state of the iron arene complex is capable of reacting with its borate counterion.

Laser flash photolysis of the iron arene borate salts confirms formation of the 2-naphthylmethyl radical for the C_6H_5CN complex. Irradiation of a tetrahydrofuran solution of $[CpFeC_6H_5CN]^+[NpCH_2B(Ph)_3]^-$ with a 20-ns light pulse at 343 nm produces a sharp transient absorption at ca. 385 nm characteristic of the 2-naphthylmethyl radical[12] (Figure 1). The absorption of the radical rises instantaneously on the time scale of this experiment and then decays following a complex kinetic law with a lifetime of 5–10 μs. In a control experiment we found that irradiation of $Me_4N^+[NpCH_2B(Ph)_3]^-$ does not give a detectable (<5% that from the complex iron salt) absorption for the naphthylmethyl radical. Significantly, laser flash photolysis of $[CpFeC_6H_5CH_3]^+[NpCH_2B(Ph)_3]^-$ in tetrahydrofuran solution also does not give evidence for the formation of the naphthylmethyl radical. Similarly, irradiation of $[CpFeC_6H_5CN]^+[NpCH_2B(Ph)_3]^-$ in acetone solution, where in contrast to the ion pairs in tetrahydrofuran, the salt should exist primarily as freely solvated ions, gives no evidence for the formation of the naphthylmethyl radical.

Astruc and co-workers report that the 19-electron species formed from the reduction of $[CpFeArH]^+$ have weak (ϵ_{max} = ca. 100 M^{-1} cm^{-1}) absorption bands at ca. 700 nm.[13] We searched unsuccessfully for the absorption of this species in the laser flash photolysis of the C_6H_5CN complex. The low extinction coefficient of this intermediate makes it difficult to detect under these conditions; its formation in a concentration equal to that of the observed naphthylmethyl radical would produce a maximum change in absorbance of only ca. 0.002 at 700 nm.

The photochemistry of the iron arene alkylborate salts can be understood within the mechanism outlined in Scheme I. Excitation of the ion pair leads to the triplet of the iron-arene complex either directly, from red light irradiation, or via the singlet excited state by means of rapid intersystem crossing (ISC) (eq 2). Electron transfer (eq 3) can occur despite the short lifetime of the triplet state because ion-pairing insures the appropriate positioning of the donor (borate) next to the acceptor (iron arene) at the moment of excitation.

The rate constant for electron transfer, k_{ET}, will depend on the free energy change for this reaction (ΔG_{ET}). This value may be calculated by means of eq 7. The oxidation potential ($E_{ox.}$) of the naphthylmethyl borate was estimated by cyclic voltammetry in acetonitrile solution to be ca. 0.3 V vs SCE from the peak of its irreversible wave. The reduction potential ($E_{red.}$) of the iron complex in acetonitrile solution is −1.10 when C_6H_5CN is the arene ligand and −1.46 V for the $C_6H_5CH_3$ complex.[14] These values can be crudely adjusted for the change of solvent from acetonitrile to tetrahydrofuran by application of the Born equation:[15] $(E_{ox.} - E_{red.})_{THF}$ = 1.86 and 1.50 V for the toluene and benzonitrile complexes in tetrahydrofuran, respectively. The triplet energies (E^{*3}) of the $[CpFeArH]^+$ complexes were calculated from their singlet–triplet absorption spectra to be 2.0 V. And the Coulombic work necessary to combine the charges (E_{work}) was estimated[15] to be 0.33 V for a center-of-charge separation in the ion pair of 6 Å in a medium with the dielectric constant of bulk tetrahydrofuran. Substitution of these values into eq 7

$$\Delta G_{ET} = E_{ox} - E_{red} - E^{*3} + E_{work} \qquad (7)$$

shows that electron transfer from the borate to the C_6H_5CN complex is exothermic (ΔG_{ET} = −0.16 V). On the other hand, this calculation predicts that the electron transfer will be endothermic (+0.19 V) for reaction of the $C_6H_5CH_3$ complex. The precise values for ΔG_{ET} revealed by these calculations must be regarded with skepticism since the oxidation of the borate is irreversible. Nevertheless, the trend is reliable and is consistent with rapid electron transfer only for the C_6H_5CN complex. This finding accounts for the observed difference in photochemistry between the C_6H_5CN and $C_6H_5CH_3$ iron complexes.

Electron transfer from the borate to the excited iron complex generates a neutral radical pair. In many such reactions back electron transfer to regenerate ground-state starting materials (eq 4) overwhelms other reaction paths. In the present case, cleavage of the carbon–boron bond in the boranyl radical (eq 5) must be sufficiently rapid to give a measurable yield of the alkyl radical, whose dimerization (eq 6) completes the reaction sequence and gives the observed product.

In summary, photolysis of iron arene cation–alkyl borate salts initiates an intra-ion-pair electron-transfer reaction when the free energy change for such a reaction is favorable. The electrically neutral radical pair produced goes on to give unique products.

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Electron-Transfer Activation of Coordinated Thiophene: Preparation and Desulfurization of $(\eta^5\text{-}C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$

Ann E. Ogilvy, Anton E. Skaugset, and Thomas B. Rauchfuss*

School of Chemical Sciences, University of Illinois
505 S. Mathews St., Urbana, Illinois 61801

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Summary: Cyclic voltammetry studies show that $[(C_5Me_5)Rh(C_4Me_4S)]^{2+}$ undergoes two reversible one-electron reductions at low potentials. The reduced product was synthesized by cobaltocene reduction and was characterized as $[(\eta^5\text{-}C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)]$. ^1H and ^{13}C NMR spectroscopic results are consistent with a symmetrical, reduced thiophene ligand. An X-ray crystallographic study confirms that the reduced complex contains a nonplanar η^4-thiophene ligand with an uncoordinated sulfur atom. The reduced complex reacts with $Fe_3(CO)_{12}$ to give $(C_5Me_5)RhC_4Me_4Fe(CO)_3$ which is analogous to a major product in the $Fe_3(CO)_{12}$ desulfurization of thiophenes. Electron-transfer activation is proposed to be relevant to the desulfurization of thiophenes by metal surfaces.

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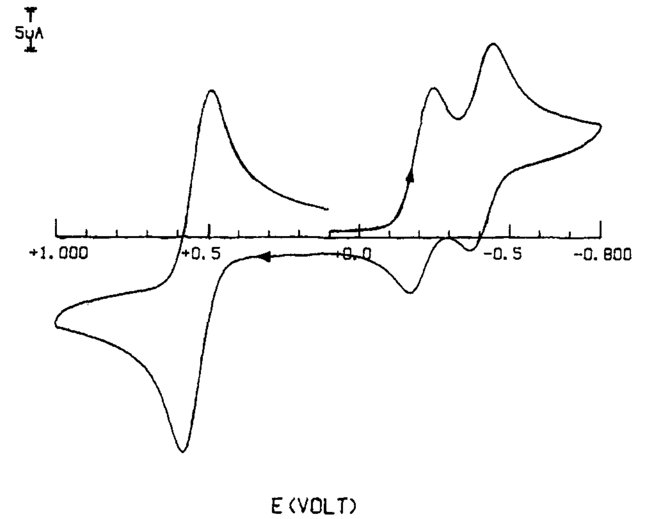


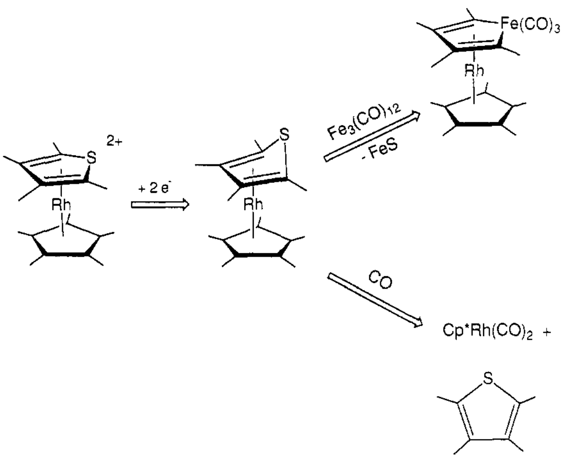
Figure 1. Cyclic voltammetry trace for an acetone solution of [Cp*Rh(TMT)](OTf)$_2$ (0.001 M) and Fe(C$_5$H$_5$)$_2$ (0.001 M). Operating conditions: 0.1 M Bu$_4$NPF$_6$; glassy carbon working electrode; Ag/AgCl, KCl (saturated) reference electrode; scan rate of 50 mV/s.

The interaction of thiophenes and metals is an aspect of organometallic chemistry with important implications in environmental and energy issues.[1] The possible effects of electron transfer on such metal–thiophene interactions came under consideration in an effort to explain the *homogeneous* desulfurization of thiophenes by Fe$_3$(CO)$_{12}$.[2] Herein we provide a preliminary account of experiments that probe the effects of electron transfer on metal-bound thiophene.

We recently showed that the sandwich compound bis(2,3,4,5-tetramethylthiophene)ruthenium(II), [Ru(TMT)$_2$]$^{2+}$, undergoes two sequential one-electron reductions at relatively mild potentials.[3] Since we have been unable to purify the reduction product [Ru(TMT)$_2$]^0, we turned our attention to the reduction of [Cp*Rh(TMT)]$^{2+}$, [1]$^{2+}$ (Cp* is η^5-C$_5$Me$_5$). We were especially encouraged by Geiger and Rheingold's successful reduction of [Cp*Rh(η^6-C$_6$R$_6$)]$^{2+}$ to [Cp*Rh(η^4-C$_6$R$_6$)]^0.[4]

We began by examining the electrochemical reduction of [1](OTf)$_2$[5] at both platinum and glassy carbon (GCE) electrodes using cyclic voltammetry. The data for the two electrodes are similar except that measurements with the platinum electrode were less reproducible possibly due to deposition of reduced products on the electrode. We observe two features associated with sequential one-electron reductions of the complex at $E_{1/2}$ = −194 and −394 mV vs Ag/AgCl[6] (Figure 1). These $E_{1/2}$ values are approximately 320 mV more positive than [Cp*Rh(C$_6$Me$_6$)]$^{2+}$, indicating that TMT is more effective than hexamethylbenzene in stabilizing the Rh(I) state. A plot of i_p vs [scan rate]$^{1/2}$ was linear for the first reduction step which confirms that this reduction is diffusion-limited and that rate-limiting chemical events do not precede the electron transfer step.[7] ΔE_p for both reduction waves using GCE changed from 100 to 60 mV as scan rates were slowed from 500 to 20 mV/s.

Scheme I



Chemical reduction was performed by the addition of 2 equiv of cobaltocene to a cold (−78 °C) acetone solution of [1](OTf)$_2$ followed by slow warming to room temperature. After removal of the solvent, the neutral products were selectively extracted into toluene leaving a residue of pale yellow Cp$_2$CoOTf, which was identified by ^{1}H NMR spectroscopy and microanalysis. Analytically pure [1]^0 was obtained in 58–66% yield as a red microcrystalline powder. The cyclic voltammetry of [1]^0 is essentially identical to that for [1]$^{2+}$. Its 70-eV EI mass spectrum is dominated by a strong molecular ion peak together with a base peak at m/z = 238 corresponding to ([1]^0 − TMT)$^+$.[8] Acetone and benzene solutions of [1]^0 are stable at room temperature under nitrogen. Carbonylation of a toluene solution of [1]^0 (60 °C, 750 psig of CO, 14 h) cleanly affords Cp*Rh(CO)$_2$[9] and free TMT as confirmed by GC–EIMS, IR, and ^{1}H NMR spectroscopy.

The 500-MHz ^{1}H NMR spectrum of [1]^0 features three peaks in the ratio 2:5:2 down to −80 °C, consistent with a symmetric molecule. However the very low-field (high-frequency) TMT ^{1}H NMR shifts indicate that the thiophene ligand is in an unusual electronic environment relative to neutral η^5-TMT compounds such as [(TMT)-

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(1) (a) An overview of catalytic hydrodesulfurization (HDS): Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw Hill: New York, 1978. (b) Theory of HDS: Zonnevylle, M. C.; Hoffmann, R.; Harris, S. *Surf. Sci.* **1988**, *199*, 320. (c) Organometallic models for HDS: Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 389. (d) The scale of HDS: Greek, B. F. *Chem. Eng. News* **1989**, May 29, 29. (e) Catalyst poisoning: Oudar, J. In *Catalyst Deactivation*; Petersen, E. E., Bell, W. T., Eds.; Marcel Dekker: New York, 1984.

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(5) Prepared from 4 equiv of AgOTf (OTf = OSO$_2$CF$_3$), excess TMT, and [Cp*RhCl$_2$]$_2$ in acetone at room temperature and isolated as pale yellow crystals from acetone/CHCl$_3$. This synthesis is based on: Russell, M. J. H.; White, C.; Yates, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 857. Anal. Calcd for C$_{20}$H$_{27}$F$_6$O$_6$RhS$_3$: C, 35.49; H, 4.02; S, 14.22. Found: C, 35.51; H, 4.07; S, 14.34. 300-MHz ^{1}H NMR (acetone-d_6): δ 2.64 (s, 6 H), 2.43 (s, 6 H), 2.24 (s, 15 H).

(6) The Ag/AgCl, KCl (saturated) couple is 197 mV more positive than the normal hydrogen electrode (NHE): Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

(7) *Laboratory Techniques in Electroanalytical Chemistry*, Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker: New York, 1984.

(8) Anal. Calcd for C$_{18}$H$_{27}$RhS: C, 57.24; H, 7.19; S, 8.47. Found: C, 57.33; H, 7.27; S, 8.20. 500-MHz ^{1}H NMR (acetone-d_6): δ 1.98 (s, 6 H), 1.71 (s, 15 H), 1.13 (s, 6 H). 125-MHz ^{13}C NMR (acetone, J(^{103}Rh,^{13}C) values (Hz) in parentheses): δ 94.58 (C_5Me$_5$, 6.2), 88.43 (C_4Me$_4$S, 7.3), 42.87 (C_4Me$_4$S, 14.8), 15.25 (C$_4$$Me_4$S), 11.31 (C$_4$$Me_4$S), 9.50 (C$_5$$Me_5$). 70-eV EIMS (probe temperature 55 °C): 378 (65%, M$^+$), 238 (100%, M$^+$ − C$_8$H$_{12}$S).

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$RuCl_2]_2$, $(TMT)RuCl_2(PR_3)$, and $(TMT)RuCl_2(NH_2R)$.[3] The reduced character on the thiophene ring is further suggested by the extremely high-field ^{13}C NMR shifts for one pair of the TMT ring carbons, the assignment being established by long-range ^1H–^{13}C chemical shift correlation spectroscopy. This very high-field ring carbon also features the largest value of $J(^{103}Rh,^{13}C)$.

A crystallographic analysis of a low quality crystal of $[1]^0$ confirms its assignment as $(\eta^5\text{-}C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$.[10] In each of the three crystallographically independent molecules, the rhodium atom is bound to nine carbon atoms and the sulfur atom is oriented away from the rhodium atom, out of the plane of the carbon atoms in the TMT ring (Scheme I). A full paper will present a detailed comparison of the structures of $[1](OTf)_2$ and $[1]^0$, contingent on the availability of suitable crystals.

The η^4-thiophene ligand in $[1]^0$ desulfurizes upon reaction with $Fe_3(CO)_{12}$ (toluene solution, 110 °C, 18 h) to give a good yield of the bright yellow compound $Cp^*Rh(C_4Me_4)Fe(CO)_3$ (**2**). On the basis of spectroscopic and analytical data, this compound[11] is assigned as a symmetrical metallacycle analogous to the ferroles $Fe_2C_4R_4(CO)_6$ isolated from the reaction of $Fe_3(CO)_{12}$ and thiophenes (see Scheme I).[2,12] The conversion $[1]^{2+} \rightarrow [1]^0 \rightarrow$ **2** involves a net replacement of a vertex on a nido RhC_4X cluster.

To summarize, we have shown that electron transfer can induce a change in hapticity from η^5- to η^4-thiophene (Scheme I). The metal ion facilitates the buckling (dearomatization?) of the thiophene ring since we found that TMT itself is not reduced in the range 0 to −2 V vs Ag/AgCl. On the basis of these results, η^4-thiophene intermediates should be considered whenever thiophenes encounter reduced metal centers as is frequently the case in the catalytic[1] and stoichiometric[13] desulfurization of thiophenes.

Compound $[1]^0$ is highly reactive and well behaved; it is therefore a likely source of new developments in thiophene coordination chemistry.

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Supplementary Material Available: Experimental conditions for crystallography, tables of atomic coordinates, bond distances, and bond angles, and ORTEP drawings (15 pages); a listing of structure factors (13 pages). Ordering information is given on any current masthead page.

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[10] Crystal data: red transparent crystal, 0.2 × 0.4 × 0.6 mm, orthorhombic $P2_12_12_1$ (D_2^4 – No. 19); $a = 35.513$ (22), $b = 10.411$ (5), $c = 14.053$ (4) Å; $Z = 12$; $\rho_{calcd} = 1.451$ g/cm^3. Diffraction data: Enraf-Nonius CAD4 automated diffractometer, Mo radiation ($K\alpha$, $\lambda = 0.71073$ Å), graphite monochromator, range $2.0 < 2\theta < 46.0°$ for $-h,-k,+l$ and $2.0 < 2\theta < 8.0°$ for $\pm h,\pm k,\pm l$, 4348 reflections, 4081 unique data, 2315 observed ($I > 2.58\sigma(I)$); corrected for anomalous dispersion, absorption, Lorentz, and polarization effects. Least-squares refinement of 2315 structure factors converged at $R = 0.130$ and $R_w = 0.15$.

[11] Anal. Calcd for $C_{21}H_{27}FeO_3Rh$: C, 51.85; H, 5.60. Found: C, 51.85; H, 5.64. ^1H NMR (benzene-d_6): δ 2.29 (s, 6 H), 1.43 (s, 15 H), 1.31 (s, 6 H). ^{13}C NMR (acetone, $J(^{103}Rh,^{13}C)$ values (Hz) in parentheses): δ 167.62 (C_4Me_4, 18.3), 113.16 (C_4Me_4), 97.13 (C_5Me_5, 7.3), 28.50 ($C_4\mathit{Me}_4$), 12.30 ($C_4\mathit{Me}_4$), 9.80 (C_5Me_5). FDMS: 486 (M^+ for ^{56}Fe). IR (hexane, cm^{-1}): 1994, 1939, 1935 (sh). Also isolated were trace amounts of two red compounds formulated as isomers of $[Cp^*Rh]_2FeS(CO)_4$ based on ^1H NMR spectroscopy (isomer A, δ 1.69; isomer B, δ 1.59), IR [isomer A (hexanes), ν_{CO} 2012, 1967, 1954 cm^{-1}; isomer B (CH_2Cl_2), ν_{CO} 1931 (br), 1758, 1751 cm^{-1}], and FDMS (676, M^+ for ^{56}Fe).

[12] Dettlaf, G.; Weiss, E. *J. Organomet. Chem.* **1976**, *108*, 213. Hübener, P.; Weiss, E. *Ibid.* **1977**, *129*, 105.

[13] Raney nickel is widely used for stoichiometric thiophene desulfurization. A recent review emphasizes that this family of alloys are "extremely useful reducing agents": Keefer, L. K.; Lunn, G. *Chem. Rev.* **1989**, *89*, 459.

[14] **Note Added in Proof.** The structure of **2** has been confirmed by X-ray crystallography.

Polymeric Organosilicon Systems. 7. Ring-Opening Polymerization of 1,2,5,6-Tetrasilacycloocta-3,7-diynes

Mitsuo Ishikawa,* Yutaka Hasegawa,[†]
Takanori Hatano, and Atsutaka Kunai

Department of Applied Chemistry, Faculty of Engineering
Hiroshima University, Higashi-Hiroshima 724, Japan

Toru Yamanaka

Mitsui Petrochemical Industries, Ltd., Nagaura, Sodegaura
Chiba 299, Japan

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Summary: Treatment of 1,2,5,6-tetramethyl(tetraphenyl)- and 1,2,5,6-tetraethyl(tetramethyl)-1,2,5,6-tetrasilacycloocta-3,7-diyne with a catalytic amount of *n*-butyllithium in THF at room temperature led to ring-opening polymerization to give the respective poly[(disilanylene)ethynylenes] with high molecular weights. Treatment of the films of these polymers with SbF_5 vapor produced highly conducting films.

Recently, we have demonstrated that the polymers in which the regular alternating arrangement of a disilanyl unit and the π-electron system such as a phenylene,[1,2] ethenylene,[3] and butenyne group[4] is found in the polymer backbone are photoactive and show conducting properties when the polymers are doped by exposure to vapor of SbF_5.

During the course of our studies concerning the synthesis of the disilanylene-containing polymers that can be used as functional material, we have discovered that treatment of 1,2,5,6-tetrasilacycloocta-3,7-diynes[5,6] with a catalytic amount of *n*-butyllithium led to ring opening polymerization to give poly[(disilanylene)ethynylenes] with high molecular weight.

The starting 1,2,5,6-tetramethyl(tetraphenyl)-1,2,5,6-tetrasilacycloocta-3,7-diyne[7] (**2a**) was prepared as follows:

[†] Present address: Tsukuba Research Laboratory, Sumitomo Chemical Co., Ltd., Kitahara, Tuskuba, Ibaraki 300, Japan.

[1] Ishikawa, M.; Nate, K. *Inorganic and organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington DC, 1988; Chapter 16.

[2] Treatment of the film of poly[*p*-(1,2-dimethyldiphenyldisilanylene)phenylene] with SbF_5 gave a highly conducting film whose conductivity was found to be 1.75 S·cm^{-1}.

[3] Ohshita, J.; Kanaya, D.; Ishikawa, M.; Yamanaka, T. *J. Organomet. Chem.* **1989**, *369*, C18.

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[6] Iwahara, T.; West, R. *J. Chem. Soc., Chem. Commun.* **1988**, 594.

[7] Compound **2a**: mp 200–202 °C; MS *m/e* 528 (M^+); IR 1428, 1249, 1108 cm^{-1}; UV λ_{max} (log ϵ) 252 nm (4.35); ^1H NMR (δ in $CDCl_3$) 0.40 (12 H, s, MeSi), 7.36–7.74 (20 H, m, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) −4.4 (MeSi), 119.9 ($C\equiv C$), 128.2, 129.5, 133.8, 134.3 (phenyl ring carbons). Anal. Calcd for $C_{32}H_{32}Si_4$: C, 72.61; H, 6.08. Found: C, 72.66; H, 6.10.

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