

Structural and Redox Properties of Novel Spirocyclic 1-Sila-3-ferracyclobutanes, $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{L}_2)\text{CH}_2\text{SiMe}_2]$, $\text{L}_2 = \text{P-P}$ (diphosphine)

Mukesh Kumar, Francisco Cervantes-Lee,[†] Hemant K. Sharma, and Keith H. Pannell*
 Department of Chemistry, University of Texas at El Paso Texas, El Paso, Texas 79968-0513

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Photochemical treatment of the 1-dimethylsila-3-ferracyclobutane $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{CH}_2\text{SiMe}_2]$ (**1**) with diphosphine ligands $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$, $n = 1, 2, 3$ (P–P), results in the formation of $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{P-P})\text{CH}_2\text{SiMe}_2]$ (**3–5**) spirocyclic complexes. The new 1-dimethylsila-3-ferracyclobutanes do not ring-open to form polymeric materials, although the X-ray structural analysis of $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{CH}_2\text{SiMe}_2]$ indicates the same ring strain as noted for analogues of **1** that do polymerize. Cyclic voltammetric studies of these complexes reveal a reversible one-electron redox process.

Introduction

Sila-metallacyclobutanes containing a transition metal atom have been explored in terms of their synthesis and reactivity.¹

For example, $\text{Cp}_2\text{M-CH}_2\text{-SiMe}_2\text{-CH}_2$ ($\text{M} = \text{Ti, Zr, Hf, Nb, Mo, Ir}$) undergo ring expansion chemistry via insertion of such reagents as paraformaldehyde, isocyanides, and carbon monoxide into the M-C bond. More recently we reported the synthesis and ring-opening behavior of 1-sila-3-ferracyclobutanes,²

$(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{CH}_2\text{SiR}_2$, and related 1,2-disilaferracyclobutanes,³ $(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{SiR}_2\text{SiR}_2$ (**A** and **B** in Figure 1). Such metallacycle ring-opening is reminiscent of the chemistry of [1]-silaferrocenophanes⁴ (**C** in Figure 1), which provides an interesting synthetic route for a new class of conducting organometallic polymers due to the presence of the redox-active ferrocenylene group in the polymer backbone.⁵ Such polymers have also been studied in nanoparticle synthesis and as magnetic materials.⁶ However, since the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ fragment does not

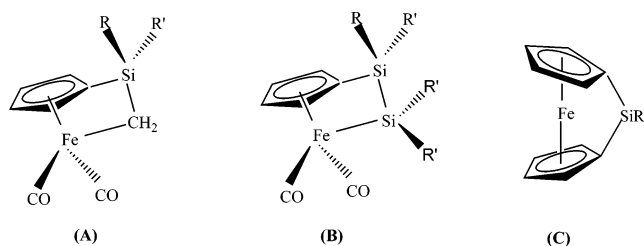


Figure 1. Schematic representation for four-membered metallacycles.

exhibit reversible redox behavior, the utility of the new organometallic polymers derived from this metal fragment is limited.

In an attempt to outline the potential for transforming the metal center of the polymer precursor 1-sila-3-ferracyclobutanes into conducting species, we now report the synthesis, characterization, and reversible redox properties of $(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{P-P})\text{CH}_2\text{SiMe}_2$ (**3–5**), $\text{P-P} = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1, 2, 3$).

Results and Discussion

The photochemical substitution of labile CO groups in $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ complexes with mono- and diphosphine ligands

(5) (a) Espada, L.; Pannell, K. H.; Papkov, V.; Larissa, L.; Bukalov, S.; Suzdalev, I.; Tanaka, M.; Hayashi, T. *Organometallics* **2002**, *21*, 3758. (b) Pannell, K. H.; Imshennik, V. I.; Maksimov, Yu. V.; Il'ina, M. N.; Sharma, H. K.; Papkov, V. S.; Suzdalev, I. P. *Chem. Mater.* **2005**, *17*, 1844. (c) Papkov, V. S.; Gerasimov, M. V.; Dubovik I. I.; Sharma, S.; Dementiev, V. V.; Pannell, K. H. *Macromolecules* **2000**, *33*, 7107. (d) Tanaka, M.; Hayashi, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 334. (e) Rulkens, R.; Resendes, R.; Varma, A.; Manners, I.; Muti, K.; Fossum, E.; Miller, P.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 8165. (f) Bakueva, L.; Sargent, E. H.; Resendes, R.; Bartole, A.; Manners, I. *J. Mater. Sci.: Mater. Electron.* **2001**, *12*, 21.

(6) (a) Clendenning, S. B.; Fournier-Bidoz, S.; Pietrangelo, A.; Yang, G.; Han, S.; Brodersen, P. M.; Yip, C. M.; Lu, Z.-H.; Ozin, G. A.; Manners, I. *J. Mater. Chem.* **2004**, *14*, 1686. (b) Wang, X.-S.; Winnik, M. A.; Manners, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 3703. (c) MacLachlan, M. J.; Ginzburg, M.; Coombs, N.; Coyle, T. W.; Raju, N. P.; Greedan, J. E.; Ozin, G. A.; Manners, I. *Science* **2000**, *287*, 1460. (d) Wang, X.; Wang, H.; Coombs, N.; Winnik, M. A.; Manners, I. *J. Am. Chem. Soc.* **2005**, *127*, 8924.

* Corresponding author. E-mail: kpannell@utep.edu.

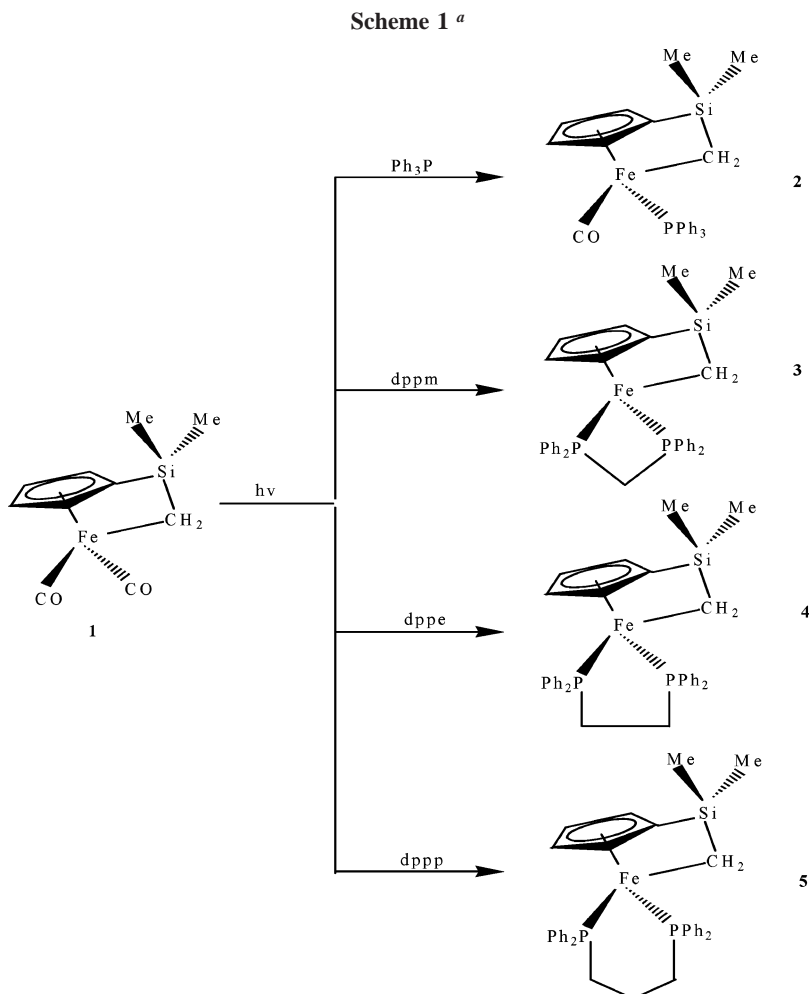
[†] Dr. Francisco (Paco) Jose Cervantes-Lee: 11/21/1950–2/15/2007.

(1) (a) Sharma, H. K.; Pannell, K. H. In *Metal-Containing and Metallo Supramolecular Polymers and Materials*; Schubert, U. S.; Newkome, G. R., Manners, I., Eds.; Oxford University Press: Washington, DC, 2006; p 457. (b) Tikkanen, W. R.; Liu, J. Z.; Egan, J. W.; Petersen, J. L. *Organometallics* **1984**, *3*, 825. (c) Tikkanen, W. R.; Liu, J. Z.; Egan, J. W.; Petersen, J. L. *Organometallics* **1984**, *3*, 1646. (d) Tikkanen, W. R.; Petersen, J. L. *Organometallics* **1984**, *3*, 1651. (e) Berg, F. J.; Petersen, J. L. *Organometallics* **1989**, *8*, 2461. (f) Petersen, J. L.; Egan, J. W. *Organometallics* **1987**, *6*, 2007. (g) Andreucci, L.; Diversi, P.; Ingrosso, G.; Lucherini, A.; Marchetti, F.; Adovasio, V.; Nardelli, M. *J. Chem. Soc., Dalton Trans.* **1986**, 477.

(2) Sharma, H. K.; Cervantes-Lee, F.; Pannell, K. H. *J. Am. Chem. Soc.* **2004**, *126*, 1326.

(3) Sharma, H. K.; Pannell, K. H. *Chem. Commun.* **2004**, 2556.

(4) (a) Foucher, D. A.; Tang, B.-Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246. (b) Nguyen, M. T.; Diaz, A. F.; Dementiev, V. V.; Sharma, H.; Pannell, K. H. *SPIE Proceedings* **1993**, *1910*, 230. (c) Flinckh, W.; Tang, B.; Foucher, D. A.; Zamble, D. B.; Ziembinski, R.; Lough, A.; Manners, I. *Organometallics* **1993**, *12*, 823. (d) Nguyen, M. T.; Diaz, A. F.; Dementiev, V. V.; Pannell, K. H. *Chem. Mater.* **1993**, *5*, 1389.



is well-established.⁷ Thus, irradiation of a freshly prepared THF solution of **1** in the presence of the appropriate phosphine ligand results in the formation of mono- (for Ph₃P) (**2**) and disubstituted derivatives, **3–5** (Scheme 1). The use of excess Ph₃P and prolonged irradiation failed to replace both the CO groups. Compounds **2–5** were isolated as red-orange solid materials soluble in common organic solvents, and they were purified by recrystallization and have been characterized by ¹H, ¹³C, and ²⁹Si NMR spectroscopy, X-ray crystallography (for **4**), and elemental analysis.

The ¹H NMR spectrum of **2** exhibited ABX quartet at δ -2.00 to -2.12 ppm (³J_{A-B} = 11.2 Hz, ³J_{A-X} = 12.6 Hz, ³J_{B-X} = 1 Hz), corresponding to two diastereotopic CH₂ hydrogens.⁸ The ¹³C NMR spectrum exhibits a phosphorus-coupled doublet at δ -50.2 ppm (²J_{P-C} = 12.9 Hz) for the FeCH₂ group, a doublet at 223.5 ppm (²J_{P-C} = 30.2 Hz) for the CO group, but singlets for the carbon atoms of the substituted cyclopentadienyl ring. The ¹H NMR spectrum of the diphosphine complexes **3–5** exhibit triplets for the CH₂ protons at δ -2.51 (³J_{P-H} = 6.0 Hz) (**3**), -3.20 (³J_{P-H} = 6.0 Hz) (**4**), and -2.53 (³J_{P-H} = 6.0 Hz) (**5**). The ¹³C NMR spectra exhibit the expected high-field CH₂ triplets at δ -48.7 (²J_{P-C} = 17.3 Hz) (**3**), -51.2 (²J_{P-C} = 17.2 Hz) (**4**), and δ -54.1 (²J_{P-C} = 15.3 Hz) (**5**). ²⁹Si NMR values of **2–5** were not changed significantly (2–3 ppm) from

that of the starting iron dicarbonyl metallacycle **1** and were noted in the range -5.0 to -7.0 ppm. ³¹P NMR signals in these compounds were observed downfield as compared to the uncoordinated phosphine ligands, exhibiting $\Delta\delta$ (ppm) values of 88 (**2**), 69 (**3**), 119 (**4**), and 83 (**5**). This behavior is in accord with the literature evidence for phosphorus-coordinated compounds.⁹

X-ray Structure of 4. The molecular structure of **4** was confirmed by single-crystal X-ray analysis of crystals formed from a benzene/hexane solvent mixture, Figure 2. The crystallographic data and selected bond lengths and angles are summarized in Tables 1 and 2, respectively. The molecule crystallizes in the orthorhombic crystal system with space group *P*(2)₂(1)₂(1). Structural analyses of several 1-metalla-3-silacyclobutanes¹ are reported in the literature; however, the presence of both the four (Fe–C–Si–C) and five (Fe–P–C–C–P) membered spirocyclic rings presents some novelty. The Si–C₆ and Si–C₁ bond distances of **4**, 1.830(4) and 1.860(5) Å, respectively, are in the range for such metallacycles. The C₁–Si–C₆ angle of 95.41(17)° is small for a tetrahedral angle and together with the C₁–Fe–C₆ bond angles of 80.39(16)° illustrates a degree of ring strain for this new structural arrangement. However, the sum of the four inner ring angles (359.9°)

(7) (a) King, R. B.; Pannell, K. H. *Inorg. Chem.* **1968**, *7*, 1510. (b) Treichel, P. M.; Shubkin, R. L.; Barnett, K. W.; Reichard, D. *Inorg. Chem.* **1966**, *5*, 1177.

(8) Pannell, K. H. *Chem. Commun.* **1969**, 1346.

(9) (a) Montigny, F.; Argouarch, G.; Costuas, K.; Halet, J.; Roisnel, T.; Toupet, L.; Lapinte, C. *Organometallics* **2005**, *24*, 4558. (b) Weyland, T.; Lapinte, C.; Frapper, G.; Calhorda, M. J.; Halet, J.; Toupet, L. *Organometallics* **1997**, *16*, 2024. (c) Scott, F.; Kruger, G. J.; Cronje, S.; Lombard, A.; Raubenheimer, H. G. *Organometallics* **1990**, *9*, 1071.

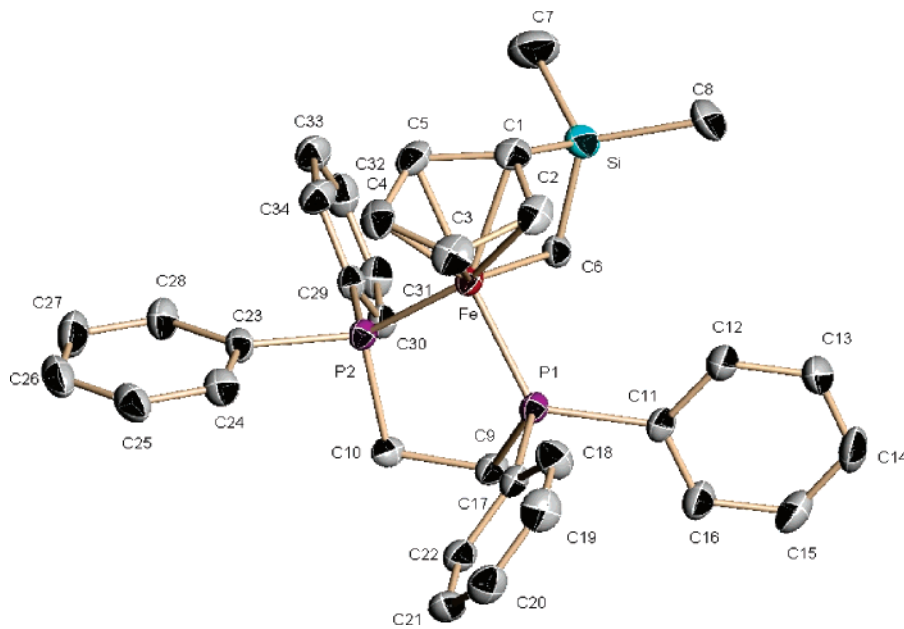


Figure 2. Molecular structure of $[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{Ph}_2\text{P})\text{CH}_2\text{SiMe}_2]$ (**4**). Thermal ellipsoids are shown at 30% probability. H atoms are omitted for clarity.

Table 1. Summary of Crystallographic Data of 4

source	synthesis
cryst color	red
cryst habit	chunk
cryst size/mm ³	0.30 × 0.30 × 0.20
<i>a</i> /Å	12.3293(17)
<i>b</i> /Å	12.9894(18)
<i>c</i> /Å	18.476(3)
α /deg	90
β /deg	90
γ /deg	90
volume/Å ³	2959.0(7)
cryst syst	orthorhombic
space group	<i>P</i> 2(1)2(1)2(1)
<i>Z</i>	4
<i>D_c</i> /g cm ⁻³	1.326
μ /mm ⁻¹	0.68
abs corr	Bruker SADABS program
temp/°C	23(2)
wavelength	0.71073 Å
monochromator	graphite
diffractometer	Bruker SMART with Apex CCD
no. of reflns collected	8805
no. of indep reflns	2825 [<i>R</i> (int) = 0.0397]
struct solution technique	direct methods
struct solution program	SHELXS-97 (Sheldrick, 1990)
refinement technique	full-matrix least-squares on <i>F</i> ²
refinement program	SHELXS-97 (Sheldrick, 1997)
function minimized	$\sum w(F_o^2 - F_c^2)^2$
goodness-of-fit on <i>F</i> ²	1.147
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b [<i>I</i> > 2 <i>s</i> (<i>I</i>)]	0.0601, 0.1218
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b (all data)	0.0691, 0.1259

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

reveals the planarity in the ring. The bite angle (P₂–Fe–P₁) for the P₂ moiety is 87.6° with Fe–P distances 2.1540(10) and 2.1716(10) Å. The bite angles (P–Fe–P) for related compounds such as Cp*(dippe)Fe–C≡C–9,10-ant-C≡C–FeCp*(dippe)^{9a} [85.4(1)°], [Cp*Fe(dippe)]₃(C≡C)₃(*μ*-1,3,5-C₆H₃)^{9b} [84.7(1)°, 83.7(4)°, 85.7(1)°], and Fc–C≡C–CpFe(dippe)^{10c} [86.7(2)°] [dippe = bis(diphenylphosphino)ethane] are smaller than that in **4**. This may be an effect of the other four-membered ring present in the molecule involving the same iron atom.

Table 2. Selected Bond Lengths and Angles of 4

Bond Lengths (Å)			
Fe–C1	2.095(4)	Fe–C6	2.134(4)
Fe–P1	2.1540(10)	Fe–P2	2.1716(10)
Si–C6	1.830(4)	Si–C7	1.860(5)
Si–C1	1.860(5)	Si–C8	1.868(4)
Bond Angles (deg)			
C1–Fe–C6	80.39(16)	Si–C1–Fe	92.25(16)
Si–C6–Fe	91.89(16)	C6–Si–C1	95.41(17)
P1–Fe–P2	87.56(4)	C6–Si–C7	115.6(2)
C7–Si–C1	109.3(3)	C6–Si–C8	114.5(2)
C7–Si–C8	108.8(3)	C1–Si–C8	112.7(2)

A comparison of the structural data of **4** with those of $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})(\text{Ph}_3\text{P})\text{CH}_2\text{Si}(n\text{-Bu})_2]^2$ [Fe–C(methylene) = 2.113(6) Å, C(methylene)–Si = 1.839(3) Å, Si–C(Cp) = 1.871(3) Å, C(Cp)–Si–C(methylene) = 94.06(11)°] and 1-silaferrocenophane, $(\eta^5\text{-C}_5\text{H}_4)_2\text{FeSiMe}_2^4$ [Fe–C(Cp) = 2.001(8) Å, 1.990(8) Å, C(Cp)–Si = 1.865(9), 1.851(9) Å, C(Cp)–Si–C(Cp) = 95.7(4)°], reflects the great similarity of the Fe–C–Si–C ring distances and angles. Thus, we conclude that the much greater disposition of the ferrocenophanes to ring-open is mainly driven by the ferrocenylene portion of the molecular geometry associated with the nonparallel character of the two-cyclopentadienyl rings.

Cyclic Voltammetric Studies. Electrochemical studies of the 1-dimethylsila-3-ferracyclobutanes **1–5** reveal that, with scan rates in the range 50/100 mV s⁻¹, the parent dicarbonyl complex **1** exhibits a completely irreversible oxidation (Figure 3a), the monophosphine-substituted **2** exhibits a slightly reversible process (Figure 3b), and the disubstituted phosphine complexes **3–5** undergo a reversible one-electron redox process, Figure 4. The reversibility of the diphosphine-substituted systems is

(10) (a) Connelly, N. G.; Geiger, W. E. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press Inc: New York, 1984; Vol. 23, p 1. (b) Treichel, P. M.; Molzahn, D. C.; Wagner, K. P. *J. Organomet. Chem.* **1979**, *174*, 191. (c) Sato, M.; Hayashi, Y.; Kumakura, S.; Shimizu, N.; Katada, M.; Kawata, S. *Organometallics* **1996**, *15*, 721. (d) Tilset, M.; Fjeldahl, I.; Hamon, J.; Hamon, P.; Toupet, L.; Saillard, J.; Costuas, K.; Haynes, A. *J. Am. Chem. Soc.* **2001**, *123*, 9984.

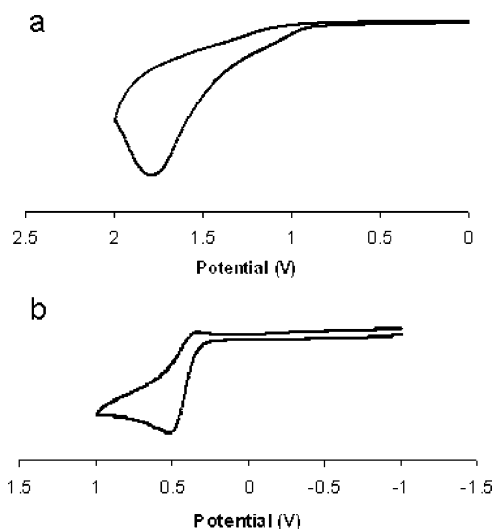


Figure 3. Cyclic voltammograms of **1** (a) and **2** (b).

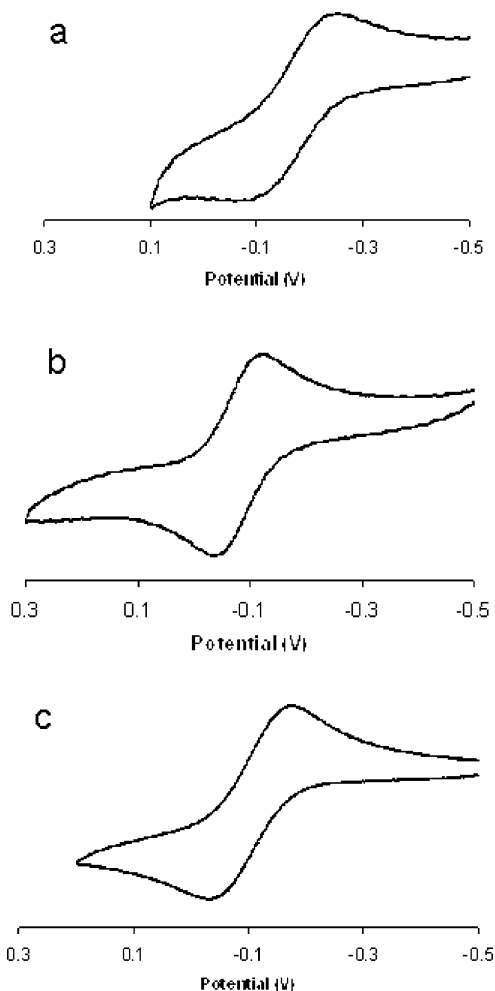


Figure 4. Cyclic voltammograms of **3** (a), **4** (b), and **5** (c).

in accord with published studies on related $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{P})_2\text{X}$ systems.^{9a,b,10} In the case of the reversible processes for **3**, **4**, and **5** the expected ($i_{\text{pa}}/i_{\text{pc}}$) ratio of unity is observed and the ΔE_{p} separation is in the range 90–145 mV. The electrochemical data are summarized in Table 3, and that for **4** ($E_{\text{ox}} = -0.037$ V, $E_{\text{red}} = -0.127$ V, $E_{1/2} = -0.082$ V, $\Delta E_{\text{p}} = 0.090$ V) resembles that of the first redox process for $[\{\text{Fe}(\text{Cp}^*)(\text{dppe})\text{-}$

Table 3. Cyclic Voltammetric Data of **1–5** in CH_2Cl_2 (0.1 M $[\text{Bu}_4\text{N}][\text{BF}_4]$; sweep rate 0.100 V s^{-1})^a

compound	E_{ox} (V)	E_{red} (V)	$E_{1/2}$ (V)	ΔE_{p} (V)
1	1.79			
2	0.512			
3	-0.096	-0.237	-0.166	0.141
4	-0.037	-0.127	-0.082	0.090
5	-0.032	-0.175	-0.103	0.143

^a References with AgCl/Ag.

$(\text{C}\equiv\text{C})_2\text{-C}_6\text{H}_4]$ ($E_{\text{ox}} = -0.060$ V, $E_{\text{red}} = -0.140$ V, $E_{1/2} = -0.100$ V, $\Delta E_{\text{p}} = 0.80$ V).^{9b}

The redox potentials of these compounds change in a systematic manner, Table 3. In the sequence $\text{Fe}(\text{CO})_2$ (**1**) \rightarrow $\text{Fe}(\text{CO})(\text{P})$ (**2**) \rightarrow $\text{Fe}(\text{P}-\text{P})$ (**3**, **4**, **5**) the oxidation potentials progressively decrease in line with the systematic increase of electron density on the iron atom as the highly retroductive electron-withdrawing CO groups are replaced by the phosphine ligands. The more subtle changes noted for **3**, **4**, and **5** possibly reflect the progressively favorable ring size of the chelating ligand complex from the strained four-membered ring to the six-membered ring. A comparison of the $E_{1/2}$ values for $\text{Fc}-\text{C}\equiv\text{C}-\text{CpFe}(\text{dppm})$ (-0.50 V) and for $\text{Fc}-\text{C}\equiv\text{C}-\text{CpFe}(\text{dppe})$ (-0.47 V), $\text{Fc} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$, indicates a slight decrease in $E_{1/2}$ by increasing the ring size.^{10c} However, in our study we found that the $E_{1/2}$ values exhibited considerable variation, -0.166 V (**3**), -0.082 V (**4**), -0.103 V (**5**).

Attempts to isolate a chemically oxidized 17-electron species by treatment of **3**, **4**, or **5** with silver tetrafluoroborate, as suggested by literature precedents,^{10b} led to black materials that were insoluble in all common solvents. Whether they are molecular or ring-opened species is unknown.

Attempted Ring-Opening Polymerization of 4. As a representative example, a toluene solution of **4** was treated with Pt(0) and Pd(0) catalysts (7–10 mol %) at both room temperature and elevated temperatures. No evidence of ring-opening of the metallacycle was observed on the basis of NMR spectroscopic analysis. In other attempts, THF solutions of **4** were treated with anionic reagents, *n*-BuLi and LDA (5–10 mol %). In neither case was ring-opening observed. However, on prolonged stirring (>24 h), small amounts of an intractable precipitate were obtained. Both reaction conditions used have been shown to result in ring-opening of the parent dicarbonyl metallacycle **1**.

Attempts to perform carbonyl substitution reactions directly with the ring-opened polymers have yielded a complex mixture of cross-linked materials involving both carbonyl insertion products and the direct carbonyl substitution reactions of the type noted here. Studies on these systems are currently in progress.

Experimental Section

All experiments were performed under an atmosphere of dry N_2 using Schlenk techniques. THF and hexanes were freshly distilled from sodium benzophenone ketyl immediately prior to use; $(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{CH}_2\text{SiMe}_2$ (**1**) was prepared according to the published procedure.² Triphenylphosphine, 1,2-bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, and 1,2-bis(diphenylphosphino)propane were purchased from Aldrich and used as received. Cyclic voltammetric measurements were performed using a Perkin-Elmer potentiostat/galvanostat CV (model # 263A) analyzer. The electrochemical cell comprised a platinum wire working electrode, a silver wire reference electrode, and a silver wire counter electrode. All measurements were made in a dry N_2

atmosphere; oxidation potentials were referenced to Ag/AgCl couple. Infrared spectra were obtained in THF solution on an ATI Mattson infinity series FTIR; ^1H , ^{13}C , ^{29}Si , and ^{31}P NMR spectra were recorded on a Bruker DPX-300 at 300, 75.4, 59.6, and 121.5 MHz, respectively. Elemental analyses were performed at Galbraith Laboratories.

Synthesis. Isolation of $[(\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2\text{CH}_2\text{SiMe}_2)]$ (1**).** **1** was prepared in solution as reported previously.² The THF was reduced slowly to ~ 10 mL and placed on a silica column packed in hexanes. Elution with hexanes produced a yellow band, which was collected and dried. The resulting orange semisolid was further purified by passing through a second silica column, and removal of the solvent resulted in the isolation of **1** as a semisolid in 50% yield. The compound is stable for several weeks stored in a refrigerator under N_2 . Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{O}_2\text{FeSi}$: C 48.19, H 4.81. Found: C 47.53, H 4.75. IR (THF, cm^{-1}): 2003, 1945 (ν CO). ^1H NMR (C_6D_6): δ -1.39 (s, 2H, FeCH_2), 0.14 (s, 6H, SiMe_2), 4.31, 4.59 (4H, Cp). ^{13}C NMR (C_6D_6): δ -50.0 (FeCH_2), -1.21 (SiMe_2), 74.5, 85.2, 92.6 (Cp), 217.8 (CO). ^{29}Si NMR (C_6D_6): δ -4.8.

Synthesis of $[(\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{Ph}_3\text{P})(\text{CO})\text{CH}_2\text{SiMe}_2)]$ (2**).** To a 30 mL THF solution of **1** (0.011 mol) in a quartz tube was added 2.89 g (0.011 mol) of PPh_3 , and the contents were degassed twice. The solution was then irradiated by a Hanovia 450 W medium-pressure lamp at a distance of 4 cm for 20 h. The progress of the photochemical reaction was monitored by infrared spectroscopy following the disappearance of the CO frequencies of **1**. After completion of reaction the solvent was removed under vacuum. The solid material obtained was extracted with a hexanes/toluene mixture and recrystallized from that solution to yield **2** as a red solid compound in 68% yield, mp 143–5 °C. Anal. Calcd for $\text{C}_{27}\text{H}_{27}\text{OPFeSi}$: C 67.21, H 5.60. Found: C 66.62, H 5.50. IR (THF, cm^{-1}): 1911 (ν CO). ^1H NMR (CDCl_3): δ -2.0 to -2.12 (2H, CH_2 , $^3J_{\text{A-B}} = 11.2$ Hz, $^3J_{\text{A-X}} = 12.6$ Hz, $^3J_{\text{B-X}} = 1$ Hz), 0.02 (s, 3H, SiMe), 0.19 (s, 3H, SiMe), 3.70 (m, 1H, Cp), 4.49 (m, 1H, Cp), 4.60 (m, 1H, Cp), 4.89 (m, 1H, Cp), 7.36 (m, 15H, Ph). ^{13}C NMR (CDCl_3): δ -50.2 (d, CH_2 , $^2J_{\text{P-C}} = 12.9$ Hz), -1.24 (SiMe), 1.33 (SiMe), 71.7, 80.6, 87.6, 90.5, 95.1 (Cp), 129.6, 130.6, 132.4, 133.7 (Ph), 223.5 (d, CO, $^2J_{\text{P-C}} = 30.2$ Hz). ^{29}Si NMR (CDCl_3): δ -6.4. ^{31}P NMR (CDCl_3): δ 83.9.

In a similar manner we obtained $[(\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)\text{CH}_2\text{SiMe}_2)]$ (**3**), $[(\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{Ph}_2\text{P})\text{CH}_2\text{SiMe}_2)]$ (**4**), and $[(\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)\text{CH}_2\text{SiMe}_2)]$ (**5**) in 60%, 65%, and 68% yields, respectively.

3. Mp: 152–6 °C. Anal. Calcd for $\text{C}_{33}\text{H}_{34}\text{P}_2\text{FeSi}$: C 68.75, H 5.90. Found: C 68.22, H 5.74. ^1H NMR (C_6D_6): δ -2.51 (t, 2H, CH_2 , $^2J_{\text{P-H}} = 6.0$ Hz), 0.41 (s, 6H, SiMe_2), 2.31 (s, 2H, PCH_2P), 4.61 (m, 2H, Cp), 4.69 (m, 2H, Cp), 6.99–7.46 (m, 20 H, Ph). ^{13}C NMR (C_6D_6): δ -48.7 (t, CH_2 , $^2J_{\text{P-C}} = 7.3$ Hz), 2.40 (SiMe_2), 44.0 (PCH_2P), 65.1, 73.6, 86.1 (Cp), 129.5, 130.1, 138.5, 142.0 (Ph). ^{29}Si NMR (C_6D_6): δ -6.11. ^{31}P NMR (C_6D_6): δ 48.4.

4. Mp: 175–8 °C. Anal. Calcd for $\text{C}_{34}\text{H}_{36}\text{P}_2\text{FeSi}$: C 69.03, H 6.09. Found: C 68.89, H 6.01. ^1H NMR (C_6D_6): δ -3.20 (t, 2H,

CH_2 , $^2J_{\text{P-H}} = 6.0$ Hz), 0.15 (s, 6H, SiMe_2), 2.21 (t, 4H, $\text{P}(\text{CH}_2)_2\text{P}$, $^2J_{\text{P-H}} = 3.9$ Hz), 4.18 (m, 2H, Cp), 4.54 (m, 2H, Cp), 7.70–7.23 (m, 20H Ph). ^{13}C NMR (CDCl_3): δ -51.2 (t, CH_2 , $^2J_{\text{P-C}} = 17.2$ Hz), 0.99 (SiMe_2), 27.4 (t, $\text{P}(\text{CH}_2)_2\text{P}$, $^1J_{\text{P-C}} = 21.7$ Hz), 65.7, 76.6, 87.2 (Cp), 128.3, 130.1, 133.6, 139.2 (Ph). ^{29}Si NMR (C_6D_6): δ -6.6. ^{31}P NMR (C_6D_6): δ 108.2.

5. Mp: 182–5 °C. Anal. Calcd for $\text{C}_{35}\text{H}_{38}\text{P}_2\text{FeSi}$: C 69.53, H 6.29. Found: C 68.82, H 6.37. ^1H NMR (C_6D_6): δ -2.53 (t, 2H, CH_2 , $J = 6$ Hz), 0.19 (s, 6H, SiMe_2), 1.93 (t, 4H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$, $^2J_{\text{P-H}} = 12.6$ Hz), 2.19 (m, 2H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$), 4.11 (m, 2H, Cp), 4.41 (m, 2H, Cp), 7.21–7.37 (m, 20H, Ph). ^{13}C NMR (CDCl_3): δ -54.1 (t, CH_2 , $^2J_{\text{P-C}} = 15.3$ Hz), 0.75 (SiMe_2), 20.3 ($\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$), 26.8 (t, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$, $^1J_{\text{P-C}} = 12.5$ Hz), 66.0, 80.2, 85.4 (Cp), 127.6, 129.3, 131.8, 138.0, 142.5 (Ph). ^{29}Si NMR (C_6D_6): δ -5.84. ^{31}P NMR (C_6D_6): δ 67.2.

Attempted Ring-Opening Polymerization of 4. In a typical experiment a 5 mL toluene solution of **4** (0.100 g) was charged into a two-neck flask fitted with a N_2 inlet tube. To the clear solution was added 7 mol % of the Karstedt's catalyst. No change in the viscosity of the solution and no changes in the ^1H and ^{13}C NMR spectral data were observed after 18 h. However, prolonged stirring, >36 h, resulted in a very small amount of insoluble precipitate. Related experiments using $\text{Pd}(\text{Ph}_3\text{P})_4$ yielded similar results, even after heating at 75 °C for 24 h.

Treatment of **1** with $\text{Pd}(\text{PPh}_3)_4$ under identical conditions noted above, 75 °C for 24 h, led to ring-opened polymerization and to polymers identical to that originally reported.²

In separate experiments similar solutions of **4** were treated with *n*-BuLi/LDA (5 mol %). The solution was then stirred at room temperature for 24 h. A small amount of an insoluble precipitate formed; however, NMR spectral analysis provided no evidence of the ring opening. The starting material was recovered in >90% yield in each case.

X-ray Crystallography. A crystal of **4** suitable for X-ray analysis was mounted on a Bruker APEX CCD diffractometer equipped with monochromatized Mo $K\alpha$ radiation. Crystallographic measurement was carried out at 296(2) K. The details of 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 F^2 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.

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Supporting Information Available: Crystallographic data in CIF format (CCDC no. 631129). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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