resulting from metal–metal interactions, do not provide useful guidelines. A hint of a more reduced chemistry has existed for several years in the $GdCl_3$–Gd system where the very incongruently melting $GdCl_{1.5}$ forms;[7] this is a compound containing elongated metal octahedra sharing edges to form chains.[16] The present results together with the checkered history of published results of the Sc–$ScCl_3$ system (cf. Introduction) should give experimentalists due caution regarding kinetic barriers in seemingly tractable systems even at as high as 877 °C, the temperature where decomposition of $ScCl_{1.5}$ seemingly first allows access to so much new chemistry. We have found evidence for a similar chemistry in the Y–YCl_3 and La–$LaCl_3$, systems where previous work did not provide any direct evidence for reduced phases,[17,18] and a preliminary note on the formation of GdCl and TbCl, isostructural with ZrCl, has just been published by Simon et al.[19]

The second more speculative implication may involve the 4d and 5d metal–halogen systems for niobium and tantalum. Their cluster chemistry is well-known but perhaps a kinetic, not a thermodynamic, barrier there limits the formation of extended metal–metal bonded structures which would be similar to those in ScCl and ZrCl. It remains to be seen whether these will be manifest as ZrX-type structures with four electrons per atom in the band, as M^VX_2 structures which are isoelectronic in the metal–metal bonding of ZrX or, perhaps most likely, as intermediate states with extended metal–metal bonding in more nearly one-dimensional aggregates (ribbons, strings, dimers, etc.), as these can better accommodate the greater number of anions.

The once totally uninteresting chemistry of the Sc–$ScCl_3$ system now seems just the opposite, rich and full of fascinating synthetic, structural, and physical problems for investigation.

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Registry No. ScCl, 17775-46-1; $ScCl_3$, 10361-84-9.

Supplementary Material Available: Listing of structure factor amplitudes (1 page). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Ferricenium Tetrachlorobismuthate

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Ferricenium tetrachlorobismuthate, $(C_5H_5)_2FeBiCl_4$, crystallizes in the monoclinic space group $P2_1/c$ with a = 10.998 (5) Å, b = 17.449 (4) Å, c = 7.569 (4) Å, β = 98.46 (5)°. There are four molecules in the unit cell. Reflection intensities were measured by the θ–2θ scan method with a Picker FACS-1 automated diffractometer, Mo Kα radiation, and a graphite monochromator. For 1374 data with $F^2 > 3\sigma(F^2)$, R_1 = 0.030 and R_2 = 0.037. The Bi atom is coordinated by six chloride ions in an irregular octahedral array; two pairs of Cl^- ions form halogen bridges with neighboring Bi ions resulting in an infinite chain of edge-sharing octahedra. There are six independent Bi–Cl bond distances: 2.50 (1) and 2.52 (1) Å to nonbridging chlorines and 2.70 (1), 2.75 (1), 2.95 (1) and 3.10 (1) Å to bridging chlorines. The bridging Cl–Bi–Cl bond angles are 80.3 and 83.9°; the ten nonbridging Cl–Bi–Cl bond angles range from 85.9 to 99.3°. The axial Cl–Bi–Cl bond angles are 166.0, 174.5, and 175.9°. The ferricenium cations stack between the polymer chains with cyclopentadiene rings in the eclipsed conformation, unlike the pure ferrocene molecule which shows staggered rings. The average C–C distance in the rings is 1.40 (2) Å, the distance between ring centers is 3.40 (2) Å, and the Fe–ring center distance is 1.70 (2) Å.

Introduction

The crystal structure of ferricenium tetrachlorobismuthate, $(C_5H_5)_2FeBiCl_4$, has been determined as part of an investigation of compounds formed between group 5 halides and ferrocene. In addition to the possibility of uncovering a novel derivative of ferrocene, studies of group 5 halide compounds have revealed interesting structural effects, such as halogen bridging[3] and infinite-chain structures.[4,5] The distance from the Fe atom to the center of the cyclopentadiene ring is also of some interest, particularly in a nonsubstituted ferricenium compound where steric influences would be less significant.

Diffraction Data

The cell dimensions and data collection details are given in Table I.

The material was isolated as black crystals by reaction of a 1:1 molar ratio of ferrocene and $BiCl_3$ in acetone. A single crystal was mounted along its needle (c) axis. Weissenberg and precession data revealed systematic extinctions for $0k0$ ($k = 2n + 1$) and $h0l$ ($l = 2n + 1$), characteristic of space group $P2_1/c$. The same crystal was placed on a Picker FACS-1 four-circle diffractometer; a scintillation counter was used to measure the scanned intensities. Unit cell dimensions were refined by a least-squares program from the diffractometer setting angles of 12 reflections measured manually. A set of three standard reflections ($00\bar{4}$, 600, 800) was checked after every 200th scan in order to test for instrumental stability and crystal decay; no systematic variation in the intensities was observed.

Standard deviations were assigned to each reflection on the basis of counting statistics where $\sigma = (C + \sigma^2(B))^{1/2}$. The standard deviation of the background count, $\sigma(B)$, was determined as the maximum value of the quantities $\sigma(B) = (t_c/2t_b)(B_1 + B_2)^{1/2}$ or $\sigma(B) = (t_c/2t_b)|B_1 - B_2|$, where t_c and t_b are the scan counting time and background counting time, respectively, and C is the number of counts recorded during the scan. The weighting parameters, w, used in the least-squares refinement were calculated as $w = 1/\sigma^2$. A "p" factor of 0.06 was

Table I. Summary of Crystal Data and Intensity Collection

Compd	$(C_5H_5)_2FeBiCl_4$
Fw	536.8296
a	10.998 (5) Å
b	17.449 (7) Å
c	7.569 (4) Å
β	98.46 (5)°
V	1436.7 Å^3
Z	4
Density (calcd)	2.482 g/cm^3
Density (obsd)	2.59 g/cm^3
Space group	$C_{2h}{}^5$-$P2_1/c$
Crystal shape and size	Irregular needle with faces 210, $\bar{2}10$, 010, $0\bar{1}0$, 001, 211; dimensions ~0.15 × ~0.08 × ~0.06 mm
Crystal vol	8.47×10^{-4} mm^3
Temp	22-23 °C
Radiation	Mo Kα (λ 0.709 26 Å), graphite monochromatized
Abs cor	1.98–2.85; average 2.32
μ	134 cm^{-1}
Receiving aperture	6 mm × 6 mm; 22 cm from crystal
Data collection method	θ-2θ scan (2°/min along 2θ)
Scan range	1.8°
Background counts	10 s; offset from scan limits by 1°
2θ limits	3.0–45.0°

Table II. Positional Parameters

Atom	*x*	*y*	*z*
Bi	0.261 27 (4)	0.189 89 (2)	0.151 36 (6)
Fe	0.769 0 (1)	0.401 36 (9)	0.952 1 (2)
Cl(1)	0.109 2 (3)	0.204 6 (2)	0.407 0 (4)
Cl(2)	0.401 9 (3)	0.184 0 (2)	−0.112 5 (4)
Cl(3)	0.394 2 (3)	0.092 2 (2)	0.334 2 (5)
Cl(4)	0.117 1 (3)	0.086 9 (2)	0.021 5 (5)
C(1)	0.825 (1)	0.403 2 (7)	0.703 (2)
C(2)	0.698 (1)	0.418 9 (8)	0.686 (1)
C(3)	0.684 (1)	0.485 8 (8)	0.785 (2)
C(4)	0.798 (1)	0.513 2 (7)	0.860 (2)
C(5)	0.886 (1)	0.461 8 (8)	0.809 (2)
C(6)	0.811 (2)	0.295 1 (8)	0.064 (2)
C(7)	0.686 (2)	0.309 (1)	0.053 (2)
C(8)	0.670 (1)	0.374 (1)	0.156 (2)
C(9)	0.791 (2)	0.3976 (9)	0.231 (2)
C(10)	0.873 (1)	0.349 (1)	0.168 (2)
H(1)	0.863	0.360	0.651
H(2)	0.634	0.389	0.620
H(3)	0.605	0.509	0.800
H(4)	0.815	0.559	0.934
H(5)	0.974	0.466	0.840
H(6)	0.848	0.254	0.005
H(7)	0.621	0.279	−0.014
H(8)	0.592	0.398	0.172
H(9)	0.813	0.441	0.311
H(10)	0.962	0.351	0.194

applied to the weighting factors in order to account for instrumental inaccuracies by the equation $\sigma = (\sigma^2 + pF_o{}^2)^{1/2}$. A full set of 3775 data was averaged to 1893 unique reflections. Lorentz and polarization corrections were made. An absorption correction[6] was applied to the data by assigning six faces to the crystal and measuring its dimensions. Azimuthal scans of integrated intensities were performed for five different reflections, and the dimensions of the crystal were adjusted to fit these scans.

Atomic scattering factors for Bi^0, Fe^0, Cl$^-$, C, and H were used[7] with all appropriately corrected for anomalous dispersion.[8]

Structure Determination

A model was provided by a three-dimensional Patterson synthesis which revealed the Bi–Bi, Bi–Fe, and Bi–Cl vectors, from which initial heavy-atom coordinates (Bi, Fe, Cl) could be deduced. The carbon atoms were located by a subsequent difference Fourier. Hydrogen atom coordinates were calculated by assuming the atoms to lie in the plane of the cyclopentadiene rings each at a distance of 0.95 Å from the appropriate carbon atom. The coordinates for the Bi, Fe, Cl, and C atoms, including anisotropic thermal parameters, were refined by a full-matrix least-squares procedure using the 1374 data for which $F^2 > 3\sigma(F^2)$. The calculated hydrogen positions, including assigned isotropic thermal parameters of 8.0 Å^2, were not refined but included as fixed parameters in the least-squares minimization. The final R_1 value $[R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|]$ was 0.03 and the final R_2 $[R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}]$ was 0.037. The goodness of fit $[\sum w(|F_o| - |F_c|)^2(m - s)]$ was 0.96, where *m* and *s* are the number of data and number of parameters, respectively. No extinction was indicated by the data and no correction for this effect was applied.

Final positional and thermal parameters are given in Tables II and III, and distances and angles are listed in Tables IV and V.

Discussion

A portion of the crystal structure is shown in Figure 1; Figure 2 gives the molecular structure of the ferricenium cation. Figure 1 is a perspective view of the *bc* plane seen down the *a* axis. The Bi atoms are surrounded by six Cl$^-$ ions in an irregular octahedron; adjacent Bi atoms are connected by halogen bridges resulting in an infinite chain of edge-sharing octahedra extending along the *c* axis. There are six separate Bi–Cl bond distances: four "long" bonds to the bridging chlorines Cl(1), Cl(2), Cl(1′), and Cl(2′) of 2.75 (1), 2.70 (1), 2.95 (1), and 3.10 (1) Å and two "short" bonds to the non-bridging chlorines Cl(3) and Cl(4) of 2.52 (1) and 2.50 (1) Å. The Cl–Bi–Cl bond angles between bridging clorines Cl(1)–Bi–Cl(2′) and Cl(2)–Bi–Cl(1′) are 80.3 (1) and 83.9 (1)°, respectively; the remaining ten interior angles range from 85.9 (1) to 99.3 (1)°, resulting in a considerably distorted octahedron.

The "short" nonbridging Bi–Cl bond distances observed in the present instance, 2.50 (1) and 2.52 (1) Å, are in good agreement with the "single-bond" value observed in an electron

Table III. Thermal Parameters[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Bi	2.40 (2)	2.41 (2)	2.48 (2)	0.04 (2)	0.60 (1)	0.05 (2)
Fe	2.87 (2)	2.36 (8)	2.93 (7)	−0.02 (6)	0.57 (6)	0.27 (6)
Cl(1)	3.2 (1)	4.3 (2)	4.2 (2)	−1.0 (1)	1.6 (1)	−1.2 (1)
Cl(2)	3.9 (1)	4.2 (2)	4.2 (2)	0.7 (1)	1.8 (1)	0.4 (1)
Cl(3)	3.5 (1)	5.2 (2)	6.0 (2)	0.9 (1)	0.4 (1)	2.2 (2)
Cl(4)	4.6 (2)	3.7 (2)	4.4 (2)	−1.0 (1)	0.9 (1)	−1.0 (1)
C(1)	5.2 (7)	2.8 (6)	3.0 (6)	0.4 (5)	1.8 (5)	−0.2 (5)
C(2)	5.7 (8)	4.9 (8)	1.3 (5)	−1.1 (6)	−0.8 (5)	−0.3 (5)
C(3)	4.3 (7)	4.5 (8)	4.6 (7)	0.5 (6)	1.0 (6)	1.4 (6)
C(4)	6.0 (8)	2.0 (6)	5.4 (7)	−0.4 (5)	1.8 (6)	0.2 (5)
C(5)	4.5 (7)	4.3 (7)	3.2 (6)	−0.4 (5)	1.3 (5)	0.6 (5)
C(6)	6.9 (9)	2.7 (7)	7.0 (9)	0.9 (6)	2.2 (8)	1.8 (6)
C(7)	5.7 (9)	6.0 (10)	5.5 (8)	−3.6 (8)	−0.2 (7)	2.8 (8)
C(8)	5.2 (8)	8.6 (12)	4.1 (7)	2.3 (8)	2.2 (6)	3.3 (8)
C(9)	7.5 (10)	5.4 (9)	3.1 (6)	−0.7 (7)	1.5 (6)	−0.5 (6)
C(10)	3.9 (7)	5.9 (9)	4.3 (7)	0.3 (7)	−0.4 (6)	2.2 (7)

[a] The form of the temperature factor is $\exp[-0.25(h^2a^{*2}B_{11} + \ldots + 2hka^*b^*B_{12} + \ldots)]$ or $\exp[-B\lambda^{-2}\sin^2\theta]$. For H(1)–H(10), B = 8.0 Å^2.

Table IV. Interatomic Distances (Å)

Bi-Cl(1)	2.749 (3)	C(1)-C(2)	1.41 (2)
Bi-Cl(2)	2.702 (3)	C(2)-C(3)	1.41 (2)
Bi-Cl(3)	2.522 (3)	C(3)-C(4)	1.39 (2)
Bi-Cl(4)	2.500 (3)	C(4)-C(5)	1.39 (2)
Bi-Cl(1′)	2.949 (3)	C(5)-C(1)	1.40 (2)
Bi-Cl(2′)	3.101 (4)	C(6)-C(7)	1.39 (2)
Fe-C(1)	2.07 (1)	C(7)-C(8)	1.40 (2)
Fe-C(2)	2.07 (1)	C(8)-C(9)	1.43 (2)
Fe-C(3)	2.07 (1)	C(9)-C(10)	1.38 (2)
Fe-C(4)	2.11 (1)	C(10)-C(6)	1.35 (2)
Fe-C(5)	2.09 (1)	C(1)-C(6)	3.34 (2)
Fe-C(6)	2.06 (1)	C(2)-C(7)	3.39 (2)
Fe-C(7)	2.05 (1)	C(3)-C(8)	3.44 (2)
Fe-C(8)	2.07 (1)	C(4)-C(9)	3.47 (2)
Fe-C(9)	2.09 (1)	C(5)-C(10)	3.38 (2)
Fe-C(10)	2.07 (1)		

Table V. Selected Angles (deg)

Cl(1)-Bi-Cl(1′)	92.0 (1)	Cl(2′)-Bi-Cl(4)	166.0 (1)
Cl(1)-Bi-Cl(2)	175.9 (1)	Cl(3)-Bi-Cl(4)	90.7 (1)
Cl(1)-Bi-Cl(2′)	80.3 (1)		
Cl(1)-Bi-Cl(3)	92.3 (1)	C(1)-C(2)-C(3)	107 (1)
Cl(1)-Bi-Cl(4)	85.9 (1)	C(2)-C(3)-C(4)	110 (1)
Cl(1′)-Bi-Cl(2)	83.9 (1)	C(3)-C(4)-C(5)	106 (1)
Cl(1′)-Bi-Cl(2′)	96.2 (1)	C(4)-C(5)-C(1)	110 (1)
Cl(1′)-Bi-Cl(3)	174.5 (1)	C(5)-C(1)-C(2)	107 (1)
Cl(1′)-Bi-Cl(4)	86.2 (1)	C(6)-C(7)-C(8)	108 (1)
Cl(2)-Bi-Cl(2′)	99.3 (1)	C(7)-C(8)-C(9)	106 (1)
Cl(2)-Bi-Cl(3)	91.8 (1)	C(8)-C(9)-C(10)	108 (1)
Cl(2)-Bi-Cl(4)	94.6 (1)	C(9)-C(10)-C(1)	119 (1)
Cl(2′)-Bi-Cl(3)	87.9 (1)	C(10)-C(6)-C(7)	109 (1)

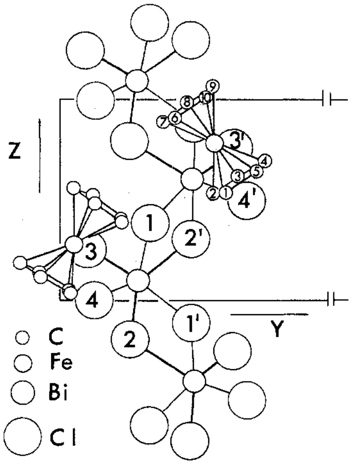

Figure 1. Schematic projection of the structure on (100). Primed numerals as superscripts refer to equivalent positions x, $^1/_2 - y$, $^1/_2 + z$, relative to the reference atom at x, y, z.

diffraction study[9] of $BiCl_3(g)$ which gave Bi–Cl = 2.48 ± 0.02 Å. However, the identification of the electron diffraction value as a single bond should be viewed with some reservation in view of a Raman spectral study[10] of $BiCl_3(g)$ which revealed modes that were interpreted as being due to chlorine bridging, suggesting that the material is not monomeric. In solid $BiCl_3$, the identification of a single-bond distance is even more ambiguous because the structure has been described[11] as a right trigonal prism with the Bi atom having a total of eight chloride neighbors, three close at 2.47 (1), 2.51 (1), and 2.52 (1) Å and five considerably more distant with values ranging from 3.22 (1) to 3.45 (1) Å. It is clear that the strong tendency to Cl bridging in Bi–Cl compounds precludes the designation of any specific value as a single-bond distance. However, the good agreement among the electron diffraction value (2.48 Å), the three short values in solid $BiCl_3$ (2.47, 2.51, 2.52 Å), and the short values for nonbridging chlorines measured in the present case (2.50, 2.52 Å) suggests that a range of values for a reasonable "single" Bi–Cl bond would be 2.47–2.52 Å.

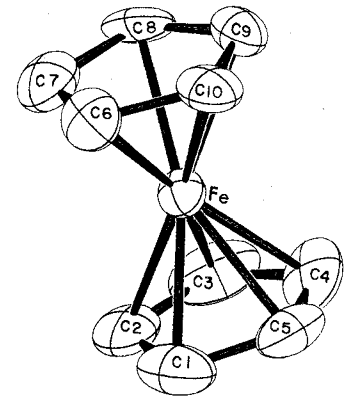

Figure 2. ORTEP diagram of the ferricenium cation.

The dihedral angle, α, between planes containing carbon atoms C(1), C(5), C(6), and C(1), C(5), C(10), respectively (Figure 2), was calculated in order to determine the extent to which the cyclopentadiene rings are staggered. The value determined, $\alpha \approx 1°$, indicates that the rings are completely eclipsed, unlike the case of pure ferrocene, in which the rings are in a staggered relationship.[12]

The specific mode of octahedral edge sharing observed in this study has been seen in three other group 5–halogen compounds, 2-picolinium tetrabromobismuthate (A),[4] 2-picolinium tetraiodobismuthate (B),[4] and pyridinium tetrachloroantimonate (C).[5] In each of the cases A, B, and C, as well as in the present study, the group 5–halogen anion MX_4^- forms an infinite chain of octahedra through pairs of bridging halogen atoms, with the organic cations, picolinium, pyridinium, or ferricenium, packing into the spaces between the chains. In A, B, and C, the heterocyclic ring cations stack in channels in the structure, essentially parallel to each other. The dihedral angle between planes formed by the rings is ~12° in A and B and ~1° in C. The ring-to-ring distance for the parallel pyridinium molecules in C is 3.49 Å, while C–C distances for the slightly inclined picolinium rings in A and B are "3.3 Å or greater". Nonparallel stacking of molecules in A and B may be due to steric constraints of the methyl group on the picolinium ion. In the present structure, the cyclopentadiene rings of the ferricenium cation are parallel to within ~2°, and the distance between the centers of the rings is 3.40 (2) Å. However, adjacent ferricenium molecules are not parallel (Figure 1) so that the parallel configuration of the rings occurs pairwise, intramolecularly, rather than in an infinite stack through the crystal as in A, B, and C. Nevertheless, the similarity among the structures A, B, and C and the present case is evident; even though the picoline and pyridine are discrete single-ring compounds, they behave very similarly to the sandwich compound ferrocene from the point of view of crystalline packing. This suggests that the pronounced tendency for halogen bridging in group 5–halogen compounds can manifest itself in infinite anion chains of type $(MX_4)_n^{n-}$ in certain instances, specifically in the presence of planar, ionizable ring compounds such as the single-ring heterocyclics, pyridine and picoline, and the double-ring sandwich compound ferrocene.

The distance from the Fe atom to the center of the cyclopentadiene ring which we have measured in ferricenium tetrachlorobismuthate (1.70 Å) is in very good agreement with values reported for ferricenium picrate,[13] ferricenium triiodide,[14] and 1,1-dimethylferricenium triiodide.[15] In the picrate and unsubstituted ferricenium triiodide, the structures were disordered so no detailed conclusions could be drawn, although Fe–ring center distances of 1.68 and 1.65 Å were reported, respectively. In the methyl-substituted ferricenium triiodide, the rings were inclined by 6.6°, and the relevant distances to each ring were 1.69 and 1.70 Å. The Fe–ring center distance in pure ferrocene[12] is 1.66 Å, which is not significantly different from the values cited above.

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Registry No. $(C_5H_5)_2FeBiCl_4$, 61026-19-5.

Supplementary Material Available: Listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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Synthesis and Spectroscopic and X-Ray Structural Characterization of Bis(diphenylphosphino(phenyl)acetylene)hexacarbonyldiiron(0), an Alkyne Derivative of Iron Pentacarbonyl

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The synthesis of $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ from phenylethynyldiphenylphosphine and $Fe_2(CO)_9$ is described. The compound has been characterized by microanalysis and mass, infrared, and Mössbauer spectroscopy, as well as by single-crystal x-ray diffraction. Crystals are monoclinic, space group $P2_1/n$, with $a = 12.032$ (6) Å, $b = 19.155$ (7) Å, $c = 17.644$ (6) Å, $\beta = 91.38$ (4)°, and $Z = 4$. The structure was solved by the heavy-atom method using the intensities of 3400 reflections measured on a Syntex $P\bar{1}$ diffractometer. Refinement converged at an R value of 0.065. In the binuclear molecule each iron atom is coordinated to three carbonyl groups, the phosphorus atom of one phosphinoalkyne, and the triple bond of the other. Each half of the molecule can be considered as a phosphine substitution product of a simple alkyne π complex $Fe(CO)_4(RC\equiv CR)$. Important intramolecular distances are Fe(1)–P(1) = 2.287 (2), Fe(2)–P(2) = 2.298 (2), Fe(1)–C(9) = 2.076 (8), Fe(1)–C(10) = 2.046 (8), Fe(2)–C(7) = 2.068 (8), Fe(2)–C(8) = 2.064 (6), C(7)–C(8) = 1.273 (11), and C(9)–C(10) = 1.260 (11) Å. Structural data and Mössbauer parameters ($\delta = 0.20$, $\Delta = 1.56$ mm s^{-1}) suggest a description of the iron–acetylene bonding intermediate between the metallocyclopropene and π-alkyne extremes. The relationship of $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ to proposed intermediates in the reactions of iron carbonyls with alkynes is discussed.

Introduction

The simple alkyne derivatives of $Fe(CO)_5$, namely $Fe(CO)_4(RC_2R')$ (I), have long been recognized as plausible intermediates in the oligomerization of acetylenes by iron carbonyls.[1-3] Evidence for the existence and structure of these compounds is scant resting mainly on the isolation of two complexes with sterically demanding alkynes. One of these $Fe(CO)_4(Me_3SiC_2SiMe_3)$[1,4] has been spectroscopically characterized,[5] but structural data for the second complex $Fe(CO)_4(Me_3CC_2CMe_3)$ have not yet been published.[4,6] In an effort to stabilize simple alkyne π complexes derived from iron carbonyls we have carried out reactions of several dialkyl- and diarylphosphinoacetylenes with diiron enneacarbonyl and triiron dodecacarbonyl. As is well established for nonbulky alkynes,[1-3] these reactions produce many exotic organometallic compounds[7] often in low yields. The present paper describes the synthesis and infrared and Mössbauer spectra as well as a complete single-crystal x-ray structure determination of $Fe_2(CO)_6(Ph_2PC\equiv CPh)_2$ a compound which can be prepared in workable yields from $Fe_2(CO)_9$ and $Ph_2PC\equiv CPh$. Each half of this binuclear molecule is derived from $Fe(CO)_5$ by substitution of an axial carbonyl by a phosphorus atom and an equatorial carbonyl by an alkyne triple bond. A preliminary report of this work has already appeared.[8]

Experimental Section

Synthesis of $Fe_2(CO)_6(Ph_2PC_2Ph)_2$. Diiron enneacarbonyl (1.8 g) and $Ph_2PC\equiv CPh$ (1.5 g) in degassed benzene (50 ml) were allowed to react for 3 days at room temperature. The resultant red solution was filtered, reduced to a small volume in vacuo, and introduced onto a Florisil column made up in petroleum ether (bp 80–100 °C). The first band, eluted with petroleum ether, contains the σ–π-acetylide complex $Fe_2(CO)_6(C_2Ph)(PPh_2)$ (II)[9] and traces of the phosphine substitution product $Fe(CO)_4(Ph_2PC\equiv CPh)$ which has a very similar R_f value. Elution of a second yellow band with a 9:1 mixture of petroleum ether–benzene afforded, on evaporation, dark yellow crystals of $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ (III) in 16% yield; mp 176–178 °C. Anal. Calcd for $Fe_2(CO)_6(Ph_2PC_2Ph)_2$: C, 64.81; H, 3.70. Found: C, 64.94; H, 3.70. IR (cm^{-1}) (Nujol): 2020 s, 2012 s, 1988 s, 1970 sh, 1940 sh, 1805 s, 1798 s (C_6H_{12}), 2044 s, 2029 s, 1980 m, 1971 s, 1946 s, 1802 w. Mass spectrum: m/e 852.0266 (calcd 852.0259) (M^+), 824, 796, 768, 740, 712, 684 ($Fe_2L_2^+$), 628, 606, 551, 530, 474, 450, 352, 342, 328, 318, 286 (L^+). A third band, eluted with a 7:3 mixture of petroleum ether–benzene gave on crystallization a 21% yield of bright yellow $Fe(CO)_3(Ph_2PC_2Ph)_2$, mp 217–218 °C. This compound is also a product of the reaction between $(\eta^4\text{-}C_7H_8)Fe(CO)_3$ and Ph_2PC_2Ph.[10]

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