ferences indicated variations in the orientation of the η^1-C_8H_{13} ring in the molecule due to restricted rotation about the Ru–C bond, which was confirmed by the determination of the crystal and molecular structures of **3a** and **3b** by X-ray diffraction.[7]

The X-ray structure analysis of **3a** and **3b** shows them to be chemically equivalent and confirms the novel Ru-(1-σ-C_8H_{13}) linkages. More importantly, however, the molecular structures of **3a** and **3b** confirm and quantify the different orientation and conformations of the cyclooctenyl ligand. In **3a** the conformation of the cyclooctenyl ligand and its orientation with respect to the rest of the molecule are such that the vinyl hydrogen atom, H(42), is directed away from the phenyl groups of the $Ph_2PCH_2PPh_2$ ligand (Figure 1). The orange form has two independent, but structurally almost identical, molecules in the asymmetric unit,[8] and in these the vinyl hydrogen atom, H(42) or H(82), is directed between two of the diphosphine phenyl groups (Figures 2 and 3). This accounts for the upfield chemical shift observed for this hydrogen in the ^1H NMR of **3b**. Calculations and inspection of space-filling models show that interconversion of the two molecular structures in **3a** and **3b** is restricted by close contacts during the transition state between the hydrogen atoms of the η^1-C_8H_{13} ring and the two nearest diphosphine phenyl groups. In particular, rotations of the η^1-C_8H_{13} ring about Ru–C produces minimum contact distances between H(42) [H(82)] or H(48B) [H(88B)] and C(121) [C(51)] or C(126) [C(516)] of between 1.31 and 1.62 Å, depending upon the direction of rotation and the specific molecule.

The conversion of a diene hydride into a metal vinyl complex is, to our knowledge, without precedent, although the reverse reaction, namely, the formation of an η^3-allyl ligand in vinylzirconium, -molybdenum, -ruthenium, and -iridium complexes has been observed.[9] Hydrido allene intermediates were preferred in the Zr, Mo and Ir systems,

leading to speculation from the present system that the stepwise isomerization of 1,5-cod to the thermodynamically favoured 1,3-cod could extend to 1,2-cod. However, our recent isolation[10] of $CpRuCl_2(\eta^3$-$CH_2C(Me)CH_2)$ from oxidative addition of Me_2C=CHCl to CpRuCl(cod) casts some doubt on a hydrido allene intermediate and has led us to consider other intermediates[11] in this process. For example, the α-hydrogen shifts in tungsten–methyl complexes[12] had led us to consider a hydrido carbene complex (Figure 4) as an intermediate in the η^3-allyl $\rightarrow$ η^1-vinyl conversion. Evidence for this intermediate is now being sought from deprotonation reactions of Ru-η^1-allyl complexes, similar to those recently reported in rhenium–alkyl systems.[13]

(6) Spectral data for **3a**: ^{1}H NMR (500 MHz, (CD₃)₂CO) δ 1.37–2.34 (m, 12 H, CH₂), 4.37 (dt, PCH$_a$P, J(HP) = 10.8 Hz, J(HH) = 13.3 Hz), 4.61 (dt, PCH$_b$P, J(HP) = 9.6 Hz, J(HH) = 13.3 Hz), 5.02 (s, Cp), 5.06 (t, =CH, J(HH) = 7.8 Hz), 6.8–7.6 (m, aromatic H); ^{13}C NMR (123 MHz, CDCl₃) δ 26.6, 27.3, 29.2, 29.5, 30.5, 41.8 (6 × s, aliphatic C), 48.6 (t, CH₂P₂, J(PC) = 20 Hz), 80.4 (s, Cp), 127–132 (aromatic C), 137.3 (t, ipso aromatic C, J(PC) = 20 Hz), 139.2 (t, =CH, J(PH) = 7 Hz), 140.8 (t, ipso aromatic C, J(PH) = 20 Hz), 146.7 (t, Ru–C, J(PH) = 15 Hz); mp 156 °C. Anal. Calcd for C₃₈H₄₀P₂Ru: C, 69.18; H, 6.11. Found: C, 69.35; H, 6.48. Spectral data for **3b**: ^{1}H NMR (500 MHz, (CD₃)₂CO) δ 1.0–2.1 (m, 12 H, CH₂), 4.36 (dt, PH$_a$P, J(HP) = 11.1 Hz, J(HH) = 13.5 Hz), 4.77 (t, =CH, J(HH) = 7.7 Hz), 4.89 (s, Cp), 4.97 (dt, PH$_b$P, J(HP) = 9.5 Hz, J(HH) = 13.8 Hz), 6.8–7.6 (m, aromatic H); ^{13}C NMR (123 MHz, CDCl₃) same as for **3a**; mp 108 °C. Anal. Calcd for C₃₈H₄₀P₂Ru: C, 69.18; H, 6.11. Found: C, 69.42; H, 6.39.

(7) Crystal data for **3a**: monoclinic, space group $P2_1/n$; a = 11.540 (2) Å, b = 27.731 (5) Å, c = 11.541 (2) Å, β = 118.44 (2)°, U = 3247.5 Å³, Z = 4, D_{calcd} = 1.349 Mg m⁻³, F(000) = 1368, Philips PW1100 diffractometer, Mo Kα radiation, λ = 0.710 69 Å, μ(Mo Kα) = 0.532 mm⁻¹. Crystal data for **3b**: triclinic, space group $P\bar{1}$; a = 10.671 (4) Å, b = 14.269 (2) Å, c = 21.106 (5) Å, α = 98.17 (2)°, β = 91.03 (3)°, γ = 98.81 (2)°, U = 3140.9 Å³, Z = 4, D_{calcd} = 1.395 Mg m⁻³, F(000) = 1368, Enraf- Nonius CAD4 diffractometer, Mo Kα radiation, μ(Mo Kα) = 0.550 mm⁻¹. The structures were solved by normal heavy-atom methods and were refined by weighted least squares [$\sum w(|F_o| - |F_c|)^2$ minimized, $w = \sigma^{-2}(F_o)$]. Anisotropic temperature factors were used for all non-hydrogen atoms. For **3a** all hydrogen atoms were located and refined; for **3b** only the hydrogen atoms of the cyclooctenyl ligands were refined; all other hydrogen atoms were added in calculated positions (d_{C-H} = 0.95 Å). The refinements converged with R = 0.0470 and R_w = 0.0454 for 3668 unique reflections with $F_o \geq 4\sigma(F_o)$ (**3a**) and R = 0.0482 and R_w = 0.0440 for 6256 unique reflections with $F_o \geq 4\sigma(F_o)$ (**3b**).

(8) One molecule and the enantiomer of the second are almost superimposable.

(9) (a) McGrady, N. D.; McDade, C.; Bercaw, J. E. In "Organometallic Compounds"; Shapiro, B. L., Ed.; Texas A&M University Press: Texas, 1983. (b) Allen, A. R.; Baker, P. K.; Barnes, S. G.; Bottrill, M.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* 1983, 927. (c) Ashworth, T. V.; Singleton, E., unpublished results. (d) Schwartz, J.; Hart, D. W.; McGiffert, B. *J. Am. Chem. Soc.* 1974, *96*, 5613.

(10) Albers, M. O.; Robinson, D. J.; Singleton, E., unpublished results.
(11) Bonding of an allyl to a transition-metal complex can open a migration corridor for the allyl α-hydrogen atom to travel intramolecularly across the suprafacial arch of the allyl ligand. There are, however, no unequivocal precedents for this type of migration. See, for example: (a) Mango, F. D. *Adv. Catal.* 1969, *20*, 291. (b) Mango, F. D. *Coord. Chem. Rev.* 1975, *15*, 109. (c) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* 1973, *95*, 8678.
(12) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* 1979, 1122.
(13) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* 1985, *107*, 4103.

Synthesis of a Phosphavinyl Complex via Shift of a Pentamethylcyclopentadienyl from Phosphorus to Iron

Dietrich Gudat and Edgar Niecke*
Fakultät für Chemie der Universität, Postfach 8640
D-4800 Bielefeld, West Germany

Atta M. Arif, Alan H. Cowley,* and Sapé Quashie
Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712

Summary: The reaction of the phosphaalkene (η^1-Me₅C₅)P=C(SiMe₃)₂ with Fe₂(CO)₉ affords the η^1 (P-bonded) complex (η^1-Me₅C₅)[(CO)₄Fe]P=C(SiMe₃)₂ (**4**). Photolysis of **4** produces the phosphavinyl complex [Fe{η^1-P=C(SiMe₃)₂}(η^5-Me₅C₅)(CO)₂] (**5**). Compound **5** can also be prepared via the metathetical reaction of (Me₃Si)₂C=PCl with K[Fe(η^5-Me₅C₅)(CO)₂]. The structure of **5** has been determined by X-ray crystallography.

Phosphaalkenes, RP=CR₂,[1] are proving to be remarkably versatile ligands. As intact units, they can coordinate

(1) (a) Klebach, T. C.; Lourens, R.; Bickelhaupt, F.; Stam, C. H.; Van Herk, A. *J. Organomet. Chem.* 1981, *210*, 211. (b) Kroto, H. W.; Nixon, J. F.; Taylor, M. J.; Frew, A. A.; Muir, K. W. *Polyhedron* 1982, *1*, 89. (c) Neilson, R. H.; Thoma, R. J.; Vickovic, I.; Watson, W. A. *Organometallics* 1984, *3*, 1132.
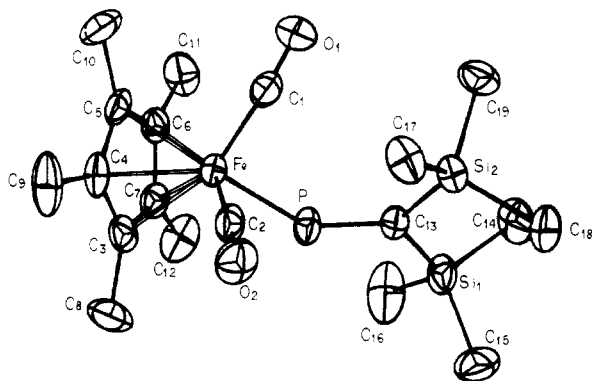
Figure 1. ORTEP drawing of [Fe{η^1-P=C(SiMe$_3$)$_2$}(η^5-Me$_5$C$_5$)-(CO)$_2$] (**5**) showing the atom numbering scheme. Important structural parameters: P–Fe = 2.256 (2) and P–C(13) = 1.680 (9) Å; Fe–P–C(13) = 126.2 (3), P–C(13)–Si(1) = 107.1 (5), P–C-(13)–Si(2) = 134.4 (5), and Si(1)–C(13)–Si(2) = 118.4 (5)°.

in an η^1 (P donor)[1] or an η^2 (P=C donor)[2] fashion. Combinations of η^1 and η^2 ligation have also been observed[3] as has equilibration between these bonding modes.[4] Further elaboration of this chemistry has become possible by the incorporation of organometallic substituents. Thus, monometalation at carbon produces **1**[5] while P-metalation results in either phosphavinyl (**2**)[6] or phosphavinylidene (**3**)[7] complexes depending on whether the phosphorus atom functions as a one- or three-electron donor. We report a novel synthesis of a phosphavinyl complex via migration of a C$_5$Me$_5$ group from phosphorus to iron.
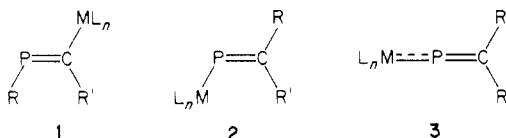
Treatment of 3.24 g (10 mmol) of (η^1-Me$_5$C$_5$)P=C-(SiMe$_3$)$_2$[8] with an equimolar quantity of Fe$_2$(CO)$_9$ for 3 days at 25 °C produced a dark red solution. After filtration and removal of the solvent and volatiles, the resulting red oil was recrystallized from 20 mL of (2:3) toluene/acetonitrile at –30 °C. The red-black crystals (mp 79 °C), which were isolated in 41% yield, were identified as the η^1-phosphaalkene complex **4** on the basis of analytical and spectroscopic data.[9] Of particular significance is the ^{31}P

chemical shift (371.5 ppm) which falls in the region typical of P-bonded phosphaalkene complexes.[1]
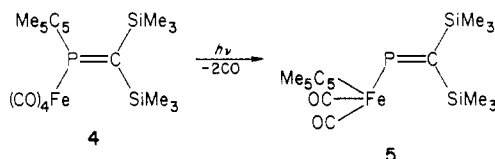
Photolysis of a *n*-hexane solution of **4** with a Hanau TQ-718 mercury lamp caused immediate gas evolution. After 3 h the carbonyl bands of **4** (2055, 1975, and 1959 cm^{-1}) disappeared and were replaced with absorptions at 1942 and 1988 cm^{-1} which are attributable to **5**. ^{31}P NMR spectroscopic assay indicated that the reaction mixture contained **5** (s, 641.5 ppm) and traces of (η^1-Me$_5$C$_5$)P=C-(SiMe$_3$)$_2$ (s, 374.5 ppm).[8] Compound **5** can also be prepared by treatment of (Me$_3$Si)$_2$C=PCl[10] with K[Fe(η^5-Me$_5$C$_5$)(CO)$_2$] in THF solution (–20 °C), and purified by recrystallization from *n*-hexane solution at –20 °C (yield 57.7%). The composition of brown, crystalline **5** (mp 117–123 °C) was established on the basis of analytical and spectroscopic data,[11] and its structure (Figure 1) was elucidated by single-crystal X-ray diffraction methods.[12] The phosphorus–carbon bond length (1.680 (9) Å) is similar to those of unmetalated phosphaalkenes;[2d,13] moreover, the sum of bond angles at C(13) is 360° within experimental error. The phosphorus–iron bond length (2.256 (2) Å) and the Fe–P–C bond angle (126.2 (3)°) indicate that the phosphorus lone pair is not involved in bonding to the metal. The fact that the Fe–P–C angle is ~15° larger than those of unmetalated phosphaalkenes seems to be a consequence of steric effects because the P–C(13)–Si(2) angle (134.4 (5)°) is considerably larger than the P–C(13)–Si(1) angle (107.1(5)°).

The scope of the Me$_5$C$_5$ (and C$_5$H$_5$) main-group/transition-metal shift reaction is presently being studied as is the reactivity of **5**.

(2) (a) Cowley, A. H.; Jones, R. A.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Zhang, H.-M. *J. Am. Chem. Soc.* **1983**, *105*, 3737. (b) Al-Resayes, A. I.; Klein, S. I.; Kroto, H. W.; Meidine, M. F.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 930. (c) Van der Knaap, Th. A.; Jenneskens, L. W.; Meerwissen, H. J.; Bickelhaupt, F.; Walther, D.; Dinjus, E.; Uhlig, E.; Spek, A. L. *J. Organomet. Chem.* **1983**, *254*, C33. (d) Cowley, A. H.; Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Zhang, H.-M. *J. Am. Chem. Soc.* **1984**, *106*, 7015. (e) Werner, H.; Paul, W.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 626.

(3) (a) Knoll, K.; Huttner, G.; Wasiucionek, M.; Zsolnai, L. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 739. (b) Holland, S.; Charrier, C.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1984**, *106*, 826. (c) Appel, R.; Casser, C.; Knoch, F. *J. Organomet. Chem.* **1985**, *293*, 213.

(4) (a) Van der Knaap, Th. A.; Bickelhaupt, F.; van der Poel, H.; van Koten, G.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 1756. Kroto, H. W.; Klein, S. I.; Meidine, M. F.; Nixon, J. F.; Harris, R. K.; Packer, K. J.; Reams, P. *J. Organomet. Chem.* **1985**, *280*, 281.

(5) Weber, L.; Reizig, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 53.

(6) Weber, L.; Reizig, K.; Boese, R.; Polk, M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 604.

(7) Cowley, A. H.; Norman, N. C.; Quashie, S. *J. Am. Chem. Soc.* **1984**, *106*, 5007.

(8) Gudat, D.; Niecke, E.; Krebs, B.; Dartmann, M. *Chimia* **1985**, *39*, 277.

(9) Anal. Calcd for C$_{21}$H$_{33}$FePO$_4$Si$_2$: C, 51.22; H, 6.75. Found: C, 51.06; H, 6.97. MS (EI, 70 eV): *m/e* (relative intensity) 492 (M$^+$, 0.4), 477 (M$^+$ – CH$_3$, 0.4), 436 (M$^+$ – 2CO, 2.7), 408 (M$^+$ – 3CO, 27.1), 380 (M$^+$ – 4CO, 76.2), 73 (SiMe$_3$$^+$, 100). ^{13}C{^{1}H} NMR: (C$_6$D$_6$, 28°C): 4.2 (d, *J* = 8.2 Hz, SiC$_3$), 5.1 (d, *J* = 4.8 Hz, SiC$_3$), 11.8 (broad, CCH$_3$), 136.5 and 142.8 (very broad, CCH$_3$), 187.8 (d, *J* = 24.5 Hz, P=C), 216.1 (d, *J* = 15 Hz, CO).

(10) Appel, R.; Westerhaus, A. *Tetrahedron Lett.* **1984**, *22*, 2159.

(11) Anal. Calcd for C$_{19}$H$_{33}$FePO$_2$Si$_2$: C, 52.29; H, 7.62. Found: C, 50.84; H, 7.72. MS (EI, 70 eV): *m/e* (relative intensity) 436 (M$^+$, 2.9), 408 (M$^+$ – CO, 44.0), 380 (M$^+$ – 2CO, 100), 73 (SiMe$_3$$^+$, 72.5). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 28 °C): 3.5 (s, SiC$_3$), 3.9 (d, *J* = 15.6 Hz, SiC$_3$), 9.3 (d, *J* = 9.2 Hz, CCH$_3$). 98.9 (s, CCH$_3$), 208.9 (d, *J* = 106.1 Hz, P=C), 217.6 ppm (s, CO).

(12) A single crystal of **5** with dimensions 0.35 × 0.35 × 0.20 mm was sealed under dry nitrogen in a Lindemann capillary. Some crystal data for **5** are as follows: C$_{19}$H$_{33}$FeO$_2$PSi$_2$, *M* = 436.47, monoclinic, space group *P*2$_1$/*n* (No. 14); *a* = 12.807 (2) Å, *b* = 9.364 (3) Å, *c* = 20.328 (3) Å, β = 103.55 (1)°; *V* = 2370 Å^3; *Z* = 4; *D*(calcd) = 1.223 g cm^{-3}, and μ = 8.1 cm^{-1}. A total of 3720 symmetry-independent reflections were recorded by using ω–2θ scans in the range 3.0 < 2θ < 48.0° using graphite-monochromated Mo Kα X-radiation with λ = 0.710 69 Å. Of these, 2339 reflections (*I* > 3.0 σ(*I*)) were used to solve (SIMPEL) and refine (full matrix, least squares) the structure of **5**. Final least-squares refinement gave *R* = 0.0572 and *R*$_w$ = 0.0746.

(13) For a review, see: Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1984**, *20*, 731.

Organometallic Chemistry of the Transition Elements. 7. A 2+ State of Bis(arene)chromium Complexes[1]

Richard J. Markle and J. J. Lagowski*

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

Summary: A new, stable oxidation state of a bis(η^6-arene)chromium complex is reported in THF. Two one-electron oxidation–reduction processes are observed for bis(hexamethylbenzene)chromium(0) at −1.630 V (reversible 1+/0 redox couple) and at −0.160 V (quasi-reversible 2+/1+ redox couple), both being measured in the presence of TBAPF$_6$ against the Ag/AgNO$_3$ couple.

The reversible or quasi-reversible oxidation–reduction processes of bis(arene)chromium(0) complexes and their corresponding bis(arene)chromium(1+) ions are well-known.[2,3] Some bis(arene)chromium redox couples are stable and sufficiently reproducible that they have been recommended as references for nonaqueous solvent systems.[4] Up to now attempts to oxidize bis(arene)chromium monocations to higher oxidation states, however, have led to irreversible oxidations and/or ligand disproportionation.[2,5]

Our work in the effects of methyl substitution on magnetic and electrochemical properties of bis(arene)chromium(0) complexes[6] has also resulted in the discovery of a new, stable, quasi-reversible oxidation state for such a complex. We report here the first example of a quasi-reversible 2+/1+ oxidation process for bis(hexamethylbenzene)chromium(0) which exhibits two redox potentials in THF.

Synthesis of Bis(hexamethylbenzene)chromium(0). Bis(hexamethylbenzene)chromium(0) was prepared by using the rotating reactor system described previously.[6,7] Chromium metal was evaporated into neat hexamethylbenzene. After workup, bis(hexamethylbenzene)chromium(0) [mp 339–340 °C dec (lit.[8] mp 400 °C dec)] was collected by sublimation [110 °C at 10^{-3} torr]. Total yield was 0.294 g or 3.66%, based on metal evaporated (HRMS calcd 376.222 20, found 376.223 13).

Electrochemical Cell and Analyses. The electrochemistry of bis(hexamethylbenzene)chromium was established by cyclic voltammetry using the apparatus illustrated in Figure 1 as described briefly here and in greater detail elsewhere.[6] The solvent THF was purified and dried by refluxing and distilling from a mixture of potassium and benzophenone and transferred to a primary
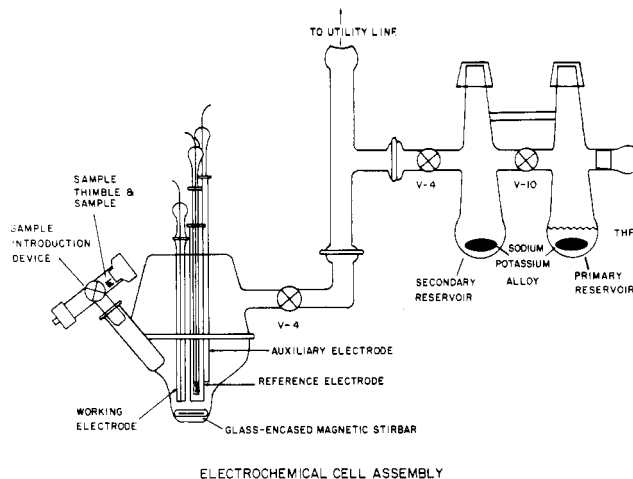

Figure 1. Electrochemical cell and related assembly used for cyclic voltammetric studies.

reservoir by using standard Schlenk techniques. The THF was stored over a 1:1 mole ratio of a sodium–potassium alloy and degassed by standard freeze–pump–thaw techniques. The THF in the reservoir was kept under static vaccum at −30 °C while the cell was dried and deoxygenated.

The supporting electrolyte, tetra-*n*-butylammonium hexafluorophosphate (TBAPF$_6$), was prepared by mixing equal molar aqueous solutions of tetra-*n*-butylammonium hydroxide and ammonium hexafluorophosphate. The product was collected, recrystallized twice from ethanol, recrystallized once from ethyl acetate, dried under vacuum, ground and dried at 140 °C, cooled, and stored in a desiccator (mp 235–237 °C, standard reference sample mp 236–238 °C). Sufficient supporting electrolyte was used in all chambers of the electrochemical cell to produce a 1.5 M solution when the appropriate amount of solvent was introduced.

The working electrode was a platinum disk (1.950-mm diameter) mounted in Pyrex glass. The platinum surface was polished to the point where no major imperfections could be observed at 50× magnification.

The reference electrode was a silver wire immersed in a solution containing TBAPF$_6$ and saturated with AgNO$_3$, the mixture being contained within a small fritted tube. A second, slightly larger fritted tube surrounded the reference electrode and contained a solution of TBAPF$_6$ in THF. The Ag/AgNO$_3$ reference electrode was thus separated from the solution containing the arene complex by two concentric fritted tubes. This reference electrode was extremely stable with reproducible potentials. Similar systems have been described by others.[3,5]

In a typical experiment, the electrochemical cell and supporting electrolyte were assembled and then dried and deoxygenated by heating under vacuum. After cooling, standard anaerobic and anhydrous handling techniques were used to incorporate the dry AgNO$_3$, the sample introduction device (and the sample), and the THF reservoir system. The assembled apparatus was then reevacuated. The solvent (THF) was flash distilled sequentially from the primary reservoir to the secondary reservoir, the secondary reservoir was isolated, and then the THF was distilled from the secondary reservoir into the electrochemical cell. Supporting electrolyte was dissolved completely and the solution allowed to equilibrate at room temperature.

All electrochemical measurements were made by using an EG&G PAR Model 175 Universal Programmer, an EG&G PAR Model 173 Potentiostat/Galvanostat, and a

(1) Paper 6 in this series: Pettijohn, T.; Shepherd, M.; Chinn, J.; Lagowski, J. J., submitted for publication.
(2) Valcher, S.; Casalbore, G.; Mastragostino, M. *J. Electroanal. Chem. Interfacial Electrochem.* **1974**, *51*, 226.
(3) Ito, N.; Saji, T.; Suga, K.; Aoyagui, S. *J. Organomet. Chem.* **1982**, *229*, 43.
(4) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461.
(5) Bailey, S.; Leung, W.; Ritchie, F. *Electrochim. Acta* **1985**, *30*, 861.
(6) Markle, R. Master's Thesis, The University of Texas at Austin, 1985.
(7) Markle, R.; Pettijohn, T.; Lagowski, J. J. *Organometallics* **1985**, *4*, 1529.
(8) Fischer, E.; Hafner, W. Brit. Pat. 829 574, 1960.