# Organometallic electron reservoirs. 33. Redox systems involving stable 17-electron iron(III)-methyl complexes

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**Registry No.** 1, 110638-28-3; $CpMn(CO)_3$, 12079-65-1; $CpMn(CO)_2$, 38548-46-8; CO, 630-08-0; $N_2$, 7727-37-9; $P(OMe)_3$, 121-45-9; $PPh_3$, 603-35-0; *n*-heptane, 142-82-5; cyclohexane, 110-82-7.

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# *Communications*

## Redox Systems Involving Stable 17-Electron Iron(III)–Methyl Complexes[1]

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*Summary:* The electron-rich, thermally stable $\sigma$-methyl complexes $[Fe^{II}Cp^*(CO)(P)(CH_3)]$ ($P = \eta^1$-dppe, **1**) and $[Fe^{II}Cp^*P_2(CH_3)]$ ($P = P(OMe)_3$, **5**, or $P_2 = \eta^2$-dppe, **6**) have been synthesized and oxidized to stable 17-electron iron(III)–methyl isostructural cations by using ferricinium or trityl salts; the latter do not undergo hydrogen atom abstraction, migratory CO insertion, ligand exchange, and $Fe-CH_3$ cleavage under ambient conditions.

Although compounds with an element–methyl bond were first found 150 years ago,[3] the finding of stable transition-metal–alkyl complexes was considerably delayed, essentially until the relatively recent recognition by Wilkinson of the kinetic basis for instability.[4,5] However, direct homolytic scission of the alkyl–metal bond is an important decomposition pathway in the absence of a closed valence shell.[6] Thus, the isolation of stable 17-electron complexes with a $\sigma$-alkyl ligand requires bulkyl alkyls (or aryls)[7] and such exemples with a methyl ligand are scarce.[7d]

We report here the first results of our strategy aimed at the stabilization of the metal–methyl bond in 17-electron complexes by using sterically protecting ancillary ligands.

The complexes $[Fe^{II}Cp^*(CO)(P)(CH_3)]$ (**1**, $P = \eta^1$-dppe, and **2**, $P = PPh_3$) were synthesized by using the classical route shown in eq 1[8] ($Cp^* = \eta^5\text{-}C_5Me_5$ throughout the text).

$$\mathrm{FeCp^*(CO)_2(CH_3)} \xrightarrow[\mathrm{P,\ 1\ h}]{h\nu\ \mathrm{(UV),\ toluene}} \begin{array}{c}\mathrm{FeCp^*(CO)(P)(CH_3)} \\ \mathbf{1},\ \mathrm{P} = \eta^1\text{-dppe} \\ \mathbf{2},\ \mathrm{P} = \mathrm{PPh_3}\end{array} \tag{1}$$

The new complex **1**[9] shows two signals in the $^{31}P$ NMR spectrum, at +76.4 ppm for the coordinated phosphine and at −13.2 ppm for the free phosphine (vs 85% $H_3PO_4$). It shows a reversible one-electron wave at $E_a = -0.3$ V vs SCE in its cyclic voltammogram (DMF, $Bu_4N^+ClO_4^-$, Pt, 20 °C). It is oxidized by a stoichiometric amount of ferricinium hexafluorophosphate in THF; after recrystallization from acetone/ether, a 90% yield of the orange $Fe^{III}$ complex **3** is obtained (eq 2).

$$\underset{\mathbf{1}}{\mathrm{Fe^{II}Cp^*(CO)(P)(CH_3)}} \xrightarrow[\mathrm{THF,\ 30\ min,\ 20\ ^\circ C}]{\mathrm{Cp_2Fe^+PF_6^-}} \begin{array}{c}[\mathrm{Fe^{III}Cp^*(CO)(P)(CH_3)}]^+\mathrm{PF_6^-} \\ \mathbf{3},\ \mathrm{P} = \eta^1\text{-dppe}\end{array} \tag{2}$$

Complex **3** shows $\nu_{CO}$ at 1950 cm$^{-1}$ (Nujol) in the infrared spectrum, new Mössbauer parameters characteristic of $Fe^{III}$ (IS = 0.55 mms$^{-1}$ vs Fe, QS = 0.62 mm s$^{-1}$, 77 K), and satisfactory elemental analyses.[10] On the other hand,

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[1] Organometallic Electron Reservoirs. 33. For part 32, see: Lacoste, M.; Astruc, D.; *J. Chem. Soc., Chem. Commun.* **1987**, 667.

[2] This work was first started by D.C. in the Laboratoire de Chimie des Organométalliques, Université de Rennes. D. C. found that oxidation of $Fe^{II}(\eta^5\text{-}C_5Me_5)(CO)(\eta^1\text{-dppe})(CH_3)$ gives the stable $Fe^{III}$ cation: 3$^e$ cycle thesis, Rennes, 1982. The first exemple of electron transfer pathway in the reaction of $Ph_3C^+$ found in our Rennes' group concerns hydride abstraction from exosubstituted cyclohexadiene Fe(0) complexes: Mandon, D. Doctorate Thesis, Rennes, 1985. Mandon, D.; Toupet, L.; Astruc, D. *J. Am. Chem. Soc.* **1986**, *108*, 1320. For literature precedents, see the work by Cooper.[16]

[3] $As_2Me_4$ was found by Bunsen in 1837; see: Sidwick N. V. *The Chemical Elements and their Compounds*; Oxford University Press: London, New York, 1962.

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[8] For the preparation of $FeCp^*(CO)_2(CH_3)$, see: Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 1094.

[9] Complex 1: a 0.79-g (3-mmol) sample of $[Fe(C_5Me_5)(CO)_2\,CH_3]$ was irradiated in 150 mL of toluene by using a high-pressure Hanover mercury lamp in the presence of 1.23 g of 1.2-bis(diphenylphosphino)ethane for 1 h at 30 °C. After the solvent was removed in vacuo, the solid residue was extracted with 3 × 30 mL of pentane; air-stable red crystals of 1 were obtained upon cooling this solution down to −80 °C (1.23 g, 65% yield): $^1H$ NMR ($CDCl_3$, $\delta$ vs TMS) 7.53 (m, 20 H, Ph), 3.60 (m, 4 H, $CH_2$), 1.40 (s, 15 h, $C_5Me_5$), −0.60 (d, 3 H, $CH_3$, $^3J_{PH} = 20$ Hz); $^{13}C$ ($C_6D_6$, $\delta$ vs TMS) 188.3 (CO), 134.0, 133.9, 133.7, 133.4, 133.2, 132.7 (coordinated $PPh_2$), 128.7, 128.6, 127.7, 126.7, 126.30 (noncoordinated $PPh_2$), 85.5 ($\mathit{C}_5Me_5$), 29.7 ($CH_2$), 10.5 ($C_5\mathit{Me}_5$), −14.9 ($CH_3$); infrared (Nujol) 1900 cm$^{-1}$ ($\nu_{CO}$, large). Complex **2** is obtained by using the same procedure.

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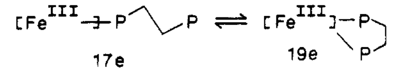
oxidation of the analogous complex 2 does not give a stable $Fe^{III}$ product. Thus, the pendent $PPh_2$ group in 3 plays a key role in the stabilization of the $Fe^{III}$ state, possibly by fast, reversible coordination[11] (eq 3).



(3)

In contrast to the Cp series,[11d] the migration of the methyl ligand onto the carbonyl is never observed upon oxidation of **1**, **2**, or FeCp*$(CO)_2$ Me, owing to the increased electron density on the iron center provided by Cp permethylation.

It has not proven possible to make chelated diphos complexes derived from **1** by removing CO either thermally or photolytically (in contrast to the Cp series[7d]) or by an oxidative pathway. The syntheses of such carbonyl free complexes proceeds by the route recently reported by Manriquez[12] and now extended to phosphines (eq 4).

$$\text{FeCp*(acac)} \xrightarrow[\text{2. P} + \text{CH}_3\text{MgI, } -80\ ^\circ\text{C}]{\text{1. P or dppe THF, } 25\ ^\circ\text{C}} \begin{array}{r} \text{FeCp*(P)}_2\text{(Me)} \\ \mathbf{4}, \text{P} = \text{PMe}_3\ (68\%) \\ \mathbf{5}, \text{P} = \text{P(OMe)}_3\ (70\%) \\ \mathbf{6}, \text{P}_2 = \text{dppe}\ (75\%) \end{array} \quad (4)$$

Crude yields around 70% (based on $Fe(acac)_2$) are obtained after extraction with pentane. Purification proceeds best by oxidation to the stable cations, and recrystallization of the latter followed by reduction. Yet, neither **4**[13] nor its one-electron oxidation product appear very stable at 20 °C. Complex **4**, an orange oil at 20 °C, is preferably stored at −40 °C and purified by pentane extraction at −80 °C immediately before use. Its anodic oxidation at −0.17 V vs SCE is chemically totally irreversible (Pt, DMF, *n*-$Bu_4NPF_6$, 20 °C) and becomes reversible at −75 °C in dichloromethane. Oxidation with ferricinium salts gave decomposition.

Complexes **5** and **6** are air-sensitive but indefinitely thermally stable under Ar and exhibited reversible one-electron anodic waves by CV[14] (Pt, DMF, *n*-$Bu_4NPF_6$, 20 °C) at −0.34 V (**5**) and −0.41 V vs SCE (**6**). They are easily oxidized by $Cp_2Fe^+PF_6^-$ or $Ph_3C^+PF_6^-$ in $CH_2Cl_2$ at 20 °C to the $Fe^{III}$ cations **7** and **8** (eq 5) which can be reduced back to $Fe^{II}$ by using Na/Hg or $[Fe^ICp(C_6Me_6)]$ in THF.

$$\begin{array}{l} \text{FeCp*(P)}_2\text{(Me)} \\ \mathbf{5}, \text{P} = \text{P(OMe)}_3 \\ \mathbf{6}, \text{P}_2 = \text{dppe} \end{array} \underset{\text{Na/Hg, THF, } 20\ ^\circ\text{C}}{\overset{\text{Cp}_2\text{Fe}^+\text{PF}_6^-\text{, CH}_2\text{Cl}_2\text{, } 20\ ^\circ\text{C}}{\rightleftarrows}} \begin{array}{r} [\text{FeCp*P}_2\text{(Me)}]^+\text{PF}_6^- \\ \mathbf{7}, \text{P} = \text{P(OMe)}_3 \\ \mathbf{8}, \text{P}_2 = \text{dppe} \end{array} \quad (5)$$

The brown complexes **7** and **8**, stable thermally and aerobically, are recrystallized from $CH_2Cl_2$ and hexane (82–92% yield).[15] Yields of complexes **5** (a bright orange oil) and **6** (a brown powder), purified via oxidation, are 30 and 45%, respectively, based on $Fe(acac)_2$. The $^1H$ and $^{13}C$ NMR spectra[15] of **4**, **5**, and **6** feature a high-field triplet assigned to the methyl ligand coupled to two equivalent phosphorus ligands ($^1H$ 0.98, − 0.87, and 1.23 ppm, respectively; $^{13}C$ for **7** −19.32 ppm ($^2J_{P-C} = 33.5$ Hz). Complexes **7** and **8** are inert toward $Ph_3C\bullet$ (from **5** or **6** + $Ph_3C^+$) in dichloromethane (25 °C). No H-atom abstraction is observed contrary to the W and Re alkyl series known to transfer $H^-$ to $Ph_3C^+$ according to an ET mechanism.[2,16–18] Complexes **7** and **8** are characterized[19] by elemental analysis, Mössbauer and EPR parameters, and magnetic susceptibility (Evans' method, $\mu_{eff} = 2.40\ \mu_B$),

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(10) Complex **3**: 0.63 g of **1** (1 mmol) and 0.33 g of $Cp_2Fe^+PF_6^-$ are stirred for 30 min in 10 mL of THF at 20 °C. After the solvent was removed in vacuo, the solid residue was dissolved in 30 mL of acetone and this solution was filtered and concentrated to 10 mL under vacuo; 20 mL of ether was added and the suspension allowed to stand overnight at −40 °C to give 0.7 g (90% yield) of **3** as orange microcrystals. Anal. Calcd for $C_{38}H_{42}FeP_3F_6O$: C, 58.70; H, 5.45; P, 11.95; Fe, 7.18. Found: C, 58.48; H, 5.45; P, 12.48; Fe, 7.89.

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(12) J.-M. Manriquez made FeCp*$(CO)_2Me$[8] by using a route analogous to that shown in eq 4: Bunuel, E. E.; Valle, L.; Manriquez, J.-M. *Organometallics* 1985, *4*, 1680. This paper also reports the preparation of FeCp*(acac).

(13) FeCp*$(PMe_3)_2$(Me) (**4**) was very recently reported by M. L. H. Green. It was made from $Fe(\eta^6\text{-}C_6H_6)(PMe_3)_2$ by successive treatments with Cp*H, $CH_2Cl_2$, and $CH_3MgI$: Green, M. L. H.; Wong, L.-L. *J. Chem. Soc., Dalton Trans.* **1987**, 411.

(14) Linear scan voltammetry (LSV) with stirring experiments verified passage of an anodic current. The constancy of $i_p v^{-1/2}$ indicate diffusion-controlled oxidations. $E_p - E_{p_a} = 60$ mV over scan speeds from 20 to 500 mV $s^{-1}$ indicated electrochemical reversibility. Over this scan range, the ratio of anodic peak current to cathodic peak current, $i_a/i_c$, is one (chemical reversibility). Ferrocene was used as an internal reference.

(15) Complex **4**: 1 g of $Fe(acac)_2$ (3.94 mmol) was dissolved in THF, and the solution was cooled to −80 °C. Cp*Li, generated in situ by adding BuLi to a THF solution of Cp*H at −80 °C followed by warming to room temperature, was slowly added by cannula into the cooled $Fe(acac)_2$ solution over a period of 5 min. The solution was allowed to warm to room temperature, and $PMe_3$ (0.814 mL 7.88 mmol) was added to the dark red solution. The solution turned a brillian violet. Cooling this solution to −80 °C and adding MeMgI (1 M, 3.94 mL) slowly yielded a brown solution upon warming to room temperature. The THF was removed in vacuo, and the product was extracted into pentane at −80 °C. Evaporation of the pentane gave a very air- and temperature-sensitive orange oil in 65% yield which is best stored at −20 °C: $^1H$ NMR (200 MHz, $C_6D_6$) $\delta$ 1.35 (s, 15 H), 0.82 (t, 18 H, $J_{P-H} = 7.8$ Hz), −0.98 (t, $J_{P-H} = 8$ Hz). Stable complexes **5** and **6** were synthesized by using the same procedure as for **4**. **5**: $^1H$ NMR (200 MHz, $CD_3COCD_3$) $\delta$ 3.55 (t, 18 H), 1.55 (s, 15 H), −0.67 (t, 3 H, $J_{P-H} = 4.8$ Hz); $^{31}P$ NMR ($CD_3COCD_3$) 183.8 ppm; $^{13}C$ NMR ($CD_3COCD_3$) $\delta$ 88.08 (s), 51.83 (tq, $J_{C-P} = 3.4$ Hz, $J_{C-H} = 144$ Hz), 9.82 (q, $J_{C-H} = 126$ Hz), −19.32 (tq, $J_{C-H} = 125$ Hz, $J_{C-P} = 33.5$ Hz). **6**: $^1H$ NMR ($C_6D_6$) $\delta$ 7.80 (s, 40 H), 1.36 (s, 15 H), 0.75–1.5 (m, 2 H), −1.35 (t, $J_{P-H} = 7.5$ Hz); $^{31}P$ NMR ($C_6D_6$) 105.7 ppm. Anal. Calcd for $C_{37}H_{36}FeO_6P_2$ (**5**); C, 44.95; H, 7.99. Found: C, 45.28; H, 8.09. Anal. Calcd for $C_{37}H_{42}FeP_2$ (**6**); C, 73.51; H, 7.00. Found: C, 73.18; H, 6.91.

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(18) (a) ET pathway in the hydride abstraction by $Ph_3C^+$ in FeCp*$(CO)_2\cdot CH_2OH$ has been reported,[18b], but latter retracted.[18c] (b) Guerchais, V.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1986**, 663. (c) Guerchais, V. Doctorate Thesis, Rennes, Jan 1987. (d) For systems probed for ET in the reaction of $Ph_3C^+$ with the $FeCp(CO)_2CH_2R$ series, see: Bly, R. S.; Bly, R. K.; Hossain, M. M.; Silverman, G. B.; Wallace, E. *Tetrahedron* **1986**, *42*, 1093.

(19) Complex **7**: to a dichloromethane solution of **5** (0.5 mmol, 0.227 g) at −50 °C was added a solution of $Cp_2Fe^+PF_6^-$ (0.5 mmol, 0.166 g). The solution was stirred for 2 h, and the solvent was removed in vacuo. The residue was washed with pentane and the mixture filtered to yield a dark brown powder which could be recrystalized from $CH_2Cl_2$–hexane (1:3) at −40 °C (82% yield): EPR (77 K) 2.35, 2.04, 2.00; Mössbauer doublet (77 K), IS vs Fe = 0.55 mm $s^{-1}$, QS = 0.60 mm $s^{-1}$. Anal. Calcd for $C_{17}H_{36}F_6FeO_6P_3$: C, 34.07; H, 6.06. Found: C, 33.87; H, 5.95. Complex 8: a THF solution of **3** (0.5 mmol, 0.302 g) and $Cp_2Fe^+PF_6^-$ was stirred for 2 h. The solvent was removed in vacuo, and the brown residue was washed with pentane and recrystallized from 40 mL of $CH_2Cl_2$–hexane–ether (1:1:1) at −40 °C (93% yield): EPR (10 K) 2.45, 2.04, 1.99. Anal. Calcd for $C_{37}H_{42}F_6FeP_3$: C, 59.29; H, 5.65. Found: C, 58.98; H, 5.64. Reduction of **5** to **7**: a THF solution of **5** (0.5 mmol, 0.227 g) was added by cannula into a Schlenk tube containing Na/Hg amalgam (0.1%, 20 g) or $FeCp(C_6Me_6)$ (0.5 mmol, 0.15 g) and stirred for 3 min or until the bright orange color of the product appeared. The solution was rapidly filtered into a third Schlenk tube, and the solvent was removed in vacuo. The oil was extracted into pentane and filtered to yield a bright orange oil in 52% yield. $^1H$ NMR spectra matched with those of *5*.

indicating the $Fe^{III}$ piano-stool, cationic structure. They do not react with CO or other two-electron donors at 25 °C in $CH_2Cl_2$. Complexes **5** and **6** react with $HBF_4 \cdot Et_2O$ under 1 atm of CO at −70 °C to give $[FeCp^*P_2(CO)]^+ BF_4^-$[8] (and presumably methane) as a consequence of protonation of the metal center. Since the reaction shown in eq 4 does not work with larger ligands such as $PBu_3$ and $P(OPh)_3$, one may conclude that adequate control of the steric bulk provides a route to both stable series of $Fe^{II}$–$CH_3$ and $Fe^{III}$–$CH_3$ complexes.

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**Registry No.** **1**, 111004-92-3; **2**, 111004-93-4; **3**, 111004-94-5; **4**, 94585-62-3; **5**, 111004-95-6; **6**, 111004-96-7; **7**, 111004-97-8; **8**, 111004-98-9; $FeCp^*(CO)_2(CH_3)$, 52409-66-2; $Fe(acac)_2$, 14024-17-0; Cp*H, 4045-44-7.

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# An Unusual Ring-Opening Reaction of (Tetrafluorobenzobicyclo[2.2.2]octatriene)tricarbonyliron

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*Summary:* Reaction of the title compound I with aryllithium reagents in ether at low temperature and subsequent alkylation of the acylmetalates formed with $Et_3OBF_4$ leads to an unusual ring-opening reaction of the bicyclodiene ligand to generate novel chelated diallyldicarbonyliron complexes II–VII. Complex V belongs to the monoclinic space group $C_{2h}^6$—$C2/c$ with $a$ = 16.870 (4) Å, $b$ = 13.707 (4) Å, $c$ = 19.361 (4) Å, $\beta$ = 107.92 (2)°, $V$ = 4259 (1) Å$^3$, and $D_{calcd}$ = 1.51 g/cm$^3$ for $Z$ = 8. Least-squares refinement based on 2481 observed reflections led to a final $R$ of 0.0409 and $R_w$ of 0.0391.

Recently, we found that several cyclic polyene ligands such as cyclohexadiene,[1] cycloheptatriene,[2] and cyclooctatetraene[3] in (cyclopolyene)tricarbonyliron complexes can be activated by the iron. A series of interesting isomerized olefin–metal carbene complexes were obtained by the reaction of the corresponding olefin–ligating metal carbonyl compounds with an aryllithium and subsequent alkylation with $Et_3OBF_4$. As an extension of our research in this field we have studied such reactions of a bicyclopolyene ligand, tetrafluorobenzobicyclo[2.2.2]octatriene. Herein we report an unusual ring-opening reaction of tetrafluorobenzobicyclo[2.2.2]octatriene tricarbonyliron (I)[4] with nucleophiles at low temperature, followed by alkylation with $Et_3OBF_4$, which led to the breaking of the tetrafluorobenzobicyclo[2.2.2]octatriene ring and the formation of novel chelated diallyldicarbonyliron complexes.

Reaction of I with about 20% excess of an aryllithium in ether at −60 °C and subsequent alkylation of the acylmetalates formed with $Et_3OBF_4$ in aqueous solution at 0 °C leads to the isolation of orange-red chelated diallyldicarbonyliron complexes II–VII.[5] Elemental analyses and spectroscopic data[6] are consistent with their compositions and assigned structures. A possible reaction mechanism is proposed in Scheme I. The alkylation of acylmetalate intermediates **a** initially gives unstable olefin-coordinated alkoxycarbene complexes **b**[7] that are transformed into metallacyclobutane intermediates **c** prior to the formation of the transition state **d**. The latter gives new carbene–alkene complexes **e** upon opening of the ring. Subsequent hydrogen migration leads to the isomerized carbene complexes II–VII.

Complexes II–VII were readily soluble in polar solvents and moderately soluble in nonpolar solvents such as pentane and petroleum ether. Several day's exposure of II–VII in the solid state to air at room temperature showed little evidence of oxidative decomposition, whereas the acylmetalate intermediates (**a**) were highly sensitive to air and temperature. These new complexes were characterized by

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(3) Chen, J.-B.; Lei, G.-X.; Xu, W.-H.; Pan, Z.-H.; Zhang, S.-W.; Zhang, Z.-Y.; Jin, X.-L.; Shao, M.-C.; Tang, Y.-Q. *Organometallics*, in press.

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(5) Experimental Procedure. To a solution of 0.20 g (0.55 mmol) of I in 30 mL of ether was added dropwise 0.65 mmol of the appropriate aryllithium, ArLi (Ar = $C_6H_5$, *o*-, *m*-, or *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-$ClC_6H_4$), in 20 mL of ether at −65 °C. After being stirred at −60 to −40 °C for 3–4 h, the resulting orange solution was concentrated to dryness under vacuum at −40 °C. The residue was dissolved in 25 mL of $N_2$-saturated water at 0 °C to give an orange-red solution, to which was added immediately $Et_3OBF_4$ in portions with vigorous stirring until the aqueous solution became acidic. The aqueous solution was extracted with petroleum ether (30–60 °C), and the combined extracts were concentrated under vacuum at −20 °C. Column chromatography of the residue on alumina at −20 °C followed (petroleum ether and then petroleum ether/ether (10/1)). The crude product was recrystallized from petroleum ether at −80 °C to give orange to red crystals of II–VII, respectively.

(6) II: yield 75%; mp 96–97 °C dec. Anal. Calcd for $C_{23}H_{16}O_3F_4Fe$: C, 58.50; H, 3.42. Found: C, 58.95; H, 3.90. IR ($\nu_{CO}$, hexane): 1992 (vs), 1943 (vs) cm$^{-1}$. $^1H$ NMR ($\delta$, $CDCl_3$): 7.30 (m, 5 H), 4.90 (t, 1 H), 4.65 (t, 1 H), 3.84 (m, 1 H), 3.52 (m, 1 H), 3.40 (m, 2 H), 1.64 (m, 1 H), 1.24 (t, 3 H), 0.86 (m, 1 H). MS: *m/e* (relative intensity) 472 ($M^+$, 10.7), 444 ($(M - CO)^+$, 7.7), 416 ($(M - 2CO)^+$, 100). III: yield 78%; mp 122 °C dec. Anal. Calcd for $C_{24}H_{18}O_3F_4Fe$: C, 59.28; H, 3.73. Found: C, 59.52; H, 3.54. IR ($\nu_{CO}$, hexane): 1985 (vs), 1938 (vs) cm$^{-1}$. $^1H$ NMR ($\delta$, acetone-$d_6$): 7.24 (m, 4 H), 5.20 (br, 1 H), 4.84 (br, 1 H), 3.86 (br, 2 H), 3.50 (m, 2 H), 2.60 (s, 3 H), 1.62 (m, 1 H), 1.24 (m, 3 H), 0.90 (m, 1 H). MS: *m/e* (relative intensity) 486 ($M^+$, 2.3), 458 ($(M - CO)^+$, 3.7), 4.30 ($(M - 2CO)^+$, 24.7). IV: yield 57%; mp 114–116 °C dec. Anal. Calcd for $C_{24}H_{18}O_3F_4Fe$: C, 59.28; H, 3.73. Found: C, 59.51; H, 3.92. IR ($\nu_{CO}$, hexane): 1990 (vs), 1943 (vs) cm$^{-1}$. $^1H$ NMR ($\delta$, acetone-$d_6$): 7.20 (m, 4 H), 4.90 (m, 1 H), 4.64 (m, 1 H), 3.84 (m, 1 H), 3.52 (m, 1 H), 3.40 (m, 2 H), 2.36 (s, 3 H), 1.60 (m, 1 H), 1.24 (m, 3 H), 0.88 (m, 1 H). MS: *m/e* (relative intensity) 486 ($M^+$, 2.3), 458 ($(M - CO)^+$, 3.3), 430 ($(M - 2CO)^+$, 7.1). V: yield 62%; mp 116–118 °C dec. Anal. Calcd for $C_{24}H_{18}O_3F_4Fe$: C, 59.28; H, 3.73. Found: C, 58.98; H, 3.66. IR ($\nu_{CO}$, hexane): 1989 (vs), 1935 (vs) cm$^{-1}$. $^1H$ NMR ($\delta$, acetone-$d_6$): 7.38 (d, 2 H), 7.10 (d, 2 H), 5.10 (t, 1 H), 4.82 (t, 1 H), 3.82 (m, 2 H), 3.50 (q, 2 H), 2.28 (s, 3 H), 1.82 (m, 1 H), 1.24 (t, 3 H), 0.92 (m, 1 H). MS: *m/e* (relative intensity) 486 ($M^+$, 27.0), 458 ($(M - CO)^+$, 22.8), 430 ($(M - 2CO)^+$, 100). VI: yield 29%; mp 124–126 °C dec. Anal. Calcd for $C_{24}H_{18}O_4F_4Fe$: C, 57.38; H, 3.61. Found: C, 57.35; H, 3.42. IR ($\nu_{CO}$, hexane): 1982 (vs), 1931 (vs) cm$^{-1}$. $^1H$ NMR ($\delta$, acetone-$d_6$): 7.42 (d, 2 H), 6.88 (d, 2 H), 5.08 (t, 1 H), 4.83 (t, 1 H), 3.74 (m, 2 H), 3.66 (s, 3 H), 3.42 (q, 2 H), 1.76 (m, 1 H), 1.18 (t, 3 H), 0.92 (m, 1 H). MS: *m/e* (relative intensity) 502 ($M^+$, 2.8), 474 ($(M - CO)^+$, 1.8), 446 ($(M - 2CO)^+$, 30.6). VII: yield 23%; mp 127–129 °C dec. Anal. Calcd for $C_{23}H_{15}O_3ClF_4Fe$: C, 54.51; H, 2.98. Found: C, 54.35; H, 2.62. IR ($\nu_{CO}$, hexane): 1993 (vs), 1945 (vs) cm$^{-1}$. $^1H$ NMR ($\delta$, acetone-$d_6$): 7.30 (dd, 4 H), 5.10 (t, 1 H), 4.82 (t, 1 H), 3.88 (m, 2 H), 3.50 (q, 2 H), 1.84 (m, 1 H), 1.18 (t, 3 H), 0.92 (m, 1 H). MS: *m/e* (relative intensity) 506 ($M^+$, 4.1), 478 ($(M - CO)^+$, 5.8), 450 ($(M - 2CO)^+$, 21.5).

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