MULTILAYERED IRON COMPLEXES OF METACYCLOPHANES. ¹H NMR BEHAVIOR

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(Received November 9th, 1981)

Summary

Syntheses are described for a series of (η^6-cyclophane)(η^5-cyclopentadienyl)-iron(II) complexes, where the cyclophane moiety is *anti*-[2.2]metacyclophane, *anti*-4,12-dimethyl[2.2]metacyclophane, *anti*-4,12-dimethyl-7,15-dimethoxy-[2.2]metacyclophane, and [2.2](2,5)thiophenophane. The triple-layered complexes (η^6,η^6-*anti*-[2.2]metacyclophane)bis[(η^5-cyclopentadienyl)iron(II)] bis(hexafluorophosphate) and (η^6,η^6-*anti*-4,12-dimethyl[2.2]metacyclophane)-bis[(η^5-cyclopentadienyl)iron(II)] bis(hexafluorophosphate) were also prepared. The NMR spectra of these compounds provide a useful insight into the nature of the iron—cyclophane bonding.

Recently, the Bennett procedure for preparing arene-metal complexes [1,2] has been used to provide simple and easy access to multilayered cyclophane-ruthenium complexes [3]. These compounds are of special interest with regard to the nature and extent of π-electron delocalization throughout the molecule [4]. Subsequently, attention has turned to the corresponding multilayered iron complexes of [2.2]paracyclophane. These have been prepared by photochemical exchange [5,6] and by ligand exchange with ferrocene catalyzed by aluminum chloride and aluminum [7,8]. We now report the preparation of a series of multilayered complexes of *anti*-[2.2]metacyclophanes.

The iron complexes shown by compounds I, II, III and IV were prepared most conveniently, and in good yield, by the photochemical method first devised by Gill and Mann [5,9].

The triple-layered complexes V and VI were prepared in reasonable yield by the aluminum chloride-catalyzed ferrocene exchange procedure [10].

As part of the characterization of these complexes, their ¹H NMR spectra have been determined. The ¹H NMR spectrum of I is particularly striking and is exhibited in Fig. 1 together with that of the corresponding hydrocarbon, *anti*-[2.2]metacyclophane (VII), and that of the triple-layered complex V. Although

(I , X = R = H ;

II , X = H ; R = CH$_3$;

III , X = OCH$_3$; R = CH$_3$)

(IV)

(V , R = H;

VI , R = CH$_3$)
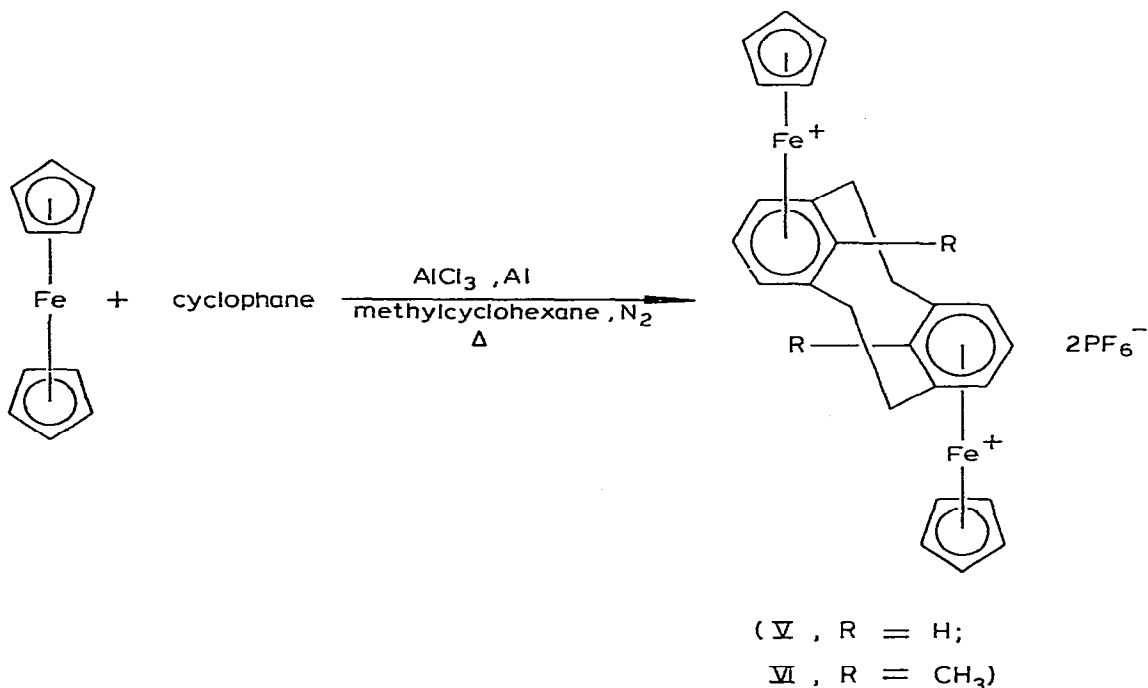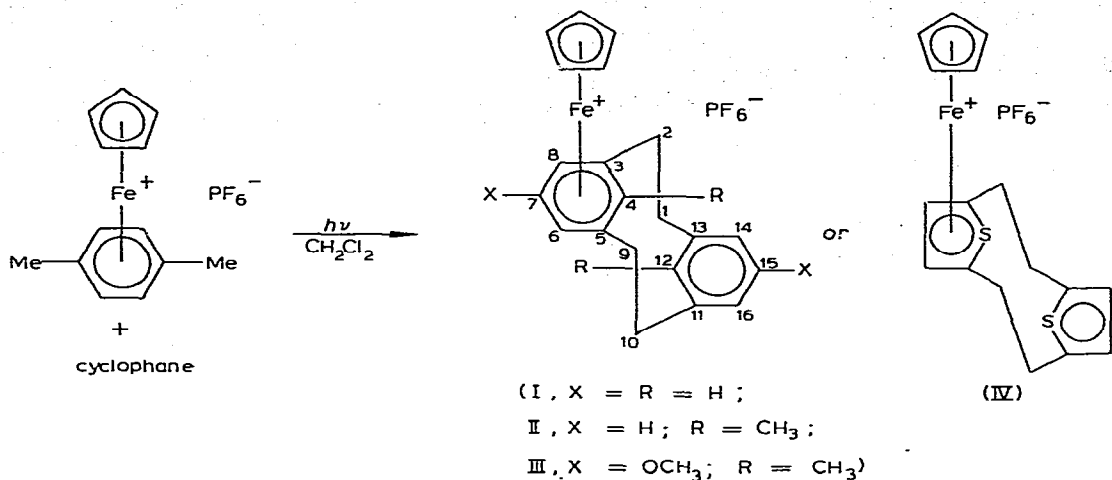
the ^{1}H NMR spectrum of *anti*-[2.2]metacyclophane (VII) has been analyzed previously [11], the multiplicities present in the original 60 MHz spectrum are greatly simplified in the 360 MHz spectrum presented in Fig. 1.

The aromatic protons of VII appear as a simplified AB$_2$X pattern: δ 7.28 (C(7) and C(15) H's, t, J_{AB} 7.5 Hz), 7.08 (C(6), C(8), C(14), and C(16) H's, d of d, J_{AB} 7.5 Hz; J_{BX} 1.4 Hz), and 4.24 ppm (C(4) and C(12) H's, t, J_{BX} 1.4 Hz) and the bridging methylene protons as symmetrical multiplets centered at δ 3.10 and 2.05 ppm.

The effect of the iron complexation is shown in the spectrum of I, where the AB$_2$X pattern of the complexed benzene ring has been markedly shifted up-
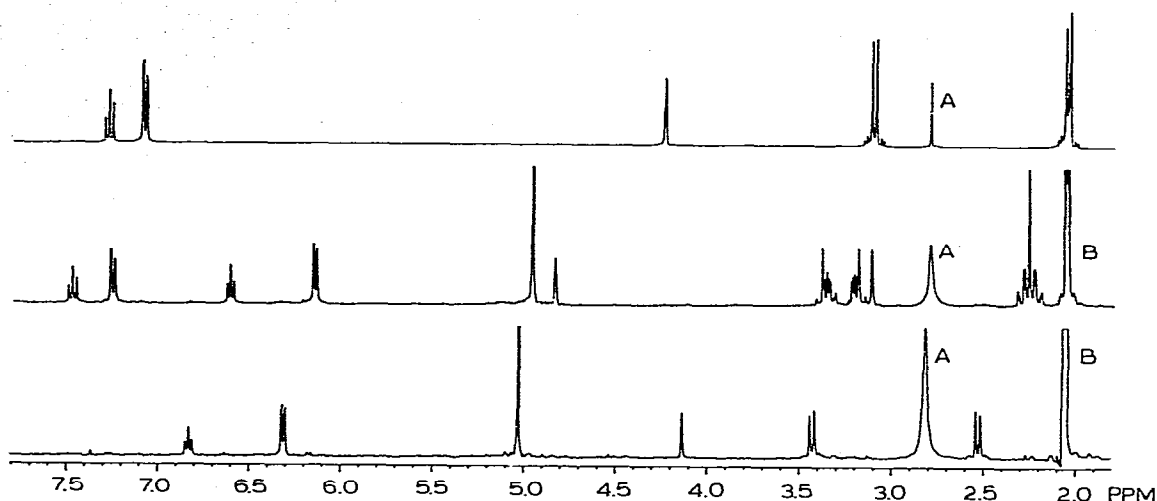
Fig. 1. (from top to bottom) ^{1}H NMR spectra of compounds VII, I and V taken in perdeuterioacetone solutions with a 360 MHz Nicolet spectrometer. (A and B are water and residual acetone signals, respectively).

field: δ 6.60 (C(7) H, t, J_{AB} 6.2 Hz), 6.14 (C(6) and C(8) H's, d of d, J_{AB} 6.2 Hz; J_{BX} 1.2 Hz), and 3.11 ppm (C(4) H, t, J_{BX} 1.2 Hz), whereas the uncomplexed benzene ring protons are shifted slightly downfield: δ 7.47 (C(15) H, t, J_{AB} 7.5 Hz), 7.25 (C(14) and C(16) H's, d of d, J_{AB} 7.5 Hz; J_{BX} 1.6 Hz), and 4.83 ppm (C(12) H, t, J_{BX} 1.6 Hz). For the triple-layered complex V both benzene rings show a single AB$_2$X pattern shifted again upfield: δ 6.83 (C(7) and C(15) H's, t, J_{AB} 6.2 Hz), 6.31 (C(6), C(8), C(14), and C(16) H's, d, J_{AB} 6.2 Hz); and 4.13 ppm (C(4) and C(12) H's, s).

From an analysis of these data, the assignment for I of which aromatic protons are attached to the benzene ring complexed to iron can be made unambiguously. The difference in chemical shift values between the A and B protons in the hydrocarbon VII is 0.20 ppm, whereas in the triple-layered complex V it is 0.52 ppm. For the upfield AB$_2$X pattern of I, the chemical shift difference between the A and B protons is 0.46 ppm, and in the downfield AB$_2$X the difference is 0.22 ppm. Thus, one can conclude without doubt that the upfield AB$_2$X pattern of I is that of the iron-complexed ring. The assignment of the C(4) proton at δ 3.11 ppm to the upfield AB$_2$X pattern and the assignment of the C(12) proton at δ 4.83 ppm to the downfield AB$_2$X pattern was confirmed by double resonance spin decoupling.

Fortunately, the geometry of *anti*-[2.2]metacyclophane (VII) is known from X-ray crystal analysis [12,13] and is depicted, somewhat exaggeratedly, in Fig. 2. Each of the benzene rings is asymmetrically boat-shaped with the internal carbons (C(4) and C(12)) being 0.143 Å out of the basal plane and the end carbons (C(7) and C(15)) being out of the plane by 0.042 Å. There is only partial overlap of the two benzene rings, but the distance between decks at C(4) and C(12) is only 2.633 Å. The protons at C(4) and C(12) are nearly over the center of the opposite benzene ring and a strong upfield shift of these

protons results from shielding due to the ring current in the opposite benzene ring.
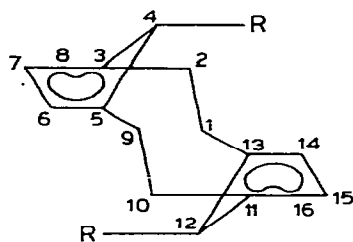
(VII , R = H ;

VIII , R = CH$_3$)

Fig. 2.

Although the factors affecting chemical shifts on complexation with transition metals are undoubtedly complex and the interpretation of such data is fraught with pitfalls [14], there are several things that seem evident in the case of *anti*-[2.2]metacyclophane. For [2.2]paracyclophane and the multibridged [2$_n$]cyclophanes ring current effects from the opposite deck have a large effect on the aromatic proton signals (the aromatic protons of [2.2]paracyclophane are shifted upfield from those of *p*-xylene by about 0.8 ppm [11]). The signals of the aromatic protons of *anti*-[2.2]metacyclophane at C(6), C(7), C(8), C(14), C(15), and C(16) are unaffected by ring current from the opposite deck and are essentially unchanged from the corresponding protons in *m*-xylene. Only the internal protons of VII at C(4) and C(12) are affected by the ring current of the opposite deck. Thus, the downfield shift of the aromatic protons at C(14), C(15), and C(16) in the uncomplexed ring of I must be due primarily to a change in electron density in that ring, an electron-withdrawing effect resulting from the metal ion complexation of the opposite deck. The enhanced downfield shift (0.41 ppm) of the aromatic proton at C(12) beyond that of the protons at C(14), C(15), and C(16) must be largely due to a decreased ring current in the complexed ring. It would be expected that metal ion complexation would change the bond orders of the aromatic carbons in the complexed ring and so lower the ring current as is observed.

Also, the change in geometry on complexation as well as a change in bond orders of the aromatic carbons should change both the relative chemical shifts and the coupling constants of the protons of the complexed ring, and this is also observed. On complexation the difference between the chemical shifts of the proton at C(7) and those at C(6) and C(8) changes from 0.20 ppm in VII to 0.46 ppm in I, while the coupling constants for these protons changes from J_{AB} 7.5 Hz to J_{AB} 6.2 Hz.

A direct influence of the magnetic anisotropy of the iron ion on neighboring protons as well as effects resulting from changes in geometry during complexation are undoubtedly present but are difficult to assess. This is borne out from a similar ^{1}H NMR analysis of *anti*-4,12-dimethyl[2.2]metacyclophane (VIII), its mono-iron complex II, and the corresponding bis-iron complex VI. The aromatic protons of VIII at C(7) and C(15) appear as a triplet at δ 6.82 ppm (J_{AB} 7.3 Hz), whereas the aromatic protons at C(6), C(8), C(14) and C(16)

are a doublet at δ 7.13 ppm (J_{AB} 7.3 Hz) and the protons of the methyl groups at C(4) and C(12) are a singlet at δ 0.58 ppm. In II, the aromatic protons at C(14) and C(16) in the uncomplexed ring appear as a doublet at δ 7.24 ppm (J_{AB} 7.4 Hz) and the proton at C(15) is at δ 6.99 ppm (J_{AB} 7.4 Hz). Thus, again there is evidently a downfield shift of the aromatic protons of the uncomplexed ring due to the electron-withdrawing effect of the iron complexation of the opposite deck. The lowering of the ring current in the complexed ring is seen in the enhanced downfield shift (0.47 ppm) of the methyl protons at C(12).

Likewise, the change in bond orders of the aromatic carbons of the complexed ring are seen again both in the changes of relative chemical shifts and coupling constants of the aromatic protons. In the case of II, the coupling constants have changed from J_{AB} 7.3 Hz (uncomplexed) to J_{AB} 6.1 Hz (complexed), while the relative chemical shift difference comparing the aromatic protons at C(6) and C(8) with that at C(7) shows an actual inversion from +0.31 ppm in VIII to —0.33 ppm in II.

The geometry of *anti*-4,12-dimethyl[2.2]metacyclophane (VIII), as determined by X-ray crystallography [15], is similar to that of *anti*-[2.2]metacyclophane (VII) itself, but even more distorted and strained. The effect of changes in geometry during metal ion complexation of VIII would, therefore, be expected to be greater than for VII. This quite probably is responsible for some of the small differences in detail of the ^{1}H NMR analyses of these two examples.

The only previous ^{1}H NMR analysis of metal complexes of cyclophanes has been that of Ohno, Horita, Otsubo, Sakata, and Misumi [16], who examined the ^{1}H NMR spectra of tricarbonylchromium complexes of multilayered [2.2]-paracyclophanes. They found that tricarbonylchromium complexation of one deck had a marked effect on the chemical shifts of the aromatic protons of all the remaining uncomplexed decks. However, for [2.2]paracyclophanes, as well as for the multibridged [2$_n$]cyclophanes, it is not possible to distinguish between ring current and electron-withdrawing effects resulting from metal ion complexation. For the reasons presented in the previous discussion, this dissection can be done only with *anti*-[2.2]metacyclophanes. Kainradl, Langer, Lehner, and Schlögel [17] have made the three possible tricarbonylchromium complexes of a carbomethoxy derivative of *anti*-[2.2]metacyclophane. Our ^{1}H NMR analysis of their data, similar to the present one for the iron complexes, leads to the conclusion that tricarbonylchromium complexation results in a large decrease in ring current of the complexed ring but has very little effect on the electron density of the uncomplexed ring.

The *anti*-[2.2]metacyclophanes appear to provide a unique insight into the magnetic consequences of metal complexation of cyclophanes, deserving of further study with other metals.

Experimental

General. Microanalyses are by Dr. Richard Wielesek of the University of Oregon Microanalytical Laboratory. ^{1}H NMR spectra were recorded on a Varian 100 XL spectrometer except for the spectra presented in Fig. 1 which were recorded using a Nicolet 360 MHz instrument. All ^{1}H NMR spectra were

measured as solutions in perdeuterioacetone.

Preparation of the double-layered iron complexes I, II, III and IV by photo-chemical exchange. General procedure. A solution of 0.20 mmoles of (η^6-*p*-xylene)(η^5-cyclopentadienyl)iron (II) hexafluorophosphate and 0.40 mmoles of cyclophane in 35 ml of dichloromethane was deaerated using nitrogen and then irradiated (150 W G.E. Reflector Flood Lamp) for 3—5 h. After filtration of the solution, the filtrate was concentrated to give a reddish-orange solid. This was treated several times with boiling heptane followed by decantation to remove unreacted cyclophane. The remaining solid was taken up in dichloromethane, filtered, and treated with ether to effect separation of the complex.

(η^6-anti-[2.2]Metacyclophane)(η^5-cyclopentadienyl)iron(II) hexafluorophosphate (I). Complex I was isolated in 43% yield as orange needles after recrystallization from absolute ethanol. Only a 3 h photolysis was used to make this particular complex. Longer irradiation resulted in extensive decomposition of the complex. The recrystallization was required to achieve pure material. (Recrystallization is unnecessary for the other double-layered iron complexes). M.p. dec. >210°C; ^{1}H NMR, δ 7.47 (C(15) H, t, J_{AB} 7.5 Hz), 7.25 (C(14) and C(16) H's, d of d, J_{AB} 7.5 Hz; J_{BX} 1.6 Hz), 6.60 ((C(7), t, J'_{AB} 6.2 Hz), 6.14 (C(6) and C(8) H's, d of d, J'_{AB} 6.2 Hz; J'_{BX} 1.2 Hz), 4.95 (5 H, s, Cp*H*), 4.83 (C(12) H, t, J_{BX} 1.6), 3.41—3.14 (4 H, m, C*H$_2$*), 3.11 (C(4) H, t, J'_{BX} 1.2 Hz), 2.32—2.19 ppm (4 H, m, C*H$_2$*). Anal. Found: C, 52.96; H, 4.03. FeC$_{21}$H$_{21}$PF$_6$ calcd.: C, 53.19; H, 4.46%.

(η^6-anti-4,12-Dimethyl[2.2]metacyclophane)(η^5-cyclopentadienyl)iron(II) hexafluorophosphate (II). Complex II was isolated in 79% yield as an orange solid. M.p. dec. >257°C; ^{1}H NMR, δ 7.24 (C(14) and C(16) H's, d, J_{AB} 7.4 Hz), 6.99 (C(15) H, t, J_{AB} 7.4 Hz), 6.57 (C(7) H, t, J'_{AB} 6.1 Hz), 6.24 (C(6) and C(8) H's, d, J'_{AB} 6.1 Hz), 4.93 (5 H, s, Cp*H*), 3.21—2.91 (8 H, m, C*H$_2$*), 1.05 (C(12), C*H$_3$*, s), 0.68 ppm (C(4), C*H$_3$*, s); Anal. Found: C, 54.90; H, 4.93. FeC$_{23}$H$_{25}$PF$_6$ calcd.: C, 55.00; H, 5.02%.

(η^6-anti-4,12-Dimethyl-7,15-dimethoxy[2.2]metacyclophane)(η^5-cyclopentadienyl)iron(II) hexafluorophosphate (III). Complex III was isolated in 61% yield as a light orange solid. M.p. dec. 240°C; ^{1}H NMR, δ 6.86 (C(14) and C(16) H's, s), 6.35 (C(6) and C(8) H's, s), 4.86 (5 H, s, Cp*H*), 4.13 (C(15), OC*H$_3$*, s), 3.76 (C(7), OC*H$_3$*, s), 3.20—2.74 (8 H, m, C*H$_2$*), 1.09 (C(12), C*H$_3$*, s), 0.69 ppm (C(4), C*H$_3$*, s). Anal. Found: C, 53.44; H, 5.12. FeC$_{25}$H$_{29}$O$_2$PF$_6$ calcd.: C, 53.40; H, 5.20%.

(η^5-[2.2]Thiophenophane)(η^5-cyclopentadienyl)iron(II) hexafluorophosphate (IV). Complex IV was isolated in 73% yield as an orange solid. M.p. dec. >200°C; ^{1}H NMR, δ 6.99 (2 H, s, Ar*H*), 6.21 (2 H, s, Ar'*H*), 5.00 (5 H, s, Cp*H*), 3.56—2.35 ppm (8 H, m, CH$_2$). (This complex showed a tendency to decompose in acetone-d_6. In perdeuterionitromethane, no such difficulty was observed.) Anal. Found: C, 42.20; H, 3.63. FeC$_{17}$H$_{17}$S$_2$PF$_6$ calcd.: C, 41.99; H, 3.52%.

Preparation of the triple-layered iron complexes V and VI, by aluminum chloride-catalyzed exchange with ferrocene. General procedure. A mixture of 0.14 mmoles of cyclophane, 0.72 mmoles of ferrocene, 0.22 mmoles of aluminum, and 2.20 mmoles of anhydrous aluminum chloride in 8 ml of methylcyclohexane was boiled under reflux and a nitrogen atmosphere for 21 h.

After the reaction mixture was cooled, 25 ml each of water and ether were added with stirring. The organic layer was separated, washed with water, and the aqueous extracts were combined. Addition of 7.59 mmoles of aqueous ammonium hydroxide to the green aqueous extract discharged the green color and precipitated a gelatinous solid. After removal of the solid by filtration, the clear yellow filtrate was treated with ammonium hexafluorophosphate, causing separation of a yellow solid. This was taken up in nitromethane and treated with ether to give a peach-colored solid. The complexes could be recrystallized from a mixture of acetone and ether.

(η^6,η^6-anti-[2.2]Metacyclophane)bis[η^5-cyclopentadienyl)iron(II)] bis(hexafluorophosphate) (V). Complex V was isolated in 44% yield as orange needles: m.p. dec. 240°C; ^{1}H NMR, δ 6.83 (C(7) and C(15) H's, t, J_{AB} 6.2 Hz), 6.31 (C(6), C(8), C(14) and C(16) H's, d, J_{AB} 6.2 Hz), 5.03 (10 H, s, CpH), 4.13 (C(4) and C(12) H's, s), 3.43 (4 H, d, CH$_2$, J 8.7 Hz), 2.53 ppm (4 H, d, CH$_2$, J 8.7 Hz). Anal. Found: C, 42.51; H, 3.54. Fe$_2$C$_{26}$H$_{26}$P$_2$F$_{12}$ calcd.: C, 42.19; H, 3.54%.

(η^6,η^6-anti-4,12-Dimethyl[2.2]metacyclophane)bis[(η^5-cyclopentadienyl)-iron(II)] bis(hexafluorophosphate) (VI). Complex VI was isolated in 43% yield as a light orange powder; m.p. dec. 275°C; ^{1}H NMR, δ 6.80 (C(7) and C(15) H's, t, J_{AB} 6.3 Hz), 6.36 (C(6), C(8), C(14) and C(16) H's, d, J_{AB} 6.3 Hz), 5.00 (10 H, s, CpH), 3.42—2.84 (8 H, m, CH$_2$), 1.20 ppm (C(4) and C(12) H's, CH$_3$, s). Anal. Found: C, 43.80; H, 4.01. Fe$_2$C$_{28}$H$_{30}$P$_2$F$_{12}$ calcd.: C, 43.78; H, 3.94%.

Acknowledgment

References

1 M.A. Bennett and T.W. Matheson, J. Organometal. Chem., 175 (1979) 87.
2 M.A. Bennett, T.W. Matheson, G.B. Robertson, A.K. Smith, and P.A. Tucker, Inorg. Chem., 19 (1980) 1014.
3 E.D. Laganis, R.G. Finke and V. Boekelheide, Tetrahedron Lett., 21 (1980) 4405.
4 R.G. Finke, R.H. Voegeli, E.D. Laganis and V. Boekelheide, J. Am. Chem. Soc., in press.
5 T.P. Gill and K.R. Mann, Inorg. Chem., 19 (1980) 3007.
6 E.D. Laganis, R.G. Finke and V. Boekelheide, Proc. Natl. Acad. Sci. USA, 78 (1981) 2657.
7 A.N. Nesmeyanov, N.A. Vol'kenau and I.N. Bolesova, Dokl. Akad. Nauk, SSSR, 149 (1963) 615.
8 A.R. Koray, J. Organometal. Chem., 212 (1981) 233.
9 Iron complexes of thiophene were first prepared by P. Bachman and H. Singer (Z. Naturforsch. B, 31 (1976) 525). The inclusion of IV in this series was prompted by its analogy to the anti-[2.2]metacyclophanes rather than its relation to the thiophenes per se.
10 C.C. Lee, B.R. Steele and R.G. Sutherland, J. Organometal. Chem., 186 (1980) 265.
11 D.J. Wilson, V. Boekelheide and R.W. Griffin, Jr., J. Am. Chem. Soc., 82 (1960) 6302.
12 C.J. Brown, J. Chem. Soc., (1953) 3278.
13 Y. Kai, N. Yasuoka and N. Kasai, Acta Crystall. B, 33 (1977) 754.
14 J. Evans and J.R. Norton, Inorg. Chem., 13 (1974) 3042.
15 A.W. Hanson, Acta Crystall., 15 (1962) 956.
16 H. Ohno, H. Horita, Y. Sakata and S. Misumi, Tetrahedron Lett., (1977) 265.
17 B. Kainraedl, E. Langer, H. Lehner and K. Schlögel, Ann., 766 (1972) 16.