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Synthesis and cyclic voltammetric studies of diiron complexes, $\text{ER}_2[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{L}_2)\text{Me}]_2$ ($\text{E} = \text{C, Si, Ge, Sn}$; $\text{R} = \text{H, alkyl}$; $\text{L}_2 =$ diphosphine) and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{L}_2)\text{ER}_2\text{Fc}$ [$\text{Fc} = (\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$]

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Summary

The cyclic voltammetric studies on $\text{ER}_2[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{L}_2)\text{Me}]_2$ ($\text{L}_2 = \text{dppe}$; $\text{ER}_2 = \text{CH}_2$ (**1a**), SiMe_2 (**2a**), GeMe_2 (**3a**), SnMe_2 (**4a**)) revealed two well resolved reversible waves [$^1\text{E}_{1/2} = -0.33$ V, $^2\text{E}_{1/2} = -0.20$ V (for **1a**); $^1\text{E}_{1/2} = -0.35$ V, $^2\text{E}_{1/2} = -0.21$ V (for **2a**); $^1\text{E}_{1/2} = -0.36$ V, $^2\text{E}_{1/2} = -0.23$ V (for **3a**); $^1\text{E}_{1/2} = -0.36$ V, $^2\text{E}_{1/2} = -0.22$ V (for **4a**)] in CH_2Cl_2 suggesting electronic communication between two iron centers which is seen for the first time in this family of organometallic complexes. The resolution between two reversible waves increases in the order of **1a** < **2a** < **3a** < **4a**; however, coordinating solvents such as pyridine, PhCN, DMSO and DMF decreased these interactions attributable to the stabilization of cationic species formed after the first oxidation. UV/Vis spectroelectrochemistry of **1a-4a** revealed two distinct absorbance patterns for both redox processes and reflected the stepwise oxidation. Homobimetallic complexes containing ferrocenyl groups, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{L}_2)\text{ER}_2\text{Fc}$ [$\text{ER}_2 = \text{none}$, $\text{L}_2 = \text{cis-dppen}$ (**5a**), $\text{ER}_2 = \text{SiMe}_2$, $\text{L}_2 = \text{cis-dppen}$ (**6a**), dppm (**6b**); $\text{ER}_2 = \text{GeMe}_2$, $\text{L}_2 = \text{cis-dppen}$ (**7a**), dppm (**7b**); $\text{ER}_2 = \text{Sn}^t\text{Bu}_2$, $\text{L}_2 = \text{dmpe}$ (**8a**); $\text{Fc} = (\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$] were prepared and studied in terms of electrochemistry. The cyclic voltammogram of **5a** exhibited two well resolved one electron reversible waves at $^1\text{E}_{1/2} = -0.21$ V and $^2\text{E}_{1/2} = 0.58$ V corresponding to oxidation of the Fe(P-P) and Fc iron atoms respectively. Other complexes in this series (**6a/6b**, **7a/7b**, **8a**) containing direct Fe-E-Fc ($\text{E} = \text{Si, Ge and Sn}$) bridging units were not stable under electrochemical conditions and rupture of the Fe-E bonds was observed.

Introduction

Organometallic complexes with two or more redox-active transition metals linked by specific bridging spacers are of interest due to possible electronic communications and mixed-valence behavior.¹ Such materials have potential properties related to semiconductivity, molecular electronics, photo-/electroluminescence, magnetism and nonlinear optics.^{1, 2} For example, bis-ferrocenyl complexes³⁻⁵ bridged by different spacers such as $(\text{SiMe}_2)_n$ (Figure 1, C) and $(\text{CH}=\text{CH})_n$ ⁵ etc. exhibit electronic interactions depending upon the value of n . Similarly, ferrocenylene-silylene polymers, $[\text{FCSiMe}_2]_n$ have been investigated in detail in terms of electrochemistry,⁶ and I_2 doping experiments on thin films of such polymers exhibited mixed-valence character and conducting properties.^{6f} Furthermore, Mossbauer spectroscopy of these

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Supporting information available. Crystallographic data in CIF format CCDC 661327 (for **6b**) and 661328 (for **9**). This material is available free of charge via Internet at <http://pubs.acs.org>.

mixed valence systems indicated significant thermal transformations from $[\text{FC}]^+$ to $[\text{FC}]$ due to the presence of the $[\text{I}_3]^-$ and $[\text{I}_5]^-$ counteranions^{6g}.

Homo/hetero bi/trimetallic complexes with conjugated and rigid spacers such as $-\text{C}\equiv\text{C}-$, $-\text{C}\equiv\text{C}-\text{aryl}-\text{C}\equiv\text{C}-$ have been utilized with a variety of transition metals and their electrochemical properties in terms of mixed-valence behavior and electron delocalization disclosed.⁷ Furthermore, the electrochemical properties of other metal complexes containing redox-active ligands, e.g. tetrathiafulvene,⁸ 1,2-dioxalenes⁹, catecholate, semiquinone/quinone⁹ and ferrocene based ligands¹⁰, have also been evaluated to create an active area of modern organometallic materials chemistry.

Recently we reported the electrochemistry of monoiron complexes, $(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{L}_2)\text{ER}_3$ [L_2 = bis-(diphenylphosphino)methane (dppm); $\text{ER}_3 = \text{CH}_3$, SiMe_3 , GeMe_3 , SnMe_3]¹¹ and 1,3-ferracyclobutanes, $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{L}_2)\text{CH}_2\text{SiMe}_2]$ ($\text{L}_2 = \text{dppm}$, dppe , dppp)¹². As part of our continuing interest in such materials we report the synthesis and electrochemical characteristics of group 14 element bridged bimetallic iron complexes involving the ferrocenyl and cyclopentadienylirondiphosphine moieties, $\text{ER}_2[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{L}_2)\text{Me}]_2$ ($\text{E} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$; $\text{R} = \text{H}, \text{Me}$; L_2 = diphosphine) and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{L}_2)\text{ER}_2\text{Fc}$ [$\text{Fc} = (\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$] (Figure 1; **A, B**).

Results and discussion

Group A Compounds

$\text{ER}_2[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{L}_2)\text{Me}]_2$ ($\text{L}_2 = \text{dppe}$; $\text{ER}_2 = \text{CH}_2$ (**1a**), SiMe_2 (**2a**), GeMe_2 (**3a**), SnMe_2 (**4a**))

Synthesis—Dicarbonyl precursors, $\text{ER}_2[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{Me}]_2$ [$\text{ER}_2 = \text{CH}_2$ (**1**), SiMe_2 (**2**)] were prepared from the reaction between $\text{ER}_2(\text{Fp}^-\text{Na}^+)_2$ [$\text{Fp} = \eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2$]¹³ and iodomethane at low temperature, equation 1. The corresponding complexes $\text{ER}_2[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{Me}]_2$ [$\text{ER}_2 = \text{GeMe}_2$ (**3**), SnMe_2 (**4**)] were synthesized by the base-induced double migration chemistry outlined in equation 2.¹⁴

(2)

The initial dicarbonyl complexes, **1-4** were treated photochemically (2-3 days) with two equivalent of the appropriate diphosphine to form the redox-active complexes; **1a-4a**, in 60-70% yield, equation 3.

(3)

The photochemical reactions were monitored by ^{31}P NMR and IR spectroscopy and the stepwise CO substitutions could be observed; however, we made no attempt to isolate the intermediate complexes formed during this process. The desired compounds were isolated as red/orange solid materials and are soluble in common organic solvents and characterized by NMR and elemental analysis.

Spectroscopic characterization—NMR spectroscopic analyses of **1-4** and **1a-4a** are in total accord with their proposed structures and are presented within the experimental section. Thus, as expected, ^{13}C NMR spectra exhibited triplets for the Fe-Me carbon due to the heteronuclear coupling with two equivalent P atoms and appeared in the range of -17.0 to -21.0 ppm. Decoupled ^{31}P NMR spectra exhibited a single resonance in each compound in the range of 109.0-112.0 ppm which is ~ 130 ppm downfield as compared to the uncoordinated diphosphine and are comparable to that observed for $[(\eta^5-C_5H_4)Fe(dppe)CH_2SiMe_2]$ ¹² and other diphosphine derivatives of iron.^{7b, 7e, 15} ^{29}Si and ^{119}Sn NMR resonances for **2a** and **4a** appeared at δ -10.6 and -27.5 ppm respectively exhibiting the expected chemical shift differences as compared to **2** and **4**.¹¹

Cyclic voltammetry—The cyclic voltammograms of the dicarbonyl derivatives, **1-4**, showed only one irreversible oxidation in the range of 1.2-1.4 V (TBAP/dichloromethane, GCE), typical of the Fp derivatives.¹⁶ No apparent intramolecular communication between the two Fe atoms is observed prior to decomposition; however, the oxidation wave is quite broad compared to those of related reversible systems and probably contain several distinct processes. On the other hand, compounds **1a-4a** exhibited two reversible waves (Figure 2). The CH_2 bridged complex (**1a**) showed a weakly resolved pair of reversible waves and they were identified at $^1E_{pa} = -0.26$ V, and $^2E_{pa} = -0.17$ V in dichloromethane (Table 1). Surprisingly the difference between the two oxidations, $^1E_{pa}$ and $^2E_{pa}$ (ΔE_{pa}) values changes relatively little

as a consequence of changing the nature of the group 14 bridge and although the resolution between the two increases in the order C<Si<Ge<Sn. The same is true for the half wave potential values ($E_{1/2}$).

The difference between the two redox processes can be expressed as $\Delta E_{1/2}$ (V) = $E_{1/2}^2 - E_{1/2}^1$ where $E_{1/2} = (E_{pa} + E_{pc})/2$ and in general this value is similar to the simpler ΔE_{pa} ($E_{pa}^2 - E_{pa}^1$). For complexes **1a-4a** such values are in the range 0.09 - 0.14 V with the single atom bridges. By comparison a series of ferrocenylpolyenes, $\text{Fc}(\text{CH}=\text{CH})_n\text{Fc}$ exhibited $E_{1/2} = 0.17$ V, $n = 1$ and 0.12 V, $n = 2$,⁵ whereas the class **C** compounds, $\text{Fc}(\text{SiMe}_2)_n\text{Fc}^4$ had values of E_{pa} ; 0.34 V, $n = 0$; 0.15 V; $n = 1$; 0.11, $n = 2$; 0.08 V, $n = 3$. These data reveal that the extent of electronic communication between two iron atoms is much higher when $n = 0$ and quickly decreases as n increases. Thus, the present complexes compare reasonably with those noted above. However, by comparison, the 1, 1'-ferrocenophanes, $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{ER}_2)]_2$, were reported to have larger $\Delta E_{1/2}$ (V) values of $\text{CH}_2 = 0.20$,¹⁷ $\text{Sn}^n\text{Bu} = 0.20$,¹⁸ $\text{SiMe}_2 = 0.25$,¹⁹ $\text{Sn}^t\text{Bu}_2 = 0.27$,²⁰ $\text{SnMe}_2 = 0.28$,²⁰ $\text{PbPh} = 0.28$,²¹ as compared to **1a-4a**.

The use of a more coordinating solvent, pyridine resulted in decrease of the resolution of both the waves and reduction in the oxidation potentials for the various processes. To determine the solvent effect on the difference between the two oxidation potentials, cyclic voltammograms for compound **4a** were recorded using the polar solvents PhCN, DMF and DMSO. A significant correlation exists between the solvent dielectric constant and $\Delta E_{1/2}$; the more polar the solvent the smaller the separation, e.g. variations from 0.90 mV in DMF to 140 mV in CH_2Cl_2 (see figure in the supplementary data). The better the stabilization of the initially formed charge by the solvent the lesser is the impact of that charge upon the neighboring metal center oxidation process.²²

The comproportionation associated with the reaction for a class II system is shown in equation 4.

(4)

The K values, K_c were calculated by using the $e[(2E_{1/2} - E_{1/2}^1)n_1n_2F]/RT$ relationship [$n_1 = n_2 = 1$; F = Faraday constant, R = gas constant, $T = 293$ K].²³ As shown in Table 1, the values for K_c (CH_2Cl_2) in the range of 170 - 260, are greater than those for $[(\text{Cp}^*(\text{dppe})\text{Fe}(-\text{C}\equiv\text{C}-))_2(1,3\text{-C}_6\text{H}_4)]$ ($K_c = 130$) and $[(\text{Cp}^*(\text{dppe})\text{Fe}(-\text{C}\equiv\text{C}-))_3(1,3,5\text{-C}_6\text{H}_4)]$ ($K_c = 130$).^{7f} These data suggest that for complexes **1a-4a** the equilibrium favors mixed-valence species.

UV/Vis spectroelectrochemistry of 1a-4a—A UV/Vis spectroelectrochemical study of **1a-4a** was performed in the region 300 - 1100 nm. The spectral changes of both **1a** and **4a** upon oxidations are available in the supplementary material. Compound **1a** showed four isosbestic points at 324, 430, 508 and 578 nm for the first oxidation at -0.20 V, while for the second oxidation process at 0.0 V three isosbestic points at 326, 426 and 497 nm are observed. Similar behavior was noted for **2a**, **3a** and **4a**. All spectral variations are reversible as are the electrochemical processes. However, due to the small changes in molar absorptivity of these compounds, no significance conclusions about the electronic transitions could be made at this time (see figure in the supplementary data). We observed no well-defined NIR bands in the region 800 - 1100 nm but the region 1100 - 2500 was not examined.

Group B compounds

$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{L}_2)\text{ER}_2\text{Fc}$ [$\text{ER}_2 = \text{none}$, $\text{L}_2 = \text{cis-dppen}$ (**5a**), $\text{ER}_2 = \text{SiMe}_2$, $\text{L}_2 = \text{cis-dppen}$ (**6a**), dppm (**6b**); $\text{ER}_2 = \text{GeMe}_2$, $\text{L}_2 = \text{cis-dppen}$ (**7a**), dppm (**7b**); $\text{ER} = \text{Sn}^t\text{Bu}_2$, $\text{L}_2 = \text{dmpe}$ (**8a**); $\text{Fc} = (\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$]

Synthesis and characterization—Compound **5**, containing a direct ferrocenyl-iron bond, was prepared by the salt-elimination reaction between FcLi and FpI [$\text{Fc} = \eta^5\text{-C}_5\text{H}_4\text{FeC}_5\text{H}_5$, $\text{Fp} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$]²⁴, equation 5. Synthesis of **6**, **7** and **8** involved quenching Fp^-Na^+ with FcECl [$\text{E} = \text{SiMe}_2$, $\text{GeMe}_2\text{Sn}(t\text{Bu})_2$]²⁵, equation 6. The synthesis of FcECl was achieved in good yield using the procedure reported in literature involving the reaction of corresponding 1-ferrocenophane with HCl .²⁶ Infrared, ^1H , ^{13}C , ^{29}Si and ^{119}Sn NMR spectroscopic analysis were in accord with their structural formulation and the data are presented in the experimental section.

(6)

Ultraviolet irradiation of **5-8** in the presence of a diphosphine (24-36 hrs) resulted in the formation of the expected CO-substituted products, equation 7. These reactions were monitored by IR and ^{31}P NMR spectroscopy and showed the stepwise replacement of the CO groups; however, we made no attempt to isolate the mono-substituted materials. The diphosphine derivatives, **5a**, **6a/6b**, **7a/7b** and **8a**, were isolated as orange/red solid materials and purified by recrystallization from toluene/hexane mixtures.

ER_2 = none (5), $SiMe_2$ (6), $GeMe_2$ (7), Sn^tBu_2 (8)

cis-dppen = Bis(diphenylphosphino)ethylene
 dppm = Bis((diphenylphosphino)methane
 dmpe = Bis((dimethylphosphino)ethane

ER_2 = none, L_2 = cis-dppen (5a)

ER_2 = $SiMe_2$, L_2 = cis-dppen (6a), dppm (6b)

ER_2 = $GeMe_2$, L_2 = cis-dppen (7a), dppm (7b)

ER_2 = Sn^tBu_2 , L_2 = dmpe (8a)

(7)

The ^1H and ^{13}C NMR spectral properties of the new complexes are in accord with their proposed structures. The ^{29}Si NMR spectra of both **6a** and **6b** showed a triplet due to two bond heteronuclear coupling for the $SiFeP_2$ moiety [26.0 ppm, $^2J_{Si-P} = 45.7$ Hz (**6a**), 26.7 ppm, $^2J_{Si-P} = 44.5$ Hz (**6b**)] reflecting the expected moderate upfield shift when compared to **6** [36.2 ppm].²⁵ Similarly, a triplet ($^2J_{Sn-P} = 409$ Hz) in the ^{119}Sn NMR spectrum of **8a** was observed at 167.0 ppm. ^{31}P NMR spectra of all these compounds showed a downfield shift as compared to free phosphine ligands.

Crystal structure of 6b—There is apparently only a single literature report concerning the structures of $Fp(L_2)R$ complexes, that of $Fp(dppm)Ph$.²⁷ The structural data reveal a piano stool arrangement at the Fe atom with Fe-P1 and Fe-P2 bond distances of 2.199 (1) and 2.174 (1) Å, respectively, with a P1-Fe-P2 bite angle of 73.8 (0)°.

The molecular structure of **6b**, as determined by single crystal X-ray analysis of a crystal formed from a benzene/hexane solvent mixture, also exhibits a piano stool arrangement at Fe as shown in Figure 3. The crystallographic data and selected bond lengths and angles are summarized in Tables 2 and 3, respectively. Compound **6b** crystallizes in a monoclinic crystal system with C2/c space group and each molecule in the unit cell crystallizes with 1.5 molecules of C_6H_6 ; however, the benzene molecule has no apparent interactions with the iron complex. The Fe_2-Si distance of 2.3786(8) Å is reminiscent of the related dicarbonyl complexes [$(\eta^5-C_5H_5)Fe(CO)_2Si_2Me_4$ ($Fe-Si = 2.375(2)$ Å)²⁸, $(\eta^5-C_5H_5)Fe(CO)_2SiMe_2SiPh_3$ ($Fe-Si = 2.346(1)$ Å)²⁹ and $(\eta^5-C_5H_5)Fe(CO)_2SiMe_2GePh_3$ ($Fe-Si = 2.328(1)$ Å)³⁰. The geometry around the Si atom is that of a slightly distorted tetrahedral ($C41-Si-C42 = 103.22(12)$, $C42-Si-C2 = 100.66(12)$, $C41-Si-C2 = 103.75(12)$ °). The Fe-P bond distances are 2.1921(7) and 2.1872(7) Å and the P2-Fe2-P1 bite angle for is found to be 74.44(3)°. Such values are almost identical to those noted above for $Fp(dppm)Ph$ ²⁷ and also those observed in $Fe(CO) dppm$ ³¹ ($P_1-Fe-P_2 = 73.5(1)$ °; $Fe-P_1 = 2.209(4)$, $Fe-P_2 = 2.225(3)$ Å). Related bidentate phosphine complexes with larger chelate rings do, as expected, have much larger bite angles, e.g. $Cp^*(dppe)Fe-C$ C-9,10-ant-CC- $FeCp^*(Dppe)$ ^{7b} (85.42(5)); $[Cp^*Fe(dppe)]_3(C\equiv C)_3(\mu-1,3,5-C_6H_3)$ ^{7c} (84.7(1), 83.7(4), 85.7(1)°) and $[Fc-C\equiv C-CpFe(dppe)]$ ^{7d} (86.7(2)°) [ant = anthracene, dppe = bis(diphenylphosphino)ethane].

The X-ray structure determination of the monoiron analog, $(\eta^5-C_5H_5)Fe(dppm)SiMe_3$ (**9**) (see reference 11 for the synthesis of **9**) was also performed in order to compare the variations in structural pattern of Fe-Si/Fe-P bond distances and PFe-P bite angles (Figure 4; Tables 2, 3).

The differences between the structures of **6b** and **9** are associated with the Fe-Si/Fe-P bond distances and P-Fe-P bite angles. The Fe-Si bond distance observed for **9** [Fe-Si = 2.4756 (10) Å] is significantly longer than other reported bond lengths Fe-Si and obviously that found in **6b** 2.3786(8) Å. Similarly the two Fe-P bond distances, Fe-P1 = 2.2789(9), Fe-P2 = 2.0878(9) exhibit a distinct variation with those in **6b** and Fp(dppm)Ph²⁷ and exhibit a greater intrametal Fe-P bond distance difference. It may also be noted that the P1-Fe-P2 bite angle in this complex is sharply reduced to 67.35(3)°. The replacement of one methyl by a ferrocenyl on the trimethylsilyl group gives rise to a large variation in the crystal structure parameters. The extra crowding around the Fe atom of the Fp group results in greater Fe-Si bond lengths, a reduced bite angle and greater asymmetry at that metal center.

Cyclic Voltammetry and UV/Vis Spectroelectrochemistry of (η^5 -C₅H₅)Fe(cisdppen)Fc (5a**)**—The cyclic voltammogram of (η^5 -C₅H₅)Fe(cis-dppen)Fc (**5a**) in dichloromethane containing 0.1 M TBAP from -0.5 to 1.0 V (vs SCE) revealed two well-separated one electron reversible redox processes at $E_{1/2}$ = -0.21 and 0.58 V with an i_{pa}/i_{pc} current ratio of 1.0. These processes were assigned to the iron centers in the Fp and Fc moieties, respectively, Figure 5. The first oxidation of the Fp moiety makes the ferrocenyl group more difficult to oxidize as found by comparison with the oxidation potential of the pure ferrocene, 0.54 V (vs. SCE). This can be accounted for by either a weak communication between the two metal centers or an electronic effect of the Fp substituent on the Fc center.

Complex **5a** exhibited a clean UV/Vis spectroelectrochemistry as illustrated in Figure 6. The first oxidation at +0.20 V revealed two isosbestic points at 314 and 402 nm. A broad and intense band is formed between 402-700 nm. The magnitude of the absorbance associated with the low energy band in the spectra are strongly suggestive of a charge transfer between the Fc and Fp(P-P) groups that occurs after the first oxidation of Fp(P-P) moiety. These low energy bands may be best described as LMCT bands.^{7b} The second oxidation at 0.80 V, Figure 6b, also exhibited two isosbestic points at 480 and 750 nm; however, the spectral pattern is different from that expected for a simple Fc/Fc⁺ transformation. Interestingly, after the second oxidation, there is a significant reduction in the absorbance in the region of the CT bands.

Cyclic Voltammetry 6a/ 6b, 7a/7b and 8a—Cyclic voltammograms of compounds **6a** and **6b**, containing a dimethylsilyl bridging group between the Fp(P-P) and Fc moieties, were obtained in dichloromethane/TBAP solution. The results for **6a** are illustrated in Figure 7 and reveal three oxidations and that of **6b** is similar, Table 5. A first reversible oxidation at ~0.0 V is reminiscent of those noted above for the Fp(P-P) part of the molecule and the third reversible oxidation in the region of ~0.5 V is typical of those associated with a ferrocenyl group. However, the system is neither simple nor clean. Recycling the electrochemistry process illustrates that the initial Fp(P-P) reversible oxidation disappears. After the initial oxidation of the Fp(P-P) group, there appears to be a cleavage of the Fe-Si bond in these complexes under these conditions. The chemical decomposition is slow compared to the electrochemical reversibility but continued spectral observation of the initially formed oxidation product illustrates the slow decomposition.

Related cyclic voltammetric studies on the germyl-bridged bimetallic complexes **7a/7b** showed four oxidations (TBAP, GCE, PtE), the first three of which resemble those observed for **6a** and **6b**. The reason for the appearance of a fourth oxidation is unclear and further illustrates the ready cleavage and decomposition of Fe-metalloid bonds as observed for the silyl complexes discussed above. The organotin analog **8a** revealed two irreversible redox in Fp(P-P) region and one reversible wave observed in Fc region all of which are of uncertain provenance but seem to indicate a lesser stability of the particular Fe-Sn bond upon oxidation.

The spectroelectrochemical UV/Vis data associated with the above processes confirm the above analysis. The spectral changes observed with the first redox processes for **6a/6b** and **7a/7b** at ~0.0 V are essentially identical and a representative spectroelectrogram of **6b** is shown in Figure 8a. Maintaining the oxidation potential in the experiment at 0.25 V, i.e. well below the potential where the subsequent oxidations become significant, results in a well-defined reversible optical change, Figure 8a. Two isosbestic points are observed at 320 nm and 375 nm, a pattern similar to those in the related Fp(dppm)SiMe₃ complex (isosbestic points at 340 nm and 395 nm, Figure 8c). The maximum wavelength of the low energy band in **6a/6b** and **7a/7b** are at ~500 nm compared to those of the Fp(P-P)EMe₃ complexes at ~430 nm, presumably an effect associated with the Fc substituent. The ferrocenyl-type redox process observed for **6a** and **7a** at ~0.5 V exhibits a typical spectral property for an Fc/Fc⁺ process as may be observed for **6b** in Figure 8b. The typical UV/vis spectral changes of Fc/Fc⁺ is shown in Figure 8d.

Attempted chemical oxidation of 6a and 7a—To investigate this reactivity we treated complexes **6a** and **7a** to a chemical oxidation reaction using AgPF₆. From the reaction mixture we were able to isolate FcSiMe₂F (or FcGeMe₂F) in good yield thereby confirming the facile oxidative cleavage of the Fe-Si/Fe-Ge bonds. FcSiMe₂F (from **6a**)³² and FcGeMe₂F (from **7a**) were isolated as hexanes soluble products while the iron compound, [CpFe(Ph₂PCH=CHPPh₂)]PF₆ was isolated as acetone soluble product from residue of both the reactions, Scheme 1.

NMR spectroscopy and elemental analysis confirmed the formation of these products and ESI Mass spectroscopy of FcGeMe₂F revealed the [M]⁺ at m/z 306 and [M⁺-F] at m/z 287. Stable 17e⁻ Cp*Fe(dppe) and its 16 e⁻ oxidized [Cp*Fe(dppe)]⁺PF₆⁻ complex are reported in the literature and analysis by X-ray crystallography revealed their structures.³³ This further proves that after oxidation the Fe-E bond was not stable and ruptured to form [FcEme + 2] species, which takes a fluoride ion from PF₆⁻ to form FcEme₂F. We have not further studied this aspect of the chemistry, but it is clear that a series of complex processes take place during the electrochemical voltammetry experiments. The second irreversible oxidation observable at ~0.4 V presumably belongs to one such material but we are unable/unwilling to speculate upon its formulation.

Experimental procedures

All experiments were performed under an atmosphere of dry N₂ using Schlenk techniques. THF and hexanes were freshly distilled from sodium benzophenone ketyl immediately prior to use; CH₂[CpFe(CO)₂Me]₂ (**1**)^{13b} and SiMe₂[(η⁵-C₅H₄)Fe(CO)₂Me]₂ (**2**) were synthesized by following the procedure reported for SiMe₂[(η⁵-C₅H₄)Fe(CO)₂SiMe₂SiMe₃]₂.¹³ GeMe₂[(η⁵-C₅H₄)Fe(CO)₂Me]₂ (**3**)¹⁴, SnMe₂[(η⁵-C₅H₄)Fe(CO)₂Me]₂ (**4**)¹⁴, (η⁵-C₅H₅Fe(CO)₂SiMe₂Fc) (**6**) and (η⁵-C₅H₅)Fe(dppe)SiMe₃ (**9**)¹¹ were prepared according to literature method. FcSn^tBu₂Cl was prepared following the procedure reported for FcSiMe₂Cl.²⁶ 1,2-bis(diphenylphosphino)ethane, cis-1,2-Bis(diphenylphosphino)ethylene, 1,2-bis(diphenylphosphino)methane and bis(dimethylphosphino)ethane, were purchased from Strem chemicals and used as received. Tetra-*n*-butylammonium perchlorate (TBAP) and dichloromethane (CH₂Cl₂, 99.5%) was obtained from Fluka Chemical Company and used as received. Other solvents for cyclic voltammetry included benzonitrile (PhCN, 99.0%); dimethyl sulfoxide (DMSO, 99.9%); *N,N*-dimethylformamide (DMF, 99.9%) and pyridine (99.9%) and were purchased from Sigma-Aldrich and used without further purification. Cyclic voltammetry was carried out at room temperature under an atmosphere of dry N₂ using a Pine Instrument Company AFCBP1 potentiostat. A three-electrode system was used and consisted of a platinum or glassy carbon disk working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the

solution by a fritted-glass bridge of low porosity that contained the solvent/supporting electrolyte mixture. UV-Vis spectroelectrochemical experiments were performed with an optically transparent platinum thin-layer electrode of the type described in the literature,³⁴ and the UV-Vis spectra were recorded with a HP 8453 diode array spectrophotometer. Infrared spectra were obtained in THF/hexane solution using ATI Mattson infinity series FTIR; ¹H, ¹³C, ²⁹Si and ³¹P NMR were recorded in C₆D₆ on a Bruker DPX-300 at 300, 75.4, 59.6 and 121.5 MHz, respectively and the values reported in ppm. Elemental analysis was performed at Galbraith Laboratories.

Synthesis of CH₂[(η⁵-C₅H₄)Fe(dppe)Me]₂ (**1a**)

To a 40 mL THF solution of **1** (0.64 g, 1.62 mmol) in a quartz tube was added (1.28 g, 3.24 mmol) of dppe and the tube was degassed twice. The solution was then irradiated by a Hanovia 450 W medium pressure lamp at a distance of 4 cm for 2-3 days. After completion of the reaction, THF was evaporated under vacuum. The solid material obtained was washed with hexanes and filtered. The hexanes insoluble orange material was collected, dried and characterized as **1a** (70 %). M. pt. 138-140°C. Anal. Calcd. For C₆₅H₆₄P₄Fe₂: C 72.23, H 5.97; found, C 72.11, H 5.90. ¹H NMR, δ -0.50 (6H, FeMe), 1.92 (s, 2H, CH₂), 2.28 (s, 8H, P(CH₂)₂P), 3.92 (s, 4H, C₅H₄), 4.37 (s, 4H, C₅H₄), 7.09-7.63 (40H, Ph); ¹³C NMR, δ -17.0 (t, FeMe, ²J_{P-C} = 26.4 Hz), 22.9 (CH₂), 27.6 (t, P(CH₂)₂P, ¹J_{P-C} = 21.5 Hz), 67.7, 75.5, 79.3 (C₅H₄), 129.2, 132.6, 139.1, 144.0 (Ph); ³¹P NMR, δ 112.3. **2a-4a** were prepared by the similar procedure and isolated in 65-70 % yield. All these compounds were purified by recrystallization from a mixture of benzene/hexanes.

SiMe₂[(η⁵-C₅H₄)Fe(CO)₂Me]₂ (2**)¹³**—(Orange oil) Anal. Calcd. For C₁₈H₂₀Fe₂O₄Si: C 49.12, H 4.58; found, C 49.01, H 4.50. IR (THF, cm⁻¹): 2010, 1956 (ν CO); ¹H NMR, δ 0.38 (s, 6H, FeMe), 0.40 (s, 6H, SiMe₂), 4.34 (s, 4H, C₅H₄), 4.41 (s, 4H, C₅H₄); C NMR, δ -22.5 (FeMe), -0.29 (SiMe₂), 84.1, 86.9, 92.1 (C₅H₄); ²⁹Si NMR, δ -10.6.

SiMe₂[(η⁵-C₅H₄)Fe(dppe)Me]₂ (2a**)**—M. pt. 148 °C (dec.). Anal. Calcd. For C₆₆H₆₈Fe₂P₄Si: C 70.47, H 6.09; found, C 69.95, H 6.10. ¹H NMR, η -0.4 (6H, FeMe), 0.22 (s, 6H, SiMe₂), 2.08 (s, 8H, P(CH₂)₂P), 4.05 (s, 4H, C₅H₄), 4.75 (s, 4H, C₅H₄), 7.10-7.68 (40H, Ph); ¹³C NMR, η -20.3 (t, FeMe, ²J_{P-C} = 26.8 Hz), -0.61 (SiMe₂), 27.6 (t, P(CH₂)₂P, ¹J_{P-C} = 21.0 Hz), 78.4, 84.3, 87.1 (C₅H₄), 129.3, 131.1, 133.3, 142.0 (Ph); ²⁹Si NMR, η -5.9; ³¹P NMR, 110.3.

GeMe₂[(η⁵-C₅H₄)Fe(dppe)Me]₂ (3a**)**—M. pt. 150 °C (dec.). Anal. Calcd. For C₆₆H₆₈Fe₂GeP₄: C 67.79, H 5.86; found, C 67.71, H 5.68. ¹H NMR, η -0.5 (6H, FeMe), 0.43 (s, 6H, GeMe₂), 2.12 (s, 8H, P(CH₂)₂P), 4.05 (s, 4H, C₅H₄), 4.74 (s, 4H, C₅H₄), 7.12-7.70 (40H, Ph); ¹³C NMR, η -20.2 (t, FeMe, ²J_{P-C} = 27.1 Hz), -1.30 (GeMe₂), 27.5 (t, P(CH₂)₂P, ¹J_{P-C} = 20.3 Hz), 77.9, 84.5, 89.5 (C₅H₄), 128.7, 132.2, 138.6, 144.4 (Ph); ³¹P NMR, η 109.0.

SnMe₂[(η⁵-C₅H₄)Fe(dppe)Me]₂ (4a**)**—M. pt. 162 °C (dec.). Anal. Calcd. For C₆₆H₆₈Fe₂P₄Sn: C 65.21, H 5.64; found, C 65.01, H 5.51. ¹H NMR, η -0.4 (6H, FeMe), 0.22 (s, 6H, SnMe₂), 2.08 (s, 8H, (CH₂)₂), 4.05 (s, 4H, C₅H₄), 4.75 (s, 4H, C₅H₄), 7.10-7.68 (40H, Ph); ¹³C NMR, η -19.2 (t, FeMe, ²J_{P-C} = 27.1 Hz), -8.10 (SnMe₂), 27.5 (t, (CH₂)₂, ¹J_{P-C} = 20.3 Hz), 78.3, 86.5, 87.1 (C₅H₄), 132.2, 132.9, 138.6, 144.5 (Ph); ¹¹⁹Sn NMR, η -27.5; ³¹P NMR, η 11.3.

General synthetic procedure for diphosphine derivatives [**5a**; **6a/6b**, **7a/7b** and **8a**]

To a 30 mL THF solution of **5** (0.25 g, 0.69 mmol) in a quartz tube was added (0.28 g, 0.69 mmol) of cis-dppen and the tube was degassed twice. The solution was then irradiated by a Hanovia 450W medium pressure lamp at a distance of 4 cm for 40-45 hours. After completion

of the reaction, THF was evaporated under vacuum. The solid material obtained was washed with hexanes and filtered. The hexane insoluble red material was collected, dried and characterized as **5a**. Recrystallization from benzene and hexanes (1:2) afforded pure compound in 68 % yield. **6a/6b**, **7a/b** and **8a** were prepared following the identical procedure as described above for **5a** in 65-70 % yields.

(η^5 -C₅H₅)Fe(cis-dppen)Fc (5a)—M. pt. 175-178°C(dec). Anal. Calcd. For C₄₁H₃₆Fe₂P₂: C 70.11, H 5.17; found, C 70.01, H 5.08. ¹H NMR, η 3.77 (s, 2H, Fc), 3.67 (s, 2H, Fc), 4.21 (5H, Fc), 4.54 (5H, C₅H₅), 7.00 (2H, CH=CH), 7.10-7.62 (20H, Ph); ¹³CNMR, η 68.3, 70.0, 73.1 (Fc), 80.7 (C₅H₅), 129.1, 132.6, 133.0, 133.3 (Ph), 148.0 (CH=CH); ³¹P NMR, η 109.0.

(η^5 -C₅H₅)Fe(cis-dppen)SiMe₂Fc (6a)—M. pt. 192-195°C (dec). Anal. Calcd. For C₄₃H₄₂Fe₂P₂Si: C 67.91, H 5.57; found, C 67.80, H 5.43. ¹H NMR, η 0.16 (s, 6H, SiMe₂), 3.40, 4.05, 4.08, 4.29 (14H, C₅H₅ + Fc), 6.92 (2H, CH=CH), 7.11-7.53 (20H, Ph); ¹³CNMR, η 7.88 (SiMe₂), 68.5, 68.7, 73.4, (Fc), 78.7 (C₅H₅), 128.7, 129.2, 132.1, 143.1, (Ph), 148.0 (t, CH=CH, ¹J_{P-C} = 33.7 Hz); ²⁹Si NMR, η 26.0 (t, ²J_{Si-P} = 45.7 Hz); ³¹P NMR, η 100.4.

(η^5 -C₅H₅)Fe(dppm)SiMe₂Fc (6b)—M. pt. 180°C (dec). Anal. Calcd. For C₄₂H₄₂Fe₂P₂Si: C 67.39, H 5.66; found, C 67.01, H 5.51. ¹H NMR, η 0.73 (s, 6H, SiMe₂), 3.20 (2H, PCH₂P), 3.95, 4.08, 4.26 (14H, C₅H₅ + Fc), 6.91-7.94 (20H, Ph); ¹³C NMR, η 8.69 (GeMe₂), 43.4 (t, PCH₂P, ¹J_{P-C} = 20.1 Hz), 68.4, 68.6, 73.8 (Fc), 76.4 (C₅H₅), 129.1, 131.3, 133.5, 143.0 (Ph); ²⁹Si NMR, η 26.7 (t, ²J_{Si-P} = 44.5 Hz); ³¹P NMR, η 39.0.

Synthesis of (η^5 -C₅H₅)Fe(CO)₂GeMe₂Fc (7)

To a 50 mL THF solution of [$(\eta^5$ -C₅H₅)Fe(CO)₂][−]Na⁺ (prepared from 2.0 g (0.011 mol) of [$(\eta^5$ -C₅H₅)Fe(CO)₂]₂) was added, *via* syringe, (3.6g, 0.011 mol) of FcGeMe₂Cl at 0°C. The solution was stirred at this temperature for 1 hour, then permitted to warm at room temperature and further stirred overnight. The solvent was removed under vacuum and the residue was extracted with 50 mL of hexanes. The solution was filtered and dried. The residue obtained placed upon a silica column and elution with hexanes developed a yellow band that was collected, dried and characterized as **7**. Recrystallization from hexanes afforded pure material in 75 % yield. M. pt. 114°C. Anal. Calcd. For C₁₉H₂₀Fe₂GeO₂: C 49.11, H 4.34; found, C 49.02, H 4.35. IR (THF, cm^{−1}): 1987, 1934 (ν CO). ¹H NMR, δ 0.92 (s, 6H, GeMe₂), 4.05 4.31 (m, 14H, C₅H₅ + Fc); ¹³C NMR, δ 5.21 (GeMe₂), 68.5, 70.0, 71.5 (Fc), 83.2 (C₅H₅), 216.2 (CO).

(η^5 -C₅H₅)Fe(cis-dppen)GeMe₂Fc (7a)—M. pt. 203°C (dec). Anal. Calcd. For C₄₃H₄₂Fe₂GeP₂: C 64.15, H 5.26; found, C 64.02, H 5.30. ¹H NMR, δ 0.19 (s, 6H, GeMe₂), 4.01-4.39 (m, 14H, C₅H₅ + Fc), 6.90 (2H, CH=CH), 6.98-7.58 (20H, Ph); ¹³C NMR, δ 5.85 (GeMe₂), 68.0, 68.2, 72.3, (Fc), 77.2 (C₅H₅), 129.2, 131.7, 133.0, 138.1 (Ph), 147.9(t, CH=CH, J_{p-c} = 33.7Hz); ³¹P NMR, δ 100.9.

(η^5 -C₅H₅)Fe(dppm)GeMe₂Fc (7b)—M. pt. 194°C (dec). Anal. Calcd. For C₄₂H₄₂Fe₂GeP₂: C 63.61, H 5.34; found, C 63.52, H 5.41. ¹H NMR, δ 0.76 (s, 6H, GeMe₂), 3.23 (2H, PCH₂P), 4.15-4.51(m, 14H, C₅H₅ + Fc), 6.90-7.41(20H, Ph); ¹³C NMR, δ 7.54 (GeMe₂), 43.3 (t, PCH₂P, J_{p-c} = 20.3 Hz), 68.2, 68.5, 73.2, (Fc), 75.4 (C₅H₅), 129.2, 131.3, 133.2, 138.9 (Ph); ³¹P NMR, δ 39.3.

FcSn^tBu₂Cl—Anal. Calcd. For C₁₈H₂₇ClFeSn: C 47.68, H 6.00; found, C 57.10, H 5.92. ¹H NMR, δ 143 (s, 18H, ^tBu), 4.02, 4.11, 4.30 (9H, Fc); ¹³C NMR, δ 30.2 (^tBu), 31.9 (*ipso*-^tBu), 68.7, 69.2, 71.4, 74.8, (Fc); ¹¹⁹Sn NMR, δ 72.3.

(η^5 -C₅H₅)Fe(CO)₂Sn^tBu₂Fc (8**)**—**8** was synthesized by the similar procedure as described for **7**. M. pt. 122–123°C. Anal. Calcd. For C₂₅H₃₂Fe₂O₂Sn: C 50.47, H 5.42; found, C 50.13, H 5.19. IR (THF, ν CO, cm⁻¹): 1990, 1935. ¹H NMR, δ 1.55 (s, 18H, ^tBu), 4.10, 4.28, 4.37 (14H, C₅H + Fc); ¹³C NMR, δ 32.7 (^tBu), 33.3 (*ipso*-^tBu), 68.7, 70.1, 74.9, 75.2 (Fc), 81.3 (C₅H₅), 216(CO); 119Sn NMR, 167.0.

(η^5 -C₅H₅)Fe(dmpe)Sn^tBu₂Fc (8a**)**—M. pt. 166°C (dec). Anal. Calcd. For C₂₉H₄₈Fe₂P₂Sn: C 50.55, H 7.02; found, C 50.20, H 6.87. ¹H NMR, δ 0.95 (6H, PMe₂), 1.46 (4H, P(CH₂)P), 1.75 (s, 18H, ^tBu), 4.09, 4.19, 4.34 (14H, C₅H + Fc); ¹³C NMR, δ 24.5 (PCH₃), 26.0 (t, P(CH₂)₂P, J_{P-C} = 12 Hz), 30.2 (*ipso*-^tBu), 35.1 (^tBu), 69.0, 69.1, 72.9 (Fc), 76.0 (C₅H₅); 119Sn NMR; δ 105.2 (t, ²J_{Sn-P} = 409 Hz); ³¹P NMR, 69.3.

Reaction of **6a/7a** with AgPF₆

To a 30 mL dichloromethane solution of **6a** (0.1 g, 0.13 mmol) was added AgPF₆ (0.033 g, 0.13 mmol) or (0.065 g, 0.26 mmol) at 0°C. The formation of black precipitate was observed during the addition of the AgPF₆ in each case. The contents were then stirred for 1 hour and dichloromethane was evaporated under vacuum. Extraction of the residue with hexane yielded the previously reported [(η^5 -C₅H₅)Fe(η^5 -C₅H₄SiMe₂F)]³¹ as a yellow solid product purified via a small silica column and characterized by NMR spectroscopy. The remaining residue was dissolved in acetone and filtered, removal of the acetone from filtrate yielded [(η^5 -C₅H₅)Fe(Ph₂PCH=CHPPh₂)]⁺PF₆⁻ as dark red solid. This compound was purified by washing with benzene until the unreacted **6a** washed away. The reaction of **7a** with AgPF₆ was performed in a similar way and yielded [(η^5 -C₅H₅)Fe(η -C₅H₄SiMe₂F)] and [CpFe(Ph₂PCH=CHPPh₂)]⁺PF₆⁻.

(η^5 -C₅H₅)Fe(η^5 -C₅H₄GeMe₂F)—M. pt. 66–67°C. Anal. Calcd. For C₁₂H₁₅FFeGe: C 46.99, H 4.93; found, C 46.95, H 4.85. ¹H NMR (C₆D₆): δ 0.62 (d, 6H, GeMe₂, ³J_{H-F} = 6.0 Hz), 4.03 (5H, Cp, Fc), 4.15 (2H, C₅H₄), 4.22 (2H, C₅H₄); ¹³C NMR (C₆D₆): δ 0.39 (d, GeMe₂, ²J_{C-F} = 16.0 Hz), 68.6 (C₅H₅), 71.5 (C₅H₄), 72.6 (C₅H₄); ESI (MS): m/z = 306.0 (M⁺), 287.0 (M⁻F).

(η^5 -C₅H₅)Fe(Ph₂PCH=CHPPh₂)]⁺PF₆⁻—M. pt. 178–182°C (dec). Anal. Calcd. For C₃₁H₂₇F₆FeP₃: C 56.22, H 4.11; found, C 55.45, H 4.01. ¹H NMR (acetone-d₆): δ 4.93 (s, 5H, C₅H₅), 7.18 (2H, CH=CH), 7.26–7.80 (20H, Ph); ¹³C NMR (acetone-d₆): 90.6 (C₅H₅), 134.6, 136.5, 137.7, 138.6 (Ph), 150.8 (CH=CH); ³¹P NMR (acetone-d₆): -137.0 (septet, PF₆⁻, ¹J_{P-F} = 710.0 Hz), 105.0 (PCH=CHP).

X-ray Crystallography

A crystal of **6b** and **9** suitable for X-ray analysis was mounted on Bruker APEX CCD diffractometer equipped with monochromatized MoK α radiation. Crystallographic measurements were carried out at 296(2) K. The details of the crystal data and refinement parameters are described in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares on F² values for all reflections using the SHELXL-97 (Sheldrick, 1997) program. All non-hydrogen atoms were assigned anisotropic displacement parameters and hydrogen atoms were constrained to ideal geometries with fixed isotropic displacement parameters.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Representation of group 14 element bridged diiron complexes.

Figure 2.
Cyclic voltammograms for 1a - 4a in CH_2Cl_2 (left) and pyridine (right)

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Figure 4. ORTEP diagram of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{Ph}_2\text{PCH}_2\text{Ph}_2\text{P})\text{SiMe}_3]$ (9). Thermal ellipsoids are drawn at the 50% probability and hydrogen atoms are deleted for clarity.

Figure 5. Cyclic voltammogram of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{cis-dppen})\text{Fc}$ (**5a**) in CH_2Cl_2 containing 0.1 M TBAP.

Figure 6. UV/Vis spectral changes for $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{cis-dppen})\text{Fc}$ (**5a**) upon the first (a) and the second (b) oxidations in CH_2Cl_2 containing 0.2 M TBAP.

Figure 7. Cyclic voltammograms of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{cis-dppen})\text{SiMe}_2\text{Fc}$ (**6a**) in CH_2Cl_2 containing 0.1 M TBAP.

Figure 8.

UV/Vis spectral changes upon oxidations for (η^5 -C₅H₅)Fe(dppm)SiMe₂Fc (a and b); (η^5 -C₅H₅)Fe(dppm)SiMe₃ (c) and Fc (d) in CH₂Cl₂, 0.2 M TBAP.

Scheme 1.
Oxidative cleavage of Fe-Si bond.

Table 1
Electrochemical Data of 1a-4a in CH₂Cl₂ and Pyridine containing 0.1 M TBAP.

Compds	Solvent	¹ E _{pa}	¹ E _{pc}	¹ E _{1/2}	² E _{pa}	² E _{pc}	² E _{1/2}	$\Delta E_{1/2}^a$	ΔE_{pa}^b	K _c
1a	CH ₂ Cl ₂	-0.26	-0.39	-0.33	-0.17	-0.23	-0.20	0.13	0.09	172
2a		-0.30	-0.40	-0.35	-0.17	-0.25	-0.21	0.14	0.13	256
3a		-0.32	-0.39	-0.36	-0.19	-0.27	-0.23	0.13	0.13	172
4a		-0.32	-0.40	-0.36	-0.18	-0.26	-0.22	0.14	0.14	256
1a	Pyridine	-0.20	-0.32	-0.26	-0.14	-0.20	-0.17	0.09	0.06	4
2a		-0.26	-0.32	-0.29	-0.14	-0.20	-0.17	0.12	0.12	116
3a		-0.27	-0.33	-0.30	-0.15	-0.23	-0.19	0.11	0.12	78
4a		-0.25	-0.33	-0.29	-0.13	-0.21	-0.17	0.12	0.12	116

^a $\Delta E_{1/2} (V) = ({}^2E_{1/2} - {}^1E_{1/2})$

^b $\Delta E_{pa} (V) = ({}^2E_{pa} - {}^1E_{pa})$

Table 2

A Summary of crystallographic data of 6b and 9.

Compound	6b	9
Source	Synthesis	Synthesis
crystal color	red	red
crystal habit	red chunk	red chunk
crystal size/mm ³	0.20 × 0.16 × 0.16	0.40 × 0.40 × 0.34
<i>a</i> /Å	10.1001(7)	12.3242(12)
<i>b</i> /Å	14.4739 (9)	12.3981(12)
<i>c</i> /Å	15.7609 (11)	19.5110(19)
<i>A</i> /deg	77.5740 (10)	90
<i>β</i> /deg	80.2480 (10)	98.403(2)
<i>γ</i> /deg	76.3780 (10)	90
volume/Å ³	2169.6 (3)	2949.2(5)
crystal system	Monoclinic	Monoclinic
space group	C2/c	P2(1)/c
<i>Z</i>	2	4
Dc/g cm ⁻³	1.325	1.303
μ/mm ⁻¹	0.805	0.681
absorption correction		
	Bruker SADABS V2.05	Bruker SADABS V2.05
temp/K	296(2)	296(2)
wavelength (Å)	0.71073	0.71073
Monochromator	graphite	graphite
	Bruker APEX CCD area	Bruker APEX CCD area
Diffractometer	detector	detector
reflections collected	13475	33312
independent reflections	9341 [R(int) = 0.0206]	7029 [R(int) = 0.0353]
structure solution technique	Direct methods	Direct methods
structure solution program	SHELXS-97 (Sheldrick, 1990)	SHELXS-97 (Sheldrick, 1990)
refinement technique	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
refinement program	SHELXL-97 (Sheldrick, 1997)	SHELXL-97 (Sheldrick, 1997)
function minimized	Σw(Fo ² - Fc ²) ²	Σw(Fo ² - Fc ²) ²
goodness-of-fit on F ²	1.047	1.155
R1 ^a , wR2 ^b [I > 2σ(I)]	R1 = 0.0486, wR2 = 0.1068	R1 = 0.0682, wR2 = 0.1586
R1 ^a , wR2 ^b (all data)	R1 = 0.0557, wR2 = 0.1112	R1 = 0.0769, wR2 = 0.1643

Table 3
Selected bond lengths (Å) and angles (°) of (η^5 -C₅H₅)Fe(dppm)SiMe₂Fe (6b) and (η^5 -C₅H₅)Fe(dppm)SiMe₃ (9).

<i>Bond lengths (Å)</i>			
For 6b			
Fe2-Si	2.3786(8)	Fe2-P1	2.1921(7)
Si-C2	1.924(3)	Si-C41	1.920 (3)
Fe2-C12	2.114 (3)	Fe2-C13	2.102 (3)
Fe2-C15	2.128(3)	Fe2-C16	2.128 (3)
For 9			
Fe-Si	2.4756(10)	Fe-P1	2.2789(9)
Si-C31	1.952(4)	Si-C32	1.812(4)
Fe-C1	1.987(4)	Fe-C2	2.263(3)
Fe-C4	2.038(3)	Fe-C5	1.837(3)
<i>Bond angles (°)</i>			
For 6b			
P2-Fe2-P1	74.44 (3)	P1-Fe2-Si	93.76 (3)
P2-Fe2-Si	94.06 (3)	C41-Si-C2	103.75 (12)
C42-Si-C2	100.66 (12)	C41-Si-C42	103.22 (12)
For 9			
P2-Fe-P1	67.35(3)	P1-Fe-Si	100.18(3)
P2-Fe-Si	105.30(3)	C32-Si-C33	110.0(2)
C32-Si-C31	99.0(2)	C33-Si-C31	90.1(2)
C32-Si-Fe	112.11(15)	C33-Si-Fe	116.74(15)
C31-Si-Fe	125.97(13)	P1-C6-P2	85.27(13)

Table 4 Cyclic voltammetric data of 5-8^a, (5a, 6a/b, 7a/b and 8a)^b

Compound	E _{pa}	E _{pc}	E _{1/2}
5	0.70	0.41	0.55
	1.65	-	-
5a	-0.17	-0.25	-0.21
	0.62	0.54	0.58
6	0.69	0.39	0.54
	1.70	-	-
6a	0.06	-0.02	0.02
	0.38	-	-
6b	0.53	0.41	0.47
	0.00	-0.07	-0.04
7	0.39	-	-
	0.53	0.45	0.49
7a	0.74	0.40	570
	1.60	-	-
7b	0.08	0.00	0.04
	0.39	-	-
8	0.53	0.44	0.49
	0.63	0.55	0.59
8a	-0.01	-0.08	-0.05
	0.38	-	-
8a	0.57	0.47	0.52
	0.72	0.43	0.57
8a	1.75	-	-
	-0.2	-	-
8a	0.03	-	-
	0.60	0.42	0.51
Ferrocene	0.54	0.46	0.50

^aOxidation potentials (V vs. Ag/AgCl, CH₂Cl₂, 0.1M TBAB).^bOxidation potentials (V vs. SCE, CH₂Cl₂, 0.1M TBAP).