Journal of Organometallic Chemistry, 421 (1991) 315–322
Elsevier Sequoia S.A., Lausanne
JOM 22195

Metal hydride oxidation chemistry: addition of a trityl cation to the cyclopentadienyl ring in $CpRu(PPh_3)_2H$ via initial electron transfer

Olav B. Ryan, Kjell-Tore Smith and Mats Tilset *
Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo (Norway)

(Received July 2nd, 1991)

Abstract

Treatment of $CpRu(PPh_3)_2H$ (**1**) with 1 equivalent of the substituted trityl reagent $Tol_3C^+PF_6^-$ (Tol = *p*-MeC_6H_4) in 9/1 dichloromethane-d_2/acetonitrile-d_3 at −80 °C led to attachment of the trityl cation to the Cp ring and generation of the ring-substituted dihydride complex *trans*-$[\eta^5\text{-}C_5H_4(Tol_3C)]Ru(PPh_3)_2H_2^+$ (**5**). At ambient temperature the reaction yielded a mixture of **5**, $CpRu(PPh_3)_2H_2^+$ (**2**), and $CpRu(PPh_3)_2(NCCD_3)^+$ (**3**-d_3). Oxidation of **1** with 1 equivalent of $Cp_2Fe^+PF_6^-$ yielded a 1:1 mixture of **2** and **3**-d_3. The mechanism of the generation of the products is discussed in the light of the experimental evidence that suggests that **5** is formed by electrophilic attack by the trityl cation at the Cp ring of **1** via initial electron transfer.

Introduction

Electrophilic addition to cyclopentadienyl (Cp) and other ligands is a well-known type of reaction in organometallic chemistry [1]. Metal-based orbitals make significant contributions to the HOMOs of coordinately saturated organometallic complexes and so it is commonly assumed that such reactions proceed by electrophilic attack at the metal center followed by transfer of the electrophile to the *endo* face of the ligand, although such a mechanism may not be general [1b]. For example, the combination of a sterically congested metal center and a sterically demanding electrophile could force the electrophilic attack to take place directly on the ligand. The bulky triphenylmethyl (trityl) cations have found widespread use as electrophilic reagents for the removal of H^- from metal hydrides and alkyls, and from saturated carbon atoms adjoining coordinated polyenes [2]. The removal of hydride from hydrocarbon ligands frequently proceeds by a two-step mechanism involving electron transfer and subsequent hydrogen atom abstraction by the trityl radical [3]. The trityl cation has been observed to undergo electrophilic addition to Re-bonded vinyl [4a], phenyl [4b], and allyl [4c] ligands, and to the exocyclic, uncomplexed double bond of $(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_5H({=}CH_2))Fe^0$ [4d]. These additions occur at carbon atoms not directly bonded to the metal, and are accompanied by an increase in the ligand hapticity or metal–carbon bond order, maintaining the 18-electron count at the metal. Trityl addition to Cp ligands has sometimes been observed; for example in the case of ferrocene [5a–c], in which it leads to electrophilic substitution, and that of nickelocene [5d], in which it causes fragmentation of the organometallic entity and formation of (triphenylmethyl)-cyclopentadiene. The latter reactions have also been proposed to proceed via a two-step electron-transfer mechanism terminated by the attachment of the trityl radical at the sterically relatively unencumbered metal centers [5d].

We present below the details of an investigation of the chemical and electrochemical oxidation of $CpRu(PPh_3)_2H$ (**1**), and report that the substituted trityl cation Tol_3C^+ (**4**; Tol = p-MeC_6H_4) undergoes smooth addition to the Cp ring in **1**, apparently by an electron-transfer mechanism.

Results and discussion

By using derivative cyclic voltammetry (DCV [6]), we have found that **1** undergoes oxidation at −0.34 V (taken as the midpoint between the anodic and cathodic waves) vs. the ferrocene/ferrocenium (Fc) couple (2.0 mM substrate, dichloromethane/0.2 M $Bu_4N^+PF_6^-$, 17 °C, 0.6 mm diameter Pt disk electrode, voltage sweep rate $\nu = 0.1$ V/s). Figure 1 shows a DCV trace for the oxidation of **1**. The cyclic voltammetry oxidation peak potential corresponds to the position at which the rapidly descending curve crosses the base line after the first derivative peak, labeled (a). The high ratio of the cathodic (b) to the anodic (a) derivative peak current intensity shows that a considerable degree of chemical reversibility pertains to the oxidation process under the experimental conditions. At a substrate concentration of 1.0 mM, the extent of reversibility is even greater, indicating a combined reaction order (with respect to $\mathbf{1}^{\cdot+}$ and **1**) for the decomposition of $\mathbf{1}^{\cdot+}$ that is greater than unity. The observed reversibility for the oxidation of **1** is in contrast with a previous report [7] of irreversible oxidation in dichloromethane and THF at −0.20 V vs. Fc.

The chemical oxidation of **1** was carried out in 9/1 dichloromethane/acetonitrile. The presence of some acetonitrile was found to give a much cleaner reaction. Thus, treatment of **1** with 1 equivalent of $Cp_2Fe^+PF_6^-$ in 9/1 dichloromethane-d_2/acetonitrile-d_3 at −80 °C produced a 1 : 1 mixture of *trans*-$CpRu(PPh_3)_2H_2^+$ (**2**) [8a] and $CpRu(PPh_3)_2(NCCD_3)^+$ (**3**-d_3) [8b] as shown in Scheme 1. The product distribution strongly suggests the occurrence of proton transfer from $\mathbf{1}^{\cdot+}$ to **1** with subsequent oxidation of the radical $CpRu(PPh_3)_2^{\cdot}$, presumably by initial acetonitrile ligation [2b,c]. Such a reaction gives a combined reaction order with respect to $\mathbf{1}^{\cdot+}$ and **1** of 2 for the reaction of $\mathbf{1}^{\cdot+}$, which is qualitatively in agreement with the voltammetric results. This proton-transfer reaction is analogous to reactions of other phosphine substituted metal hydride cation radicals [2b–d].

We attempted to effect hydride abstraction by treatment of **1** with $Tol_3C^+PF_6^-$ (**4**-PF_6; Tol = p-MeC_6H_4; $E_{red} = -0.35$ V vs. Fc) in 9/1 dichloromethane-d_2/acetonitrile-d_3 at −80 °C, but observed that the expected product **3**-d_3 was not formed at all. Instead, an instantaneous reaction resulted in the appearence of two new hydride signals in the ^1H NMR spectrum, at δ −5.53 (t, J 23 Hz, 1H) and −7.36 (t, J 27 Hz, 1H), suggesting the presence of a dihydride species. The two

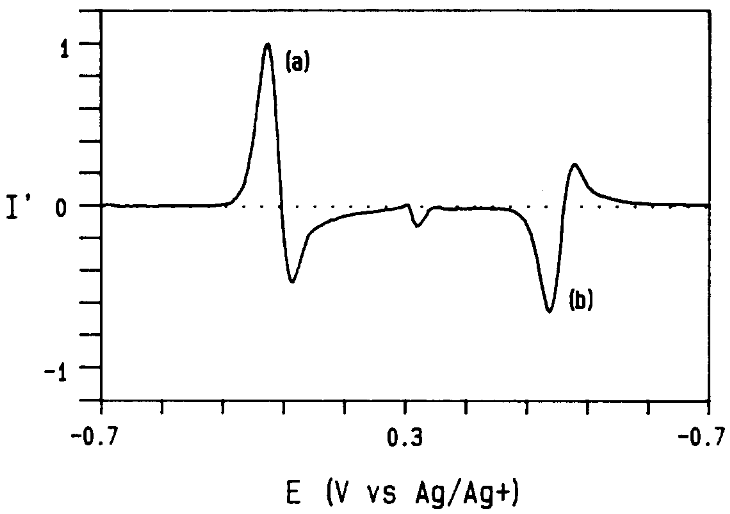
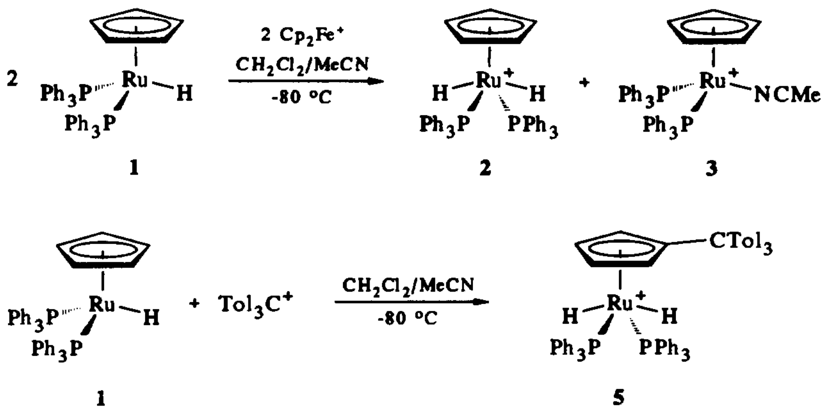


Fig. 1. Derivative cyclic voltammogram for the oxidation of **1** (2.0 m*M* substrate, dichloromethane/0.2 *M* $Bu_4N^+PF_6^-$, 17 °C, 0.6 mm diameter Pt disk electrode, voltage sweep rate $\nu = 0.1$ V/s).

signals reversibly merged with the baseline at 20 °C (300 MHz), corresponding to a free energy of activation, $\Delta G^{\#}$, for the fluxional process of 13.3 kcal/mol [9*]. Two Cp resonances were present at δ 5.29 (br t, 2H) and 3.83 (br t, 2H), in addition to a methyl singlet at δ 2.21 (9H) and multiplets in the aromatic region (δ 6.9–7.4, 42H). Only the hydride signals underwent observable changes when the sample was heated. The NMR data suggest that the product was *trans*-[η^5-$C_5H_4(Tol_3C)]Ru(PPh_3)_2H_2^+$ (**5**; Scheme 1) [10*]. Owing to interligand repulsive forces, the conformation in which the trityl group lies between the PPh_3 ligands, as shown in Scheme 1, is most stable. This is in accord with the observation of two nonequivalent hydride signals in the low-temperature ^1H NMR spectrum.



Scheme 1

---

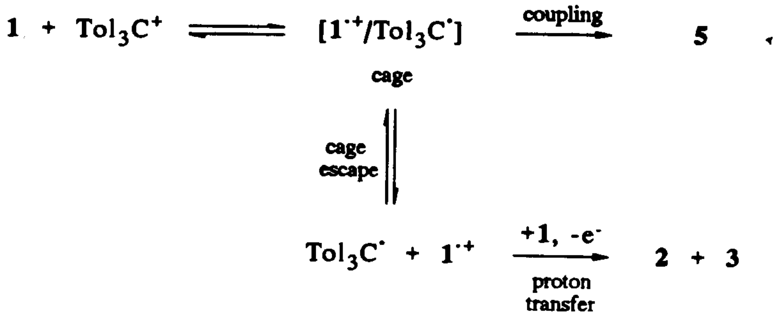
* Reference number with asterisk indicates a note in the list of references.

Attempts to obtain a limiting high-temperature spectrum in 1,1,2,2-tetrachloroethane-d_2 were unsuccessful. At 80 ° C, a temperature at which sample decomposition was seen to take place within minutes, the averaged hydride signal had not yet appeared. Provided that the fluxional process is intramolecular in nature, the dynamic behavior may be due to a hindered rotation around the metal–cyclopentadienyl bond axis arising from severe steric interactions between the bulky PPh_3 ligands and the trityl substituent on the ring [11]. Alternatively, a facile equilibrium between **5** and a corresponding (unobserved) dihydrogen complex $[\eta^5\text{-}C_5H_4(Tol_3C)]Ru(PPh_3)_2(\eta^2\text{-}H_2)^+$, in which rapid rotation around the Ru–$(\eta^2\text{-}H_2)$ bond axis is expected, could be the source of the exchange [12]. Experiments that are aimed at distinguishing between these exchange mechanisms are being planned.

In accord with the proposed structure, deprotonation of **5** with pyrrolidine [13*] gave the neutral hydride $[\eta^5\text{-}C_5H_4(Tol_3C)]Ru(PPh_3)_2H$ (**6**). On a preparative scale, **6** was obtained in 75% yield from **1** and was characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and elemental analysis (see Experimental section for details). The number of signals derived from the trityl substituent in the $^{13}C\{^1H\}$ NMR spectrum shows unambiguously that it is the central carbon atom of the trityl group that has been attached to the Cp ring. Treatment of **6** with $HBF_4 \cdot Et_2O$ regenerated **5** quantitatively (^1H NMR).

Two distinctly different mechanisms, both of which may proceed by initial electron transfer, must be considered for the addition reaction: (i) electrophilic attack on the *exo* face of the Cp ring, followed by migration of the *endo* H to the metal; and (ii) electrophilic attack on the metal and migration of the trityl group to the *endo* face of the ring. This reaction could be terminated either by proton removal from the *exo* face and reprotonation at the metal center [14*], or by [1,5]-hydrogen shifts on the *exo* face of the ring and insertion of the metal into an *endo* C–H bond. Alternative (ii) appears highly unlikely for two reasons; firstly, if the attacks were to take place on the metal, then the bulky trityl reagent would approach from the hydride side [15*] and this should result in hydride abstraction. Steric hindrance is probably the main reason why the normal hydride abstraction does not occur at all in this system. Second, the *exo* deprotonation step should be facilitated by **1**, presumably the strongest base in solution, to yield **6** and **2** initially. Proton transfer from **2** to the metal center of **6** then would provide the product **5** as well as **1**. The viability of the last step is discounted by the observation that an equilibrium mixture of the products of the proton transfer between **5** and **1**, generated from **1** and substoichiometric quantities of **4**-PF_6 at −80 ° C, was not formed (^1H NMR) until the sample was heated to ca. −40 ° C.

Although the trityl reactions did not proceed to generate the same products as the outer-sphere electron-transfer reaction of $Cp_2Fe^+PF_6^-$, the electron-transfer mechanism may still be operative. The virtually identical redox potentials for the **1**/**1**$^{\cdot+}$ and $Tol_3C^+/Tol_3C^{\cdot}$ couples certainly hints at the possibility of a facile electron-transfer preequilibrium between **1** and **4**. The different outcomes of the two reactions may attributed to rapid **1**$^{\cdot+}/Tol_3C^{\cdot}$ coupling, possibly within a solvent cage, before diffusional separation of these intermediates [16a*]. In order to test for the intermediacy of $Tol_3C^{\cdot}$ radicals, the reaction between **1** and **4** was performed in the presence of air. The $Ph_3C^{\cdot}$ radical is known to react with O_2 at near diffusion-controlled rates to generate $Ph_3COO^{\cdot}$ [17*]. The reaction between



Scheme 2

1 and 4 in the presence of air in 9/1 dichloromethane-d_2/acetonitrile-d_3 at −80 °C gave a mixture (by ^{1}H NMR) of 2 (13%), 3-d_3 (29%), and 5 (58%). The formation of 2 and 3-d_3 strongly indicates an electron-transfer mechanism. The formation of more 3-d_3, than 2 may be the result of a hydrogen atom abstraction from $1^{\cdot +}$ by the sterically less demanding $Tol_3COO^{\cdot}$ radical. The fact that 5 was seen under these conditions shows that the $1^{\cdot +}/Tol_3C^{\cdot}$ coupling is indeed very rapid.

When the reaction between 1 and 4 was performed at ambient temperature but otherwise under identical conditions, a mixture of 2 (7%), 3-d_3 (16%), 5 (61%), and small amounts of as yet unidentified products (17%) was obtained. Taken together with the evidence presented above, this suggests that as expected the escape of $1^{\cdot +}$ and $Tol_3C\cdot$ from the cage becomes more efficient at higher temperatures. Also, to the extent that $1^{\cdot +}/Tol_3C^{\cdot}$ coupling might take place after escape from the cage the higher temperature would render the proton-transfer reaction kinetically more favorable relative to the coupling process. This is a result of the higher activation energy expected for this reaction, which involves cleavage of bonds, than for the coupling reaction between a neutral and a charged species, in which there is no bond cleavage. The proposed reaction mechanism is summarized in Scheme 2.

In conclusion, the experimental evidence appears to favor trityl addition to the Cp ligand of 1, rather than to the metal, following electron transfer. Work is underway to examine the electron-transfer reactions of electron rich, sterically hindered metal hydrides.

Experimental

General procedures

All handling of organometallic complexes was performed under an inert atmosphere by the use of standard vacuum line, Schlenk, syringe, or drybox techniques. Acetonitrile was distilled from P_2O_5, and acetonitrile-d_3, dichloromethane, and dichloromethane-d_2 were distilled from CaH_2. ^{1}H NMR spectra were recorded on Varian XL-300 or Varian Gemini-200 instruments. Chemical shifts are reported downfield from tetramethylsilane with the residual solvent proton resonances as internal standards (δ 1.93 for acetonitrile, and 5.32 for dichloromethane). Melting points were measured on a Büchi melting point apparatus in capillary tubes sealed under vacuum. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany.

The electrochemical cells, data-handling procedures and electrodes were as previously described [6a,18]. Electrolytes used for electrochemical experiments were passed through a column of active neutral alumina before use in order to remove water and protic impurities. The electrolyte was freed of air by purging with purified argon, and all measurements were carried out under a blanket of solvent-saturated argon gas. Preparative electrochemical oxidations and coulometry experiments were performed at a Pt-gauze working electrode in an H-shaped cell, the compartments of which were separated by a fritted-glass junction.

The compounds $CpRu(PPh_3)_2H$ [8b], $Cp_2Fe^+PF_6^-$ [19a] and $Tol_3C^+PF_6^-$ [19b] were prepared by published procedures. All other chemicals were obtained commercially and used as received.

[η^5-$C_5H_4(Tol_3C)$]$Ru(PPh_3)_2H$ (6)

Solid $Tol_3C^+PF_6^-$ (86 mg, 0.20 mmol) was added to a vigorously stirred orange solution of **1** (138 mg, 0.20 mmol) in 9/1 dichloromethane/acetonitrile (30 mL) at −80 °C. The color changed to yellow almost instantaneously. The solution was heated to 0 °C and pyrrolidine (25 μL, 0.30 mmol) was added. The solvent was removed by vacuum transfer and the residue purified by column chromatography (Alumina III, hexane/benzene eluent). A yellow band was eluted, and removal of the solvent followed by recrystallization from benzene/pentane yielded the product as a yellow powder (146 mg, 75%): m.p. 250–253 °C; ^1H NMR (dichloromethane-d_2, 200 MHz) δ −10.29 (t, J 35 Hz, 1H), 2.29 (s, 9H), 3.14 (br "t", 2H), 4.67 (br "t", 2H), 6.8–7.4 (m, 42H); $^{13}C\{^1H\}$ NMR (dichloromethane-d_2, 50 MHz) δ 21.3, 58.1, 81.0, 82.7, 120.1, 126.3 (br "t"), 127.1, 127.4, 130.4, 133.3, (br "t"), 134.6, 140.1 (m), 144.7. Anal. Found: C, 77.81; H, 5.99. $C_{63}H_{56}P_2Ru$ calc.: C, 77.52; H, 5.78%.

Trans-[η^5-$C_5H_4(Tol_3C)$]$Ru(PPh_3)_2H_2^+BF_4^-$ (5-BF_4)

A stirred solution of **1** (100 mg, 0.14 mmol) in dichloromethane (20 mL) was treated with $HBF_4 \cdot Et_2O$ (27 μL, ca. 0.2 mmol) at ambient temperature. Addition of ether caused the product to separate as a white powder. The solvent was decanted, and the product was washed with ether and dried in vacuo (76 mg, 51%). The white solid turned pink within hours when left at ambient temperature, but still gave a reasonably good elemental analysis. ^1H NMR (dichloromethane-d_2, 300 MHz, −80 °C) δ −7.36 (t, J 23 Hz, 1H), −5.55 (t, J 27 Hz, 1H), 2.21 (s, 9H), 3.83 (br t, 2H), 5.29 (br t, 2H), 6.9–7.4 (m, 42H). Anal. Found: C, 71.11; H, 6.00. $C_{63}H_{57}BF_4P_2Ru$ calc.: C, 71.12; H, 5.40%.

Oxidation of 1 with $Cp_2Fe^+PF_6^-$

An NMR tube equipped with a ground-glass joint was charged with **1** (10 mg, 0.014 mmol) and $Cp_2Fe^+PF_6^-$ (4.5 mg, 0.014 mmol). The tube was attached to the vacuum line and cooled in liquid nitrogen, and dichloromethane-d_2 (0.45 mL) and acetonitrile-d_3 (0.05 mL) were introduced by vacuum transfer. The tube was sealed under vacuum and inserted into the NMR probe precooled to −80 °C. The ^1H NMR spectrum revealed the presence of **2** (δ −7.90 (t, J 23.0 Hz, 2H), 4.80 (s, 5H)), **3**-d_3 (δ 4.35 (s)), and ferrocene (δ 4.05) in a 1/1/1 molar ratio. The identities of the products were confirmed by comparison of their spectroscopic data with those for independently prepared samples of **2** [8a] and **3** [8b].

Monitoring of the reaction between 1 and $Tol_3C^+PF_6^-$ *by* ^1H *NMR*

An NMR tube equipped with a ground-glass joint was loaded with **1** (10 mg, 0.014 mmol) and $Tol_3C^+PF_6^-$ (6.2 mg, 0.014 mmol). The tube was attached to the vacuum line and cooled in liquid nitrogen, and dichloromethane-d_2 (0.45 mL) and acetonitrile-d_3 (0.05 mL) were introduced by vacuum transfer. The tube was sealed under vacuum and inserted into the NMR probe precooled to −80 ° C. The ^1H NMR spectrum was recorded immediately and revealed the presence of **5** as the only product. An analogous experiment was carried out in which **1** and $Tol_3C^+PF_6^-$ were dissolved in the dichloromethane-d_2/acetonitrile-d_3 solvent mixture at ambient temperature and the ^1H NMR spectrum immediately recorded. In this case, a mixture of **2** (7%), **3**-d_3 (16%), **5** (61%) and unidentified products, giving rise to signals at δ 3.70 and 4.58 (17% combined), was obtained. It was confirmed that **2** and **5** were stable on the time scale of this experiment.

Reaction between 1 and $Tol_3C^+PF_6^-$ *in the presence of air*

An NMR tube equipped with a ground-glass joint was charged with **1** (10 mg, 0.014 mmol). Dichloromethane-d_2 (0.9 mL) and acetonitrile-d_3 (0.1 mL) were added, and dry air (15 mL) was bubbled through the solution at −80 ° C. Solid $Tol_3C^+PF_6^-$ (6.2 mg, 0.014 mmol) was added, and the tube sealed under vacuum and inserted into the precooled NMR probe. The ^1H NMR spectrum was recorded immediately, and revealed the presence of **2** (13%), **3**-d_3 (29%), and **5** (58%).

Preparative electrolysis of 1 in acetonitrile

A solution of **1** (42.7 mg, 0.0617 mmol) in acetonitrile/0.05 *M* $Me_4N^+BF_4^-$ (20 mL) was electrolyzed for the time required for the passage of 1.0 faraday/mol of charge. The solution was left for 30 min at ambient temperature before it was concentrated by rotary evaporation. The residue was extracted with dichloromethane (5 mL) and the extract was filtered and concentrated. The product **3**-BF_4 (49.3 mg, 97%) was obtained by crystallization from dichloromethane/ether, and was judged to be pure by ^1H NMR spectroscopy. The NMR spectrum was identical with that of an authentic sample.

Acknowledgement

We gratefully acknowledge support from Statoil under the VISTA program, administered by the Norwegian Academy of Science and Letters (stipend to O.B.R.) and from the Norwegian Council for Science and the Humanities, NAVF.

References and notes

1 (a) W.E. Watts, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organonometallic Chemistry, Vol. 8, Pergamon, New York, 1982, p. 1019; (b) J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, 1987.

2 For examples of H^- removal from metal hydrides, see: (a) W. Beck and K. Sünkel, Chem. Rev., 88 (1988) 1405 and references cited therein; (b) O.B. Ryan, M. Tilset and V.D. Parker, J. Am. Chem. Soc., 112 (1990) 2618; (c) O.B. Ryan, M. Tilset and V.D. Parker, Organometallics, 10 (1991) 298; (d)

D.E. Westerberg, L.F. Rhodes, J. Edwin, W.E. Geiger and K.G. Caulton, Inorg. Chem., 30 (1991) 1107.

3 (a) J.C. Hayes and N.J. Cooper, J. Am. Chem. Soc., 104 (1982) 5570; (b) D. Mandon, L. Toupet and D. Astruc, J. Am. Chem. Soc., 108 (1986) 1320; (c) V. Guerchais and C. Lapinte, J. Chem. Soc., Chem. Commun., (1986) 663; (d) G.S. Bodner, J.A. Gladysz, M.F. Nielsen and V.D. Parker, J. Am. Chem. Soc., 109 (1987) 1757; (e) D. Mandon and D. Astruc, Organometallics, 8 (1989) 2372.

4 (a) G.S. Bodner, D.E. Smith, W.G. Hatton, P.C. Heah, S. Georgiou, A.L. Rheingold, S.J. Geib, J.P. Hutchinson and J.A. Gladysz, J. Am. Chem. Soc., 109 (1987) 7688; (b) S.K. Agbossou, G.S. Bodner, A.T. Patton and J.A. Gladysz, Organometallics, 9 (1990) 1184; (c) G.S. Bodner, T.-S. Peng, A.M. Arif and J.A. Gladysz, Organometallics, 9 (1990) 1191; (d) D. Astruc, D. Mandon, A. Madonik, P. Michaud, N. Ardoin and F. Varret, Organometallics, 9 (1990) 2155.

5 (a) M.F. Hawthorne, J. Org. Chem., 21 (1956) 363; (b) E.W. Neuse and D.S. Trifan, J. Am. Chem. Soc., 84 (1962) 1850; (c) P.L. Pauson, M.A. Sandhu and W.E. Watts, J. Chem. Soc. C, (1966) 251; (d) H. Werner, G. Mattmann, A. Salzer and T. Winkler, J. Organomet. Chem., 25 (1970) 461.

6 (a) E. Ahlberg and V.D. Parker, J. Electroanal. Chem. Interfacial Electrochem., 121 (1981) 73; (b) V.D. Parker, Electroanal. Chem., 14 (1986) 1.

7 G. Jia and R.H. Morris, J. Am. Chem. Soc., 113 (1991) 875.

8 (a) T. Wilczewski, J. Organomet. Chem., 361 (1989) 219; (b) P.M. Treichel, D.A. Komar and P.J. Vincenti, Synth. React. Inorg. Met.-Org. Chem., 14 (1984) 383.

9 $k_c = \pi \Delta v/2^{1/2}$ and $\Delta G^{\#} = 2.301RT(10.32 + \log(T_c/k_c))$: J.B. Lambet, H.F. Shurvell, L. Verbit, R.G. Cooks and G.H. Stout, Organic Structure Analysis, Macmillan, New York, 1976, p. 116.

10 The generation of **5** is reminiscent of the reaction between $CpM(CO)_3^-$ (M = Mo, W) with the tri-tert-butylcyclopropenium cation (R^+), which resulted in $(\eta^5\text{-}C_5H_4R)\text{-}M(CO)_3H$: M. Green and R.P. Hughes, J. Chem. Soc., Chem. Commun., (1975) 862.

11 For recent examples of sterically inhibited rotation around metal-Cp bonds, see: (a) F. Mao, S.K. Sur and D.R. Tyler, J. Am. Chem. Soc., 111 (1989) 7627; (b) F. Mao, C.E. Philbin, T.J.R. Weakley and D.R. Tyler, Organometallics, 9 (1990) 1510; (c) R. Mynott, H. Lehmkuhl, E.-M. Kreuzer and E. Joussen, Angew. Chem., Int. Ed. Engl., 29 (1990) 289; (d) H. Sitzmann, Chem. Ber., 123 (1990) 2311; (e) M. Fei, S.K. Sur and D.R. Tyler, Organometallics, 10 (1991) 419.

12 For recent discussions of $M(H)_2/M(\eta^2\text{-}H_2)$ equilibria, see ref. 7 and (a) M.S. Chinn and D.M. Heinekey, J. Am. Chem. Soc., 112 (1990) 5166; (b) R.H. Crabtree, Acc. Chem. Res., 23 (1990) 95; (c) G.J. Kubas, Acc. Chem. Res., 21 (1988) 120.

13 pK_a data in acetonitrile: **2**, 16.0 by converting reported aqueous values [7] to acetonitrile; pyrrolidine, 19.6: J.F. Coetzee, Prog. Phys. Org. Chem., 4 (1967) 45.

14 A similar deprotonation/reprotonation sequence has been verified for the electrophilic substitution of $CpCo(PMe_3)_2$ with Me_3CBr and Me_2CHBr: H. Werner and W. Hofmann, Angew. Chem., Int. Ed. Engl., 16 (1977) 794.

15 Hydride abstraction from the dynamic 1:1 mixture of *cis* and *trans* $CpW(CO)_2(PMe_3)H$ in acetonitrile generated the thermodynamically least stable *trans*-$CpW(CO)_2(PMe_3)(NCMe)^+$ as the kinetic product, indicating a strong preference for reaction with the *trans* isomer and implying significant steric effects on the direction of approach of the trityl reagent [2b].

16 (a) The presence of acetonitrile is not a prerequisite for the outcome of this reaction, which also proceeded smoothly in neat dichloromethane. This appears to disfavor the possibility of a reaction between $Tol_3C^{\cdot}$ and a 19-electron solvent adduct $CpRu(PPh_3)_2(NCMe)^{\cdot +}$ which may be expected [16b–e] to have excess electron density located at the Cp ring. Also, acetonitrile then is apparently not needed to stabilize the initial 16-electron cyclopentadiene complex $[\eta^4\text{-}C_5H_5(Tol_3C)]\text{-}Ru(PPh_3)_2H^+$; (b) J.P. Blaha and M.S. Wrighton, J. Am. Chem. Soc., 107 (1985) 2694; (c) D. Astruc, Chem. Rev., 88 (1988) 1189; (d) D.R. Tyler, C. Philbin and M. Fei, in M. Chanon, M. Julliard and J.C. Poite (Eds.), Paramagnetic Organometallic Species in Activation/Selectivity, Catalysis, Kluwer Academic, Dordrecht, 1989, p. 201; (e) D. Astruc, Acc. Chem. Res., 24 (1991) 36.

17 The second-order rate constant for the reaction between $Ph_3C^{\cdot}$ and O_2 has been estimated to be $10^7\ M^{-1}\ s^{-1}$ or greater in dichloromethane at −60 °C [3d]. Employing the same method and criteria as those in ref. 3d, we find the same to hold true for the reaction between $Tol_3C^{\cdot}$ and O_2.

18 (a) E. Ahlberg and V.D. Parker, Electroanal. Chem. Interfacial Electrochem., 121 (1981) 57; (b) E. Ahlberg and V.D. Parker, Acta Chem. Scand., Ser. B, 34B (1980) 97.

19 (a) I.R. Lyatifov, S.P. Solodovnikov, V.N. Babin and R.B. Materikova, Z. Naturforsch. B, 34B (1979) 863; (b) H.J. Dauben, L.R. Honnen and K.M. Harmon, J. Org. Chem., 25 (1960) 1442.