Short Communication

Stable zwitterions of indenyl and fluorenyl Cp*Ru(η^6-arene) complexes

Dale E. Wheeler** and Thomas E. Bitterwolf

Department of Chemistry, University of Wisconsin-Parkside, Kenosha, WI 53141 (USA) and University of Idaho, Moscow, ID 83843 (USA)

(Received July 27, 1992; revised October 22, 1992)

Abstract

The novel complexes $[Cp^*Ru(\eta^6\text{-}C_9H_8)]^+O_3SCF_3^-$ and $[Cp^*Ru(\eta^6\text{-}C_{13}H_{10})]^+O_3SCF_3^-$ (where $Cp^* = C_5(CH_3)_5$; C_9H_8 = indene; $C_{13}H_{10}$ = fluorene) are formed from the reaction of $[Cp^*Ru(NCCH_3)_3]^+O_3SCF_3^-$ with indene and fluorene, respectively. These complexes react with NaH forming the stable zwitterionic complexes $Na[Cp^*Ru(\eta^6\text{-}C_9H_7)O_3SCF_3]$ and $Na[Cp^*Ru(\eta^6\text{-}C_{13}H_9)O_3SCF_3]$. Since no evidence for η^6-to-η^5 haptotropic rearrangement is observed at ambient temperatures, we believe that the barrier to metal migration must be high resulting in the stability of these zwitterionic complexes. ^1H and ^{13}C NMR data for these complexes are reported.

Introduction

Osiecki and Hoffman [1] reported $(\eta^5\text{-}C_9H_7)_2Ru$ as the first indenyl ruthenium compound in 1965. Several η^5-indenyl [2] ruthenium compounds have since been reported including $[Cp^*Ru(\mu\text{-}\eta^5\text{:}\eta^6\text{-}C_9H_7)RuCp^*]PF_6$ [3] ($Cp^* = C_5(CH_3)_5$) and the unusual $Ru_4(CO)_7(\mu\text{-}CO)_2(\eta^2\text{:}\eta^5\text{:}\eta^2\text{-}C_9H_7)(\eta^5\text{-}C_9H_9)$ [4]. The only previously reported η^6-indene ruthenium compound is $[(\eta^5\text{-}Cp)Ru(\eta^6\text{-}C_9H_8)]PF_6$ [5]. Gassman and Winter [6] reported $Cp^*Ru(\eta^5\text{-}C_{13}H_9)$ as the first ruthenium fluorenyl compound in 1988. Rybinskaya and co-workers [7] have since reported $[Cp^*Ru(\eta^6\text{-}C_{13}H_{10})]PF_6$ as the only other isolated fluorene ruthenium compound. Slight differences in the NMR data are attributed to the differences in anions, PF_6 versus O_3SCF_3 and the difference in solvents $CDCl_3$ versus d_8-THF.

Fagen *et al.* [8] recently reported the usefulness of $[Cp^*Ru(NCCH_3)_3]^+O_3SCF_3^-$ (**1**) in the preparation of $Cp^*(\eta^6\text{-arene})Ru(II)$ complexes. We now report the novel complexes $[Cp^*Ru(\eta^6\text{-}C_9H_8)]^+O_3SCF_3^-$ (**2**) and $[Cp^*Ru(\eta^6\text{-}C_{13}H_{10})]^+O_3SCF_3^-$ (**3**) formed from the reactions of **1** with indene and fluorene as analytically pure, fine powders. Several attempts to grow crystallographic quality crystals were unsuccessful.

Experimental

Materials

CH_3OH was dried over Mg/I_2, CH_3CN was dried over CaH_2, and $(CH_3CH_2)_2O$, CH_2Cl_2 and THF were dried over Na/K. $RuCl_3 \cdot xH_2O$ and $C_5(CH_3)_5H$ were purchased from Aldrich Chemical Co. and used without further purification. Indene (C_9H_8) was freshly distilled prior to use and fluorene ($C_{13}H_{10}$) was used without further purification. $[Cp^*RuCl_2]_n$ was synthesized using a modified procedure of Oshima *et al.* [9]. $[Cp^*Ru(\mu^3\text{-}Cl)]_4$ and $[Cp^*Ru(NCCH_3)_3]^+O_3SCF_3^-$ were synthesized using the published procedures of Fagen *et al.* [10].

Instrumentation

^1H and ^{13}C NMR spectra were measured at 300 MHz on a Bruker IBM AF 300 Fourier transform spectrometer. Chemical shifts were referenced to the solvent. The 2D COSY and JRES spectra were also obtained on this instrument. Mass spectra were obtained by fast atom bombardment on a VG Micromass 7070 HS mass spectrometer with an 11/250 data system. IR data was obtained on a Perkin-Elmer 1750 FT-IR instrument as KBr pellets. Elemental analyses were performed by Desert Analytics of Tucson, AZ.

Syntheses

All synthetic procedures were carried out under vacuum or a nitrogen atmosphere with standard Schlenkware using standard Schlenk techniques, unless otherwise noted.

Synthesis of $[Cp^*Ru(\eta^6\text{-}C_9H_8)]^+O_3SCF_3^-$ (2)

To 50 ml CH_2Cl_2, $[Cp^*Ru(NCCH_3)_3]^+O_3SCF_3^-$ (0.50 g, 0.98 mmol), was added followed by addition of 0.20 g, 1.72 mmol freshly distilled indene at ambient temperature. The solution was stirred for 4 h and the solution turned pale yellow. The solution was filtered and the solvent was removed under vacuum leaving a pale yellow solid. The product was purified by reprecipitation from CH_2Cl_2 with diethyl ether twice leaving a light-tan hygroscopic powder.

**Author to whom correspondence should be addressed.

0020-1693/93/$6.00

TABLE 1. IR[a], FAB mass spectrometric and analytical[b] data

Compound	ν (cm^{-1})	Mass data (amu)	Analysis (%)
$[Cp^*Ru(\eta^6\text{-}C_9H_8)]^+O_3SCF_3^-$ (**2**)	3078.4 s, 3063.9 vs., 2920.2 vs., 1383.9 s, 1271.1 vs., 1261.4 vs., 1221.9 s, 1163.1 vs., 1029.0 vs., 745.5 s, 635.5 vs., 516.9 s.	353 amu $Cp^*Ru(C_9H_8)^+$ 233 amu Cp^*Ru^+ 218 amu $Ru(C_9H_8)^+$	C 47.13 (47.90) H 4.57 (4.62) S 5.32 (6.39)
$[Cp^*Ru(\eta^6\text{-}C_{13}H_{10})]^+O_3SCF_3^-$ (**3**)	3064.9 vs, 1473.6 s, 1431.2 s, 1403.2 s, 1384.9 vs, 1278.8 vs, 1253.7 vs, 1153.4 s, 1030.0 vs, 770.6 s, 728.1 s, 639.4 s, 636.5 s, 517.9 vs, 454.2 vs.	402 amu $Cp^*Ru(C_{13}H_{10})^+$ 267 amu $Ru(C_{13}H_{10})^+$ 233 amu Cp^*Ru^+	C 52.02 (52.26) H 4.23 (4.57) S 5.63 (5.81)

[a] IR spectra were obtained as KBr pellets. [b] Calculated values are given in parentheses.

Synthesis of $[Cp^*Ru(\eta^6\text{-}C_{13}H_{10})]^+O_3SCF_3^-$ *(3)*

To 50 ml CH_2Cl_2, $[Cp^*Ru(NCCH_3)_3]^+O_3SCF_3^-$ (0.65 g, 1.28 mmol), was added followed by addition of 0.22 g, 1.32 mmol fluorene at ambient temperature. The solution was stirred for 4 h and the solution turned pale yellow. The solution was filtered and the solvent was removed under vacuum leaving a pale yellow solid. The product was purified by reprecipitation from CH_2Cl_2 with diethyl ether twice leaving an off-white hygroscopic powder.

Synthesis of $Na[Cp^*Ru(\eta^6\text{-}C_9H_7)O_3SCF_3]$ *(4)*

4 was generated *in situ* by adding a small molar excess of NaH to the d_8-THF solution of **2**. No attempt was made to isolate the product.

Synthesis of $Na[Cp^*Ru(\eta^6\text{-}C_{13}H_9)O_3SCF_3]$ *(5)*

5 was generated *in situ* by adding a small molar excess of NaH to a d_8-THF solution of **3**. No attempt was made to isolate this product.

IR, FAB mass spectrometric and analytical data for compounds **2** and **3** are given in Table 1.

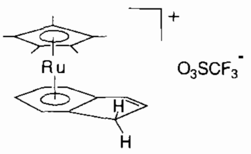

Fig. 1. Compound **2**: $[Cp^*Ru(\eta^6\text{-}C_9H_8)]^+O_3SCF_3^-$.

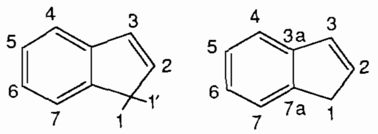

Fig. 2. Numbering scheme for ^1H NMR and ^{13}C NMR spectra assignments.

Results and discussion

Compound **2** (Fig. 1) was characterized by ^1H and ^{13}C NMR spectroscopy. (The ^{13}C NMR assignments were made by comparison with $[(\eta^6\text{-}C_9H_8)Re(\eta^5\text{-}C_9H_7)]$ [11].) The methylene protons are magnetically inequivalent and appear as an AB signal centered at 3.16 ppm with a coupling constant of −23.6 Hz. The coordinated ring protons display an average upfield shift of 1.28 ppm from free indene. The 2D COSY ^1H NMR spectrum of **2** clearly shows the coupling of the protons throughout the spectrum [12]. Combined with a JRES spectrum, it was possible to assign the resonances for all protons. The numbering scheme is given in Fig. 2.

TABLE 2. ^{1}H and ^{13}C NMR data[a] for the indenyl complexes

Compound	^{1}H(δ)[b]	^{13}C(δ)[c]
$[Cp^*Ru(\eta^6\text{-}C_9H_8)]^+O_3SCF_3^-$ (2)	6.88 (m, 1H, H(2)), 6.58 (m, 1H, H(3)), 6.32 (m, 1H, H(7)), 6.10 (m, 1H, H(4)), 5.81 (m, 1H, H(5)), 5.80 (m, 1H, H(6)), 3.16 (AB, 2H, H(1) and H(1'); $J(1,1') = -23.6$), 1.57 (s, 15H, $C_5(CH_3)_5$)[d]	140.3 (C(2)), 127.5 (C(3)), 107.6 (C(3a)), 104.3 (C(7a)), 94.7 (Cp* ring C's), 86.1, 85.7, 84.8, 82.7, (C(5), C(6), C(4), C((7); the exact assignment has not been made), 37.4 (C(1)), 9.89 (Cp* methyl Cs)[e]
$Na[Cp^*Ru(\eta^6\text{-}C_9H_7)O_3SCF_3]$ (4)	7.41 (m, 1H, H(2)), 5.81 (m, 2H, H(4) and H(7)), 5.47 (m, 2H, H(1) and H(3)), 4.84 (m, 2H, H(5) and H(6)), 1.47 (s, 15H, $C_5(CH_3)_5$)	133.8 (C(2)), 91.9 (C(1) and C(3)), 87.4 (C(3a) and C(7a)), 86.4 (Cp* ring Cs), 80.4 (C(5) and C(6)), 78.7 (C(4) and C(7)), 9.25 (Cp* methyl Cs)[e]

[a] Chemical shifts δ in ppm, coupling constants in Hz and measurements at ambient temperature. Chemical shifts relative to internal solvent d_8-THF. [b] ^{1}H NMR (d_8-THF, 300 MHz, δ). [c] ^{13}C NMR (d_8-THF, 300 MHz, δ). [d] The ^{1}H NMR assignments were made with the aid of a COSY spectrum. [e] The ^{13}C NMR assignments were compared to $[(\eta^6\text{-}C_9H_7)Re(\eta^5\text{-}C_9H_7)]^-$ [11].

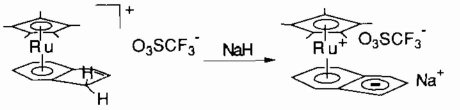

Fig. 3. The reaction of **2** with NaH yields the stable zwitterionic species $Na[Cp^*Ru(\eta^6\text{-}C_9H_7)O_3SCF_3]$ (**4**).

TABLE 3. Experimental proton coupling constants (Hz) for $[Cp^*Ru(\eta^6\text{-}C_9H_8)]^+O_3SCF_3^-$ (2)

Indene [15]	$[Cp^*Ru(\eta^6\text{-}C_9H_8)]^+O_3SCF_3^-$[a]
	$J(1,1') = -23.6$
$J(1,2) = 2.1$	$J(1,2) = 2.1$
$J(1,3) = 2.1$	$J(1,3) = 2.1$
$J(1,7) = 0.8$	$J(1,7) = 0.6$
$J(2,3) = 5.6$	$J(2,3) = 6.0$
$J(3,7) = 0.7$	$J(3,7) = 0.5$
$J(4,5) = 6.8$	$J(4,5) = 6.9$
$J(4,6) = 1.3$	$J(4,6) = 0.8$
$J(4,7) = 0.6$	$J(4,7) = 1.0$
$J(5,6) = 7.4$	$J(5,6) = 7.4$
$J(5,7) = 1.3$	$J(5,7) = 0.5$
$J(6,7) = 6.9$	$J(6,7) = 6.9$

[a] Coupling constants (Hz) for $[Cp^*Ru(\eta^6\text{-}C_9H_8)]^+O_3SCF_3^-$ were obtained from a simulated spectrum calculation.

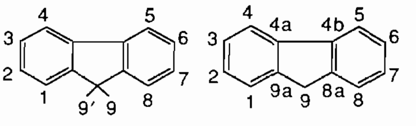

Fig. 4. Numbering scheme for ^{1}H NMR and ^{13}C spectra assignments.

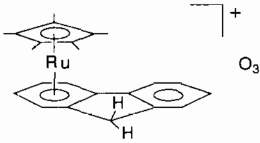

Fig. 5. Compound **3**: $[Cp^*Ru(\eta^6\text{-}C_{13}H_{10})]^+O_3SCF_3^-$.

TABLE 4. Experimental coupling constants (Hz) for $[Cp^*Ru(\eta^6\text{-}C_{13}H_{10})]^+O_3SCF_3^-$ (3)

Fluorene [15b]	$[Cp^*Ru(\eta^6\text{-}C_{13}H_{10})]^+O_3SCF_3^-$
$J(5,6) = 7.61$	$J(5,6) = 5.77$
$J(6,7) = 7.61$	$J(6,7) = 5.63$
$J(7,8) = 7.77$	$J(7,8) = 5.71$
	$J(9,9') = -21.97$

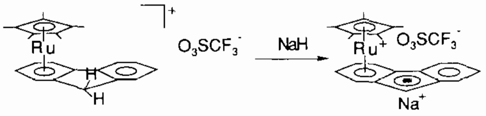

Fig. 6. The reaction **3** with NaH yields the stable zwitterionic species $Na[Cp^*Ru(\eta^6\text{-}C_{13}H_9)O_3SCF_3]$ (**5**).

An eight spin simulation of the ^{1}H NMR spectrum of **2** was used to determine the magnitude of the proton coupling constants. Calculations were performed with the PMR Spectrum Simulator Algorithm from Yale University courtesy of M. Saunders. Elleman and Manatt [13] first reported and Elvidge and Foster [14] confirmed a strong, small coupling of 0.7 Hz for $J(3,7)$, exceptional in that it occurs over five bonds. Comparison of the calculated indene coupling constants of **2** with those reported for free indene reveal that complexation has little effect on the magnitude of the coupling constants [15]. ^{1}H and ^{13}C NMR data for the indenyl complexes is given in Table 2.

A solution of **2** in degassed d_8-THF reacts with NaH producing an intensely colored orange solution (see Fig. 3). The ^{1}H and ^{13}C NMR spectra indicate that coordination of the metal to the six-membered ring is retained resulting in the formation of the zwitterionic species, $Na[Cp^*Ru(\eta^6\text{-}C_9H_7)O_3SCF_3]$ (**4**). No decomposition was observed by ^{1}H NMR after 24 h in solution at ambient temperature and exclusion from light. This

TABLE 5. ^1H and ^{13}C NMR data[a] for the fluorenyl complexes

Compound	$^1H(\delta)$[b]	$^{13}C(\delta)$[c]
$[Cp^*Ru(\eta^6\text{-}C_{13}H_{10})]^+O_3SCF_3^-$ (**3**)	[e]7.70, 7.52 (m, 2H, H(1) and H(4))[d], 7.40, 7.39 (m, 2H, H(2) and H(3))[d], 6.48, 6.38 (m, 2H, H(5) and H(8))[d], 5.93, 5.86 (m, 2H, H(6) and H(7))[d]	142.1 (C(8a)), 134.9 (C(4b)), 129.4, 127.6, 125.0, 121.6 (C(6), C(7), C(8) C(5))[d], 103.8, 103.4 (C(9a) and C(4a))[d], 94.9 (Cp* ring C's), 86.2 86.1, 84.9, 80.3, (C(3), C(2), C(1), C(4)[d], 34.3 (C(9)), 9.14 (Cp* methyl Cs)[f]
$Na[Cp^*Ru(\eta^6\text{-}C_{13}H_9)O_3SCF_3]$ (**5**)	7.74 (m, 1H, H(4)), 7.32 (m, 1H, H(3)), 7.09 (m, 1H, H(2)), 6.63 (m, 1H, H(1)), 6.22 (m, 1H, H(5)), 5.64 (m, 1H, H(6)), 5.36 (s, 1H, H(9)), 5.03 (m, 2H, H(7) and H(8)), 1.50 (s, 15H, $C_5(CH_3)_5$)	[f]147.2 (C(8a)), 130.3 (C(4b)), 124.7 121.2, 118.5, 114.6 (C(6), C(7), C(8) C(5))[d], 88.4 (Cp* ring C's), 82.7 (C(9)), 79.8 (C(9a)), 79.8, 79.0, 76.2 75.6 (C(3), C(2), C(1), C(4)[d], 9.44 (Cp* methyl Cs)[f]

[a] Chemical shifts δ in ppm, coupling constants in Hz and measurements at ambient temperature. Chemical shifts relative to internal solvent d_8-THF. [b] ^1H NMR (d_8-THF, 300 MHz, δ). [c] ^{13}C NMR (d_8-THF, 300 MHz, δ). [d] The exact assignment has not been made. [e] The ^1H NMR assignments were made with the aid of a COSY spectrum. [f] The ^{13}C NMR assignments were made by comparison with $[(\eta^5\text{-}Cp)Fe(\eta^6\text{-}C_{13}H_9)]^-$ [17].

observation indicates the zwitterion is quite stable and that the barrier of η^6-to-η^5 haptotropic rearrangement must be unusually high. Experimental proton coupling constants for **2** are given in Table 3.

Samples of the indenyl zwitterionic solution underwent photolysis in sunlight to give an intense purple solution. The visible spectrum displayed two absorption bands with peak maximum values at 561 and 737 nm and an intensity ratio of 1.00:0.51. A possible explanation is the indene analog of the purple fluorene trimer reported by Minabe and Suzuki [16]. The numbering scheme is given in Fig. 4.

The fluorenyl compound **3** (Fig. 5) was characterized by ^1H and ^{13}C NMR. (The ^{13}C NMR assignments were compared to $[(\eta^5\text{-}Cp)Fe(\eta^6\text{-}C_{13}H_{10})]$ [17].) The methylene protons are magnetically inequivalent and appear as an AB signal centered at 3.64 ppm with a coupling constant of -22.0 Hz. The coordinated ring protons display an average upfield shift of 1.25 ppm and the free ring protons display an average downfield shift of 0.09 ppm from fluorene. Coupling constants, derived from experimental ^1H NMR spectral data, are given in Table 4.

A degassed d_8-THF solution of **3** also reacts with NaH producing an intensely colored dark orange solution. Similarly, coordination of the metal to the six-membered ring is retained resulting in formation of the zwitterionic species, $Na[Cp^*Ru(\eta^6\text{-}C_{13}H_9)O_3SCF_3]$ (**5**) (Fig. 6), verified by ^1H and ^{13}C NMR spectroscopy. Only slight decomposition was observed by ^1H NMR after 24 h in solution at ambient temperature without exposure to light. This observation indicates that the fluorenyl zwitterion is quite stable and that the barrier of η^6-to-η^5 haptotropic rearrangement must be high. Table 5 gives ^1H and ^{13}C NMR data for the fluorenyl complexes.

Under mild conditions, $[CpFe(\eta^6\text{-}C_{13}H_{10})]^+$ can be deprotonated to yield a stable zwitterion in which the CpFe moiety remains coordinated through the six-membered ring. Helling and Hendrickson [17] found no evidence of haptotropic rearrangement even when the zwitterionic compound was heated to 100 °C. In contrast, Russian workers [18] have reported that heating the zwitterion in toluene at 80 °C induces haptotropic rearrangement in 70% yield. We believe that $[CpFe(\eta^6\text{-toluene})]^+$ may be formed as an intermediate providing a non-haptotropic pathway for conversion.

The behavior of these zwitterionic materials at elevated temperatures has not been examined. Since it is now known that both η^6- and η^5-indenyl and fluorenyl Cp*Ru complexes are stable, isolable species, it would appear that the barrier to metal migration must be substantial. It is not clear whether this barrier is electronic or steric in nature. Continuing research of the synthetic applications, experimental and theoretical aspects of these complexes is being pursued.

References

1 J. H. Osiecki and C. J. Hoffman, *J. Organomet. Chem*, *3* (1965) 107.

2 (a) N. S. Crossley, J. C. Green, A. Nagy and G. Stringer, *J. Chem. Soc., Dalton Trans.*, (1989) 2139; (b) F. Morandini, G. Consiglio, A. Sironi and M. Moret, *J. Organomet. Chem.*, *370* (1989) 305; (c) P. G. Gassman and C. H. Winter, *J. Am. Chem. Soc.*, *110* (1988) 6130; (d) L. A. Oro, M. A. Ciriano, M. Campo, C. Foces-Foces and F. H. Cano, *J. Organomet.*

Chem.. *289* (1985) 117; (e) H. P. Fritz and C. G. Kreiter, *J. Organomet. Chem.*, *4* (1965) 198.

3 A. R. Kudinov and M. I. Rybinskaya, *Metalloorg. Khim.*, *1* (1988) 1429.

4 A. Eisenstadt, F. Frolow and A. Efraty, *J. Chem. Soc., Chem. Commun.*, (1982) 642.

5 M. O. Albers, D. J. Robinson, A. Shaver and E. Singleton, *Organometallics*, *5* (1986) 2199.

6 P. G. Gassman and C. H. Winter, *J. Am. Chem. Soc.*, *110* (1988) 6130.

7 A. R. Kudinov, L. S. Shul'pina, P. V. Petrovskii and M. I. Rybinskaya, *Metalloorg. Khim.*, *3* (1990) 1391.

8 P. J. Fagen, W. S. Mahoney, J. C. Calabrese and I. D. Williams, *Organometallics*, *9* (1990) 1843.

9 N. Oshima, H. Suzuki and Y. Moro-Oka, *Chem. Lett.*, (1984) 1161.

10 P. J. Fagen, M. D. Ward and J. C. Calabrese, *J. Am. Chem. Soc.*, *111* (1989) 1698.

11 M. L. H. Green, N. D. Lowe and D. O'Hare, *J. Organomet. Chem.*, *355* (1988) 315.

12 D. E. Wheeler, *Ph.D. Dissertation*, University of Idaho, 1990, Ch. 9.

13 D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, *36* (1962) 2346.

14 J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, (1963) 590.

15 (a) M. Barfield and B. Chakrabarti, *J. Am. Chem. Soc.*, *91* (1969) 4346; (b) J. Douris and A. Mathieu, *Bull. Soc. Chim. Fr.*, *9* (1971) 3365.

16 (a) M. Minabe and K. Suzuki, *J. Org. Chem.*, *40* (1975) 1298; (b) *Bull. Chem. Soc. Jpn.*, *48* (1975) 1301.

17 J. F. Helling and W. A. Henderickson, *J. Organomet. Chem.*, *99* (1977) 141.

18 (a) N. A. Ustynyuk, N. A. Pomazanova, L.N. Novikova, D. N. Kravtsow and Y. A. Ustynyuk, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1986) 1688; (b) N. A. Ustynyuk, L. I.Denisovich, M. G. Peterleitner, L. N. Novikova, N. A. Pomazanova and D. N. Kravstov, *Metalloorg. Khim.*, *216* (1988) 1.