Organometallics **1992,** *11,* 3947-3953

Calcd for $C_{22}H_{24}Cl_2Ti_2$ (**21**): C, 54.69; H, 5.01. Found: C, 54.33; H, 4.75. Mass spectrum (m/z): M^+, 482 (^{48}Ti, ^{35}Cl). Anal. Calcd for $C_{25}H_{28}Cl_2SiTi_2$ (**22**): C, 57.39; H, 5.39. Found: C, 57.09; H, 5.43. Mass spectrum (m/z): M^+, 522 (^{48}Ti, ^{35}Cl). Anal. Calcd for $C_{24}H_{28}Cl_2Si_2Ti_2$ (**23**): C, 53.45; H, 5.23. Found: C, 53.17; H, 5.09. Mass spectrum (m/z): M^+, 538 (^{48}Ti, ^{35}Cl).

Supplementary Material Available: Tables of crystallographic parameters, positional and thermal parameters, and bond lengths and bond angles (13 pages). Ordering information is given on any current masthead page.

OM9202276

Enthalpies of Reaction of $Cp^*Ru(CH_3CN)_3{}^+O_3SCF_3{}^-$ (Cp^* = η^5-C_5Me_5) with Arenes. Solution Thermochemical Study of Arene Binding to the Cp^*Ru^+ Fragment

Steven P. Nolan,* Kenneth L. Martin, and Edwin D. Stevens

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

Paul J. Fagan*

Central Research and Development Department, E. I. du Pont de Nemours & Co., Inc., Experimental Station, P.O. Box 80328, Wilmington, Delaware 19880-0328

Received July 1, 1992

The enthalpies of reaction of $Cp^*Ru(CH_3CN)_3OTf$ (Cp^* = η^5-$C_5(CH_3)_5$, OTf = O_3SCF_3) with a series of arenes have been measured by solution calorimetry. The results of this study are used to establish the following relative stability scale leading to the formation of $Cp^*Ru(arene)OTf$ complexes in THF (in kcal/mol): naphthalene, −1.7 ± 0.1; benzene, −3.4 ± 0.1; biphenyl, −3.6 ± 0.1; toluene, −4.3 ± 0.2; *p*-xylene, −4.6 ± 0.2; (trimethylsilyl)benzene, −5.0 ± 0.2; anisole, −5.4 ± 0.2; mesitylene, −5.5 ± 0.1; indole, −7.3 ± 0.2; *N,N*-dimethylaniline, −7.5 ± 0.1; *p*-bis(dimethylamino)benzene, −8.3 ± 0.2. The solid-state structure of one of these arene complexes, $Cp^*Ru[C_6H_5(Si(CH_3)_3)]OTf$, was determined by a low-temperature data collection X-ray crystallographic study. This investigation illustrates the presence of steric interactions between the phenyl TMS methyl groups and the Cp^* methyl group and explains the small measured enthalpy of reaction. The enthalpies of arene substitution from $Cp^*Ru(CH_3CN)_3OTf$ span some 6.6 kcal/mol and vary as a function of the electron-donating ability of the arene. Factors affecting the Ru–arene bond energy are discussed, and thermodynamic comparisons with other organometallic systems are presented.

Introduction

A better knowledge of metal–ligand bond energies is vital to a complete understanding of the driving forces behind important organotransition-metal-mediated reactions. A variety of methods have been used to obtain metal–ligand bond disruption enthalpies for organometallic systems.[1-3] These include kinetic,[2c,h,4] photoacoustic,[2i,5] laser pyrolytic,[6] and one-[7,8] and two-electron-redox[2d,j,9] approaches. A thermochemical technique which has proven successful for a number of oganometallic systems is solution calorimetry. Some of these solution calorimetric studies have led to the determination of relative and absolute bond disruption enthalpies, the latter through an accessible thermodynamic anchor[7,10a] or estimation of a thermodynamic anchor point.[8-10] Even though the knowledge of absolute bond dissociation energies is fundamental to a complete understanding of a transition-metal system, as they allow direct thermodynamic comparison between different systems, relative bond disruption

---

(1) (a) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629–688. (b) Marks, T. J., Ed. Metal-Ligand Bonding Energetics in Organotransition Metal Compounds. *Polyhedron* **1988**, *7*. (c) Marks, T. J., Ed. *Bonding Energetics in Organometallic Compounds*; ACS Symposium Series 428; American Chemical Society: Worthington, DC, 1990. (d) Hoff, C. D. *Prog. Inorg. Chem.* **1992**, *40*, 503–561.

(2) For some leading references, see also: (a) Pilcher, G.; Skinner, H. H. In *The Chemistry of the Metal-Carbon Bond*; Harley, F. R., Patai, S., Eds.; Wiley: New York, 1982; pp 43–90. (b) Connor, J. A. *Top Curr. Chem.* **1977**, 71–110. (c) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238–244. (d) Mondal, J. U.; Blake, D. M. *Coord. Chem. Rev.* **1983**, *47*, 204–238. (e) Mansson, M. *Pure Appl. Chem.* **1983**, *55*, 417–426. (f) Skinner, H. A.; Connor, J. A. *Pure Appl. Chem.* **1985**, *57*, 79–88. (g) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41–59. (h) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41–48. (i) Nolan, S. P.; Hoff, C. D.; Stoutland, P. O.; Newman, L. J.; Buchanan, J. M.; Bergman, R. G.; Yang, G. K.; Peters, K. G. *J. Am. Chem. Soc.* **1987**, *109*, 3143–3145 and references therein. (j) Dias, A. R.; Salema, M. S.; Martinho-Simoes, J. A. *J. Organomet. Chem.* **1981**, *222*, 69–78.

(3) (a) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701–7715. (b) Dias, A. R.; Simoes, J. A. M. In ref 1b, pp 1531–1544. (c) Lappert, M. F.; Patil, D.; Pedley, J. B. *J. Chem. Soc., Chem. Commun.* **1975**, 830–831.

(4) (a) Halpern, J. In ref 1b, pp 1483–1490. (b) Hay, B. P.; Finke, R. G. In ref 1b, pp 1469–1481. (c) Koenig, T. W.; Hay, B. P.; Finke, R. G. In ref 1b, pp 1499–1516. (d) Wayland, B. B. In ref 1b, pp 1545–1455. (e) Geno, M. K.; Halpern, J. *J. Chem. Soc., Chem. Commun.* **1987**, 1052–1053.

(5) (a) Yang, G. K.; Vaida, V.; Peters, K. S. In ref 1b, pp 1619–1622. (b) Rothberg, L. J.; Simon, J. D.; Bernstein, M.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 3464–3470.

(6) Smith, G. P. In ref 1b, pp 1605–1608.

(7) (a) Nolan, S. P.; Stern, D. L.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844–7853. (b) Toscano, P. J.; Seligson, A. L.; Curran, M. T.; Skrobutt, A. T.; Sonnenberger, D. C. *Inorg. Chem.* **1989**, *28*, 166–168.

(8) (a) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824–6832. (b) Sonnenberger, D. C.; Morss, L. R.; Marks, T. J. *Organometallics* **1985**, *4*, 352–355. (c) Bruno, J. W.; Stecher, H. A.; Morss, L. R.; Sonnenberger, D. C.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7275–7280 and ref 4. (d) Nolan, S. P.; Stern, D. L.; Hedden, D.; Marks, T. J. In ref 1c, pp 159–174. (e) Nolan, S. P.; Porchia, M.; Marks, T. J. *Organometallics* **1991**, *10*, 1087–1090.

(9) Stoutland, P. O.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. In ref 1b, pp 1429–1440.

(10) (a) Nolan, S. P.; Lopez de la Vega, R.; Hoff, C. D. *Organometallics* **1986**, *5*, 2529–2537. (b) Nolan, S. P.; Hoff, C. D.; Landrum, J. T. *J. Organomet. Chem.* **1985**, *282*, 357–362. (c) Hoff, C. D.; Nolan, S. P. *J. Organomet. Chem.* **1985**, *290*, 365–373. (d) Nolan, S. P.; Lopez de la Vega, R.; Mukerjee, S. L.; Hoff, C. D. *Inorg. Chem.* **1986**, *25*, 1160–1165. (e) Mukerjee, S. L.; Nolan, S. P.; Lopez de la Vega, R.; Hoff, C. D. *Inorg. Chem.* **1988**, *27*, 81–85.

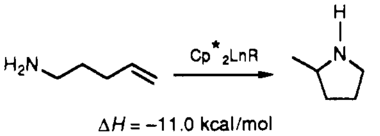
0276-7333/92/2311-3947$03.00/0

enthalpies suffice to predict the feasibility of reactions revolving around a metal center having a constant ancillary ligation (eq 1).

$$L_nM\text{-}X + Y \rightarrow L_nM\text{-}Y + X \qquad (1)$$

$$L_n = \text{ancillary ligation}$$

Recent developments in the area of organometallic thermochemistry have led to prediction of the thermodynamic feasibility of lanthanide-mediated cyclization of N-unprotected aminoolefins[11] (eq 2) as well as to the design



(2)

and implementation of high-yield synthetic pathways for molybdenum complexes[12] (eq 3).

$$(p\text{-xylene})Mo(CO)_3 + C_5H_6 \xrightarrow{THF} HMo(C_5H_5)(CO)_3 + p\text{-xylene} \qquad (3)$$

$$\Delta H = -11.1 \pm 0.5\ \text{kcal/mol}$$

Although the number of organometallic systems subjected to solution calorimetric studies has increased in the recent past,[1a] the thermochemistry of a a large number of organometallic systems remains unexplored. Ligand substitution reactions represent a specific case where thermodynamic data would prove greatly informative, since the ease of such ligand substitutions is at the heart of catalytic transformations[13] where an active catalyst, due to low energy barriers with regard to ligand exchange and interconversion, may be subject to important thermodynamic constraints.

One ruthenium system of particular interest to us centers on the chemistry of the $Cp'Ru^+$ ($Cp' = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5Me_5$) fragment, which has has been shown to effectively bind arenes.[14,15] One of us has recently reported on the synthesis and utilization of $Cp^*Ru(CH_3CN)_3{}^+OTf^-$ ($OTf^- = O_3SCF_3{}^-$; $Cp^* = \eta^5\text{-}C_5Me_5$) as a versatile organometallic building block and precursor leading to the isolation of $Cp^*Ru(arene)^+OTf^-$ complexes,[15] as illustrated in eq 4. We report in the present contribution a solution calorimetric study probing the relative thermodynamic stability of ruthenium–arene complexes.

$$Cp^*Ru(CH_3CN)_3OTf + \text{arene} \rightarrow Cp^*Ru(\text{arene})OTf + 3CH_3CN \qquad (4)$$

Experimental Section

General Considerations. All manipulations were carried out under an inert atmosphere of nitrogen or argon using standard Schlenk tube techniques or in a Vacuum Atmospheres glovebox with less than 1 ppm oxygen and water. Tetrahydrofuran (THF) was purified by distillation from calcium hydride and subsequent drying over Na/K alloy prior to use. Other reagents and arenes were obtained from commercial sources and purified by standard procedures.[16] Only high-purity materials were used in calorimetric experiments. Calorimetric measurements were performed as described below using a Calvet C-80 calorimeter. The calorimeter was calibrated using the TRIS reaction[17] and the enthalpy of solution of KCl in water;[18] both methods gave satisfactory results compared to literature values. Prior to every calorimetric experiment, a known amount of the organoruthenium complex and the arene of interest were weighed into a J. Young NMR tube (tube is equipped with a Teflon valve which enables easy handling of air-sensitive complexes) in the glovebox and THF-d_8 was subsequently added. The reaction was monitored by ^{1}H NMR, and each reported reaction was found to be rapid and quantitative, a condition necessary for accurate and meaningful calorimetric results. NMR spectra were recorded on a Gemini 300-MHz or a GE 300-MHz instrument. All resonances are referenced to tetramethylsilane. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Synthesis. Known organoruthenium complexes were prepared using procedures described in the literature.[15] All syntheses were carried out in a glovebox equipped with a constant dinitrogen flush. Solvents were dried and distilled under dinitrogen before use by employing the following drying agents: tetrahydrofuran (THF) (Na dispersion); CH_3CN (P_2O_5); CD_3NO_2 (vacuum transferred from P_2O_5) Note: THF should not be distilled from Na/benzophenone ketyl. This leads to contamination of this solvent by trace amounts of benzene, which reacts with $Cp^*Ru(CH_3CN)_3{}^+OTf^-$, forming the cation $Cp^*Ru(\eta\text{-}C_6H_6)^+$; this can contaminate the final product. The reagent $Cp^*Ru(CH_3CN)_3{}^+OTf^-$ ($OTf = O_3SCF_3$) was synthesized as described previously.[15] For ^{13}C NMR data, observed two-bond ^{13}C–H coupling constants ($J \leq 10$ Hz) are not reported. The $PF_6{}^-$ salts of the (naphthalene)- and (biphenyl)ruthenium complexes have been reported previously.[19,20]

$Cp^*Ru(\eta^6$-naphthalene)$^+OTf^-$. A 50-mL round-bottomed flask was charged with 1.00 g (7.80 mmol) of naphthalene and 10 mL of benzene-free THF. To this was added 0.200 g (0.393 mmol) of $Cp^*Ru(CH_3CN)_3{}^+OTf^-$. After the mixture was stirred for 1 h, 10 mL of hexane was added to the flask and the solid in the flask was collected by filtration, washed several times with a total of ca. 100 mL of hexane, and dried in vacuo: yield 0.200 g (97%). ^{1}H NMR (300 MHz, CD_3NO_2, 25 °C): δ 1.68 (s, 15 H, Cp*), 6.05 (m, 2 H, naphthalene), 6.54 (m, 2 H, naphthalene), 7.59 (m, 2 H, naphthalene), 7.74 (m, 2 H, naphthalene). ^{13}C NMR (75.5 MHz, CD_3NO_2, 25 °C): δ 9.8 (q, J_{CH} = 129 Hz, Cp*), 86.7 (d, J_{CH} = 179 Hz, $\eta^6\text{-}C_6H_4$), 89.7 (d, J_{CH} = 178 Hz, $\eta^6\text{-}C_6H_4$), 95.4 (s, Cp*), 98.5 (s, $\eta^6\text{-}C_6H_4$), 128.9 (d, J_{CH} = 169 Hz, C_4H_4), 132.4 (d, J_{CH} = 165 Hz, C_4H_4). Anal. Calcd for $C_{21}H_{23}F_3O_3SRu$: C, 49.12; H, 4.51. Found: C, 48.59; H, 4.26.

$Cp^*Ru(\eta^6$-biphenyl)$^+OTf^-$. A procedure similar to that for the synthesis of $Cp^*Ru(\eta^6\text{-naphthalene})^+OTf^-$ was performed using 1.500 g (9.73 mmol) of biphenyl, 10 mL of benzene-free THF, and 0.200 g (0.393 mmol) of $Cp^*Ru(CH_3CN)_3{}^+OTf^-$. A large excess of biphenyl was required in order to prevent formation of $[(Cp^*Ru)_2(\eta^6{:}\eta^6\text{-biphenyl})]^{2+}(O_3SCF_3{}^-)_2$: yield 0.210 g (99%). ^{1}H NMR (300 MHz, CD_3NO_2, 25 °C): δ 1.86 (s, 15 H, Cp*), 5.96 (m, 1 H, Ru–η^6-phenyl), 6.04 (m, 2 H, Ru–η^6-phenyl), 6.40 (m, 2 H, Ru–η^6-phenyl), 7.5–7.6 (multiplets, 3 H, phenyl), 7.75 (multiplet, 2 H, phenyl). ^{13}C NMR (75.5 MHz, CD_3NO_2, 25 °C): δ 10.5 (q, Cp*, J_{CH} = 129 Hz), 86.2 (d, η^6-phenyl, J_{CH} = 172 Hz), 88.8 (d, η^6-phenyl, J_{CH} = 172 Hz), 88.8 (d, shoulder, η^6-phenyl, J_{CH} ca. 172 Hz), 98.2 (s, Cp*), 102.8 (s, η^6-phenyl), 128.5 (d, phenyl, J_{CH} = 159 Hz), 130.8 (d, phenyl, J_{CH} = 163 Hz), 131.4 (d, phenyl, J_{CH} = 163 Hz), 134.2 (s, phenyl). Anal. Calcd for $C_{23}H_{25}F_3O_3SRu$: C, 51.20; H, 4.67. Found: C, 50.94; H, 4.52.

$Cp^*Ru(\eta^6$-anisole)$^+OTf^-$. A 50-mL round-bottomed flask was charged with 0.200 g (1.85 mmol) of anisole and 10 mL of benzene-free THF. To this was added 0.200 g (0.393 mmol) of $Cp^*Ru(CH_3CN)_3{}^+OTf^-$. After the mixture was stirred for 1 h, 10 mL of hexane was added to the flask and the solid was collected

---

(11) (a) Gagné, M. R.; Nolan, S. P.; Seyam, A. M.; Stern, D.; Marks, T. J. *Metal-Metal Bonds and Clusters in Chemistry and Catalysis*; Fackler, J. P., Jr., Ed.; Plenum Press: New York, 1990; pp 113–125. (b) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108–4109. (c) Gagné, M. R.; Nolan, S. P.; Marks, T. J. *Organometallics* **1990**, *9*, 1716–1718.

(12) Nolan, S. P.; Hoff, C. D. *Organomet. Synth.* **1990**, *4*, 58–65.

(13) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; Univeristy Science: Mill Valley, CA, 1987.

(14) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485–488.

(15) (a) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981–2983. (b) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698–1719 and references therein.

(16) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, NY, 1988.

(17) Ojelund, G.; Wadsö, I. *Acta Chem. Scand.* **1968**, *22*, 2691–2699.

(18) Kilday, M. V. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1980**, *85*, 467–481.

(19) Chavez, I.; Cisternas, A.; Otero, M.; Roman, E.; Mueller, U. *Z. Naturforsch., B* **1990**, *45*, 658–666.

(20) McNair, A. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 2519–2527.

by filtration, washed twice with 5 mL of hexane, and dried in vacuo: yield 0.188 g (97%). ^{1}H NMR (300 MHz, CD_3NO_2, 25 °C): δ 2.01 (s, 15 H, Cp*), 3.83 (s, 3 H, OCH_3), 5.64 (t, 1 H, phenyl), 5.83 (overlapping multiplets, 4 H, phenyl). ^{13}C NMR (75.5 MHz, CD_3NO_2, 25 °C): δ 10.8 (q, J_{CH} = 129 Hz, Cp*), 57.6 (q, J_{CH} = 146 Hz, OCH_3), 76.9 (d, J_{CH} = 177 Hz, η^6-phenyl), 86.2 (d, J_{CH} = 178 Hz, η^6-phenyl), 87.2 (d, J_{CH} = 178 Hz, η^6-phenyl), 97.6 (s, Cp*), 133.9 (s, OCH_3). Anal. Calcd for $C_{18}H_{23}F_3O_4SRu$: C, 43.18; H, 4.70. Found: C, 43.95; H, 4.57.

Cp*Ru(η^6-indole)$^+$OTf$^-$. A procedure similar to that for the synthesis of Cp*Ru(η^6-anisole)$^+$OTf$^-$ was carried out using 0.100 g (0.853 mmol) of indole and 0.200 g (0.393 mmol) of Cp*Ru(CH_3CN)$_3$$^+OTf^-$: yield 0.198 g (100%). ^{1}H NMR (300 MHz, CD_3NO_2, 25 °C): δ 1.70 (s, 15 H, Cp*), 5.58 (d of t, 2 H, η^6-C_6H_4), 6.36 (multiplet overlap d, 2 H, η^6-C_6H_4 and NCH=C*H*), 6.49 (d, 1 H, NC*H*=CH, J_{HH} = 6 Hz), 7.80 (multiplet, 1 H, η^6-C_6H_4), 9.55 (broad s, 1 H, NH). ^{13}C NMR (75.5 MHz, CD_3NO_2, 25 °C): δ 9.7 (q, J_{CH} = 128 Hz, Cp*), 74.7 (d, J_{CH} = 171 Hz, η^6-C_6H_4), 80.9 (d, J_{CH} = 174 Hz, η^6-C_6H_4), 85.0 (d, J_{CH} = 174 Hz, η^6-C_6H_4), 85.1 (d, J_{CH} = 174 Hz, η^6-C_6H_4), 93.8 (s, Cp*), 98.0 (s, η^6-C_6H_4), 101.5 (d, J_{CH} = 184 Hz, NCH=*C*H), 110.1 (s, η^6-C_6H_4), 134.4 (d, J_{CH} = 187 Hz, N*C*H=CH). Anal. Calcd for $C_{19}H_{21}F_3NO_3SRu$: C, 45.51; H, 4.22; N, 2.79. Found: C, 45.15; H, 4.19; N, 2.72.

Cp*Ru(η^6-*N,N*-dimethylaniline)$^+$OTf$^-$. A procedure similar to that for the synthesis of Cp*Ru(η^6-anisole)$^+$OTf$^-$ was carried out using 1.00 g (0.825 mmol) of *N,N*-dimethylaniline and 0.200 g (0.393 mmol) of Cp*Ru(CH_3CN)$_3$$^+OTf^-$: yield 0.200 g (100%). ^{1}H NMR (300 MHz, CD_3NO_2, 25 °C): δ 2.00 (s, 15 H, Cp*), 3.01 (s, 12 H, $N(CH_3)_2$), 5.48 (multiplet, 3 H, η^6-C_6H_5), 5.64 (multiplet, 2 H, η^6-C_6H_5). ^{13}C NMR (75.5 MHz, CD_3NO_2, 25 °C): δ 11.3 (q, J_{CH} = 128 Hz, Cp*); 40.1 (q, J_{CH} = 138 Hz, NCH_3), 70.7 (d, J_{CH} = 173 Hz, η^6-phenyl), 83.6 (d, J_{CH} = 177 Hz, η^6-phenyl), 86.7 (d, J_{CH} = 177 Hz, η^6-phenyl), 96.1 (s, Cp*), 127.9 (s, $(CH_3)_2N$*C*). Anal. Calcd for $C_{19}H_{26}F_3NO_3SRu$: C, 45.05; H, 5.17; N, 2.77. Found: C, 45.18; H, 5.14; N, 2.76.

Cp*Ru[η^6-*p*-bis(dimethylamino)benzene]$^+$OTf$^-$. A procedure similar to that for the synthesis of Cp*Ru(η^6-anisole)$^+$OTf$^-$ was carried out using 0.100 g (0.609 mmol) of *p*-bis(dimethylamino)benzene and 0.200 g (0.393 mmol) of Cp*Ru(CH_3CN)$_3$$^+OTf^-$: yield 0.218 g (100%). ^{1}H NMR (300 MHz, CD_3NO_2, 25 °C): δ 1.98 (s, 15 H, Cp*), 2.94 (s, 12 H, $N(CH_3)_2$), 5.27 (s, 4 H, η^6-C_6H_4). ^{13}C NMR (75.5 MHz, CD_3NO_2, 25 °C): δ 11.8 (q, J_{CH} = 128 Hz, Cp*), 40.3 (q, J_{CH} = 137 Hz, NCH_3), 68.9 (d, J_{CH} = 173 Hz, η^6-C_6H_4), 95.2 (s, Cp*), 123.9 (s, $(CH_3)_2N$*C*). Anal. Calcd for $C_{21}H_{31}F_3N_2O_3SRu$: C, 45.89; H, 5.69; N, 5.10. Found: C, 45.85; H, 5.81; N, 5.38.

Cp*Ru[η^6-(trimethylsilyl)benzene]$^+$OTf$^-$. A procedure similar to that for the synthesis of Cp*Ru(η^6-anisole)$^+$OTf$^-$ was carried out using 0.200 g (1.33 mmol) of (trimethylsilyl)benzene and 0.200 g (0.393 mmol) of Cp*Ru(CH_3CN)$_3$$^+OTf^-$. The reaction mixture was stirred for 24 h before adding the 10 mL of hexane: yield 0.196 g (93%). ^{1}H NMR (300 MHz, CD_3NO_2, 25 °C): δ 0.36 (s, 9 H, $Si(CH_3)_3$), 2.02 (s, 15 H, Cp*), 5.83 (multiplet, 5 H, η^6-phenyl). ^{13}C NMR (75.5 MHz, CD_3NO_2, 25 °C): δ −1.31 (q, J_{CH} = 120 Hz, $Si(CH_3)_3$, 11.3 (q, J_{CH} = 129 Hz, Cp*), 88.8 (d, J_{CH} = 179 Hz, η^6-phenyl), 88.9 (d, J_{CH} = 176 Hz, η^6-phenyl), 90.7 (d, J_{CH} = 175 Hz, η^6-phenyl), 98.1 (s, Cp*), 98.4 (s, $(CH_3)_3Si$*C*). Anal. Calcd for $C_{20}H_{29}F_3O_3SSiRu$: C, 44.85; H, 5.46. Found: C, 44.39; H, 5.27.

Cp*Ru(η^6-*p*-xylene)$^+$OTf$^-$. A procedure similar to that for the synthesis of Cp*Ru(η^6-anisole)$^+$OTf$^-$ was carried out using 0.100 g (0.942 mmol) of *p*-xylene and 0.200 g (0.393 mmol) of Cp*Ru(CH_3CN)$_3$$^+OTf^-$: yield 0.194 g (100%). ^{1}H NMR (300 MHz, CD_3NO_2, 25 °C): δ 1.95 (s, 15 H, Cp*), 2.20 (s, 6 H, CH_3), 5.68 (s, 4 H, C_6H_4). ^{13}C NMR (75.5 MHz, CD_3NO_2, 25 °C): δ 10.7 (q, Cp*, J_{CH} = 128 Hz), 18.3 (q, J_{CH} = 130 Hz, xylene CH_3), 89.3 (d, J_{CH} = 175 Hz, xylene), 96.8 (s, Cp*), 100.3 (s, xylene CH_3*C*). Anal. Calcd for $C_{19}H_{25}F_3O_3SRu$: C, 46.43; H, 5.13. Found: C, 46.46; H, 4.87.

Calorimetric Measurements for Reaction of Cp*Ru(CH_3CN)$_3$OTf with Indole. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven at 150 °C, and then taken into the glovebox. The cell was assembled in the glovebox, where in a typical experiment, 10–20 mg of 1 was transferred into a 2-mL volumetric flask and accurately weighed on a high-precision balance placed inside the glovebox. The yellow solid was dissolved in 2 mL of a 1% CH_3CN in THF solution and the resulting yellow solution syringed into the inner section of the calorimetric cell. Two milliliters of a stock solution containing 1.0 g of indole in 10 mL of THF, previously prepared in the glovebox, was syringed into the outer cell chamber. The vessel was then closed, taken out of the glovebox, and loaded in the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no organoruthenium complex 1 was added to the inner cell compartment. After the calorimeter had reached thermal equilibrium at 30.0 ± 0.1 °C (ca. 2 h), the reaction was initiated by inverting the calorimeter. At the end of the reaction (1–2 h) the reaction vessel was removed from the calorimeter and taken inside the glovebox. There the cell was opened, the solvent removed in vacuo, the residue taken in THF-d_8, and an ^{1}H NMR spectrum recorded that showed conversion to Cp*Ru(η^6-indole)OTf to be quantitative. The enthalpy of reaction, −7.3 ± 0.2 kcal/mol, is the average of five separate determinations. This represents the general protocol established for all calorimetric determinations reported in the present study.

Table I. Summary of Crystallographic Data for Cp*Ru(C_6H_5TMS)OTf

empirical formula	$C_{20}H_{29}O_3F_3SiSRu$
space group	$P2_1/n$
unit cell dimens	
a, Å	10.811 (2)
b, Å	14.232 (2)
c, Å	14.756 (3)
α, deg	90
β, deg	92.71 (2)
γ, deg	90
V, Å^3	2268 (1)
Z	4
density (calcd), g/cm^3	1.569
wavelength, Å	0.71073
monochromator	highly ordered graphite crystal
temp, K	97 (2)
abs cor	empirical (4-scan method)
diffractometer	Enraf-Nonius CAD 4
scan type	θ-2θ
data collected	$-12 \le h \le 11, 0 \le k \le 16, 0 \le l \le 20$
2θ range, deg	4.0–50.0
no. of collected rflns	7593
no. of unique rflns	6605
no. of observed rflns	3642
R_I, %	2.2
R_F(obsd data), %	3.3
R_{wF}, %	3.6
goodness of fit	1.27
no. of variables	378

Crystallographic Study of Cp*Ru[η^6-$C_6H_5(Si(CH_3)_3)$]OTf. A colorless crystal of approximate dimensions 0.25 × 0.25 × 0.12 mm, grown by slow solvent evaporation from a tetrahydrofuran solution, was mounted on an Enraf-Nonius CAD 4 diffractometer, and data were collected at 97 K. The structure was solved using direct methods and refined by full-matrix least-squares techniques. The crystal data and data collection parameters are summarized in Table I. Selected bond distances and angles are presented in Table II.

Results and Discussion

The ease with which the ruthenium arene compounds are formed in eq 5 shows complex 1 to represent a practical entryway into the thermochemistry of the Cp*Ru$^+$ system.

$$\underset{1}{\text{Cp*Ru}(\text{CH}_3\text{CN})_3\text{OTf}} + \text{arene} \xrightarrow[30\ ^\circ\text{C}]{\text{THF}} \text{Cp*Ru(arene)OTf} + 3\text{CH}_3\text{CN} \quad (5)$$

Reactions suitable for calorimetric determination, as determined by ^{1}H NMR spectroscopy, were carried out in THF solution at 30 °C. The reactions described are rapid and quantitative for a number of arenes, and enthalpies of reaction with all species in solution are reported in Table III. The experimental protocol adopted (see Experimental Section) was selected in view of the relatively large en-

Table II. Selected Bond Distances (Å) and Bond Angles (deg) for $Cp^*Ru[C_6H_5(Si(CH_3)_3)]OTf$

Bond Lengths			
Ru-C(5)	2.256 (3)	Ru-C(6)	2.212 (3)
Ru-C(7)	2.195 (3)	Ru-C(8)	2.205 (3)
Ru-C(9)	2.211 (3)	Ru-C(10)	2.214 (4)
Ru-C(11)	2.193 (4)	Ru-C(12)	2.202 (3)
Ru-C(13)	2.186 (3)	Ru-C(14)	2.162 (3)
Ru-C(15)	2.176 (4)	Si-C(2)	1.848 (5)
Si-C(3)	1.848 (5)	Si-C(4)	1.850 (4)
Si-C(5)	1.881 (4)	Ru-Cp*(centroid)	1.815 (4)
Ru-arene(centroid) 1.705 (4)			
Bond Angles			
C(5)-Ru-C(6)	37.1 (2)	C(5)-Ru-C(7)	67.3 (1)
C(7)-Ru-C(14)	107.1 (1)	C(6)-Ru-C(12)	118.0 (1)
C(9)-Ru-C(15)	105.5 (1)	C(10)-Ru-C(11)	108.5 (1)
C(5)-Ru-C(12)	109.9 (1)	Si-C(5)-Ru	133.8 (1)
C(7)-Ru-C(14)	107.1 (1)	C(6)-Ru-C(12)	118.0 (1)
Ru-C(8)-C(9)	71.7 (2)	Ru-C(8)-C(7)	70.8 (2)
Ru-C(5)-C(6)	69.8 (2)	Ru-C(5)-C(10)	69.9 (2)
Cp*(centroid)-Ru-arene(centroid) 177.1 (2)			

thalpy of solution of 1 (+6.0 ± 0.2 kcal/mol) when compared with the experimentally measured enthalpies of reaction. This method allows for greater experimental accuracy and eliminates the need to independently consider the enthalpy of solution for 1. The addition of 1% acetonitrile, by volume, in the tetrahydrofuran solution was adopted in view of the lability of the first coordinated acetonitrile (see below). The effects of the electron-donating ability of the arenes were investigated by examining various substituted aromatic compounds. The order of stability ranges from the least stable naphthalene complex, with an enthalpy of substitution of only −1.7 ± 0.1 kcal/mol, to the most stable [bis(dimethylamino)benzene]ruthenium complex, with an enthalpy of substitution of −8.3 ± 0.2 kcal/mol.

The primary goal of this work is to begin to shed light on the thermodynamic requirements governing organoruthenium reactions such as reaction 6. The tabulated

$$Cp^*Ru(arene')OTf\ (soln) + arene\ (soln) \xrightarrow[30\ ^\circ C]{THF} Cp^*Ru(arene)OTf\ (soln) + arene'\ (soln) \quad (6)$$

enthalpies of reaction (Table III) allow a relative stability scale to be established where the enthalpy of arene exchange for any two arenes can be calculated simply by subtracting the enthalpy values of the appropriate arenes of interest. Subtraction of eq 8 from eq 7 leads directly

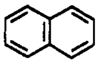
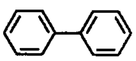
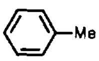
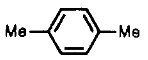
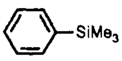
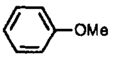
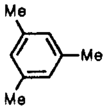
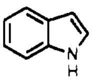
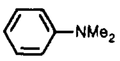
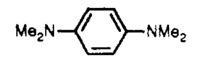
$$Cp^*Ru(CH_3CN)_3OTf\ (soln) + arene\ (soln) \xrightarrow[30\ ^\circ C]{THF} Cp^*Ru(arene)OTf\ (soln) + 3CH_3CN\ (soln) \quad (7)$$

$$Cp^*Ru(CH_3CN)_3OTf\ (soln) + arene'\ (soln) \xrightarrow[30\ ^\circ C]{THF} Cp^*Ru(arene')OTf\ (soln) + 3CH_3CN\ (soln) \quad (8)$$

to a calculated enthalpy of arene exchange in THF solution at 30 °C shown in eq 6.[21] Since the complexes studied are generated in THF solution, isolation and separate determination of the heats of solution of the crystalline compounds are not necessary.[22] This was tested on several isolated complexes, and within experimental error the enthalpies of solution, in tetrahydrofuran, of ruthenium-containing starting material and products cancel out. However, it should be kept in mind that because of the ionic nature of the complexes studied, transfer of the present set of data to other solvents or to the gas phase would yield sizable errors. In the present system, relative bond energy terms discussed refer only to solution values. The possibility of ion pair formation contributing to the enthalpy of reaction was also considered, and within 0.1 kcal/mol the enthalpy cf solution of the tris(acetonitrile) ruthenium and (arene)ruthenium complexes are similar within experimental error.

Table III. Enthalpies of Arene Substitution (kcal/mol) in the Reaction

$$Cp^*Ru(CH_3CN)_3OTf\ (soln) + arene\ (soln) \xrightarrow[30\ ^\circ C]{THF} Cp^*Ru(arene)OTf\ (soln) + 3CH_3CN\ (soln)$$

arene		$-\Delta H_{reacn}$
naphthalene		1.7 ± 0.1
benzene		3.4 ± 0.1
biphenyl		3.6 ± 0.1
toluene		4.3 ± 0.2
p-xylene		4.6 ± 0.2
(trimethylsilyl)benzene		5.0 ± 0.2
anisole		5.4 ± 0.2
mesitylene		5.5 ± 0.1
indole		7.3 ± 0.2
dimethylaniline		7.5 ± 0.1
p-bis(dimethylamino)benzene		8.3 ± 0.2

Attention must be taken in establishing a correct calorimetric measurement protocol in view of the lability of the first coordinated acetonitrile molecule[23] (eq 9). In

$$\underset{\mathbf{1}}{Cp^*Ru(CH_3CN)_3OTf} + THF \rightleftharpoons \underset{\mathbf{2}}{Cp^*Ru(CH_3CN)_2(THF)OTf} + CH_3CN \quad (9)$$

order to eliminate the substitution of THF for CH_3CN, acetonitrile was added (1% by volume) to drive the equilibrium to the left. This protocol has successfully been applied to other organometallic systems.[24] Calorimetric measurements were performed using this protocol for all arenes investigated. In order to estimate the difference between the first Ru-$NCCH_3$ and Ru-THF bonds, calorimetry was also performed in neat tetrahydrofuran solutions. A difference of 1.3 kcal/mol in the measured enthalpy of reaction was measured for two diffrent arenes (benzene and toluene). This increase in the measured enthalpy of reaction illustrates the difference between performing calorimetric measurements from 1 or 2.

The least stable of all arene complexes investigated is the Cp*Ru(naphthalene) complex (ΔH_{reacn} = −1.7 ± 0.1

---

(21) Although eq 9 allows for calculated enthalpies of arene exchange, direct exchange reactions appear to be extremely slow.

(22) Hoff, C. D. *J. Organomet. Chem.* **1985**, *282*, 201–214.

(23) Fagan, P. J. Unpublished results.

(24) Mukerjee, S. L.; Lang, R.; Ju, T.; Kiss, G.; Hoff, C. D.; Nolan, S. P. *Inorg. Chem.*, in press.

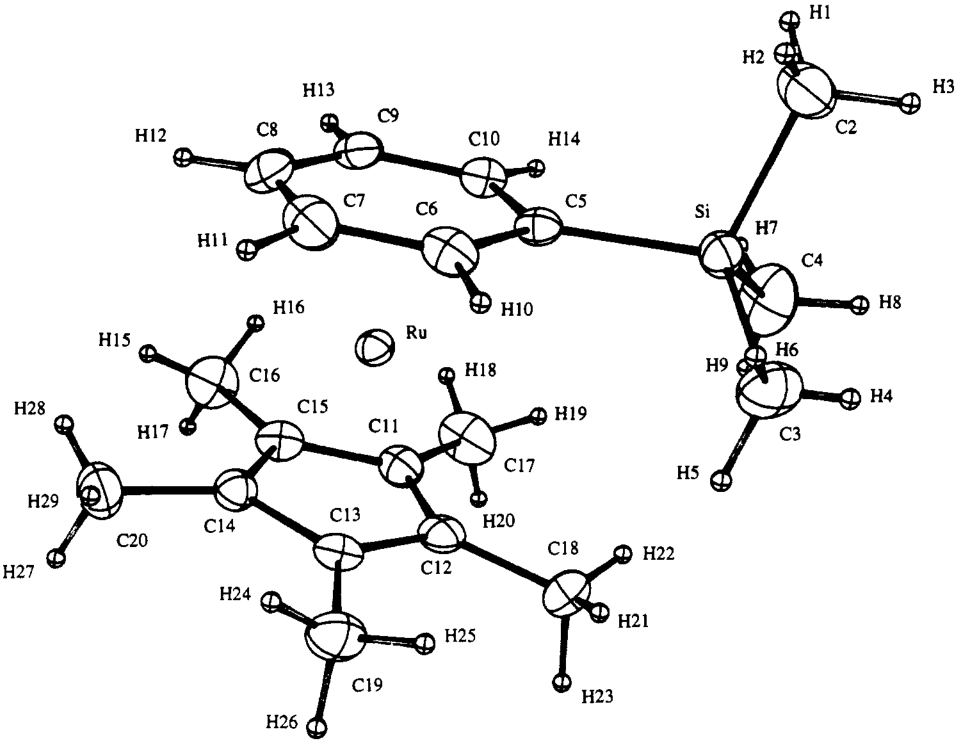
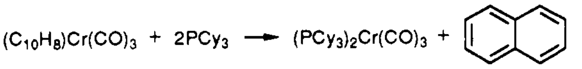


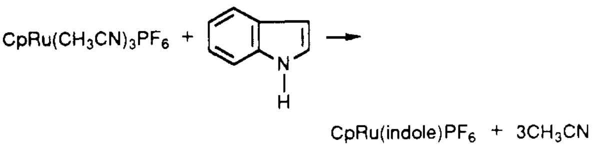
Figure 1. Molecular structure of $Cp^*Ru[C_6H_5(Si(CH_3)_3)]OTf$ with probability ellipsoids drawn at the 50% level.

kcal/mol). The relative weakness of the metal–naphthalene bond has recently been measured in the (arene)$Cr(CO)_3$ system.[25] The chromium–naphthalene bond disruption enthalpy (BDE) was found to be 6.3 kcal/mol less stable than for the benzene complex and 17 kcal/mol less stable than for the tris(acetonitrile) complex. This compares to a ruthenium–naphthalene BDE 1.3 kcal/mol less stable than the benzene complex and 1.7 kcal/mol more stable than the tris(acetonitrile) adduct. The relatively weak chromium–naphthalene BDE present in the (arene)$Cr(CO)_3$ system[25] suggested to Hoff and co-workers a synthesis of the chromium analogue to the molybdenum and tungsten complexes investigated by Kubas[26] (eq 10).



(10)

The use of metal-indole complexes in a variety of systems[27] prompted our thermochemical investigation of this ligand. Recent work has centered on the use of the ruthenium compound $CpRu(CH_3CN)_3PF_6$ ($Cp = C_5H_5$) as a precursor for ruthenium indole and other complexes[28,29] (eq 11). Coordination of the indole ligand to the ruthenium(II) center markedly influences its reactivity toward nucleophilic attack and direct substitution reactions.[30] The thermodynamic preference for the indole ligand exhibited by ruthenium(II) (−7.3 kcal/mol) is presumably applicable to the related $CpRu(CH_3CN)_3PF_6$ system. Our solution thermochemical investigation offers a first glimpse at the magnitude of the enthalpic driving force behind eq 11. Investigation of the steric and electronic factors influencing the ruthenium–indole bond energy term is presently underway.[31]



(11)

The trend observed for $Cp^*Ru(CH_3CN)_3OTf$ shows that an increase in the electron-donating ability of the arene is accompanied by an increase in magnitude in measured enthalpy of substitution. One notable exception to this trend is phenyltrimethylsilane. To clarify the steric requirements present in this complex, a low-temperature data collection X-ray diffraction structural determination was performed and the resulting ORTEP drawing is presented in Figure 1. A summary of crystallographic data for $Cp^*Ru(C_6H_5TMS)OTf$ (**3**) is shown in Table I. Selected bond lengths and bond angles are given in Table II. All hydrogen atoms were located by a difference Fourier map. The structure consists of a Cp* ligand and a phenyltrimethylsilane ligand bound to ruthenium in a η^5 and η^6 fashion, respectively. The average C–C(ring) and the C–Me distances of the η^5-C_5Me_5 ligand are 1.427 (4) and 1.499 (4) Å, respectively. The average C–C(ring) distance of the PhTMS ring is 1.415 (5) Å. The planes of the two ring ligands are almost parallel with a 3.52-Å interplanar separation. The Ru–centroid distance for the η^6-C_6H_5TMS ligand is 1.70 (1) Å, and the Ru–Cp*(centroid) distance is 1.82 (1) Å. The angle formed by the ring centroids and the ruthenium atom is 177.1 (2)°. The structure of **3** shows important differences when compared to the reported one of $Cp^*Ru(C_6Me_6)^+$.[15] The smaller arene(centroid)–Ru–Cp*(centroid) angle in **3**, compared to 178.8 (9)° for the

---

[25] (a) Gonzalez, A. A.; Mukerjee, S. L.; Chou, S.-J.; Kai, Z.; Hoff, C. D. *J. Am. Chem. Soc.* **1988**, *110*, 4419–4421. (b) Kubas, G. J.; Kiss, G.; Hoff, C. D. *Organometallics* **1991**, *10*, 2870–2876.

[26] Zhang, K.; Gonzalez, A. A.; Mukerjee, S. L.; Chou, S.-J.; Hoff, C. D.; Kubat-Martin, K. A.; Barnhart, D.; Kubas, G. J. *J. Am. Chem. Soc.* **1991**, *113*, 9170–9176 and references therein.

[27] Pannell, K. H.; Kolsotra, B. L.; Parkanyi, C. *J. Heterocycl. Chem.* **1978**, *15*, 1057–1081.

[28] Gill. U. S.; Moriarty, R. M.; Ku, Y. Y.; Butler, I. R. *J. Organomet. Chem.* **1991**, *417*, 313–325.

[29] The use of a metal tris(acetonitrile) precursor has also been employed in the rhodium-mediated hydrogenation of heteroaromatic compounds: Fish, R. H.; Baralt, E.; Smith, S. J. *Organometallics* **1991**, *10*, 54–56 and references therein.

[30] Moriarty, R. M.; Ku, Y. Y.; Guo, L. *J. Chem. Soc., Chem. Commun.* **1988**, 1621–1622.

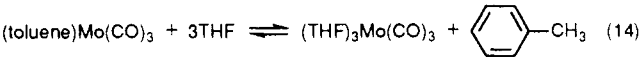
[31] Trudell, M. L.; Nolan, S. P. Work in progress.

hexamethylbenzene complex, shows the presence of steric repulsion between the TMS group and the C(18)-centered methyl group of the two ring systems in **3**. A more persuasive argument for steric interaction between the two rings is illustrated by distortions present in the Cp ligand. The Cp(centroid)–C(12)–C(18) angle of 174.2 (3)° compared to the Cp(centroid)–C(14)–C(20) angle of 177.1 (3)° emphasizes the steric repulsion present between the phenyl TMS group and the Cp*Me substituent occupying the same side of the molecule. This steric interaction explains the lower experimental enthalpy of substitution and emphasizes the importance of both steric and electronic factors in the present system.

A study performed by Connor and co-workers on the carbonyl-insertion reaction illustrated in eq 12 has focused on estimating the loss of rotational and translational entropy of CO gas in this reaction ($\Delta S = -36$ eu, which translates to $-T\Delta S = +10\text{–}14$ kcal/mol in the temperature range 25–100 °C).[32,33] This entropic barrier must be overcome in order to obtain net thermodynamic stability. Entropic contribution has also been extracted from temperature variation of the equilibrium constant in the system illustrated in eq 13. This more sterically congested system shows a room-temperature entropic contribution of −10.6 ± 0.4 kcal/mol.[34] We take the closely related molybdenum(0) equilibrium, illustrated in eq 14, as a more accurate approximation of the entropic contribution at play in the present ruthenium system. A $\Delta S°$ value of −41.5 eu has been reported for this reaction,[22] which translates into a $-T\Delta S$ thermodynamic contribution at 30 °C of 12.5 kcal/mol. This value is taken as an estimate of the entropic contribution to the overall free energy in the ruthenium system. Considering the range of measured enthalpies of reaction, indications are that the $T\Delta S$ term is an extremely important thermodynamic factor leading to product formation in the present system. This importance of entropic factors explains the successful experimental isolation of arene complexes bearing electron-withdrawing groups, although we were unable to measure noticeable exothermic enthalpies for such processes.[35]

$$H_3CMn(CO)_5 + CO \rightleftharpoons H_3CC(O)Mn(CO)_3 \qquad (12)$$

$$[CpCr(CO)_3]_2 \rightleftharpoons 2CpCr(CO)_3^{\bullet} \qquad (13)$$



$$(\text{toluene})Mo(CO)_3 + 3THF \rightleftharpoons (THF)_3Mo(CO)_3 + C_6H_5CH_3 \qquad (14)$$

Comparison to Other Organometallic Systems. With the exception of the investigations of Bercaw and co-workers[36] on the equilibrium constant variation for a series of ligands (eq 15) and the kinetic study of Collman and co-workers[37] on the ruthenium–ethyl bond-cleavage process illustrated in eq 16, very few solution thermochemical and, to our knowledge, no solution calorimetric investigations have been carried out on organoruthenium systems.[38,39] Parallels can be drawn between our Ru(II) compounds and the isoelectronic iridium(III) and rhodium(III) Cp*M(arene)(PF$_6$)$_2$ complexes studied by Maitlis and co-workers.[40] In these investigations, competition reactions were used to establish a relative M–arene stability scale: naphthalene < benzene < alkylbenzene < indole. This trend is similar to the one observed in the present ruthenium(II) system.

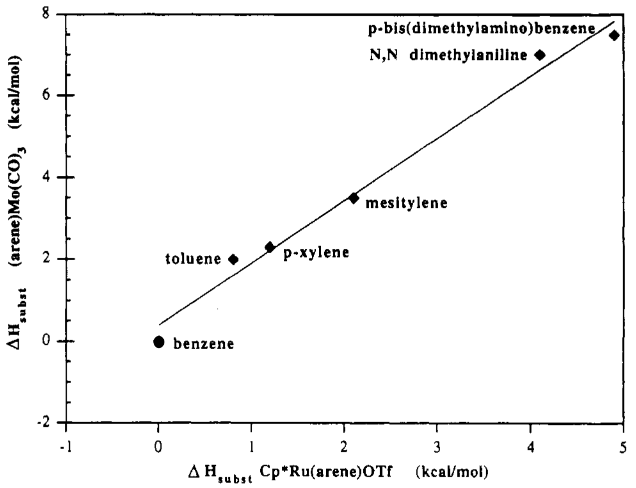


Figure 2. Relative enthalpies of arene substitution in the (arene)Mo(CO)$_3$ vs Cp*Ru(arene)OTf systems. Enthalpies are related to their respective enthalpy of reaction with the benzene value (set to 0 kcal/mol) ($R = 0.993$, slope 1.52).

$$Cp^*Ru(PMe_3)_2OH\ (soln) + HL\ (soln) \rightarrow Cp^*Ru(PMe_3)_2L\ (soln) + H_2O\ (soln) \qquad (15)$$

$$(OEP)RuEt_2\ (soln) \rightarrow (OEP)RuEt\ (soln) + Et\ (soln) \qquad (16)$$

$$Cp^*Ir(CH_3CN)_3(PF_6)_2 + \text{arene} \rightarrow Cp^*Ir(\text{arene})(PF_6)_2 + 3CH_3CN \qquad (17)$$

The experimental trend observed in the present study correlates the electron-donating ability of the arene with a proportional increase in the magnitude of the enthalpy of substitution, reflecting the greater thermodynamic stability of complexes containing electron-donating arenes. The same has been observed by Hoff and co-workers in their solution calorimetric investigation of the (arene)Mo(CO)$_3$ system, where the enthalpies of substitution for a series of these arene complexes by pyridine were measured:[10a,41]

$$(\text{arene})Mo(CO)_3 + 3py \rightarrow (py)_3Mo(CO)_3 + \text{arene} \qquad (18)$$

---

(32) Connor, J.; Zafarani-Moattar, M. T.; Bickerton, J. B.; El Saied, N. I.; Suradi, S.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166–1174.

(33) A number of of additional studies of equilibria similar to eq 13 have been reported: (a) Fachinetti, G.; Fochi, G.; Floriani, C. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1946–1950. (b) Moloy, K. J.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051–7064. (c) Lee, C.; James, B. R.; Nelson, D. R.; Haller, R. T. *Organometallics* **1984**, *3*, 1360–1364.

(34) McLain, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 643–644.

(35) Nolan, S. P.; Fagan, P. J. *Unpublished* results.

(36) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444–1456.

(37) Collman, J. P.; McElwee-White, L.; Brothers, P. J.; Rose, E. *J. Am. Chem. Soc.* **1986**, *108*, 1332–1333.

(38) Calorimetric studies of coordination complexes have been reported for complexes of type $[(NH_3)_5RuOH_2]^{2+}$; see for example:[38] (a) Wishart, J. F.; Taube, H.; Breslauer, K. L.; Isied, S. S. *Inorg. Chem.* **1986**, *25*, 1479–1481. (b) Wishart, J. F.; Taube, H.; Breslauer, K. L.; Isied, S. S. *Inorg. Chem.* **1984**, *23*, 2997–3001.

(39) Related cobalt coordination complexes have been examined via solution calorimetry: Uzice, J. L.; Lopez de la Vega, R. *Inorg. Chem.* **1990**, *29*, 382–384.

(40) (a) White, C.; Maitlis, P. M. *J. Chem. Soc. A* **1971**, 3322–3326. (b) Thompson, S. J.; Bailey, P. M.; White, C.; Maitlis, P. M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 490–491. (c) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1976**, 409–410. (d) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654–1661.

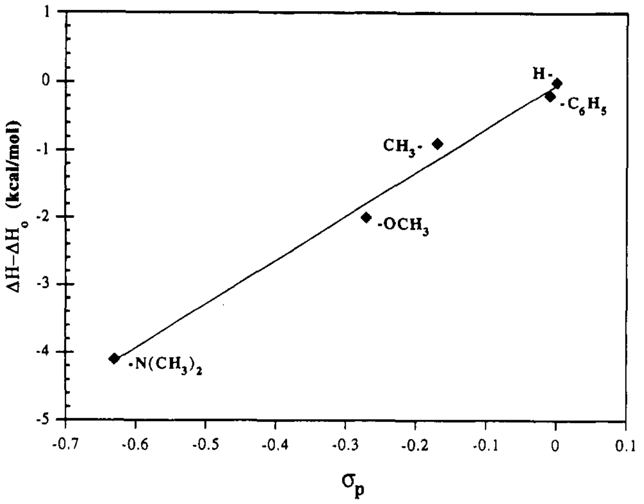
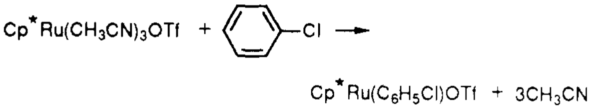


Figure 3. Correlation between enthalpies of reaction compared to that of benzene (set to 0 kcal/mol) and arene substituent Hammett σ_p parameter (R = 0.995, slope 6.49).

A comparison between the molybdenum–arene BDE to the present ruthenium results proves interesting. Figure 2 illustrates such a comparison of the relative enthalpies of reaction (normalized to the appropriate M–benzene value) between the two systems. As can be seen, an excellent fit exists between the molybdenum and ruthenium systems (R = 0.993) for six arene complexes. Moreover, from the slope of this plot, the metal–arene bond energy in the molybdenum system appears more sensitive than the Ru–arene bond energy to electronic variations on the arenes. A qualitative look also emphasizes the presence of a proportionality between electron donation and enthalpy of substitution. The value for the phenyltrimethylsilane has been omitted in Figure 2. On the basis of simple electronic considerations, the expected enthalpy of substitution from the benzene complex leading to the formation of the ruthenium–PhTMS complex can be estimated as −3.2 kcal/mol. The measured enthalpy difference is actually 1.6 kcal/mol more stable than the Ru–benzene BDE. The difference is attributed to steric effects present in the PhTMS complex (vide infra).

Linear Free Energy Relationship. Linear free energy relationships (LFER) have been shown to correlate substituent constants of arenes with a variety of physical properties.[42] The present ruthenium(II) system offers an excellent opportunity to investigate whether such a LFER exists between the enthalpy of ligand substitution and the Hammett σ_p arene substituent parameter.[43] This relationship is illustrated in Figure 3, and the data show an excellent fit (R = 0.995) for five monosubstituted arenes investigated. The thermochemistry of anisole was used to test the relationship, for it was investigated after the relationship had been established. A predicted enthalpy of reaction of −5.1 kcal/mol was estimated from the σ value of the free arene, and an enthalpy of substitution of −5.3 kcal/mol was measured. Here again the Ru–PhTMS bond enthalpy value is not included in view of the steric hindrance present in this complex. To our knowledge this relationship has not been explored for organometallic systems without doubt because of the paucity of such thermochemical data. An important use of the established LFER is the ability to estimate enthalpy data not accessible via direct calorimetric measurements (e.g. arenes bearing an electron-withdrawing group). For example, the enthalpy of substitution illustrated in eq 19 can be estimated. On the basis of our observations concerning the Ru–PhTMS complex, meaningful and accurate enthalpy of reaction estimates from such a linear free energy relationship appear to greatly depend on steric factors present in the ruthenium–arene complexes.



(19)

$\Delta H_{calcd} = -1.5$ kcal/mol

Conclusion

Solution calorimetric results show a variation of 6.6 kcal/mol in the Ru(II)–arene BDE. The entropic contribution appears to be an important factor in dictating the thermodynamic feasibility of a given arene reaction. A comparison of the present ruthenium system to available thermodynamic data on the (arene)Mo(CO)$_3$ system shows important similarities, although the ruthenium system appears less sensitive to the electronic requirements of the arene ligand. A linear free energy relationship is established which allows estimation of Ru–arene BDE values not readily available from solution calorimetric studies. These data allow estimation of enthalpies of reaction of a ruthenium-mediated reaction. Further thermochemical investigations based on these and related compounds are in progress.

Acknowledgment. S.P.N. acknowledges support of this work through a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society. The Louisiana Board of Regents is also acknowledged for allocating funds for the purchase of NMR equipment under Grant LEQSF-ENH-53 (1990–1991).

Supplementary Material Available: Tables of positional parameters, selected distances and angles, and anisotropic thermal parameters for Cp*Ru(C$_6$H$_5$TMS)OTf (12 pages). Ordering information is given on any current masthead page.

OM9203946

---

(41) Although substantial work has been carried out on the (arene)Cr(CO)$_3$ system,[41a–c] we have only considered in this discussion the results of another second-row transition metal, although the comparison appears to qualitatively hold for the chromium system as well: (a) Connor, J. A.; Martinho-Simoes, J. A.; Skinner, H. A.; Zafari-Moattar, M. T. *J. Organomet. Chem.* **1979**, *179*, 331–356. (b) Brown, D. L. S.; Connor, J. A.; Demain, C. P.; Leung, M. L.; Martinho-Simoes, J. A.; Skinner, H. A.; Zafari-Moattar, M. T. *J. Organomet. Chem.* **1977**, *142*, 321–335. (c) Adedeji, F. A.; Brown, D. L. S.; Connor, J. A.; Leung, M. L.; Paz-Andrade, I. M.; Skinner, H. A. *J. Organomet. Chem.* **1975**, *97*, 221–228.

(42) Wells, P. R. *Linear Free Energy Relationships*; Academic Press: New York, 1968. (b) Charton, M. *Prog. Phys. Org. Chem.* **1973**, *10*, 81–204.

(43) A relationship linking the enthalpy of formation of (arene)Cr(CO)$_3$ complexes to the enthalpy of formation of the ligand has previously been published with R = 0.98 for 10 complexes: Al-Talkin, G.; Connor, J. A.; Skinner, H. A.; Zafari-Moattar, M. T. *J. Organomet. Chem.* **1984**, *260*, 189–197.