	0.349	0.028
C(135)	0.3918 (4)	0.3980 (3)	0.0426 (3)	5.61 (18)	0.367	0.460	0.022
C(136)	0.5020 (3)	0.3759 (3)	0.0685 (2)	4.49 (16)	0.556	0.422	0.066
C(211)	0.7922 (4)	−0.0057 (3)	0.3204 (2)	3.30 (13)			
C(212)	0.8912 (3)	−0.0218 (3)	0.3157 (2)	4.47 (15)	0.939	0.032	0.317
C(213)	0.9229 (3)	−0.1132 (3)	0.3094 (3)	5.48 (18)	0.994	−0.125	0.306
C(214)	0.8556 (4)	−0.1886 (3)	0.3078 (3)	6.22 (20)	0.878	−0.254	0.303
C(215)	0.7566 (4)	−0.1725 (3)	0.3126 (3)	6.39 (20)	0.708	−0.227	0.311
C(216)	0.7249 (3)	−0.0811 (3)	0.3189 (2)	5.47 (18)	0.653	−0.070	0.322
C(221)	0.8590 (3)	0.1646 (3)	0.3934 (2)	3.08 (13)			
C(222)	0.9120 (4)	0.1073 (2)	0.4465 (2)	4.46 (16)	0.896	0.039	0.445
C(223)	0.9884 (4)	0.1459 (3)	0.5026 (2)	5.05 (17)	1.027	0.106	0.541
C(224)	1.0117 (4)	0.2417 (3)	0.5057 (2)	4.82 (16)	1.067	0.270	0.546
C(225)	0.9587 (4)	0.2989 (2)	0.4527 (2)	4.56 (16)	0.976	0.368	0.455
C(226)	0.8823 (3)	0.2604 (3)	0.3965 (2)	3.75 (14)	0.845	0.302	0.358
C(231)	0.6324 (3)	0.1158 (3)	0.3378 (2)	3.57 (14)			
C(232)	0.5366 (4)	0.0816 (3)	0.2908 (2)	4.90 (16)	0.536	0.057	0.249
C(233)	0.4408 (3)	0.0828 (4)	0.3010 (2)	5.96 (19)	0.372	0.059	0.267
C(234)	0.4408 (3)	0.1182 (4)	0.3583 (2)	6.17 (20)	0.372	0.120	0.365
C(235)	0.5366 (4)	0.1523 (4)	0.4053 (2)	5.57 (18)	0.537	0.178	0.446
C(236)	0.6324 (3)	0.1511 (3)	0.3951 (2)	4.41 (15)	0.701	0.175	0.429
C(11)	0.7082 (3)	−0.0543 (3)	0.1468 (2)	3.73 (14)			
C(12)	0.8147 (3)	−0.0353 (3)	0.1549 (2)	4.47 (16)	0.850	0.025	0.175
C(13)	0.8724 (3)	−0.1005 (4)	0.1350 (3)	5.51 (18)	0.949	−0.086	0.141
C(14)	0.8235 (4)	−0.1849 (3)	0.1070 (3)	6.14 (20)	0.865	−0.231	0.093
C(15)	0.7170 (4)	−0.2039 (3)	0.0989 (3)	6.65 (22)	0.683	−0.264	0.079
C(16)	0.6593 (3)	−0.1386 (3)	0.1188 (3)	5.18 (17)	0.584	−0.152	0.113

[a] C (*xx*1) is attached to P, and the atoms in the ring are sequentially numbered around the ring. [b] The units are Å^2; the isotropic thermal parameters for the hydrogen atoms were taken to be the same as those for the respective carbon atoms to which they are attached.

value of ν(NN) for the neutral complex $FeCl(CO)(N_2Ph)(PPh_3)_2$.[34]

Other than those already noted, there are three other similar structures of the type $M(CO)_2(L)P_2$: $Os(CO)_3(PPh_3)_2$,[35] $Os(CO)_2(NO)(PPh_3)_2^+$ (Os–N = 1.89 (1) Å),[36] and $Mn(CO)_2(NO)(PPh_3)_2$ (Mn–N = 1.73 (1) Å).[37] All three are trigonal bipyramidal[38] as well as are $RuI(CO)(NO)(PPh_3)_2$[39] and $CoCl_2(NO)(PPh_2Me)_2$[40] though the geometry of the cobalt nitrosyl complex is rather distorted. Although the structure of $Ir(CO)(NO)(PPh_3)_2$[41] is straightforward, the anomalously long Os–N distance observed in the osmium–dicarbonyl–nitrosyl complex must be viewed with caution in light of the CO–NO disorder problems in $Fe(CO)(NO)_2(PPh_3)$,[28] $Co(CO)_2(NO)(PPh_3)$,[42] $Co(CO)(NO)(PPh_3)_2$,[42] $Co(CO)_2(NO)(AsPh_3)$,[43] and $Mo(HBPz_3)(CO)_2(NO)$.[44] Although the structures of $Mn(CO)_2(N_2Ph)(PPh_3)_2$[13] and $FeCl(CO)(N_2Ph)(PPh_3)_2$[34] are not known, these two aryldiazo complexes of first-row transition metals are isoelectronic with the iron complex herein reported and probably have trigonal-bipyramidal geometries with singly bent phenyldiazo ligands. The value of ν(NN) for the Mn complex would be a useful piece of information to test this prediction. The only other iron–aryldiazo complex is the four-coordinate $Fe(CO)(NO)(N_2Ph)(PPh_3)$[45] whose structure is probably similar to the pseudotetrahedral analog $Fe(CO)(NO)_2(PPh_3)$.[28]

Although much of the discussion concerning the structures of diazo ligands is technically limited to aryldiazo ligands, we feel that most, if not all, also applies to other monodentate alkyl–, acyl–, or aroyldiazo ligands. To date, all X-ray structural studies have been performed on aryldiazo complexes except for one rhenium–benzoyldiazo complex.[5] One must be cautious, however, in extending the generality too far because an alkyldiazo group would be expected to be a poorer π acceptor than its aryl analog. It is, however, this metal–ligand π interaction which apparently stabilizes the diazo ligand, reduces its tendency to decompose *via* N_2 liberation, and causes the ligand to adopt geometry A in preference to C.

Although the reaction chemistry of the iron–dicarbonyl–phenyldiazo cation[34] is different from that of the ruthenium and osmium analogs[46]

$$Fe(CO)_2(N_2Ph)P_2^+ + Cl^- \rightarrow FeCl(CO)(N_2Ph)P_2 + CO\uparrow$$

$$Os(CO)_2(N_2Ph)P_2^+ + Cl^- \rightarrow OsCl(CO)_2(N_2Ph)P_2$$

all three of them probably possess the same general trigonal-bipyramidal structure with singly bent diazo groups. The alternate square-pyramidal structure with an apical diazo ligand is probably not found owing to the unfavorable arrangement of trans carbonyl ligands. Although the weakening of the Fe–C(1) bond resulting from steric interactions offers a convenient explanation for the relative ease with which CO

Table V. Selected Distances (Å) and Angles (deg) in $[Fe(CO)_2(N_2Ph)(PPh_3)_2][BF_4]$

	Bond Distances		
Fe-P(1)	2.261 (2)	P(1)-C(121)	1.812 (6)
Fe-P(2)	2.266 (2)	P(1)-C(131)	1.810 (4)
Fe-C(1)	1.818 (9)	P(2)-C(211)	1.807 (4)
Fe-C(2)	1.767 (9)	P(2)-C(221)	1.816 (4)
Fe-N(1)	1.702 (6)	P(2)-C(231)	1.807 (5)
N(2)-N(1)	1.201 (7)	B-F(1)	1.316 (13)
N(2)-C(11)	1.404 (8)	B-F(2)	1.325 (12)
C(1)-O(1)	1.138 (8)	B-F(3)	1.437 (13)
C(2)-O(2)	1.141 (8)	B-F(4)	1.263 (14)
P(1)-C(111)	1.817 (4)		
	Intramolecular Nonbonded Distances		
N(1)-H(12)	2.62	P(2)-C(1)	2.867 (8)
N(1)-C(11)	2.304 (8)	P(2)-C(2)	2.927 (8)
N(2)-H(12)	2.68	P(2)-N(1)	2.815 (6)
N(2)-H(16)	2.56	N(1)-C(1)	3.204 (11)
P(1)-C(1)	2.873 (8)	N(1)-C(2)	3.026 (10)
P(1)-C(2)	2.909 (8)	C(1)-C(2)	2.892 (12)
P(1)-N(1)	2.834 (6)		
	Bond Angles		
N(1)-Fe-C(2)	121.4 (3)	F(2)-B-F(4)	113.4 (13)
N(1)-Fe-C(1)	131.0 (3)	F(3)-B-F(4)	105.8 (10)
N(1)-Fe-P(1)	90.15 (18)	F(1)-B-F(2)	110.6 (9)
N(1)-Fe-P(2)	89.19 (18)	F(1)-B-F(3)	107.9 (10)
C(2)-Fe-C(1)	107.6 (3)	F(2)-B-F(3)	104.3 (10)
C(2)-Fe-P(1)	91.6 (2)	Fe-P(1)-C(131)	110.6 (2)
C(2)-Fe-P(2)	92.2 (2)	Fe-P(1)-C(121)	112.7 (2)
C(1)-Fe-P(1)	88.9 (2)	Fe-P(1)-C(111)	116.6 (2)
C(1)-Fe-P(2)	88.5 (2)	C(111)-P(1)-C(121)	105.3 (2)
P(1)-Fe-P(2)	175.85 (8)	C(111)-P(1)-C(131)	105.4 (2)
Fe-C(1)-O(1)	175.1 (7)	C(121)-P(1)-C(131)	105.4 (2)
Fe-C(2)-O(2)	174.5 (7)	Fe-P(2)-C(211)	110.8 (2)
Fe-N(1)-N(2)	179.2 (5)	Fe-P(2)-C(221)	117.6 (2)
N(1)-N(2)-C(11)	124.2 (6)	Fe-P(2)-C(231)	110.1 (2)
N(2)-C(11)-C(12)	123.2 (4)	C(211)-P(2)-C(221)	105.2 (2)
N(2)-C(11)-C(16)	116.7 (4)	C(211)-P(2)-C(231)	107.0 (2)
F(1)-B-F(4)	114.1 (11)	C(221)-P(2)-C(231)	105.5 (2)
	Dihedral Angles		
N(1)-C(1)-C(2) O(1)-C(1)-Fe	6 (8)[a]	P(1)-C(111)-C(112) C(111)-Fe-P(1)	34.9 (4)
Fe-C(2)-O(2) N(1)-C(1)-C(2)	2 (7)[a]	P(1)-C(122)-C(121) Fe-C(121)-P(1)	73.4 (4)
N(1)-C(1)-C(2) N(2)-N(1)-Fe	3 (38)[a]	P(1)-C(132)-C(131) Fe-C(131)-P(1)	42.5 (4)
N(1)-C(11)-N(2) Fe-N(2)-N(1)	5 (39)[a]	Fe-P(2)-C(211) P(2)-C(211)-C(212)	66.5 (4)
N(2)-C(12)-C(11) N(1)-C(11)-N(2)	6.2 (9)	Fe-P(2)-C(221) P(2)-C(221)-C(226)	29.4 (5)
C(11)-N(1)-N(2) C(1)-N(1)-C(2)	2.1 (6)	Fe-P(2)-C(231) P(2)-C(231)-C(232)	52.0 (4)
C(11)-C(12)-C(16) C(2)-N(1)-C(1)	7.2 (3)		

[a] Large errors result from the near collinearity of Fe–C–O or Fe–N–N; these values are tabulated in order to indicate the direction of the bending about C(1), C(2), and N(1).

is lost during substitution reactions, the same steric repulsions (assuming no radical change in the conformation of the phosphine phenyl groups) would result when Cl^- had replaced CO. More important in this respect, however, are the larger d orbitals and greater basicity of Ru(0) and Os(0), both of which stabilize the $M^{II}(PhN_2^-)$ formulations over the analogous Fe(0) compounds.

One set of authors reported the title complex to be paramagnetic[15] while another reported it to be diamagnetic.[14] Using a Faraday balance, we determined that many of our own samples were paramagnetic (~0.6 BM). However, very careful recrystallization resulted in a diamagnetic product. Indeed, only by growing large single crystals and carefully selecting them by hand could a diamagnetic product be obtained. This diamagnetism is consistent with the formulation of the iron–aryldiazo complex as one containing Fe(0).

The Mössbauer spectra of $Fe(CO)_3P_2$, $Fe(CO)_2(NO)P_2^+$, and $Fe(CO)_2(N_2Ph)P_2^+$ do not lend themselves to ready interpretation. The isomer shifts (δ) increase along the series and the quadrupole splittings ($|\Delta|$) dramatically decrease. The aryldiazo complex has one of the smallest Δ values for a trigonal-bipyramidal complex.[14,15] Although we suggested previously that PhN_2 is a better π acceptor than NO,[8] we now suggest that the relationship between linear NO and singly bent RN_2 ligands is the same as that between CO and N_2, namely, that (1) RN_2 is a very good π acceptor but not quite so good as NO and (2) that PhN_2 is a much poorer σ donor than NO. The result is that the diazo ligand is better at reducing the total electron density on the metal although NO is better at reducing the π-electron density on the metal. We believe that this suggestion is more in harmony with infrared (relative values of ν(CO)), nuclear magnetic resonance[32] (σ values for ^{19}F), and Mössbauer[14,15] (σ values) spectroscopic data. Furthermore, this view is consistent with the observation that NO^- has a stronger trans-weakening influence than PhN_2^-.

$$IrCl(CO)(N_2Ph)(PPh_3)_2^+ + Cl^- \rightarrow IrCl_2(CO)(N_2Ph)(PPh_3)_2{}^{8}$$

$$IrCl(CO)(NO)(PPh_3)_2^+ + Cl^- \rightarrow \text{no reaction}^{47}$$

Thus, $OsCl(CO)(NO)P_2$, $OsCl(CO)(N_2Ph)P_2$, and $OsCl(CO)_2(N_2Ph)P_2$ are all known, but not the six-coordinate osmium dicarbonyl nitrosyl. Apparently in five-coordinate complexes, the NO^+ (18 electron) → NO^- (16 electron) transformation is frequently incomplete, and the addition of a sixth ligand is usually energetically unfavorable; but because the diazo ligand more effectively reduces the total electron density on the metal, this transformation is more facile, and the addition of the sixth ligand to the N_2Ph^- (16 electron) system is favored.

Since we describe the iron–aryldiazo complex as containing Fe(0), it is appropriate to discuss briefly the utility of formal oxidation states for complexes which contain aryldiazo or similar nitrogen ligands that can form multiple bonds with transition metals. Five-coordinate, low-spin complexes are usually trigonal bipyramidal when the central metal has a d^8 or d^{10} configuration and they are usually square-pyramidal when the metal is d^4 or d^6. Similarly, four-coordinate, low-spin complexes are tetrahedral when the metal is d^0 or d^{10}, but they are square-planar when the metal is d^2, d^4, d^6, or d^8.[48] Although it is not necessary to assign oxidation states to metals or ligands for the purpose of determining whether the EAN (18-electron) rule is obeyed, it is necessary to do so in order to determine the formal electronic configuration of the metal. Although several systems for assigning oxidation states exist, we favor that system which gives one pair of bonding electrons to the metal in metal–nitrogen double and triple bonds. We now illustrate the utility of this system.

If one considers the linear nitrosyl ligand to be NO^+, then $Ir(CO)(NO)(PPh_3)_2$,[41] $Ir(NO)_2(PPh_3)_2^+$,[49] $Os(NO)_2(PPh_3)_2$,[46] and $Ni(N_3)(NO)(PPh_3)_2$[50] contain d^{10} metals and are pseudotetrahedral, while $CoCl_2(NO)(PMePh_2)_2$,[40] $Mn(CO)_2(NO)(PPh_3)_2$,[37] and $Ru(NO)(diphos)_2^+$ [51] contain d^8 metals and are trigonal bipyramidal. If one considers a bent nitrosyl ligand to be NO^-, then $IrCl_2(NO)(PPh_3)_2$,[52] $IrCl(CO)(NO)(PPh_3)_2^+$,[53] and $Os(OH)(NO)(NO)(PPh_3)_2^+$ [54] contain d^6 metals and are square pyramidal. This same formalism may also be applied successfully to aryldiazo complexes. The complexes $RhCl(NNAr)(ppp)^+$ [6] (Rh(III)) and $PtCl(NNAr)(PEt_3)_2$[55] (Pt(II)) contain the doubly bent ArN_2^- ligand and, as expected, possess square-pyramidal and square-planar geometries, respectively. In contrast the present Fe(0) complex, $Fe(CO)_2(NNAr)(PPh_3)_2^+$, contains a singly bent ArN_2^+ ligand and is trigonal bipyramidal. Although the

Table VI. Bond Distances (Å) in Mononuclear Iron–Carbonyl–Phosphine Complexes

Compd[a]	Fe–P	Fe–C	P–C	C–O
$FeCp(C_4H_3S)(CO)(PPh_3)$[g]	2.22 (1)	1.75 (3)	1.83 (3)[b]	1.14 (4)
$FeCpPh(CO)(PPh_3)$[h]	2.23 (1)	1.78 (2)	1.83 (2), 1.84 (2), 1.84 (2)	1.18 (4)
$FeI(C_3H_5)(CO)(PPh_3)$[i]	2.23 (1)	1.77 (2), 1.79 (2)	1.85 (2)[b]	1.18 (3), 1.19 (3)
$Fe(CO)_3(P_2C_3H_6O_3)_2$[e,j]	2.190 (4)	1.81 (1), 1.78 (2)	1.80 (1), 1.82 (1)	1.15 (1), 1.15 (2)
$Fe(CO)_2(Ph_2P(C_8H_7))_2$[f,k]	2.238 (3)	1.73 (1), 1.77 (1)	. . .[c]	1.15 (3), 1.19 (3)
$Fe(CO)_4(PHPh_2)$[d,l]	2.237 (2)	1.803 (9), 1.787 (9), 1.789 (9)	1.820 (6), 1.819 (7)	1.16 (1), 1.16 (1), 1.15 (1)
$(CO)_4Fe(Ph_2PPPh_2)Fe(CO)_4$[d,m]	2.260 (5)	1.78 (2), 1.78 (2), 1.79 (2)	1.82 (2), 1.82 (2)	1.14 (2), 1.17 (2), 1.18 (2)
$[Fe(CO)_2(N_2Ph)(PPh_3)_2][BF_4]$[n]	2.261 (2), 2.266 (2)	1.818 (9), 1.767 (9)	1.807 (5)–1.817 (4)	1.138 (8), 1.141 (8)

[a] Abbreviations used: $Ph = C_6H_5$, $Cp = C_5H_5$. [b] Average value reported. [c] Value not reported. [d] Data for axial carbonyl ligands omitted. [e] Data for phosphite ligand omitted. [f] Data for chelating phosphine ligand omitted. [g] V. G. Andrianov, G. N. Sergeeva, Y. T. Struchkov, K. N. Anisimov, N. E. Kolohova, and A. S. Beschastnov, *J. Struct. Chem.* (*USSR*), **11**, 163 (1970). [h] V. A. Semion and Y. T. Struchkov, *ibid.*, 10, 80 (1969). [i] M. K. Minasyants, V. G. Andrianov, and Y. T. Struchkov, *ibid.*, 9, 939 (1968). [j] D. A. Allison, J. Clardy, and J. G. Verkade, *Inorg. Chem.*, **11**, 2804 (1972). [k] M. A. Bennett, G. B. Robertson, I. B. Tomkins, and P. O. Whimp, *Chem. Commun.*, 341 (1971). [l] B. T. Kilbourn, U. A. Raeburn, and D. T. Thompson, *J. Chem. Soc. A*, 1906 (1969). [m] J. A. J. Jarvis, R. H. B. Mais, P. G. Owston, and D. T. Thompson, *ibid.*, 622 (1968). [n] This work.

Table VII. Bond Angles and Distances for Singly Bent Aryldiazo Ligands

Compd[a]	M–N[b]	N–N	N–C	N–N–C[c]	M–N–N
$ReCl_2(N_2Ph)(PPhMe_2)_3$[d]	1.77 (2)	1.23 (2)	1.43 (2)	119 (2)	173 (2)
$Mo(HBPz_3)(CO)_2(N_2Ph)$[e]	1.825 (4)	1.211 (6)	1.432 (17)	121.1 (2)	174.2 (1)
$[Fe(CO)_2(N_2Ph)(PPh_3)_2][BF_4]$[f]	1.702 (6)	1.201 (7)	1.404 (8)	124.2 (6)	179.2 (5)
$RuCl_3(N_2To)(PPh_3)_2$[g]	1.784 (5)	1.158 (6)	1.376 (6)	137.1 (5)	171.9 (5)

[a] Abbreviations used: $Ph = C_6H_5$, $Me = CH_3$, To = p-$CH_3C_6H_4$, $Pz = C_3H_3N_2$, M = metal. [b] Distances given in angstroms. [c] Angles given in degrees. [d] Reference 5. [e] Reference 11. [f] This work. [g] B. L. Haymore and J. A. Ibers, unpublished work. See also ref 12.

nitrido ligand is traditionally described as a trinegative ligand, this system makes it a uninegative ligand. Thus using this system the complexes $ReN(S_2CNEt_2)_2$,[56] $ReNCl_2(PPh_3)_2$,[57] $RuNCl_4^-$,[58] and $OsNCl_4^-$ [58] contain d^4 metals, which is consistent with their having square-pyramidal geometries.

All oxidation state formalisms are to some extent artificial, especially when the complexes being considered contain strong π-bonding ligands. Nevertheless the present system has particular utility. As a final example, the complexes $ReCl_2(NO)(PPh_3)_2$[59] and $Fe(CO)(NO)(NNAr)(PPh_3)$[45] have high enough values of $\nu(NO)$ and $\nu(NN)$ to expect that they contain a linear nitrosyl and a singly bent aryldiazo ligand, respectively. From the resulting d^6 and d^{10} configurations we then expect that the respective geometries will be square pyramidal and pseudotetrahedral.

In conclusion we believe that further structural, synthetic, and magnetic studies of aryldiazo, nitrosyl, and related ligands will prove valuable for the understanding of the nature of dinitrogen and diazo ligands and will further our knowledge of metal–nitrogen bonding.

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Registry No. $[Fe(CO)_2(N_2C_6H_5)(P(C_6H_5)_3)_2][BF_4]$, 41830-38-0.

Supplementary Material Available. Table IV, the root-mean-square amplitudes of vibration, and the table of observed and calculated structure 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 $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC40639Q.

References and Notes

(1) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 300 (1966).
(2) G. W. Parshall, *J. Am. Chem. Soc.*, **89**, 1822 (1967).
(3) J. Chatt, G. A. Heath, and G. J. Leigh, *J. Chem. Soc., Chem. Commun.*, 444 (1972); J. Chatt, J. R. Dilworth, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 612 (1973).
(4) J. Chatt, G. A. Heath, N. E. Hooper, and G. J. Leigh, *J. Organomet. Chem.*, **57**, C67 (1973).
(5) V. F. Duckworth, P. G. Douglas, R. Mason, and B. L. Shaw, *Chem. Commun.*, 1083 (1970); R. Mason, K. M. Thomas, J. A. Zubieta, P. G. Douglas, A. R. Galbraith, and B. L. Shaw, *J. Am. Chem. Soc.*, **96**, 260 (1974).
(6) A. P. Gaughan, Jr., B. L. Haymore, J. A. Ibers, W. H. Myers, T. E. Nappier, and D. W. Meek, *J. Am. Chem. Soc.*, **95**, 6859 (1973).
(7) K. R. Laing, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 2713 (1973).
(8) B. L. Haymore and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 3052 (1973).
(9) Abbreviations used: $Ph = C_6H_5$, $Me = CH_3$, $Pz = C_3N_2H_3$, $Cp = C_5H_5$, diphos = $Ph_2PCH_2CH_2PPh_2$, M = metal, P = tertiary phosphine, To = p-$CH_3C_6H_4$, Et = C_2H_5.
(10) B. L. Haymore, Abstracts, 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973, No. INOR-64.
(11) G. Avitable, P. Ganis, and M. Nemiroff, *Acta Crystallogr., Sect. B*, **27**, 725 (1971).
(12) J. A. McArdle, A. J. Schultz, B. J. Corden, and R. Eisenberg, *Inorg. Chem.*, **12**, 1676 (1973). An independent structural determination of this complex in this laboratory is in good agreement with that of this reference.
(13) E. W. Abel, G. A. Burton, M. R. Churchill, and K. G. Lin, *J. Chem. Soc., Chem. Commun.*, 268 (1974).
(14) W. E. Carroll and F. J. Lalor, *J. Chem. Soc., Dalton Trans.*, 1754 (1973).
(15) D. R. Fisher and D. Sutton, *Can. J. Chem.*, **51**, 1697 (1973).
(16) A. F. Clifford and A. K. Mukherjee, *Inorg. Syn.*, **8**, 185 (1966).
(17) A. I. Vogel, "Practical Organic Chemistry", 3rd ed, Longmans, Green and Co., New York, N.Y., 1956, p 609.
(18) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).
(19) The Northwestern absorption program, AGNOST, includes the Coppens–Leiserowitz–Rabinovich logic for gaussian integration. In addition to various local programs for the CDC 6400 computer, modified versions of the following programs were employed: Zalkin's FORDAP Fourier summation program, Johnson's ORTEP thermal ellipsoid plotting program, Busing and Levy's error function program, and Lawton's TRACER cell reduction program. Our full-matrix, least-squares program, NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program.
(20) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2A. For hydrogens atoms, see R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965). For $\Delta f'$ and $\Delta f''$ for Fe and P, see D. T. Cromer and D. Liberman, *ibid.*, **53**, 1891 (1970).
(21) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).
(22) Supplementary material.

(23) For reasons which are not clear, the metal–carbon distances for the two carbonyl ligands in $Mo(HBPz_3)(CO)_2(N_2Ph)$ are also different by 0.047 (8) Å.

(24) C. P. Brock and J. A. Ibers, *Acta Crystallogr., Sect. B*, **29**, 2426 (1973), and references therein.

(25) C. J. Brown, *Acta Crystallogr.*, **21**, 146, 153 (1966).

(26) G. R. Davies, J. A. Jarvis, B. T. Kilbourn, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A*, 1275 (1970).

(27) L. F. Dahl, E. R. deGil, and R. D. Feltham, *J. Am. Chem. Soc.*, **91**, 1653 (1969).

(28) V. G. Albano, A. Araneo, P. L. Bellon, G. Ciani, and M. Manassero, *J. Organomet. Chem.*, **67**, 413 (1974).

(29) W. Harrison and J. Trotter, *J. Chem. Soc. A*, 1542 (1971).

(30) C. Romming and T. Tjornhom, *Acta Chem. Scand.*, **22**, 2934 (1968); C. Romming, *ibid.*, **17**, 1444 (1963).

(31) G. C. Hampson and J. M. Robertson, *J. Chem. Soc.*, 409 (1941).

(32) D. Sutton, *Can. J. Chem.*, **52**, 2634 (1974); W. E. Carroll, M. E. Deane, and F. J. Lalor, *J. Chem. Soc., Dalton Trans.*, 1837 (1974).

(33) This value is for the bis(phosphine)ammine complex, not for the tris(phosphine) complex: R. Mason and B. L. Shaw, personal communication.

(34) W. E. Carroll, F. A. Deeney, and F. J. Lalor, *J. Chem. Soc., Dalton Trans.*, 1430 (1974).

(35) J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, **8**, 419 (1969).

(36) G. R. Clark, K. R. Grundy, W. R. Roper, J. M. Waters, and K. R. Whittle, *J. Chem. Soc., Chem. Commun.*, 119 (1972).

(37) J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, **6**, 1575 (1967).

(38) In contrast, there are some very similar complexes which are square pyramidal with nonlinear nitrosyl ligands, $IrCl(CO)(NO)P_2^+$, $RuCl(NO)_2P_2^+$, $IrCl_2(NO)P_2$, etc: B. A. Frenz and J. A. Ibers, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Phys. Chem., Ser. One*, **11**, 33 (1972).

(39) D. Hall and R. B. Williamson quoted by K. R. Laing and W. R. Roper, *J. Chem. Soc. A*, 2149 (1970).

(40) C. P. Brock, J. P. Collman, G. Dolcetti, P. H. Farnham, J. A. Ibers, J. E. Lester, and C. A. Reed, *Inorg. Chem.*, **12**, 1304 (1973).

(41) C. P. Brock and J. A. Ibers, *Inorg. Chem.*, **11**, 2812 (1972).

(42) V. Albano, P. L. Bellon, and G. Ciani, *J. Organomet. Chem.*, **38**, 155 (1972).

(43) G. Gilli, M. Sacerdoti, and G. Reichenbach, *Acta Crystallogr., Sect. B*, **29**, 2306 (1973).

(44) S. Holt, quoted in ref 11.

(45) W. E. Carroll and F. J. Lalor, *J. Organomet. Chem.*, **54**, C37 (1973).

(46) B. L. Haymore and J. A. Ibers, submitted for publication.

(47) With a large excess of halide ion, there appears to be a reversible color change, but only the starting materials could be isolated. No reaction occurs at room temperature, but in refluxing ethanol small amounts of $IrCl_2(NO)(PPh_3)_2$ are produced with the apparent loss of CO.

(48) R. G. Pearson, *J. Am. Chem. Soc.*, **91**, 1252, 4947 (1969); B. A. Frenz and J. A. Ibers, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Phys. Chem., Ser. One*, **11**, 33 (1972).

(49) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **9**, 1105 (1970).

(50) J. H. Enemark, *Inorg. Chem.*, **10**, 1952 (1971).

(51) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **12**, 199 (1973).

(52) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1035 (1971).

(53) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968).

(54) J. M. Waters and K. R. Whittle, *Chem. Commun.*, 518 (1971).

(55) S. Krogsrud, S. D. Ittel, and J. A. Ibers, Abstracts, American Crystallographic Association Summer Meeting, University Park, Pa., Aug 1974, No. E7.

(56) S. R. Fletcher and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1079 (1972).

(57) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

(58) S. R. Fletcher, W. P. Griffith, D. Pawson, F. L. Phillips, and A. C. Skapski, *Inorg. Nucl. Chem. Lett.*, **9**, 1117 (1973).

(59) R. W. Adams, J. Chatt, N. E. Hooper, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1075 (1974).

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Structural Characterization of a Chloride-Bridged Lanthanide Cyclopentadienyl Dimer, $[Yb(C_5H_4CH_3)_2Cl]_2$

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The structure of $[Yb(C_5H_4CH_3)_2Cl]_2$ has been determined from three-dimensional X-ray diffraction data collected by counter methods. The molecular unit is a dimer which is located about a crystallographic inversion center with a Yb–Yb distance of 3.979 (1) Å. The five cyclopentadienyl carbon atoms of each ring form a plane equidistant from the Yb atom with an average Yb–C distance of 2.585 (7) Å. The coordination about the ytterbium ions is distorted tetrahedral; the bridging unit is symmetrical and approximately square with an average Yb–Cl distance of 2.64 Å and a Yb–Cl–Yb angle of 97.95 (5)°. Orange-red platelets crystallized from benzene conform to space group $C2/c$ with $a = 20.377$ (6) Å, $b = 9.185$ (2) Å, $c = 13.235$ (4) Å, $\beta = 108.97$ (2)°, $Z = 4$, and $\rho_{\text{calcd}} = 2.08$. A total of 7786 reflections were collected of which 2751 independent reflections with $F^2 > 3\sigma(F^2)$ were used in the final refinement by full-matrix least-squares methods to give weighted and unweighted R factors of 3.69 and 3.46%, respectively.

Introduction

Interest in the organometallic compounds of the lanthanides and actinides has expanded rapidly in recent years.[2] Possible applications as chemical shift reagents[3] or homogeneous catalysts in organic reactions have contributed to this interest.[4] Although the chemistry of π-carbocyclic complexes of f transition metals is now extensive, the nature of the bonding in these compounds and the extent of involvement of the f electrons are still in question. The synthesis of lanthanide dicyclopentadienyl chlorides and related phenoxy and carboxylate derivatives by Maginn, Manastyrskyj, and Dubeck[5] stands out both because of the fact that these compounds appear to be somewhat more stable than the parent tricyclopentadienides and because of the suggestion by Dubeck that these complexes may be dimeric in noncoordinating solvents. This latter supposition was particularly intriguing because, if true, it would allow a unique opportunity to study the magnetic interaction between two isolated f-series paramagnetic ions in close proximity. Furthermore, as a dimeric cerium complex containing the cyclooctatetraene ligand is already known,[6,7] the effect of changing the bridging group and/or carbocyclic ligand could be examined. The only other previous study of relevance has been of a scandium dimer[8] which, while structurally similar, contains no f electrons. Thus a single-crystal X-ray diffraction study of the ytterbium member of the lanthanide bis(methylcyclopentadienyl) chloride series was undertaken. The ytterbium member of the series was chosen because of its f^{13} configuration. The methyl-substituted cyclopentadienyl complex was used because of its greater solubility in benzene and because of the fact that we wanted to reduce rotation of the cyclopentadienyl rings in the solid.

Experimental Section

Crystals of $[Yb(C_5H_4CH_3)_2Cl]_2$ suitable for diffraction analysis were grown using a modification[9] of the literature preparation[5] of the monomer followed by slow, controlled evaporation from benzene. Several crystals were sealed in thin-walled glass capillaries under a nitrogen atmosphere. A series of precession photographs exhibited