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Facile, Redox-Promoted Formation of Rhodocenium Complexes Bearing the 1,2,3-Tri-*tert*-butylcyclopentadienyl Ligand

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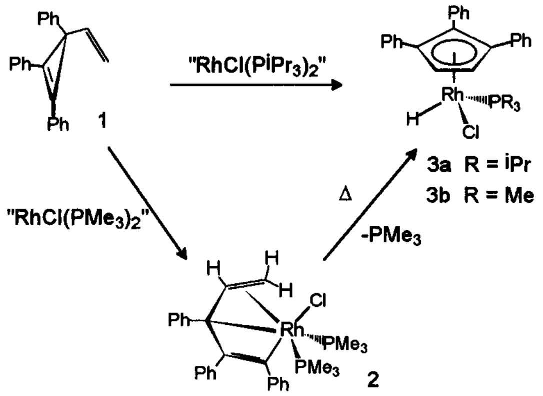
Summary: Although pentadienediyl complex ***6b*** *does not react when heated for months in refluxing toluene, it rapidly converts to the rhodocenium product* $\boldsymbol{7b}^+$ *when subjected to electrochemical or chemical oxidizing conditions. Oxidation of the indenyl pentadienediyl complex* ***6a*** *likewise affords rhodocenium complex* $\boldsymbol{7a}^+$*.*

The transition-metal-promoted reactions of 3-vinyl-1-cyclopropenes are of synthetic use and mechanistic interest.[1] Products of these reactions include complexes containing substituted η^4-cyclopentadiene or η^5-cyclopentadienyl ligands,[2−6] free cyclopentadienes,[4] 1,2,3,5-η- or 1,5-η-pentadienediyl complexes,[2,4,5,7,8] and, after incorporation of CO, phenols and cyclohexadienones.[4,9,10] These transformations are relevant to the synthetically useful Dötz reaction in which five- and six-membered organic rings are produced by treating Fischer carbenes with alkynes.[11,12] The production of complexes containing substituted η^5-cyclopentadienyl ligands is illustrated by the reaction of 1,2,3-triphenyl-3-vinyl-1-cyclopropene

Scheme 1



[⊗] Abstract published in *Advance ACS Abstracts*, February 15, 1997.

(1) For thermal and photochemical reactions of vinylcyclopropenes, see: (a) Zimmerman, H. E.; Wilson, D. W. *J. Org. Chem.* **1995**, *60*, 692 and references therein. (b) Padwa, A. *Org. Photochem.* **1979**, *4*, 261. (c) Breslow, R. In *Molecular Rearrangements;* deMayo, P., Ed.; Wiley: New York, 1963; Part 1, p 263.

(2) Egan, J. W.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1578.

(3) Hughes, R. P.; Robinson, D. J. *Organometallics* **1989**, *8*, 1015.

(4) Grabowski, N. A.; Hughes, R. P.; Jaynes, B. S.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1694.

(5) (a) Donovan, B. T.; Hughes, R. P.; Trujillo, H. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7076. (b) Donovan, B. T.; Hughes, R. P.; Trujillo, H. A.; Rheingold, A. L. *Organometallics* **1992**, *11*, 64.

(6) Donovan, B. T.; Hughes, R. P.; Kowalski, A. S.; Trujillo, H. A.; Rheingold, A. L. *Organometallics* **1993**, *12*, 1038.

(7) Donovan, B. T.; Egan, J. W.; Hughes, R. P.; Spara, P. P.; Trujillo, H. A.; Rheingold, A. L. *Isr. J. Chem.* **1990**, *30*, 351.

(8) Hughes, R. P.; Kowalski, A. S.; Donovan, B. T. *J. Organomet. Chem.* **1994**, *472*, C18.

(9) Cho, S. H.; Liebeskind, L. S. *J. Org. Chem.* **1987**, *52*, 2631.

(10) (a) Semmelhack, M. F.; Ho, S.; Steigerwald, M.; Lee, M. C. *J. Am. Chem. Soc.* **1987**, *109*, 4397. (b) Semmelhack, M. F.; Ho, S.; Cohen, D.; Steigerwald, M.; Lee, M. C.; Lee, G.; Gilbert, A. M.; Wulff, W. D.; Ball, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7108.

(11) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (b) Bos, M. E.; Wulff, W. D.; Miller, R. A.; Chamberlin, S.; Brandvold, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 9293.

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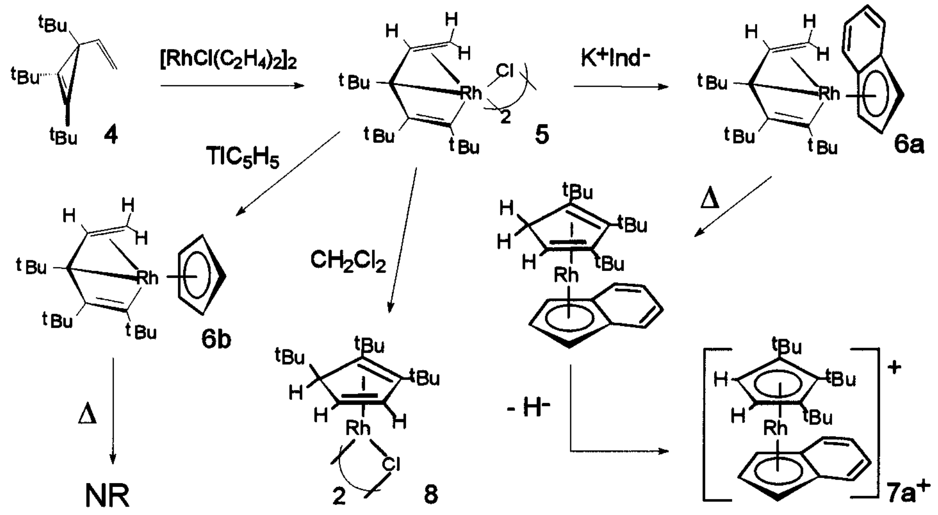
Scheme 2



(**1**) (Scheme 1) with Rh(I) to generate complexes **3a**,**b**.[2] Isolation of an intermediate 1,2,3,5-η-pentadienediyl complex **2** revealed the stepwise nature of this transformation. 1,2,3-Tri-*tert*-butyl-3-vinyl-1-cyclopropene (**4**) (Scheme 2), the tri-*tert*-butyl analogue of **1**, reacts with $[RhCl(C_2H_4)_2]_2$ to form dimer **5**,[7] which can be converted to mononuclear indenyl (**6a**)[5] and cyclopentadienyl (**6b**)[7] derivatives. Although the tri-*tert*-butyl complexes **5** and **6a**,**b** are analogues of intermediate **2**, reported attempts[5-7] to convert these complexes to rhodocenium products bearing the novel η^5-1,2,3-tri-*tert*-butylcyclopentadienyl ligand (1,2,3-^{t}Bu$_3$Cp) have been successful only for the transformation **6a** → **7a**$^+$.[13]

We report here the first electrochemistry studies of pentadienediyl complexes **6a**,**b** and demonstrate that oxidation of these compounds results in their *rapid* conversion to rhodocenium products **7a**$^+$ and **7b**$^+$, respectively. In addition to providing a facile route to rhodium complexes bearing the novel 1,2,3-^{t}Bu$_3$Cp ligand, the oxidatively-promoted transformation illustrates a striking example of the differences in reactivity of 17 e$^-$ vs 18e$^-$ organometallic complexes.[14]

Figure 1 displays two cyclic voltammetry scans of **6b** in THF solution. A chemically irreversible wave (labeled A) at $Ep_a = +0.02$ V [15] is observed when the scan is initiated in the positive potential direction (scan represented by solid line). The fact that wave A is chemically irreversible at scan rates ranging from 0.05 to 2 V/s indicates the occurrence of a rapid reaction of **6b**$^+$, the radical cation generated by oxidation of **6b**. Reversal of the scan direction after traversing the anodic portion of wave A reveals a wave of limited chemical reversibility (labeled B) at $E° = -1.83$ V. Wave B is observed only if wave A is traversed first and hence is absent in the scan depicted by the dashed line. Furthermore, if a holding time of 10 s is imposed immediately after peak A is traversed, the cathodic peak current of wave B is larger than in experiments which do not employ a holding time.[16] We will demonstrate (*vide infra*) that wave A arises from an EC process[17] in which **6b**$^+$ undergoes ring closure and loss of hydrogen (in the form H$^•$)[18] to afford rhodocenium complex **7b**$^+$ (Scheme 3) and that wave B arises from the reversible reduction of **7b**$^+$ (an E process).

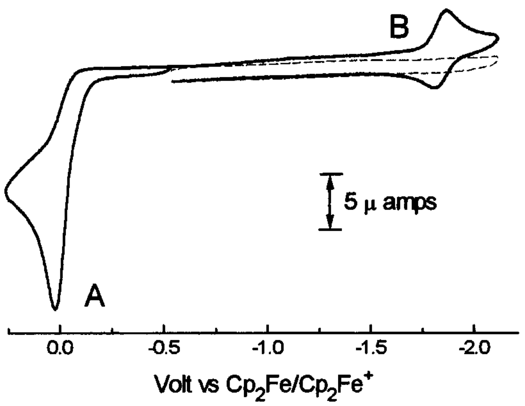


Figure 1. Cyclic voltammetry scans of 0.7 mM **6b** in THF solution. The scan represented by the solid line was initiated in the positive potential direction, while the scan represented by the dashed line was initiated in the negative potential direction. The lettered waves arise from the following reactions: (A) **6b** → **7b**$^+$ + e$^-$; (B) **7b**$^+$ + e$^-$ $\rightleftarrows$ **7b**. A glassy carbon working electrode was used with scan rate = 200 mV/s.

The one-electron nature of wave A was confirmed by exhaustive bulk electrochemical oxidation. CV scans obtained after electrolysis of **6b** show the absence of wave A and the presence of wave B regardless of the initial scan direction. Oxidation of **6b** was also accomplished by chemical means, using a stoichiometric

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[12] For a discussion of the relevance of the transition-metal-promoted ring expansion reactions of 3-vinyl-1-cyclopropenes to the Dötz reaction, see: Hughes, R. P.; Trujillo, H. A.; Gauri, A. J. *Organometallics* **1995**, *14*, 4319.

[13] As shown in Scheme 2, indenyl derivative **6a** reacts in a two-step process to afford **7a**$^+$, the only complex bearing the 1,2,3-^{t}Bu$_3$Cp ligand reported to date.[5] Chloride-bridged dimer **5**, however, produces η^4-cyclopentadiene complex **8** on prolonged standing in methylene chloride solution.[6] Cyclopentadienyl complex **6b** does not react even when heated in refluxing toluene solution for several months.[7]

[14] (a) Sun, S.; Sweigart, D. A. *Adv. Organomet. Chem.* **1996**, *40*, 171. (b) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217. (c) Astruc, D. *Acc. Chem Res.* **1991**, *24*, 36. (d) Evans, D. H. *Chem. Rev.* **1990**, *90*, 739.

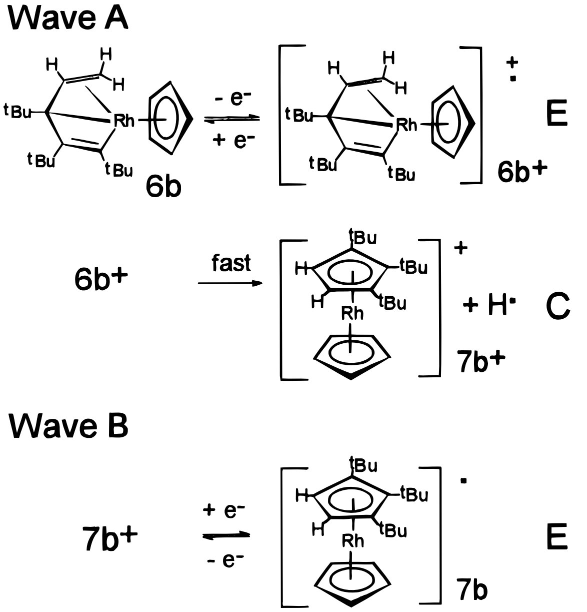
[15] All potentials are reported versus the ferrocene/ferrocenium redox couple, which has an $E_{1/2}$ value of +0.56 V vs the saturated calomel electrode (SCE) under identical experimental conditions.

[16] The holding time allows a greater concentration of the oxidation product to develop near the electrode surface.

[17] E represents an electron transfer process, and C, a chemical reaction. See: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 429.

[18] The H$^•$ generated presumably reacts with solvent molecules. No gas evolution (indicating the formation of H$_2$) was observed during the chemical or electrochemical oxidations.

Scheme 3



amount of ferrocenium hexafluorophosphate as the oxidizing agent. The isolated product was identified as rhodocenium complex **7b**$^+$.[19] The cyclic voltammetry of **7b**$^+$, shown in Figure 2, is identical to that obtained after bulk electrochemical oxidation of **6b**. A comparison of wave heights in voltammograms recorded before and after electrolysis showed the conversion to be almost quantitative.[21] This facile, redox-promoted reaction of **6b** provides the only known route to **7b**$^+$. Although **6b** does not react when heated for extended periods, it converts to **7b**$^+$ in less than 0.5 s when subjected to oxidation conditions.

The oxidatively-promoted transformation is not limited to the cyclopentadienyl derivative. Indeed, the conversion **6a** → **7a**$^+$ occurs rapidly when **6a** is subjected to chemical or electrochemical oxidation conditions identical to those used to promote reaction of **6b**.[22] Although **7a**$^+$ can also be prepared using thermally-promoted methods,[5] the redox synthesis of **7a**$^+$ offers the advantage of being a rapid, one-step reaction that provides a comparable yield to that obtained using the literature procedure.

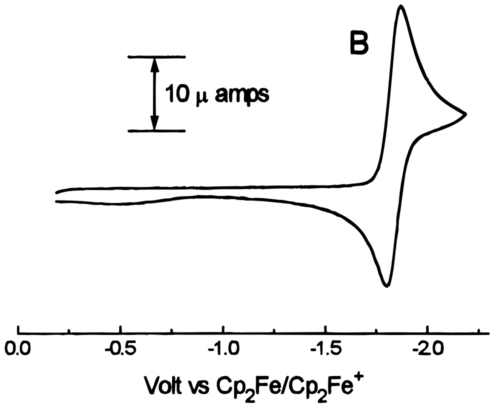


Figure 2. Cyclic voltammetry of 0.7 mM **7b**$^+$ in THF solution. A glassy carbon working electrode was used with scan rate = 300 mV/s.

The results reported here represent the first studies of the redox behavior of 1,2,3,5-η-pentadienediyl complexes. Theoretical studies aimed at more fully understanding how the redox-promoted reaction occurs are in progress. We are also exploring the redox chemistry of other pentadienediyl complexes and are investigating the consequences of reducing the new rhodocenium products. Reactions of pentadienediyl complexes with other reagents, including hydride abstracting reagents, are also under investigation. These results will be reported in due course.

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[19] **7b**$^+$: Isolated as the PF$_6^-$ salt, white solid, mp 280–282 °C (dec) ^{1}H NMR (acetone-d_6): δ 1.53 (s, 18H, ^{t}Bu), 1.64 (s, 9H, ^{t}Bu), 6.09 (s, 2H, C$_5{}^t$Bu$_3$$H_2$), 6.19 (s, 5H, C$_5$$H_5$). Anal. Calcd for C$_{22}H_{34}F_6$PRh: C, 48.36; H, 6.27. Found: C, 48.39; H, 6.33. The structure was confirmed by the results of a single-crystal X-ray diffraction study.[20]

[20] Rheingold, A. L. Private communication.

[21] This comparison of wave heights assumes that the diffusion coefficients of **6b** and **7b**$^+$ are similar. See: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 218.

[22] The spectroscopic data for **7a**$^+$ matched that reported in the literature.[5]