Journal of Organometallic Chemistry, 127 (1977) 223—236
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

PREPARATION AND STRUCTURAL CHARACTERIZATION OF $[Fe_3(h^5\text{-}C_5H_5)_3(CO)_5As_4O_5]^+BF_4^-$: AN UNUSUAL TRANSITION METAL DERIVATIVE OF As_4O_6

CHARLES F. CAMPANA *, J. DOUGLAS SINCLAIR ** and LAWRENCE F. DAHL*
Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706 (U.S.A.)

(Received July 14th, 1976)

Summary

The reaction of arsenic trifluoride with a *m*-xylene solution of cyclopentadienyliron dicarbonyl dimer contained in a Pyrex-glass vessel has unexpectedly produced the tetrafluoroborate salt of the highly unusual $[Fe_3(h^5\text{-}C_5H_5)_3(CO)_5As_4O_5]^+$ monocation. An X-ray diffraction analysis has elucidated unequivocally both the stoichiometry and atomic arrangement of this compound in complete harmony with its physical and chemical properties. The diamagnetic monocation may be envisioned as arising from the cubic T_d bird-cage As_4O_6 molecule through the replacement of one of its six edge-bridged oxygen atoms with an iron-bridged $[Fe(h^5\text{-}C_5H_5)(CO)]^+$ species together with the concomitant addition of a terminal one-electron donating $[Fe(h^5\text{-}C_5H_5)(CO)_2]$ ligand to each of the two iron-bridged arsenic atoms in order for them to maintain a closed-shell electronic configuration. The resulting $[As_4O_5Fe]$ core closely conforms to C_{2v}-$2mm$ symmetry, while the entire monocation has an approximate mirror plane. A salient structural feature is that there is no appreciable structural influence on the As_4O_6 architecture due to this formal transmutation into the monocation other than an increase of 0.06 Å along the iron-bridged edge of the nonbonded tetrahedron of arsenic atoms. The orange-red compound crystallizes with four monocations and four BF_4^- anions in a monoclinic unit cell of $P2_1/c$ symmetry with $a = 15.571(3)$, $b = 14.800(3)$, $c = 15.389(3)$ Å, and $\beta = 126.176(6)°$. The crystal structure has been refined to a final unweighted R_1 value of 4.5% for 2400 independent diffractometry-collected data with $I \geqslant 2.0\ \sigma(I)$.

Introduction

Recent synthetic and structural studies in our laboratories [1] of a number of cubane-like $[M_4(h^5\text{-}C_5H_5)_4(\mu_3\text{-}X)_4]^n$ complexes have been directed primarily to-

---

* Present address: Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131 (U.S.A.).
** Present address: Bell Laboratories, Holmdel, New Jersey 07733 (U.S.A.).

ward a stereochemical systemization concerning the detailed nature of the metal—metal interactions in a given central M_4X_4 core. A qualitative molecular orbital model [2] has demonstrated that the observed differences in geometry among members of this intriguing family of tetramers may be satisfactorily accounted for on the basis of the number of electrons in the so-called metal cluster orbitals. In particular, this MO scheme assumes that a cubane-like $[M_4(h^5\text{-}C_5H_5)_4(\mu_3\text{-}X)_4]^n$ complex has six bonding and six higher-energy, antibonding metal cluster orbitals such that a 12-electron system (with twelve bonding and zero antibonding electrons directly involved in the tetrametal interactions) possesses a completely bonding metal tetrahedron of total bond order six, while a 24-electron system (with twelve bonding and twelve antibonding electrons) has a completely nonbonding metal tetrahedron of total bond order zero. The 13- to 23-electron systems, which with partial occupancy of the antibonding metal cluster orbitals correspond to intermediate tetrametal bonding representations possessing a total limiting metal—metal valence bond order between six and zero, are predicted via application of first-order Jahn—Teller effect to produce certain vibronically-allowed distortions in the normally idealized cubic T_d geometry of the M_4X_4 core. To date, cubane-like $[M_4(h^5\text{-}C_5H_5)_4(\mu_3\text{-}X)_4]^n$ complexes have been prepared and structurally characterized for neutral 12- [1a—1c], 20- [1d—1h], and 24-electron [1i] molecules as well as for the oxidized 18- [1j], 19- [1k], and 23-electron [1i] species.

The work reported here is an outgrowth of our research designed to prepare and structurally analyze the cubane-like $Fe_4(h^5\text{-}C_5H_5)_4(\mu_3\text{-}As)_4$ molecule as a representative member of the as yet unknown 16-electron metal cluster system. The recent syntheses and structural determinations of the $[Ni_4(h^5\text{-}C_5H_5)_4(\mu_3\text{-}As)_3]^+BF_4^-$ [3], $Fe_3(CO)_9(\mu_3\text{-}As)_2$ [4], and $[Co_4(h^5\text{-}C_5H_5)_4(\mu_3\text{-}As)_4]$ [1f] complexes provided examples of metal clusters in which "bare" arsenic atoms serve as bridging ligands coordinated to three transition metal atoms. Since these complexes were prepared by the reaction of arsenic trihalides with iron pentacarbonyl, nickelocene and cyclopentadienylcobalt dicarbonyl, respectively, it was thought that the reaction of cyclopentadienyliron dicarbonyl dimer with arsenic trifluoride might provide a convenient route to the preparation of $Fe_4(h^5\text{-}C_5H_5)_4(\mu_3\text{-}As)_4$. Although this reaction did not yield the desired cyclopentadienyliron—arsenic tetramer, a new type of organo(transition metal)—arsenic complex was isolated. This paper presents the synthesis and structural characterization of $[Fe_3(h^5\text{-}C_5H_5)_3(CO)_5As_4O_5]^+BF_4^-$, which is believed to be the first organometallic derivative of As_4O_6.

Experimental

Preparation and properties

30 ml of anhydrous arsenic trifluoride (ROC/RIC Chemical Co.) were added to a *m*-xylene solution of 10 g of cyclopentadienyliron dicarbonyl dimer (Strem Chemical Co.) in a Pyrex glass reaction vessel at 80°C under a nitrogen atmosphere. The solution was heated to 110°C and maintained at that temperature for 12 h with continuous stirring, from which the formation of an orange-red precipitate resulted. The solution was filtered and the residue washed with pentane and then dissolved in dichloromethane. The addition of small amounts of pentane precipitated a yellow powder. This sample, which exhibited carbonyl

stretching frequencies (Beckman IR-8; dichloromethane solution) at 1858 w, 1902 s, and 1950 s cm^{-1}, was not further characterized.

An infrared spectrum of the remaining red dichloromethane solution exhibited carbonyl stretching frequencies at 1955 s, 2000 s, and 2040 s cm^{-1} as well as bands indicating the presence of cyclopentadienyl and BF_4^- groups. A solid-state (KBr pellet) infrared spectrum of the purified residue displayed nearly identical bands. An EPR measurement (Varian E-3) gave no resonance, while a proton NMR spectrum (Varian HA-100) showed two sharp singlets at δ 5.45 and 5.10 ppm in a 2 : 1 ratio corresponding to two different types of cyclopentadienyl protons. Although independent elemental analyses yielded highly varying percentages of iron, arsenic, carbon, hydrogen, and fluorine, one analysis indicated an iron-to-arsenic ratio of 3 : 4 *. The actual stoichiometry as well as the structure of $[Fe_3(h^5\text{-}C_5H_5)_3(CO)_5As_4O_5]^+BF_4^-$ was established by an X-ray diffraction examination. Crystals suitable for an X-ray analysis were grown by a slow evaporation of a chloroform/heptane solution at —10°C.

Single crystal data collection

An orange needle-shaped crystal with approximate dimensions of 0.06 mm × 0.60 mm × 0.20 mm in the [100], [010], and [201] directions, respectively, was used to collect the intensity data. The crystal was glued to the end of a thin glass fiber with epoxy cement, sealed in an argon-filled Lindemann glass capillary and mounted such that the unique axis of a monoclinic unit cell was parallel to the goniometer axis. Preliminary oscillation and Weissenberg photographs exhibited monoclinic $C_{2h}\text{-}2/m$ Laue symmetry. The observed systematic absences of $l = 2n + 1$ for $\{h0l\}$ and of $k = 2n + 1$ for $\{0k0\}$ uniquely indicated the space group $P2_1/c$ (C_{2h}^5, No. 14), which was confirmed by the successful refinement of the structure.

The crystal was transferred to a General Electric XRD-6 Datex-controlled diffractometer equipped with a full-circle E & A goniometer. After careful optical and X-ray alignment of the crystal, 21 reflections were manually centered and used in least-squares refinement to determine the lattice constants of $a = 15.571(3)$, $b = 14.800(3)$, $c = 15.389(3)$ Å and $\beta = 126.176(6)°$. Diffractometer angle settings for the collection of intensity data were obtained from the refined lattice parameters and instrument orientation parameters. Intensity data were collected by the $\theta - 2\theta$ scan technique at a take-off angle of 2° with constant speeds of 2°/min in 2θ. Symmetric scan widths of 2.5° in 2θ were used for $5° \leqslant 2\theta \leqslant 10°$, 2.0° for $10° < 2\theta \leqslant 20°$, and 1.5° for $20° < 2\theta \leqslant 45°$. (Stationary crystal) — (stationary counter) background measurements were done for 20 sec at both extremes of each scan range. Zirconium-filtered Mo-K_α radiation (with λ 0.71069 Å) was used with a scintillation detector, followed by a

---

* Microanalyses by two different commercial laboratories on the same sample inexplicably gave widely differing results. (Found: Fe, 18.15; As, 11.88; C, 31.10; H, 2.36; B, 3.66; F, 14.83 vs Fe, 23.28 (23.33); As, 43.56 (37.01); C, 18.36 (19.45); H, 1.63 (1.44); F, (5.20), where the latter values in parentheses are those from a second sample. $Fe_3As_4C_{20}H_{15}O_{10}BF_4$ calcd.: Fe, 17.28; As, 30.92; C, 24.78; H, 1.56; O, 16.50; B, 1.12; F, 7.84%). Of importance is that the microanalyses at least established the presence of the above elements in harmony with the composition unequivocally obtained from the structural determination. The immense power of the X-ray diffraction method to analyze unambiguously in most cases both the constitution and atomic arrangement of crystalline compounds is clearly illustrated, especially here for an unexpected reaction product.

pulse-height analyzer adjusted to accept about 90% of the Mo—K_α pulse distribution. Intensity data from ca. 3700 nonsystematically-absent reflections were measured twice for an asymmetrical hkl, $\bar{h}kl$ unit of the reciprocal lattice. Four standard reflections, measured every 100 reflections, showed similar linear decreases in intensities by ca. 5% over the total data collection time; hence, a linear decay correction of the data was made. After correction of the data for background and Lorentz-polarization effects, structure factor amplitudes and corresponding standard deviations were obtained in a manner described elsewhere [5] *. Equivalent reflections were merged to yield 2400 independent reflections with $I \geqslant 2\sigma(I)$. The data were corrected for absorption effects on the basis of a calculated linear absorption coefficient, μ, of 64.64 cm^{-1} for Mo-K_α radiation with extreme values of the transmission coefficients ranging from 0.29—0.68.

The experimental density of 2.25 g/cm^3 measured by the flotation method is in accord with a value of 2.23 g/cm^3 calculated for a unit cell volume of 2862 $Å^3$ containing four $[Fe_3(h^5\text{-}C_5H_5)_3(CO)_5As_4O_5]^+BF_4^-$ formula species. All atoms occupy the general fourfold set of positions (4e): $\pm(x, y, z; x, 1/2 - y, 1/2 + z)$. The total number of electrons in the unit cell, $F(000)$, is 1544.

Structural determination and refinement

The approximate positions of the four arsenic and three iron atoms were determined from an interpretation of a Patterson map, and the coordinates of the remaining nonhydrogen atoms were obtained from subsequent Fourier syntheses. The structure was refined by least squares to values of R_1 13.2 and R_2 14.8% with positions and isotropic temperature factors for all nonhydrogen atoms being varied. At this point, hydrogen atoms were fitted to each cyclopentadienyl ring in idealized positions; least-squares refinement was then carried out with anisotropic thermal parameters utilized for all nonhydrogen atoms along with fixed-atom contributions from the cyclopendadienyl hydrogen atoms, for which isotropic temperature factors were assigned and new idealized coordinates were calculated from the new coordinates of the carbon atoms after several least-squares cycles. At convergence the final discrepancy values were R_1 4.5 and R_2 5.1% with no Δ/σ values greater than 0.9 and with a final goodness-of-fit value of 1.34 **. A final Fourier difference map showed no unusual features with the largest peak maximum being 1.2 $e^-/Å^3$. The atomic scattering factors for all nonhydrogen atoms are from Cromer and Mann [6a], while those for hydrogen atoms are from Stewart, et al. [6b]. Real and imaginary corrections for anomalous dispersion (viz., $\Delta f'$ 0.4, $\Delta f''$ 1.0 for Fe; $\Delta f'$ 0.1, $\Delta f''$ 2.2 for As) [7] were included in the calculations.

The positional and thermal parameters from the output of the full-matrix least-squares cycle are given in Table 1 ***. Interatomic distances and bond angles

(continued on p. 231)

---

* The programs utilized for the data collection and reduction, the structural determination and refinement and error analyses are given elsewhere [5], if not otherwise referenced.

** $R_1 = (\Sigma ||F_o| - |F_c|| / \Sigma |F_o|) \times 100$ and $R_2 = (\Sigma \omega_i ||F_o| - |F_c||^2 / \Sigma \omega_i |F_o|^2)^{1/2} \times 100$. All least-squares refinements were based on the minimization of $\Sigma \omega_i ||F_o| - |F_c||^2$ with individual weights $\omega_i = 1/\sigma(|F_o|)^2$.

*** See NAPS document no. 02952 for supplementary material involving a listing of the observed and calculated structure factors for $[Fe_3(h^5\text{-}C_5H_5)_3(CO)_5As_4O_5]^+BF_4^-$..Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y., 10017. Remit in advance for each NAPS accession number \$1.50 for microfiche or \$5.00 for photo-

TABLE 1

ATOMIC PARAMETERS [a] FOR $[\mathrm{Fe_3}(h^5\text{-}\mathrm{C_5H_5})_3(\mathrm{CO})_5\mathrm{As_4O_5}]^+\mathrm{BF_4^-}$

A. Positional parameters

Atoms	*x*	*y*	*z*
As(1)	−0.0913(1)	0.1572(1)	0.0846(1)
As(2)	0.1585(1)	0.1537(1)	0.2895(1)
As(3)	0.0682(1)	0.3129(1)	0.1172(1)
As(4)	0.0874(1)	0.1131(1)	0.0508(1)
O(1)	0.0967(8)	0.2344(6)	0.0511(7)
O(2)	−0.0573(7)	0.2710(5)	0.0759(6)
O(3)	−0.0416(7)	0.0997(6)	0.0180(6)
O(4)	0.1516(7)	0.2694(6)	0.2489(7)
O(5)	0.1670(7)	0.0943(6)	0.1921(7)
Fe(1)	−0.2740(1)	0.1552(1)	−0.0451(1)
Fe(2)	0.3348(1)	0.1476(1)	0.4390(1)
Fe(3)	0.0020(1)	0.1162(1)	0.2626(1)
C(1-1)	−0.2538(12)	0.1644(12)	−0.1470(11)
O(1-1)	−0.2465(10)	0.1722(11)	−0.2158(9)
C(1-2)	−0.2829(11)	0.0351(12)	−0.0516(13)
O(1-2)	−0.2932(10)	−0.0398(8)	−0.0572(12)
C(2-1)	0.3695(12)	0.1632(13)	0.3494(12)
O(2-1)	0.3909(11)	0.1742(11)	0.2915(10)
C(2-2)	0.3393(12)	0.0318(11)	0.4336(12)
O(2-2)	0.3487(11)	−0.0468(9)	0.4323(11)
C(3-1)	−0.0146(11)	0.2244(10)	0.2939(9)
O(3-1)	−0.0297(8)	0.2960(6)	0.3129(7)
C(1)	−0.3672(18)	0.1690(15)	0.0083(18)
C(2)	−0.2896(16)	0.2348(18)	0.0547(12)
C(3)	−0.3094(13)	0.2848(12)	−0.0317(17)
C(4)	−0.3962(14)	0.2501(13)	−0.1225(14)
C(5)	−0.4321(13)	0.1776(13)	−0.1001(14)
H(1)	−0.3682	0.1112	0.0580
H(2)	−0.2222	0.2453	0.1410
H(3)	−0.2631	0.3495	−0.0238
H(4)	−0.4344	0.2798	−0.2086
H(5)	−0.4993	0.1325	−0.1581
C(6)	0.3303(14)	0.1686(14)	0.5691(12)
C(7)	0.3008(14)	0.2491(13)	0.5091(12)
C(8)	0.3862(16)	0.2761(11)	0.5089(13)
C(9)	0.4692(13)	0.2129(14)	0.5691(13)
C(10)	0.4350(15)	0.1473(13)	0.6065(11)
H(6)	0.2803	0.1298	0.5853
H(7)	0.2235	0.2841	0.4695
H(8)	0.3888	0.3375	0.4683
H(9)	0.5478	0.2162	0.5834
H(10)	0.4807	0.0879	0.6557
C(11)	−0.0462(13)	0.0546(9)	0.3500(12)
C(12)	0.0592(13)	0.0307(11)	0.3932(11)
C(13)	0.0571(12)	−0.0161(10)	0.3103(13)
C(14)	−0.0479(11)	−0.0183(8)	0.2174(10)
C(15)	−0.1118(10)	0.0258(9)	0.2428(10)
H(11)	−0.0714	0.0913	0.3939
H(12)	0.1303	0.0423	0.4752
H(13)	0.1270	−0.0443	0.3186
H(14)	−0.0766	−0.0489	0.1405
H(15)	−0.1992	0.0349	0.1870
B	0.6478(12)	0.0263(11)	0.2524(11)
F(1)	0.5698(12)	0.0210(11)	0.2580(14)
F(2)	0.6674(14)	0.1113(10)	0.2364(13)
F(3)	0.7334(13)	0.0029(15)	0.3454(13)
F(4)	0.6390(13)	−0.0195(14)	0.1793(16)

(Table to be continued)

TABLE 1 (continued)

B. Anisotropic thermal factors ($\times 10^4$)^{b,c}

Atoms	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
As(1)	50	35	45	5	28	−1
As(2)	51	35	47	−5	28	−1
As(3)	88	35	60	−5	47	2
As(4)	63	48	57	−2	40	−10
O(1)	105	52	66	−12	61	3
O(2)	77	35	64	6	42	5
O(3)	64	47	55	−4	37	−13
O(4)	85	43	65	−21	48	−9
O(5)	54	58	70	0	35	−3
Fe(1)	52	54	53	11	28	−3
Fe(2)	50	58	53	−10	25	−4
Fe(3)	52	30	43	−3	28	−1
C(1-1)	63	93	58	15	18	−3
O(1-1)	127	195	67	37	62	22
C(1-2)	41	69	110	3	31	−1
O(1-2)	106	57	227	−11	84	−21
C(2-1)	76	106	93	−38	48	−28
O(2-1)	125	201	127	−81	96	−56
C(2-2)	77	62	91	14	33	7
O(2-2)	147	63	206	19	88	15
C(3-1)	62	57	44	−11	31	11
O(3-1)	134	33	92	10	75	−3
C(1)	160	136	149	86	135	65
C(2)	112	197	36	102	−1	−37
C(3)	55	71	175	15	41	−40
C(4)	87	109	120	46	71	32
C(5)	71	99	119	11	59	−2
C(6)	102	136	68	−64	53	−42
C(7)	101	90	68	−12	40	−26
C(8)	140	63	91	−39	67	−35
C(9)	77	115	101	−42	49	−36
C(10)	104	104	48	−15	23	3
C(11)	120	48	87	−16	81	−7
C(12)	99	68	54	−20	27	30
C(13)	93	49	117	12	77	26
C(14)	79	25	74	−5	44	−2
C(15)	56	40	64	−7	32	6
B	71	49	35	−12	39	8
F(1)	195	183	326	6	198	31
F(2)	346	128	267	−17	242	5
F(3)	173	306	223	−34	41	145
F(4)	220	241	401	−117	202	−16

[a] The standard deviations of the last significant figure are listed in parentheses after the number. [b] The anisotropic temperature factors are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2\,hk\beta_{12} + 2\,hl\beta_{13} + 2\,kl\beta_{23})]$. [c] The hydrogen thermal parameters were assigned a fixed isotropic value of 5.0 Å^2.

TABLE 2

DISTANCES AND ANGLES FOR $[Fe_3(h^5\text{-}C_5H_5)_3(CO)_5As_4O_5]^+BF_4^-$

A. Within the $[As_4O_5Fe]$ *core*

Atoms	Distances (Å)	Average		Atoms	Distances (Å)	Average	
		a	*b*			*a*	*b*
As(1)···As(2)	3.255(2)	3.255	3.255	As(1)···O(4)	3.488(9)	3.48	
				As(2)···O(2)	3.473(8)		
As(1)···As(3)	3.203(2)	3.194					3.48
As(2)···As(3)	3.186(2)						
			3.195	As(1)···O(5)	3.454(8)	3.49	

TABLE 2 (continued)

A. Within the [As_4O_5Fe] core

Atoms	Distances (Å)	Average *a*	Average *b*
As(3)···As(4)	3.199(2)	3.199	3.199
Fe(3)—As(1)	2.298(2)	2.29	2.29
Fe(3)—As(2)	2.287(2)		
As(1)—O(2)	1.795(8)	1.80	181
As(2)—O(4)	1.803(9)		
As(1)—O(3)	1.819(8)	1.81	
As(2)—O(5)	1.808(8)		
As(3)—O(2)	1.772(9)	1.77	1.77
As(3)—O(4)	1.761(9)		
As(4)—O(3)	1.771(8)	1.77	
As(4)—O(5)	1.778(8)		
As(3)—O(1)	1.764(9)	1.76	1.78
As(4)—O(1)	1.800(9)	1.80	
Fe(3)···O(2)	3.350(8)	3.35	3.36
Fe(3)···O(4)	3.345(8)		
Fe(3)···O(3)	3.416(8)	3.38	
Fe(3)···O(5)	3.343(8)		
O(2)···O(3)	2.74(1)	2.76	2.75
O(4)···O(5)	2.79(1)		
O(2)···O(4)	2.73(1)	2.73	
O(3)···O(5)	2.73(1)		
O(1)···O(2)	2.69(1)	2.68	2.71
O(1)···O(4)	2.68(1)		
O(1)···O(3)	2.75(1)	2.74	
O(1)···O(5)	2.72(1)		

Atoms	Distances (Å)	Average *a*	Average *b*
As(1)···O(1)	3.453(9)	3.43	3.42
As(2)···O(1)	3.411(8)		
As(3)···O(3)	3.482(8)	3.48	3.46
As(3)···O(5)	3.473(9)		
As(4)···O(2)	3.422(8)	3.45	
As(4)···O(4)	3.470(8)		
	Angles (°)		
Fe(3)—As(1)—O(2)	109.2(7)	109.2	109.7
Fe(3)—As(2)—O(4)	109.2(8)		
Fe(3)—As(1)—O(3)	111.6(8)	110.2	
Fe(3)—As(2)—O(5)	108.9(7)		
O(2)—As(1)—O(3)	99.0(8)	100.0	100.0
O(4)—As(2)—O(5)	101.1(9)		
O(1)—As(3)—O(2)	99.3(9)	99.1	99.5
O(1)—As(3)—O(4)	98.9(8)		
O(1)—As(4)—O(3)	100.9(8)	99.9	
O(1)—As(4)—O(5)	98.9(8)		
O(2)—As(3)—O(4)	101.1(7)	101.1	100.9
O(3)—As(4)—O(5)	100.7(8)	100.7	90.5
As(1)—Fe(3)—As(2)	90.5(1)	90.5	
As(1)—O(2)—As(3)	127.8(5)	127.3	126.6
As(2)—O(4)—As(3)	126.8(5)		
As(1)—O(3)—As(4)	125.0(6)	125.9	
As(2)—O(5)—As(4)	126.8(5)		
As(3)—O(1)—As(4)	127.8(5)	127.8	127.8

B. Between the [As_4O_5Fe] core and cyclopentadienyliron carbonyl fragments

Atoms	Distances (Å)	Average[a]	Atoms	Bond angles (°)	Average[a]
Fe(1)—As(1)	2.318(2)	2.318	Fe(1)—As(1)—Fe(3)	127.9(2)	130.4
Fe(2)—As(2)	2.319(2)		Fe(2)—As(2)—Fe(3)	132.9(1)	
As(1)···C(1-1)	2.911(14)	2.88	As(1)—Fe(3)—C(3-1)	89.7(7)	91.1
As(2)···C(2-1)	2.843(16)		As(2)—Fe(3)—C(3-1)	92.5(7)	
As(1)···C(1-2)	3.029(15)	2.99	As(1)—Fe(3)—Cp(3)	122.6	122.9
As(2)···C(2-2)	2.955(15)		As(2)—Fe(3)—Cp(3)	123.2	
As(1)···C(3-1)	2.872(12)	2.90	As(1)—Fe(1)—C(1-1)	89.6(6)	88.4
As(2)···C(3-1)	2.930(14)		As(2)—Fe(2)—C(2-1)	87.2(7)	
As(1)···C(2)	3.064(17)	3.07	As(1)—Fe(1)—C(1-2)	94.5(6)	93.7
As(2)···C(7)	3.080(14)		As(2)—Fe(2)—C(2-2)	92.9(6)	
As(1)···C(3)	3.336(16)	3.48	As(1)—Fe(1)—Cp(1)	122.6	122.9

(Table to be continued)

TABLE 2 (continued)

B. Between the [As_4O_5Fe] core and cyclopentadienyliron carbonyl fragments

Atoms	Bond length (Å)	Average [a]	Atoms	Bond angles (°)	Average [a]
As(2)---C(8)	3.621(16)		As(2)—Fe(2)—Cp(2)	123.2	
As(1)---C(14)	3.122(12)	3.10	Fe(1)—As(1)—O(2)	102.4(8)	101.2
As(2)---C(13)	3.084(14)		Fe(2)—As(2)—O(4)	100.0(8)	
As(1)---C(15)	3.274(12)	3.31	Fe(1)—As(1)—O(3)	102.8(7)	101.6
As(2)---C(12)	3.342(14)		Fe(2)—As(2)—O(5)	100.4(8)	

C. Within the cyclopentadienyl carbonyl fragments

Atoms	Bond lengths (Å)	Atoms	Bond angles (°)
Fe(1)—C(1-1)	1.778(16)	C(1-1)—Fe(1)—C(1-2)	94.1(7)
Fe(1)—C(1-2)	1.780(17)	C(2-1)—Fe(2)—C(2-2)	93.1(7)
Fe(2)—C(2-1)	1.768(16)	Fe(1)—C(1-1)—O(1-1)	176(2)
Fe(2)—C(2-2)	1.719(17)	Fe(1)—C(1-2)—O(1-2)	177(2)
Fe(3)—C(3-1)	1.735(15)	Fe(2)—C(2-1)—O(2-1)	179(2)
C(1-1)—O(1-1)	1.136(15)	Fe(2)—C(2-2)—O(2-2)	176(2)
C(1-2)—O(1-2)	1.116(17)	Fe(3)—C(3-1)—O(3-1)	177(2)
C(2-1)—O(2-1)	1.132(16)		
C(2-2)—O(2-2)	1.174(17)	C(1-1)—Fe(1)—Cp(1)	123.6
C(3-1)—O(3-1)	1.159(15)	C(2-1)—Fe(2)—Cp(2)	124.3
		C(1-2)—Fe(1)—Cp(1)	123.5
Fe(1)—C(1)	2.06(1)	C(2-2)—Fe(2)—Cp(2)	126.0
Fe(1)—C(2)	2.06(1)	C(3-1)—Fe(3)—Cp(3)	128.1
Fe(1)—C(3)	2.04(2)		
Fe(1)—C(4)	2.08(2)		
Fe(1)—C(5)	2.10(2)		
Fe(2)—C(6)	2.07(1)		
Fe(2)—C(7)	2.09(2)		
Fe(2)—C(8)	2.10(2)		
Fe(2)—C(9)	2.09(2)		
Fe(2)—C(10)	2.08(1)		
Fe(3)—C(11)	2.10(1)		
Fe(3)—C(12)	2.08(1)		
Fe(3)—C(13)	2.09(1)		
Fe(3)—C(14)	2.10(1)		
Fe(3)—C(15)	2.09(1)		
Fe(1)—Cp(1) [c]	1.71		
Fe(2)—Cp(2)	1.71		
Fe(3)—Cp(3)	1.71		
C(1)—C(2)	1.38(3)		
C(2)—C(3)	1.39(3)		
C(3)—C(4)	1.35(2)		
C(4)—C(5)	1.35(2)		
C(5)—C(1)	1.35(2)		
C(6)—C(7)	1.41(2)		
C(7)—C(8)	1.39(2)		
C(8)—C(9)	1.41(2)		
C(9)—C(10)	1.39(2)		
C(10)—C(6)	1.41(2)		
C(11)—C(12)	1.40(2)		
C(12)—C(13)	1.43(2)		
C(13)—C(14)	1.40(2)		
C(14)—C(15)	1.42(2)		
C(15)—C(11)	1.40(2)		

(Table to be continued)

TABLE 2 (continued)

C. Within the cyclopentadienyl carbonyl fragments

Atoms	Bond length (Å)
C(1)—H(1)	1.15
C(2)—H(2)	1.12
C(3)—H(3)	1.16
C(4)—H(4)	1.17
C(5)—H(5)	1.11
C(6)—H(6)	1.11
C(7)—H(7)	1.11
C(8)—H(8)	1.12
C(9)—H(9)	1.11
C(10)—H(10)	1.10
C(11)—H(11)	1.10
C(12)—H(12)	1.09
C(13)—H(13)	1.10
C(14)—H(14)	1.09
C(15)—H(15)	1.11

D. Within the BF_4^- monoanion

Atoms	Bond lengths (Å)	Atoms	Bond angles (°)
B—F(1)	1.27(2)	F(1)—B—F(2)	114(4)
B—F(2)	1.35(2)	F(1)—B—F(3)	107(3)
B—F(3)	1.30(2)	F(1)—B—F(4)	115(4)
B—F(4)	1.25(2)	F(2)—B—F(3)	105(3)
		F(2)—B—B(4)	106(3)
F(1)···F(2)	2.20(2)	F(3)—B—F(4)	110(4)
F(1)···F(3)	2.08(2)		
F(1)···F(4)	2.13(2)		
F(2)···F(3)	2.11(2)		
F(2)···F(4)	2.06(2)		
F(3)···F(4)	2.10(2)		

[a] Averaged in accord with an assumed C_s-m geometry for the entire monocation. [b] Averaged in accord with an assumed C_{2v}-$2mm$ geometry for the $[As_4O_5Fe]$ core. [c] Cp(n) denotes the centroid of the nth cyclopentadienyl ring.

(with estimated standard deviations calculated from the variance-covariance matrix) are listed in Table 2. The least-squares planes defined by specific atoms with perpendicular displacements of these and other atoms from these planes and the angles between the normals to these planes are presented in Table 3.

Results and discussion

General comments

The reaction in a Pyrex-glass flask of arsenic trifluoride with cyclopentadienyliron dicarbonyl dimer in *m*-xylene solution has produced the tetrafluoroborate salt of the $[Fe_3(h^5\text{-}C_5H_5)_3(CO)_5As_4O_5]^+$ monocation which is an unusual organometallic derivative of the bird-cage As_4O_6 molecule. Analogous solid-state and solution spectra of this compound show absorption bands characteristic of the tetrafluorborate anion as well as of the cyclopentadienyl and terminal carbonyl

TABLE 3

DISTANCES OF ATOMS FROM SELECTED LEAST-SQUARES PLANES[a] IN THE $[Fe_3(h^5\text{-}C_5H_5)_3(CO)_5As_4O_5]^+$ MONOCATION, AND ANGLES BETWEEN THE NORMALS TO THESE PLANES

A. Distances (Å) from the Plane Formed by As(3), As(4) and the midpoint of As(1) and As(2)

$-0.627X + 0.026Y - 0.779Z + 1.013 = 0$

As(1)	1.63	Fe(3)	−0.01	O(2)	1.38
As(2)	−1.63	C(3-1)	0.07	O(3)	1.36
Fe(1)	3.93	O(3-1)	0.17	O(4)	−1.36
Fe(2)	−3.94	O(1)	−0.03	O(5)	−1.36

B. Distances (Å) from the Plane Formed by As(1), As(2) and the midpoint of As(3) and As(4)

$0.229X - 0.925Y - 0.248Z + 3.044 = 0$

As(3)	−1.60	Fe(3)	−0.04	O(4)	−1.38
As(4)	1.60	O(1)	−0.01	O(5)	1.40
Fe(1)	−0.05	O(2)	−1.36		
Fe(2)	0.02	O(3)	1.39		

C. Distances (Å) from the Plane Formed by C(1), C(2), C(3), C(4) and C(5)

$0.796X - 0.600Y - 0.076Z + 6.122 = 0$

Fe(1)	1.72	C(2)	−0.01	C(4)	0.00
C(1)	0.01	C(3)	0.01	C(5)	0.00

D. Distances (Å) from the Plane Formed by C(6), C(7), C(8), C(9) and C(10)

$0.160X - 0.535Y - 0.830Z + 7.210 = 0$

Fe(2)	1.71	C(7)	0.00	C(9)	0.01
C(6)	0.01	C(8)	0.00	C(10)	−0.01

E. Distances (Å) from the Plane Formed by C(11), C(12), C(13), C(14) and C(15)

$0.390X + 0.870Y - 0.301Z + 2.120 = 0$

Fe(3)	1.72	C(12)	0.01	C(14)	0.00
C(11)	−0.01	C(13)	−0.01	C(15)	0.00

F. Angles (Degrees Between Normals to the Planes

A and B	90.6	A and D	62.8
A and C	57.9	A and E	89.4

[a] The equations of the planes are given in an orthogonal Angstrom coordinate system (XYZ), which is related to a monoclinic fractional unit cell coordinate system (xyz) by the transformation: $X = xa + zc \cos\beta$, $Y = yb$, $Z = cz \sin\beta$.

groups. The diamagnetism of the orange-red compound was established in solution from the lack of an EPR resonance and from a sharp proton NMR spectrum which indicated the presence of two different types of cyclopentadienyl protons in a 2 : 1 ratio. The actual composition as well as detailed atomic arrangement of the compound was ascertained from an X-ray crystallographic investigation. Although the origin of the boron and oxygen atoms in the isolated product (whose yield is expectedly low and variable) is somewhat uncertain, it is presumed that these atoms were leached from the Pyrex glass of the reaction vessel in that the ability of fluorine-containing reagents to attack glass is well known [3,8,9].

Description of the crystal structure

The compound is comprised of discrete monocations and BF_4^- counteranions. The configuration elucidated for the $[Fe_3(h^5\text{-}C_5H_5)_3(CO)_5As_4O_5]^+$ monocation is formally based on a bird-cage As_4O_6 unit in which one of the siz bridging oxygen

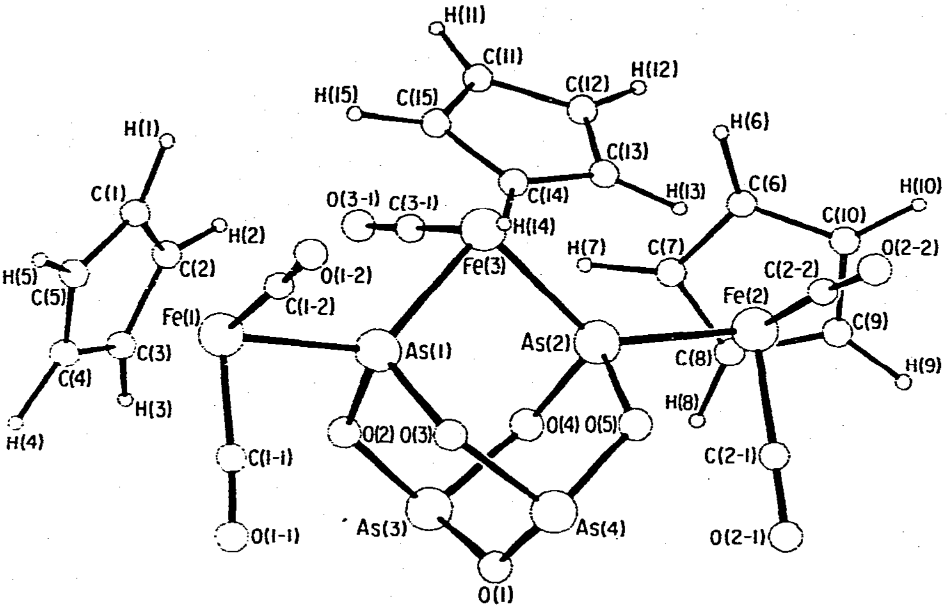

Fig. 1. A view of the $[Fe_3(h^5\text{-}C_5H_5)_3(CO)_5As_4O_5]^+$ monocation showing the atom labeling scheme.

atoms has been replaced with a bridging $[Fe(h^5\text{-}C_5H_5)(CO)]^+$ moiety and two one-electron donating $[Fe(h^5\text{-}C_5H_5)(CO)_2]$ fragments have been added as terminal ligands to the two iron-bridged arsenic atoms.

The crystalline arrangement of the four monocations and four BF_4^- monoanions in the monoclinic unit cell gives rise to no unusual interionic contacts. The shortest H---F separations of 2.30 and 2.38 Å, respectively, indicate at most weak hydrogen bonding between the cyclopentadienyl hydrogen and fluorine atoms. The BF_4^- monoanion possesses a nearly regular tetrahedral configuration with mean B—F and F---F separations of 1.29 and 2.11 Å, respectively, and F—B—F angles ranging from 105(3)° to 115(4)°. These values are similar to those found in tetrafluoroborate salts of several other metal cluster cations [3, 8,10].

The $[Fe_3(h^5\text{-}C_5H_5)_3(CO)_5As_4O_5]^+$ monocation

(a) Stereochemical relationship of its central $[As_4O_5Fe]$ core with the As_4O_6 molecule. Fig. 1 exhibits a nonbonded tetrahedral array of arsenic atoms linked to one another on five edges by oxygen atoms and bridged on the sixth edge between As(1) and As(2) by the Fe(3) atom of a $[Fe(h^5\text{-}C_5H_5)(CO)]^+$ group. The additional coordination of a terminal $[Fe(h^5\text{-}C_5H_5)(CO)_2]$ ligand via an electron-pair Fe—As σ-bond to both As(1) and As(2) is necessary in order to satisfy the closed-shell electronic requirements of each arsenic and each iron atom in accord with the diamagnetic character of the monocation *. Fig. 2 shows that the entire

---

* On the basis of the $[Fe(h^5\text{-}C_5H_5)(CO)]^+$ moiety being formally regarded as a monopositive species, the bridging Fe(3) completes its closed-shell electronic configuration by acquiring four electrons from As(1) and As(2) through the formation of two coordinate covalent As → Fe bonds. The concomitant addition of a one-electron donating $[Fe(h^5\text{-}C_5H_5)(CO)_2]$ ligand to both As(1) and As(2) is thereby required for each of these tetrahedral-like arsenic atoms to maintain a valence octet of electrons.

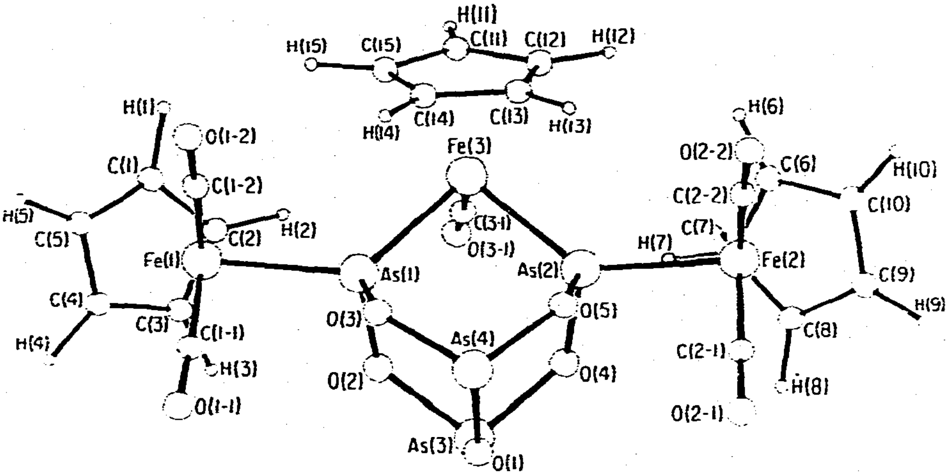

Fig. 2. A view of the [$Fe_3(h^5\text{-}C_5H_5)_3(CO)_5As_4O_5$]$^+$ monocation showing the idealized C_s-m geometry.

monocation ideally possesses a mirror plane, which is defined (Table 3, plane A) by As(3), As(4) and the midpoint of As(1) and As(2) which also passes through O(1), Fe(3), its bonded carbonyl ligand, and one carbon and its attached hydrogen of the bisected cyclopentadienyl ring. This approximate mirror plane symmetry is also revealed from the corresponding equivalent distances and bond angles in Table 2. A further examination of this table reveals that the [As_4O_5Fe] kernel of the monocation conforms to a pseudo C_{2v}-$2mm$ geometry with the second vertical mirror plane (Table 3, plane B) defined by As(1), As(2), and the midpoint of As(3) and As(4). The line of intersection of these two perpendicular mirror planes (dihedral angle, 90.6°) generates the twofold axis passing through Fe(3) and O(1).

Of prime interest is a comparison in Table 4 of the mean distances and bond angles for the [As_4O_5Fe] kernel with those for the cubic T_d As_4O_6 molecule from which the monocation is formally derived. The molecular parameters in Table 4 for As_4O_6 are those obtained from the crystal structure of arsenolite [11], the cubic form of As_4O_6, which consists of a diamond-like array of discrete As_4O_6 molecules [12] *. The only significant distortion apparently imposed on the As_4O_6 architecture due to the formal replacement of one bridging oxygen atom by the bridging iron fragment is a 0.06 Å increase in the As(1)···As(2) separation to 3.255(2) Å compared to the mean As···As separation of 3.196 Å for the other five oxygen-bridged edges. The two As—Fe(3) bond lengths of 2.287(2) and 2.298(2) Å are slightly smaller than the terminal As(1)—Fe(1) and As(2)—Fe(2) bond length of 2.318(2) and 2.319(2) Å, respectively. These values are not unlike the mean As—Fe bond lengths reported for $Fe_2(CO)_6[(\mu_2\text{-}AsCH_3)_2As_2(CH_3)_2]$ (2.323 [14a] and 2.309 Å [14b]), $Fe(CO)_4[As(CH_3)_3]$ (2.30(3) Å) [15], and $Fe_3(CO)_9(\mu_3\text{-}As)_2$ (2.348(2) Å) [4]. It is noteworthy that Hampson and Stosick [12b] concluded from their electron diffraction investigation of As_4O_6 that the observed As—O bond lengths, which are 0.1 Å less than the calculated

---

* These molecular parameters are essentially identical with those obtained from electron diffraction studies [12] of gaseous As_4O_6. The best determined values [12a] based on assumed T_d symmetry are As···As, O···O, and As—O distances of 3.20(2) 2.73(2) and 1.79(2) Å, respectively, with As—O—As and O—As—O bond angles of 128(2) and 99(2)°, respectively.

TABLE 4

COMPARISON BETWEEN THE MEAN DISTANCES AND BOND ANGLES FOR As_4O_6 AND FOR THE $[As_4O_5Fe]$ FRAGMENT OF THE $[Fe_3(h^5\text{-}C_5H_5)_3(CO)_5(CO)_5As_4O_5]^+$ MONOCATION

Distance		As_4O_6 (T_d)[a] (Å)		$[As_4O_5Fe]$ (C_{2v})[a] (Å)
As—O	(12)[b]	1.80 ± 0.03(av)[c]	(4)[d]	1.803 ± 0.008(av)
			(4)	1.771 ± 0.0009(av)
			(2)	1.782 ± 0.009(av)
As···As	(6)	3.23 ± 0.03(av)	(1)[e]	3.255 ± 0.002
			(4)	3.195 ± 0.002(av)
			(1)	3.199 ± 0.002
O···O	(12)	2.73 ± 0.03(av)	(4)[f]	2.75 ± 0.001(av)
			(4)	2.71 ± 0.01(av)
Angle		As_4O_6(T_d)[a] (°)		$[As_4O_5Fe]$(C_{2v})[a] (°)
As—O—As	(6)	126 ± 3(av)	(4)	126.6 ± 0.5(av)
			(1)	127.8 ± 0.5
O—As—O	(12)	100 ± 2(av)	(2)[g]	100.0 ± 0.9(av)
			(2)	100.9 ± 0.8(av)
			(4)	99.5 ± 0.9(av)

[a] The molecular parameters are averaged in accord with an idealized geometry of T_d symmetry for As_4O_6 and of C_{2v} symmetry for the $[As_4O_5Fe]$ framework of the monocation. [b] ( ) denotes the number of distances or bond angles having the values listed in the right column. [c] The average value of the e.s.d. denotes the arithmetic mean of the individual e.s.d.'s of the equivalent distances or bond angles. [d] This set of four equivalent As—O distances involves As(1) and As(2). [e] This nonbonding distance is between As(1) and As(2). [f] This set of four closest nonbonding O···O distances involves O(2), O(3), O(4), and O(5). [g] This set comprises O(2)—As(1)—O(3) and O(4)—As(2)—O(5).

sum of 1.87 Å for the covalent single-bond radii [13] of arsenic and oxygen, are the result of double-bond character arising from the interactions of the unshared electron pairs on the oxygen atoms with the arsenic atoms.

The $[Fe_3(h^5\text{-}C_5H_5)_3(CO)_5As_4O_5]^+$ monocation, which on account of its $[As_4O_5Fe]$ core may be considered as a substituted derivative of the As_4O_6 molecule, is distinctly different in coordination mode from the previously known adduct-type nickel tricarbonyl complexes of the isostructural P_4O_6 molecule. These latter complexes were shown by Riess and Van Wazer [16] from an elegant ^{31}P NMR analysis to arise from P_4O_6 being successively coordinated by one to four nickel tricarbonyl fragments via donation of the normally unshared electron pair of a given phosphorus atom to the Lewis acid $Ni(CO)_3$ fragment. The expected cubic T_d geometry of the isolated $P_4O_6[Ni(CO)_3]_4$ molecule, which crystallizes in the cubic lattice system, was substantiated from a structural characterization by powder X-ray diffractometry (in the absence of suitable single crystals) [17]. Other analogous adduct-type metal carbonyl complexes of the adamantoid P_4O_6 molecule have subsequently been produced by Mills and co-workers [18] who characterized them via ^{31}P NMR, infrared, and mass spectral analyses; these include $P_4O_6[Fe(CO)_4]_n$ (where $n = 1$—4) [18a], $Fe(CO)_3(P_4O_6)_2$ where the two phosphorus-coordinated P_4O_6 ligands were assigned at axial sites of a trigonal bypyramidal D_{3h} molecule [18a], and the mono-coordinated $P_4O_6M(CO)_5$ molecules (where M = Cr, Mo, W) [18b].

(b) The terminal $[Fe(h^5\text{-}C_5H_5)(CO)_2]$ and bridging $[Fe(h^5\text{-}C_5H_5)(CO)]$ ligands

Each iron atom of these two different ligands expectedly possesses an octahedral-like environment with the cyclopentadienyl ring sterically occupying three coordination sites. The As(1)—Fe(3)—As(2) and As—Fe(3)—CO bond angles for the [Fe(h^5-C_5H_5)(CO)]$^+$ ligand as well as the corresponding As—Fe—CO and OC—Fe—CO bond angles for the two [Fe(h^5-C_5H_5)$(CO)_2$] ligands are all close to 90°. The analogous geometries and distances found for these two ligands are similar to those found for the corresponding fragments in other complexes [2d, 19].

Acknowledgments

We are grateful to the National Science Foundation for their financial support of this research. The use of the UNIVAC 1110 computer at the Academic Computing Center of the University of Wisconsin (Madison) was made available through partial support of the National Science Foundation administered through the University Research Committee.

References

1 (a) M.A. Neuman, Trinh-Toan and L.F. Dahl, J. Amer. Chem. Soc., 94 (1972) 3383; (b) Trinh-Toan, W.P. Fehlhammer and L.F. Dahl, J. Amer. Chem. Soc., 94 (1972) 3389; (c) T.M. Burger, C.H. Wei and L.F. Dahl, to be published; (d) C.H. Wei, R.G. Wilkes, P.M. Treichel and L.F. Dahl, Inorg. Chem., 5 (1966) 900; (e) G.L. Simon and L.F. Dahl, J. Amer. Chem. Soc., 95 (1973) 2175; (f) M.S. Paquette and L.F. Dahl, to be published; (g) R.M. Roder and L.F. Dahl, submitted for publication; (h) R.M. Roder, Ph.D. Thesis, University of Wisconsin (Madison), 1973; (i) G.L. Simon and L.F. Dahl, J. Amer. Chem. Soc., 95 (1973) 2164; (j) Trinh-Toan, B.K. Teo, J.A. Ferguson, T.J. Meyer and L.F. Dahl, J. Amer. Chem. Soc., in press; (k) Trinh-Toan, W.P. Fehlhammer and L.F. Dahl, J. Amer. Chem. Soc., in press.

2 (a) Trinh-Toan, Ph.D. Thesis, University of Wisconsin (Madison), 1972; (b) B.K. Teo, Ph.D. Thesis, University of Wisconsin (Madison), 1973; (c) L.F. Dahl, Abstracts of Papers, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, INOR 6; (d) L.F. Dahl, J.D. Sinclair and B.K. Teo, in E.A. Koerner von Gustorf, (Ed.), The Organic Chemistry of Iron, Academic Press, New York, N.Y.; (e) B.K. Teo, Trinh-Toan, and L.F. Dahl, to be submitted for publication.

3 (a) J.D. Sinclair and L.F. Dahl, to be published; (b) J.D. Sinclair, Ph.D. Thesis, University of Wisconsin (Madison), 1973.

4 L.T.J. Delbaere, L.J. Kruczynski and D.W. McBride, J. Chem. Soc. Dalton, (1973) 307.

5 (a) C.F. Campana, Ph.D. Thesis, University of Wisconsin (Madison), 1976; (b) V.A. Uchtman and L.F. Dahl, J. Amer. Chem. Soc., 91 (1969) 3756.

6 (a) D.T. Cromer and J.F. Mann, Acta Crystallogr., Sect A, 24 (1968) 321; (b) R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys.; 42 (1965) 3175.

7 International Tables for X-Ray Crystallography, Vol. III, The Kynoch Press, Birmingham, England, 1962, p. 215.

8 C.F. Campana and L.F. Dahl, J. Organometal. Chem., 127 (1977) 209.

9 H.C. Clark, P.W.R. Corfield, K.R. Dixon and J.A. Ibers, J. Amer. Chem. Soc., 89 (1967) 3360.

10 P.D. Frisch and L.F. Dahl, submitted for publication.

11 K.E. Almin and A. Westgren, Arkiv Kemi, Mineral. Geol., 15B (1942) 22.

12 (a) C.-S. Lu and J. Donohue, J. Amer. Chem. Soc., 66 (1944) 818; (b) G.C. Hampson and A.J. Stosick, J. Amer. Chem. Soc., 60 (1938) 1814; (c) L.R. Maxwell, S.B. Hendricks and L.S. Deming, J. Chem. Phys., 5 (1937) 626.

13 L. Pauling, The Chemical Bond, Cornell University Press, 1967, p. 176.

14 (a) B.M. Gatehouse, Chem. Commun., (1969) 948; (b) A.S. Foust, Jr., Ph.D. Thesis, University of Wisconsin (Madison) 1970.

15 J.J. Legendre, C. Girard and M. Huber, Bull. Soc. Chim. Fr., 6 (1971) 1998.

16 J.G. Riess and J.R. Van Wazer, J. Amer. Chem. Soc., 88 (1966) 2166.

17 E.D. Pierron, P.J. Wheatley and J.G. Riess, Acta Crystallogr., 21 (1966) 288.

18 (a) M.L. Walker and J.L. Mills, Inorg. Chem., 14 (1975) 2438; (b) M.L. Walker, D.E. Peckenpaugh and J.L. Mills, Abstracts, 172nd ACS National Meeting, San Francisco, California, Aug. 30—Sept. 3, 1976, No. INOR-152; J. Organometal. Chem., in press.

19 (a) Trinh-Toan and L.F. Dahl, Inorg. Chem., in press; (b) M.R. Churchill, B.G. De Boer, K.L. Kalra, P. Reich-Rohrwig and A.J. Wojcicki, J. Chem. Soc. Chem. Commun., (1972) 981; M.R. Churchill, B.G.