convergence with $R = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [\sum w(||F_o| - |F_c||)^2/\sum wF_o^2]^{1/2}$, having values listed in Table VIII. Criteria for a satisfactory complete analysis were the ratios of root-mean-square (rms) shift to standard deviation being less than 0.1 and no significant features in final difference maps. Atomic coordinates are given in Table IX.

Supplementary Material Available: Tables of anisotropic temperature factors, hydrogen coordinates, and bond distances and angles for CO ligands (10 pages); tables of observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

---

(33) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr. Sect. A: Cryst. Phys. Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

(34) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *39*, 158.

Preparation and Stoichiometric and Catalytic Reactivity of Hydrido Organometallic Ruthenium Complexes. X-ray Crystal Structure of $[RuH(\eta^5\text{-}C_8H_{11})_2]BF_4$

Faouzi Bouachir, Bruno Chaudret,* Françoise Dahan, Francine Agbossou, and Igor Tkatchenko*

Laboratoire de Chimie de Coordination du CNRS, UP"8241 liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205 Route de Narbonne, 31077 Toulouse Cedex, France

Received April 12, 1990

Protonation of $Ru(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_8H_{10})$ by $HBF_4{\cdot}Et_2O$ at −80 °C initially produces $[RuH(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_8H_{10})]BF_4$ (**1**). Complex **1** isomerizes in solution to $[RuH(\eta^5\text{-}C_8H_{11})_2]BF_4$ (**2**) through a mechanism that has been specifically studied by freezing the reaction through deprotonations. The X-ray crystal structure of **2** shows the complex to be a ruthenium(IV) hydride lacking any agostic interactions: space group $C_{2h}^6\text{-}C2/c$; $a = 10.962$ (1) Å, $b = 9.922$ (1) Å, $c = 15.077$ (1) Å, $\beta = 98.71$ (1)°; $V = 1620.9$ (5) Å^3; $Z = 4$. Complex **2** reacts with acetone to give an equilibrium mixture of **2** and $[Ru(\eta^5\text{-}C_8H_{11})(\eta^4\text{-}C_8H_{12})(\text{acetone})]BF_4$ (**3**), thus demonstrating the ease of hydrogen transfer in the system. The reaction of **1** with S (S = MeCN, H_2O) produces $[Ru(\eta^5\text{-}C_8H_{11})S_3]BF_4$ (**5** and **4**, respectively), while with C_5Me_5H the complex $[Ru(\eta^5\text{-}C_5Me_5)(C_8H_{12})]BF_4$ (**7**) is formed and shown by ^1H and ^{13}C NMR studies to adopt a ruthenium(II) structure with an agostic interaction. With cyclopentene, a similar complex is obtained for which the formula $[Ru(\eta^5\text{-}C_5H_5)(C_8H_{12})]BF_4$ (**9**) is proposed. **1** also reacts with $PMePh_2$ to yield $[Ru(\eta^5\text{-}C_8H_{11})(PMePh_2)_3]BF_4$ (**6**) and with C_6Me_6 to yield $[Ru(\eta^5\text{-}C_8H_{11})(\eta^6\text{-}C_6Me_6)]BF_4$ (**10**). Complex **1** or its derivatives are catalysts for 1-alkene isomerization, ethylene dimerization, and ring-opening polymerization of norbornene.

Introduction

Cationic organometallic derivatives and more specifically cationic allyl species of group 10 have shown high reactivity toward olefins and exhibit remarkable catalytic properties.[1] We have recently attempted the preparation of similar ruthenium complexes in order to compare their reactivities with those of group 10 metals and to develop new reactions.[2] In this regard, ruthenium complexes are increasingly studied in view of their potential catalytic applications.[3] For example, ruthenium hydride[4] compounds or derivatives of Ru(COD)(COT)[3] (COD is cyclooctadiene, COT is cyclooctatetraene) have been used for the linear codimerization of butadiene and acetylenes. However, the cationic complexes that we obtained, $[Ru(1\text{-}3\text{:}5\text{-}6\text{-}\eta\text{-}C_8H_{11})(\eta^6\text{-}C_8H_{10})]PF_6$ or $[Ru(1\text{-}3\text{:}5\text{-}6\text{-}\eta\text{-}C_8H_{11})(\eta^6\text{-}C_6H_6)]PF_6$,[2] were electronically saturated and did not show high catalytic activity.

On the other hand, the protonation of low-valent olefinic organometallic complexes usually does not lead to hydride species but rather to unsaturated species that may show a strong C–H–M or agostic interaction.[5,6] A much greater reactivity was thus expected from these unsaturated or agostic species in which the three-center interaction can be easily broken. This property has been used for catalytic reactions such as the recent polymerization of ethylene using cobalt complexes.[4d] As part of our interest for hydrogen-transfer reactions related to the study of C–H activation,[7] we have examined the protonation of Ru(COD)(COT) and shown that the ruthenium complex can undergo numerous hydrogen-transfer reactions. The stoichiometric and catalytic reactivity of these species toward unsaturated hydrocarbons has been studied. However, problems of stability, in particular in the pres-

---

(1) (a) Grenouillet, P.; Neibecker, D.; Tkatchenko, I. *Organometallics* **1984**, *3*, 1130. (b) Grenouillet, P.; Neibecker, D.; Poirier, J.; Tkatchenko, I. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 767. (c) Pardy, R. B. A.; Tkatchenko, I. *J. Chem. Soc., Chem. Commun.* **1981**, 49.

(2) Bouachir, F.; Chaudret, B.; Neibecker, D.; Tkatchenko, I. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 347.

(3) Mitsudo, T.; Hori, Y.; Watanabe, Y. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3201 and references therein.

(4) Mitsudo, T.; Nakagawa, Y.; Watanabe, K.; Hori, Y.; Misawa, H.; Watanabe, H.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 565.

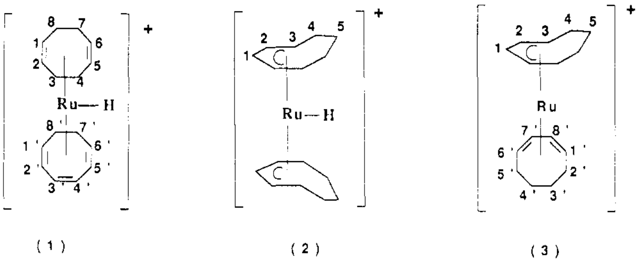
(5) (a) Cotton, F. A.; La Cour, T.; Stanislowski, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 754. (b) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(6) For selected examples of protonation leading to complexes containing an agostic interaction, see, for example: (a) Ittel, S. D.; Van-Catledge, F. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 6905. (b) Timmers, F.; Brookhart, M. *Organometallics* **1985**, *4*, 1365 and references therein. (c) Bennett, M. A.; McMahon, I. J.; Pelling, S.; Robertson, G. B.; Wickramasinghe, W. A. *Organometallics* **1985**, *4*, 754. (d) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443.

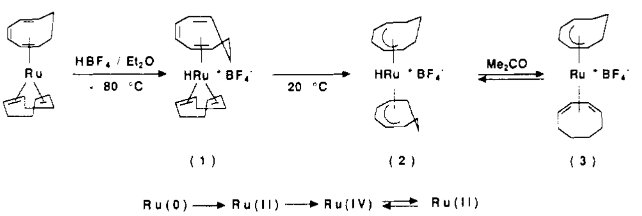
(7) Arliguie, T.; Chaudret, B. *J. Chem. Soc., Chem. Commun.* **1986**, 985.

0276-7333/91/2310-0455$02.50/0 © 1991 American Chemical Society

Chart I. Proposed Structures for 1–3 Showing the Numbering Scheme



Scheme I. Reactions of the Protonation of Ru(COD)(COT)



ence of hydrogen, led us to attempt ring-exchange reactions. The reactions are outstandingly facile and have led both to the preparation of arene complexes and to that of substituted cyclopentadienyl derivatives.

Arene organometallic ruthenium complexes can be obtained from Ru(COD)(COT) either by hydrogenation in the presence of arenes[8] or by protonation in the neat arene.[9] However, in either case, no C_6Me_6 compound had been obtained. The source of such complexes is $[RuCl_2C_6Me_6]_2$,[10] which has led to interesting chemistry such as arene hydrogenation[11] and C–H activation.[12]

For (pentamethylcyclopentadienyl)ruthenium compounds, the main starting materials are $[Cp^*Ru(CO)_2]_2$[13] and $[Cp^*RuCl_2]_n$.[14] The latter complex has led to a recent and major development of the chemistry of carbonyl-free complexes including the synthesis of the trihydrides $RuH_3Cp^*PR_3$ (R = Me, Ph, Pr, Cy)[7,15–18] and ruthenium(IV) organometallic alkyl derivatives,[19–22] such as the remarkable complex $Cp^*Ru(\eta^3\text{-}C_3H_5)Me_2$.[22] The catalytic properties of these ruthenium(IV) species have been explored, and interesting results such as the linear trimerization of butadiene have been obtained.[23] These results led us to examine the reactivity of these compounds and to the observation that, in contrast with the product of the protonation of Ru(COD)(COT), which is a ruthenium(IV) hydride species, the pentamethylcyclopentadienyl derivative shows an agostic interaction. The full details of this work are described here; preliminary accounts of part of this work have been published.[24,25]

Table I. ^{1}H and ^{13}C NMR Spectra of $[RuH(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_8H_{10})]BF_4$ in CD_2Cl_2 at −80 °C

^{1}H NMR

δ C_8H_{10}	δ C_8H_{10}	δ
0.37 (m, ^{1}H, H_{8endo}, m, 1 H, H_1); 1.4–2.5 (m large, 4 H, H_2, $H_{7'}$, H_7, H_{8exo}); 3.63 (1 H, below Et_2O, H_3); 4.08 (t, ^{1}H, J = 7.5 Hz, H_4); 5.13 (q, 1 H, J = 7.5 Hz, H_6); 7.36 (t, 1 H, J = 7.5 Hz, H_5)	1.85 (m, 1 H, $H_{8'}$); 1.4–2.5 (m, 1 H, $H_{3'}$); 2.32 (m, 1 H, $H_{7'}$), 2.5 (m, 3 H, $H_{4'}$, $H_{7'}$, $H_{8'}$); 2.84 (m, 1 H, $H_{4'}$); 3.12 (m, 1 H, $H_{3'}$); 3.42 (t, 1 H, J = 7.5 Hz, $H_{2'}$); 3.96 (m, 2 H, $H_{5'}$, $H_{6'}$); 6.07 (q, 1 H, J = 7.5 Hz, $H_{1'}$)	−5.48 (dt, $J_{H\text{-}H}$ = 7.5 Hz)

^{13}C NMR

δ CH	δ CH_2
32.6; 54.7; 74.9; 82.7; 88.9; 89.2	16.9; 17.6; 19.7; 25.2; 26.1; 34.6

Results and Discussion

Synthesis and Characterization. Ru(COD)(COT) reacts readily with stoichiometric amounts of $HBF_4{\cdot}Et_2O$ at −80 °C in CH_2Cl_2 to give a yellow solution from which yellow microcrystals of $[RuH(C_8H_{12})(C_8H_{10})]BF_4$ (1) were obtained upon addition of diethyl ether. The complex was found to be thermally unstable, slowly turning brown in the solid state. ^{1}H NMR spectra in CD_2Cl_2 show that the complex is fluxional at room temperature and also that it slowly transforms into another species. However, when a solution of $Ru(C_8H_{12})(C_8H_{10})$ in CD_2Cl_2 is protonated at low temperature and when the ^{1}H NMR spectrum is run shortly afterwards at −80 °C, we could observe a spectrum consistent with the presence of a single rigid hydrido species. The spectrum is very complex, but we could assign each peak by using selective decoupling experiments (see Table I, Scheme I, and Chart I for assignments). The most noticeable feature of this spectrum is the presence of a high field signal at δ −5.48 ppm as a doublet of triplets (J_{HH} = 7.5, 5 Hz) due to coupling to three ring protons, one olefinic (H_6) and two aliphatic ones among $H_{4'}$ $H_{7'}$, and $H_{8'}$, respectively We propose that these are through-space couplings.

The $^{13}C\{^1H\}$ NMR spectrum of 1 at −80 °C only shows 14 resonances (8 CH and 6 CH_2) instead of the expected 16 (Table I). This is probably due to carbons resonating fortuitously at the same frequency. No anomalously low $J_{C\text{-}H}$ was detected when the ^{13}C NMR spectrum was recorded, and thus, we favor a complex with a terminal hydride ligand rather than with a hydrocarbon cycle

---

(8) Pertici, P.; Vitulli, G.; Lazzaroni, R.; Salvadori, P. *J. Chem. Soc., Dalton Trans.* **1982**, 1019.

(9) Vitulli, G.; Pertici, P.; Bigelli, C. *Gazz. Chim. It.* **1985**, *115*, 75.

(10) Bennett, M. A.; Huang, T. N.; Matheson, T. W.; Smith, A. K.; checked by Ittel, S.; Nickerson, W. *Inorg. Synth.* **1982**, *21*, 74.

(11) Bennett, M. A.; Huang, T. N.; Smith, A. K.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* **1978**, 582.

(12) (a) Kletzin, H.; Werner, H. *Angew. Chem.* **1983**, *95*, 916. (b) Morris, R. H.; Shiralian, M. *J. Organomet. Chem.* **1984**, *260*, C47.

(13) (a) King, R. G.; Iqbal, M. A.; King, A. D. *J. Organomet. Chem.* **1979**, *171*, 53. (b) Nelson, G. O.; Summer, C. E. *Organometallics* **1986**, *5*, 1983.

(14) (a) Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274. (b) Oshima, N.; Suzuki, H.; Moro-Oka, Y. *Chem. Lett.* **1984**, 1161.

(15) Paciello, R.; Bercaw, J. E. *Abstracts of Papers*, 191st National Meeting of the American Chemical Society, New York, April 1986; American Chemical Society: Washington, DC, 1986; Inor 82.

(16) Oshima, N.; Suzuki, H.; Moro-Oka, Y. *J. Organomet. Chem.* **1986**, *314*, C46.

(17) Suzuki, H.; Lee, D. H.; Oshima, N.; Moro-Oka, Y. *J. Organomet. Chem.* **1986**, *317*, C45.

(18) (a) Arliguie, T.; Chaudret, B.; Devillers, J.; Poilblanc, R. *C. R. Seances Acad. Sci., Ser. 2* **1987**, *305*, 1523. (b) Arliguie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989**, *9*, 308.

(19) Nagashima, H.; Mukai, K.; Itoh, K. *Organometallics* **1984**, *3*, 1314.

(20) Nagashima, H.; Mukai, K.; Shlota, Y.; Ara, K.; Itoh, K.; Suzuki, H.; Oshima, N.; Moro-Oka, Y. *Organometallics* **1985**, *4*, 1314.

(21) Nagashima, H.; Yamaguchi, K.; Mukai, K.; Itoh, K. *J. Organomet. Chem.* **1985**, *291*, C20.

(22) Nagashima, H.; Ara, K.; Yamaguchi, K.; Itoh, K. *J. Organomet. Chem.* **1987**, *319*, C11.

(23) Itoh, K.; Fukahori, T.; Ara, K.; Nagashima, H.; Nishiyama, H. Proc. Kobe AIO.

(24) Bouachir, F.; Chaudret, B.; Tkatchenko, I. *J. Chem. Soc., Chem. Commun.* **1986**, 94.

(25) Bouachir, F.; Chaudret, B.; Dahan, F.; Tkatchenko, I. *New. J. Chem.* **1987**, *11*, 527.

Table II. ^1H NMR Data for New Cyclooctadienyl Derivatives

	δ H_1 (Hz)	δ H_2 (Hz)	δ H_3 (Hz)	δ H_4 (Hz)	δ H_5 endo (Hz)	δ H_5 exo (Hz)	δ others
$[RuH(C_8H_{11})]_2^+$ (**2**)[b,c]	6.25 t (6.8)	4.67 t (7.5)	4.06 br	1.73 t (13.7) 2.06 d (13.7)	1.33 d (13.7)	0.38 q (13.7)	–5.6, s, RuH
$[Ru(C_8H_{11})(C_8H_{12})]^+$ (**3**)[a,d]	6.45 t (6.2)	3.99 t (7.5)	3.48 br	1.5–20	1.07 cl (13.0)	–0.49 q (13.0)	5.89 d+, 5.71 dd+, 2.27 d+; 10.4 10.4, 7 1.5–2
$[Ru(C_8H_{11})(MeCN)_3]^+$ (**5**)[b,d]	6.03 t (6.2)	3.91 dd (9.0, 6.7)	2.77 br	1.3–16 br	0.90 (13.2)	–0.41 (13.2)	2.19, MeCN free; 2.31, 2.43, 2.54, MeCN coordinated
$[Ru(C_8H_{11})(H_2O)_3]^+$ (**4**)[a,e]	5.83 br t	obsured by H_2O	3.7 br	2.3–1.7	0.94 br	–0.56 br	4.82, H_2O
$[Ru(C_5Me_5)(C_8H_{12})]^+$ (**7**)[b,c]	6.93 t (7.0)	5.38 dd (7.0, 10.5)	3.81 br	1.84 t (14) 2.05 br	1.57 cl (13.7)	0.57 q (13.7)	–9.77, s, RuHC 2.17, s, C_5Me_5
$[Ru(C_5Me_5)(C_8H_{11})]$ (**8**)[a,d]	5.47 t (5.9)	3.68 dd (5.9, 8.1)	3.06	2.2–1.4	2.2–1.4	0.35 q t (13.2, 3)	1.76, s, C_5Me_5
$[Ru(C_5H_5)(C_8H_{12})]^+$ (**9**)[b,c]	7.4 br	5.8 br	3.2 br	0.8–3 br	0.8–3 br	0.8–3 br	–9.6, s, RuHC; 6.5, C_5H_5
$[Ru(C_6Me_6)(C_8H_{11})]^+$ (**10**)[a,d]	6.45 (6.6)	4.49 t (7.5)	3.6 m	2–1.2 m	2–1.2 m	0.2 m	2.43, C_6Me_6
$[Ru(C_8H_{11})(PMePh_2)]^+$ (**6**)[a,d]	6.84 t	5.09 br	2.7 br	1.2–1.5	1.03	0.9–0.2	0.9–0.2, $PMePh_2$; 7.2–7.7, $PMePh_2$

[a] Room temperature. [b] 200 K. [c] CD_2Cl_2 solvent. [d] $(CD_3)_2CO$. [e] D_2O. [f] Apparent cyclooctadienyl derivative (effect of fluxionality, see text).

Table III. ^{13}C NMR Data for Some Cyclooctadienylruthenium Derivatives

	δ C_1 (Hz)	δ C_2 (Hz)	δ C_3 (Hz)	δ C_4 (Hz)	δ C_5 (Hz)	δ others (Hz)
$[RuH(C_8H_{11})_2]^+$ (**2**)[a]	107.3 (d, 167)	88.6 (d, 88)	55.7 (d, 160)	25.6 (t, 130)	17.9 (t, 127)	
$[Ru(C_5Me_5)(C_8H_{12})]^+$ (**7**)[b]	106.3 (d, 166)	83.9 (d, 171)	40.3 (dd, 150, 34)	21.0 (t, 128)	18.5 (t, 135)	97.8 (C_5Me_5), 8.6 ($C_5\mathit{Me}_5$) (q, 128)
$[Ru(C_8H_{11})(PMePh_2)_3]^+$ (**6**)[b]	97.6	89.4	58.1	24.9	18.9	3.6 ($P\mathit{Me}Ph_2$), 130.8–135.0 ($PMe\mathit{Ph}_2$)
$[Ru(C_8H_{11})(C_6Me_6)]^+$ (**10**)[c]	106.3	84.2	60.9	27.0	19.1	104.8 (C_6Me_6), 15.7 ($C_6\mathit{Me}_6$)

[a] Spectra recorded in CD_2Cl_2. [b] Spectra recorded in acetone-d_6. [c] Spectra recorded in $CDCl_3$.

showing an "agostic" Ru–H–C interaction. Complex **1** can be deprotonated easily with NEt_3 at low temperature to give back Ru(COD)(COT) in agreement with our proposed structure. It represents the first example of an isolated hydridometal complex stabilized only by alicyclic hydrocarbon ligands.

When a solution of **1** in CH_2Cl_2 was allowed to warm to room temperature for various periods of time and then cooled again, a number of small uncharacterized peaks appeared in the ^1H NMR spectrum, but we could only follow the growth of one new complex, **2** (see Scheme I). When the same kind of experiment was carried out by ^{13}C NMR, only the appearance and growth of **2** was detected. Complex **2** could be obtained in pure form by allowing the mixture to react for 5 h at room temperature. The NMR spectra (^1H and ^{13}C) are broad at room temperature, while at 200 K very simple spectra are observed (Tables II and III). The ^1H NMR spectrum shows a single high field peak at δ –5.6 ppm together with peaks characteristic of a η^5-cyclooctadienyl ligand (Table II and Chart I). H_1 may be observed as a triplet at δ 6.25 ppm ($J_{H_1H_2}$ = 6.8 Hz), H_2 as a pseudotriplet ($J_{H_1H_2} = J_{H_2H_3}$), H_3 as a rather broad peak at δ 4.06 ppm, H_5 exo as a doublet (J_{HH} = 13.3 Hz), and $H_{5'}$ endo as a quartet at δ 0.38 ppm (integration ratio: hydride:H_1:H_2:H_3:H_{5exo}:H_{5endo} = 1:2:4:4:2:2). The $^{13}C\{^1H\}$ NMR spectrum at 203 K is also very simple, showing 5 peaks at δ 107.31, 88.65, 25.66, and 17.93 ppm for C_1, C_2, C_3, C_4, and C_5, respectively. It should be noted that the peak for C_3 is broad but only gives a doublet in the ^{13}C NMR spectrum. The C–H coupling constant (160 Hz) is typical of a sp^2 carbon. At 294 K, the spectrum is basically similar but much broader. These data together with those of the microanalysis are in agreement with the proposed structure, $[RuH(\eta^5\text{-}C_8H_{11})_2]BF_4$, for **2**. Again the absence of an anomalous C–H coupling constant and the equivalence of the two C_8 rings favors a ruthenium(IV) hydride structure rather than of a ruthenium(II) complex showing a C–H–Ru interaction. The spectra are similar to those of the corresponding neutral $Ru(\eta^5\text{-}C_8H_{11})_2$[26] except that this complex is rigid at all temperatures.

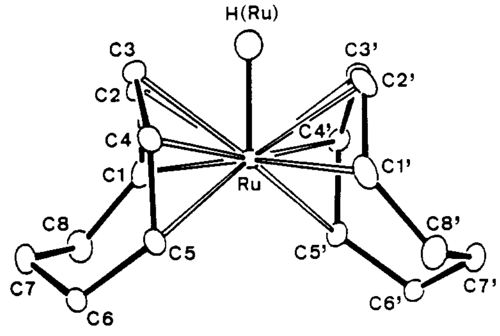


Figure 1. ORTEP view of $[RuH(C_8H_{11})_2]$ cation with ellipsoids drawn at 20% probability. All hydrogen atoms except the hydride are omitted.

However, since it seemed surprising that simple protonation of Ru(COD)(COT) led to a ruthenium(IV) complex, an X-ray crystal structure determination was carried out. The results are summarized in Figure 1 and Tables IV–VI. The molecule adopts a typical sandwich conformation consisting of two cyclooctadienyl rings related by symmetry about a 2-fold rotation axis containing the ruthenium and the hydride ligand. The five metal-bound carbon atoms of the ring are planar within ±0.055 (4) Å. The metal lies 1.581 (4) Å from the plane. The Ru–H distance (1.67 (6) Å) is typical of a terminal hydride. The

---

(26) Itoh, K.; Nagashima, H.; Ohshima, T.; Nishiyama, H. *J. Organomet. Chem.* **1984**, *272*, 179.

Table IV. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for 2[a]

Ru–H(Ru)	1.67 (6)	Ru–C(3)	2.209 (4)
Ru–C(1)	2.263 (5)	Ru–C(4)	2.155 (4)
Ru–C(2)	2.186 (5)	Ru–C(5)	2.283 (4)
H(Ru)–Ru–C(1)	94.8 (1)	C(1)–Ru–C(1)′	170.4 (3)
H(Ru)–Ru–C(2)	60.0 (1)	C(1)–Ru–C(2)′	150.3 (2)
H(Ru)–Ru–C(3)	55.2 (1)	C(1)–Ru–C(3)′	117.0 (2)
H(Ru)–Ru–C(4)	82.4 (1)	C(1)–Ru–C(4)′	92.1 (2)
H(Ru)–Ru–C(5)	120.3 (1)	C(1)–Ru–C(5)′	90.8 (2)
C(1)–Ru–C(2)	38.3 (2)	C(2)–Ru–C(2)′	120.1 (3)
C(1)–Ru–C(3)	69.0 (2)	C(2)–Ru–C(3)′	103.3 (2)
C(1)–Ru–C(4)	89.2 (1)	C(2)–Ru–C(4)′	101.6 (2)
C(1)–Ru–C(5)	84.3 (2)	C(2)–RU–C(5)′	120.9 (2)
C(2)–Ru–C(3)	36.9 (2)	C(3)–Ru–C(3)′	110.5 (2)
C(2)–Ru–C(4)	70.5 (2)	C(3)–Ru–C(4)′	130.0 (2)
C(2)–Ru–C(5)	89.4 (2)	C(3)–Ru–C(5)′	157.8 (2)
C(3)–Ru–C(4)	37.5 (2)	C(4)–Ru–C(4)′	164.8 (2)
C(3)–Ru–C(5)	69.5 (2)	C(4)–Ru–C(5)′	157.2 (2)
C(4)–Ru–C(5)	37.9 (2)	C(5)–Ru–C(5)′	119.5 (2)
C(1)–C(2)	1.460 (8)	C(5)–C(6)	1.505 (6)
C(2)–C(3)	1.389 (7)	C(6)–C(7)	1.479 (7)
C(3)–C(4)	1.405 (6)	C(7)–C(8)	1.487 (6)
C(4)–C(5)	1.447 (6)	C(8)–C(1)	1.513 (8)
C(8)–C(1)–C(2)	127.3 (4)	C(4)–C(5)–C(6)	123.6 (4)
C(1)–C(2)–C(3)	125.5 (5)	C(5)–C(6)–C(7)	117.0 (4)
C(2)–C(3)–C(4)	127.4 (4)	C(6)–C(7)–C(8)	111.8 (4)
C(3)–C(4)–C(5)	127.6 (4)	C(7)–C(8)–C(1)	117.2 (4)

[a] ′ denotes the symmetry operation $1 - x, y, {}^3/_2 - z$.

Table V. Crystal Data and Data Collection Details for 2

	Crystal Data
formula	$BC_{16}F_4H_{23}Ru$
fw	403.2
cryst system	monoclinic
space group	C_{2h}^6-$C2/c$
a, Å	10.962 (1)
b, Å	9.922 (1)
c, Å	15.077 (1)
β, deg	98.71 (1)
V, Å^3	1620.9 (5)
Z	4
$F(000)$	816
D(calcd),g·cm^{-3}	1.65
cryst size, mm	0.50 × 0.20 × 0.05
μ(Mo Kα), cm^{-1}	9.8
	Data Collection
temp, °C	20
radiation	Mo Kα (λ = 0.71073 Å) from graphite monochromator
θ(min–max), deg	1.5–30
scan mode	ω–2θ
scan range, deg	0.80 + 0.35 tan θ
scan speed, deg min^{-1}	1.1–10.1
receiving aperture, mm	4.0 × 4.0
take-off angle, deg	3.5
intensity stds	208, 153, 33$\bar{6}$ monitored every 2 h
orientation reflectns	0.29, 260, 60$\bar{4}$ checked every 200 reflectns
collected reflectns	2465 ($h,k,\pm l$)
non-zero unique reflectns	2180

bonding Ru–C distances (around 2.2 Å, see Table IV) and the C–C distances are also in the range expected for such a structure.[27] The interesting point of this structure is the position of the hydride which lies between C_3 and $C_{3'}$ and not close to C_1 or C_5 as would be expected when considering the ease of the **2** = **3** equilibrium (vide infra).

Table VI. Fractional Atomic Coordinates with Estimated Standard Deviations in Parentheses[a]

atom	x/a	y/b	z/c
Ru	$^1/_2$	0.34140 (4)	$^3/_4$
H(Ru)	$^1/_2$	0.509 (6)	$^3/_4$
C(1)	0.6113 (4)	0.3222 (6)	0.6359 (3)
C(2)	0.5472 (4)	0.4514 (5)	0.6343 (3)
C(3)	0.4215 (4)	0.4683 (4)	0.6350 (3)
C(4)	0.3363 (3)	0.3701 (4)	0.6531 (3)
C(5)	0.3531 (3)	0.2254 (4)	0.6567 (3)
C(6)	0.3735 (4)	0.1415 (4)	0.5771 (3)
C(7)	0.4593 (4)	0.1957 (5)	0.5192 (3)
C(8)	0.5870 (4)	0.2088 (6)	0.5685 (3)
B	$^1/_2$	0.1591 (5)	$^1/_4$
F(1)	0.4353 (5)	0.0483 (5)	0.2709 (4)
F(2)	0.4113 (5)	0.2534 (6)	0.2217 (5)
F(3)	0.5706 (7)	0.1337 (10)	0.1843 (4)
F(4)	0.5697 (5)	0.2038 (6)	0.3277 (3)

[a] Fluorine atoms have an occupancy factor of 0.5 for **2**.

This structure confirms that protonation of the zero-valent Ru(COD)(COT) leads eventually to a hydrido ruthenium(IV) complex. To our knowledge, this is the first structure of a hydrido organometallic ruthenium(IV) derivative.

If now the protonation reaction is carried out in acetone and the reaction mixture allowed to react at room temperature for the same period of time as before (5 h), another complex (**3**) is observed. Like **1** and **2**, it is fluxional but the high-temperature limit spectrum is observed at 298 K in the ^{1}H NMR spectrum whereas at 200 K the spectrum is more complicated. An η^5-coordinated cyclooctadienyl ring is clearly observed (Table II) together with a coordinated 1,3-cyclooctadiene. Two interesting features are present in the spectra: (1) a high field shift of the endo proton of the methylene C_5 group (δH −0.48 ppm, J_{HH} = 13 Hz), which can be related to a steric effect (coordinated acetone?) pushing the ring so that the endo proton of C_5 (see Chart I) becomes parallel to the plane of the five ruthenium-bonded carbons of the η^5-cyclooctadienyl group, and (ii) **2** and **3** are in equilibrium in acetone since at 200 K the spectra of both compounds are visible. Dissolution of crystalline samples of **2** in acetone and cooling to −80 °C afforded the same mixture.

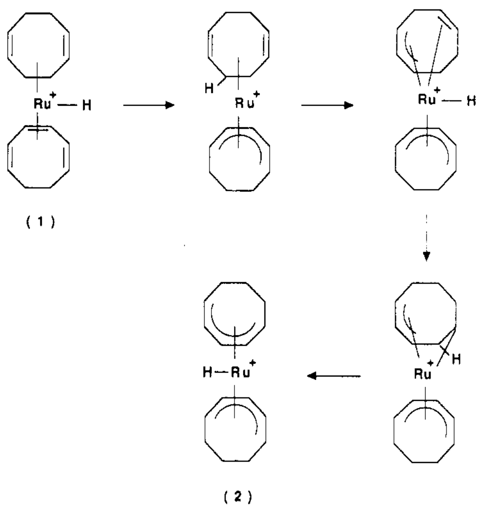
The net result of these reactions is the facile solvent-induced transfer of hydrogen from the metal to the hydrocarbon. The mechanism of this reaction most probably involves a species containing a two-electron three-center interaction (Ru–H–C), but no spectroscopic evidence was found for it. However, this mechanism is very likely since such an interaction has been demonstrated in a very similar complex (vide infra). Complex **3** apparently only exists in solution, and **2** is obtained again by recrystallization. Such an equilibrium involving a proton migration from metal to hydrocarbon has only rarely been observed spectroscopically.[28] This equilibrium must be very slow on the NMR time scale since both complexes are clearly observed. It also seems to be temperature-dependent. Thus, after dissolving **2** in acetone and cooling, the initially observed **2**:**3** ratio slowly increased as a function of time but we could not reach good equilibrium values. Two proposals can be made for the structure of **3**. Since the complex is yellow and fairly stable, it is likely to be coordinatively and electronically saturated. It can thus either contain an agostic interaction between one proton of 1,3-COD and the metal (but no evidence was found for such an interaction; vide infra) or more likely a solvent molecule is loosely bonded to ruthenium.

---

(27) (a) Trimarchi, M. C. L.; Green, M. A.; Huffmann, J. C.; Caulton, K. G. *Organometallics* **1985**, *4*, 514. (b) Ashworth, T. V.; Chalmers, A. A.; Liles, D. C.; Meintjes, E.; Oosthuizen, H. E.; Singleton, E. *J. Organomet. Chem* **1985**, *284*, C19.

(28) Derome, A. E.; Green, M. L. H.; O'Hare, D. *J. Chem. Soc., Dalton Trans.* **1986**, 343.

Scheme II. Proposed Mechanism for Hydrogen Transfer in 1



In order to prove this proposal, we have reacted **2** with better coordinating solvents, but NMR studies show that we have obtained substitution of the 1,3-cyclooctadiene and formation of $[Ru(\eta^5\text{-}C_8H_{11})S_3]BF_4$ (S = H_2O (**4**) or MeCN (**5**)). It is noteworthy that, in the case of the reaction with acetonitrile, the system is fluxional at room temperature, showing only a broad resonance between δ 2 and 3 ppm, together with the classical peaks for the η^5-coordinated cyclooctadienyl ligand. However, at low temperatures, the peak for free MeCN appears at δ 2.43 ppm and two sharp peaks are visible at δ 2.31 and 2.54 ppm for the three coordinated acetonitrile molecules.

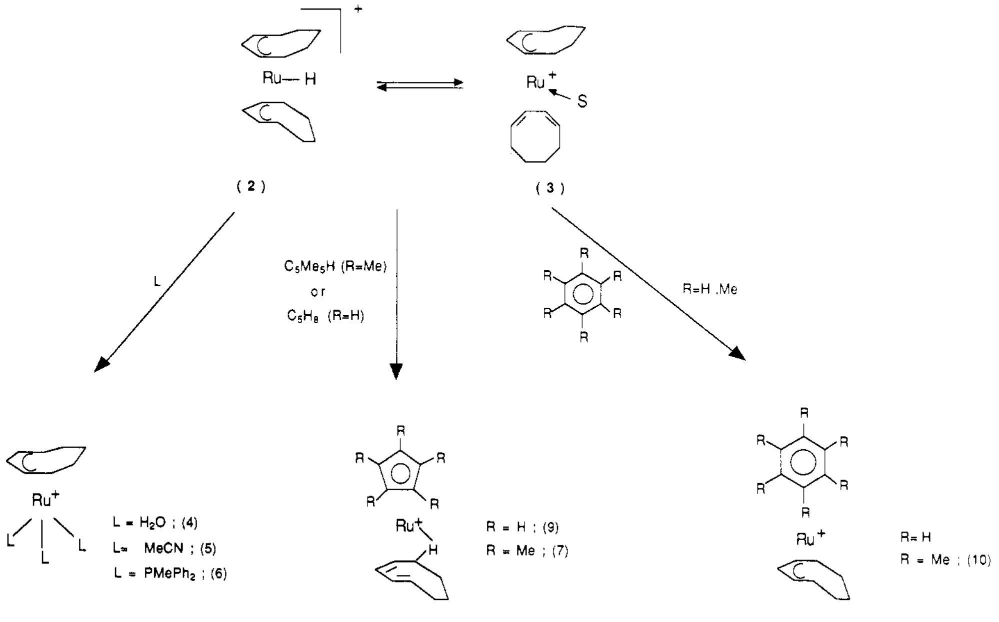
Itoh et al.[26] have recently reported a study concerning the preparation and isomerization of Ru(COD)(COT). They found that the first product of the reaction of ruthenium trichloride hydrate with cyclooctadiene in the presence of zinc is bis(1–3:5–6-η-cyclooctadienyl)ruthenium(II), which isomerizes at 70 °C into Ru(COD)(COT), the kinetic product, then into $Ru^{II}(1\text{–}5\text{-}\eta\text{-}C_8H_{11})(1\text{–}3\text{:}5\text{–}6\text{-}\eta\text{-}C_8H_{11})$, and eventually into $Ru(\eta^5\text{-}C_8H_{11})_2$ in refluxing toluene. In this neutral system, hydrogen transfer occurs at elevated temperatures (first 70 °C and then 110 °C), whereas we have seen that in our case it occurs at low temperatures (−70 °C to room temperature). In order to shed some light on the hydrogen-transfer mechanism, we attempted to deprotonate reaction solutions during the conversion of **1** into **2**, as this was expected to freeze the reaction. As described earlier, when NEt_3 was added to the reaction mixture after protonation at low temperatures, Ru(COD)(COT) was obtained almost quantitatively, only contaminated with small amounts of $Ru(\eta^5\text{-}C_8H_{11})(1\text{–}3\text{:}5\text{–}6\text{-}\eta\text{-}C_8H_{11})$. When NEt_3 was added after allowing the reaction mixture to react for 1 h at room temperature, $Ru(\eta^5\text{-}C_8H_{11})_2$ was the major product observed. However, when the solution was left at room temperature for various periods of time before deprotonation occurred, various yields of $Ru(\eta^5\text{-}C_8H_{11})(1\text{–}3\text{:}5\text{–}6\text{-}\eta\text{-}C_8H_{11})$ were obtained (first minor product mixed with Ru(COD)(COT), then major product, finally minor product mixed with $Ru(\eta^5\text{-}C_8H_{11})_2$). This suggests that the process of isomerization in the cationic ruthenium(IV) system is very similar to that observed in the neutral species but much more rapid due to the presence of an extra hydrogen (see Scheme II).

The ^1H NMR spectrum did not allow us to detect a cationic species corresponding to neutral $Ru(1\text{–}3\text{:}5\text{–}6\text{-}\eta\text{-}C_8H_{11})(\eta^5\text{-}C_8H_{11})$, but presumably this results from its high fluxionality. Another interesting phenomenon specific to the cationic system is that the bis(η^5-cyclooctadienyl) complex is no longer a dead-end; it equilibrates with the product of hydride migration to give coordinated 1,3-cyclooctadiene. This then explains the much higher reactivity of the cationic compounds.

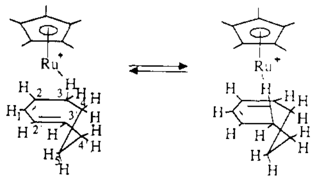
Reactivity of the Cationic Complexes (See Scheme III). The first reaction which was tried was to show that hydrogen transfer could be initiated by reactions with good donor ligands. Thus, in the presence of 3 equiv of $PMePh_2$, **2** reacts in CH_2Cl_2 to give after recrystallization white crystals of $[Ru(\eta^5\text{-}C_8H_{11})(PMePh_2)_3]BF_4$ (**6**). Spectroscopic data (^1H and ^{13}C NMR) confirm the presence of a 1,5-coordinated cyclooctadienyl ring and three phosphines. The complex is presumably very similar to that recently reported by Ashworth et al., $[Ru(\eta^5\text{-}C_8H_{11})(PMe_2Ph)_3]$,[27b] and to the tris solvato derivatives and was not studied further.

A somewhat similar ligand-exchange reaction was attempted with pentamethylcyclopentadiene. Hydrogen transfer was expected to lead to a similar (C_5Me_5) ruthe-

Scheme III. Reactions of 2 with Cyclic Hydrocarbons, Phosphines, and Donor Solvent



Scheme IV. Proposed Equilibrium Explaining the Spectroscopic Properties of 7



nium complex. 1 or 2 reacts with C_5Me_5H at room temperature, affording after 15 h a pale-yellow solution from which pale-yellow crystals of $[Ru(\eta^5\text{-}C_5Me_5)(C_8H_{12})]BF_4$ (7) could be obtained after recrystallization from CH_2Cl_2/Et_2O. The microanalytical data agree with this formulation, whereas the spectroscopic data (^1H and ^{13}C NMR data at 200 K or below) confirm the presence of a C_5Me_5 ring and of a η^5-coordinated cyclooctadienyl group in the complex (Tables II and III). Furthermore, a singlet at δ -9.77 ppm in ^1H NMR spectrum indicated the presence of hydrogen coordinated to ruthenium. At room temperature, the spectra only show broad peaks because of the fluxionality of the complexes. However, in the ^{13}C NMR spectra, all peaks are sharp except the one for C_3, which remains broad down to 168 K. Furthermore, the chemical shift of this carbon is significantly shifted upfield when compared to the corresponding one of 2. The most interesting feature is the observation of a doublet of doublets in the hydrogen-coupled spectrum (J_{C-H} = 150, 34 Hz). The 34-Hz coupling constant arises from coupling with the hydrogen near δ -10 ppm as shown by a selective decoupling experiment. In order to explain this coupling, we propose that the hydrogen at δ -9.77 ppm is part of a three-center Ru-H-C interaction. However, since the molecule is presumably symmetrical, the jump of the proton from one carbon (C_3) to the other ($C_{3'}$) is most probably a very low energy process (Scheme IV) and is rapid even at -70 °C. This would render the two carbons equivalent and explain the observation of a coupling constant of 34 Hz, which would be a mean value since it is about half of what is expected for H-C coupling in a three-center M-H-C agostic interaction (compare, for example, the value of 78 Hz in $[Ru(C_{10}H_{23})(C_6Me_6)]PF_6$,[6c] 66 Hz in the corresponding osmium complex,[6c] 50 Hz in $[Ir(C_{10}H_{13})(C_5Me_5)]PF_6$,[6c] and 61 Hz in $[Co(C_5Me_5)(C_2H_5)(P(OMe)_3)]BF_4$,[6d]).

Alternative possibilities exist for the structure of 7: (i) a hydride complex coupled to the C_8 ring via the metal or a through-space interaction, but to our knowledge this has never been observed; or (ii) proton capping a MC_2 triangle. This also has never been observed and would not explain why C_3 remains broad down to 168 K. It is noteworthy that, in the isoelectronic $[ReH(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_8H_{11})]^+$, which is clearly a hydride complex, no anomalous J_{C-H} was observed.[28]

It is not clear why 2 is a hydrido complex whereas 7 shows an agostic interaction. First, empirically the higher electron-releasing effect of C_5Me_5 when compared to C_8H_{11} would make the metal less reactive to break the C-H bond. Second, although in the crystal structure the hydride was observed far from the C_3 and $C_{3'}$ carbons, in agreement with molecular mechanics calculations, an equilibrium between the hydride and an agostic interaction involving rapid conversion from one carbon C_3 to $C_{3'}$ could exist. Thus, the resonance for C_3 is broad at low temperatures in the ^{13}C NMR spectrum in CD_2Cl_2, and we know that, in the presence of a donor solvent such as acetone or a ligand such as phosphine, rapid hydride migration to give coordinated 1,3-COD is observed even at low temperatures.

Complex 7 does not react with H_2 in acetone. Its reaction with P^iPr_3 only leads to deprotonation, which also occurs with NEt_3. We could then quantitatively isolate $Ru(C_5Me_5)(C_8H_{11})$ (8) as a white crystalline alkane soluble compound. Its ^1H NMR spectrum (Table II) is very similar to that of 5: a singlet for C_5Me_5 and the usual pattern for the η^5-cyclooctadienyl ring only shifted upfield when compared to 7. Neither 7 nor 8 react with hydrogen at room temperature, and in the case of 8, even at 100 °C no reaction was observed.

Reactions of 1, 2, and 3 with Olefins. Complexes 1, 2, and 3 have been shown to undergo rapid intramolecular transfer of hydrogen and also easy substitution reaction. We have been interested in testing whether we could use this high reactivity for stoichiometic and catalytic reactions involving transformation of alkenes.

Reactions with Ethylene. When ethylene is bubbled through a dichloromethane solution of 1 at 0°C, no apparent change in the solution is observed. We monitored this reaction by running ^{13}C NMR spectra of 1 at -80 °C, bubbling ethylene through the solution at 0 °C for 5 min and running a new NMR spectrum at -80 °C. What we observed was only a slight transformation of 1 into 2 and the formation of no other complex but the appearance of peaks corresponding to *cis*- and *trans*-2-butenes. The same reaction was performed in a bomb at 0°C under 30 atm of C_2H_4. We obtained mainly butenes (90%, [1-butene]:[*cis*-2-butene]:[*trans*-2-butene], 10:70:20) and small amounts of higher oligomers with a high turnover (1000 h^{-1}).

Reaction with 1-Hexene. The reaction was performed in acetone in the presence of a large excess of hexene after initial addition of 1 at -50 °C. We did not observe the formation of a new complex but rather obtained the 2 ⇔ 3 equilibrium, as expected. However, we observed by gas-liquid chromatography (GLC) that 1-hexene was isomerized. We carried out the same reaction under catalytic conditions ([1] 10^{-4}, 0.1 mol of 1-hexene or 1-octene). The system was found to be very active for isomerization (3200 turnover h^{-1}, [2-alkenes]:[3-alkenes], 40:60). It is noteworthy that, under 1 atm of H_2 in the same catalytic conditions, 1-hexene is quantitatively converted into hexane at room temperature (2 h, turnover 1200 h^{-1}). The reaction proceeds also in biphasic conditions, the catalysts being dissolved in water (12 h, turnover 36 h^{-1}). However, in both cases, the catalyst is decomposed at the end of the reaction.

Reaction with Norbornene. Complex 2 catalyses the ring-opening polymerization of norbornene under very mild conditions (see Table VI). In ethanol, the reaction proceeds at room temperature and yields a white precipitate of the polymer (turnover 67 h^{-1}). In dichloromethane, the initial rate of the reaction is high but decreases rapidly because of the increasing viscosity of the solution which becomes a gel. Interestingly, the two polymers show different fractions of cis (c) and trans (t) double bonds (in ethanol σ-C = 0.56 whereas in CH_2Cl_2 σ-C = 0.69); furthermore their location is different (ethanol r_c = cc/ct = 7.04, r_t = tt/tc = 1.74; CH_2Cl_2 r_c = 7.04, r_t = 1).[29] It is noteworthy that the polymers found in these reactions show a high amount of cis double bonds whereas almost only trans double bonds are in the polymers obtained from $RuCl_3 \cdot 3H_2O$ (σ-C = 0.05).[30] This could be related to the

---

(29) For detailed definitions and discussion of these factors see: Ardill, H. E.; Greene, R. M. E.; Hamilton, J. G.; Ho, H. T.; Irin, K. J.; Lapienis, G.; McCann, G. M.; Rooney, J. J. *ACS Symp. Ser.* **1985**, *286*, 275.

(30) Gillan, E. M. D.; Hamilton, J. G.; McKey, O. N. D.; Rooney, J. J. *J. Mol. Catal.* **1988**, *46*, 359.

presence of sterically more demanding ligands on **2**.

Reaction with Cyclopentene and Benzene. Compound **2** can react in two ways with cyclopentene. It can give rise either to hydrogen transfer or to ring-opening polymerization. Thus, cyclopentene reacts with protonated solutions of Ru(COD)(COT) to give oils which were shown to undergo rapid fluxional processes even at 200 K. However, ^{1}H NMR spectra at −80 °C of the complex obtained (**9**) clearly showed the presence of a cyclopentadienyl ring at δ 6.5 ppm, a high field proton at δ −9.6 ppm, and broad peaks at the positions expected for an η^5-coordinated ring. It is thus obvious that hydrogen transfer is more rapid that polymerization. Only a small amount of polymers were found in the reaction mixtures and are not characterized. Unfortunately, we do not have good enough spectroscopic data to decide whether complex **9** is a ruthenium(IV) hydride complex or a ruthenium(II) derivative showing an agostic interaction (both are probably present in the fluxional process of the molecule). At room temperature, only the Cp ring and the high field proton are visible at the same chemical shift. The presence of a similar cyclopentadienyl ring between **5** and **9** and the high field proton observed at the same chemical shift is in favor of a similar agostic structure, i.e., $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_8H_{12})]BF_4$.

In the case of cyclohexene, a very complex reaction was observed and was not elucidated. However, we checked that no benzene complex was present by reacting **2** with 1 equiv of C_6H_6 at room temperature, affording after 15 h yellow cationic $[Ru(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_8H_{11})]BF_4$, which had been previously obtained by Vitulli, et al. by direct protonation of Ru(COD)(COT) in benzene.[9]

Note that the latter reaction is general. Vitulli et al. have prepared a number of $[Ru(arene)(C_8H_{11})]^+$ derivatives by direct protonation of Ru(COD)(COT) in the neat liquid arene. However, we have been able to extend this reaction to solid arenes. Thus, $[Ru^{II}(\eta^5\text{-}C_8H_{11})_2]BF_4$ reacts with stoichiometric amounts of C_6Me_6 to give a crystalline cationic derivative, $[Ru(\eta^6\text{-}C_6Me_6)(\eta^5\text{-}C_8H_{11})]BF_4$ (**10**), which shows an ^{1}H NMR spectrum very similar to the benzene complex.

Experimental Section

All experiments were conducted under dry argon by using conventional Schlenk tube techniques. Infrared spectra were recorded as Nujol mulls by using a Perkin-Elmer grating diffractometer. ^{1}H NMR spectra were recorded by using a WH90 or WM250 Bruker FT NMR spectrometer. Microanalyses were performed by the "Centre de Microanalyse du CNRS" or in the lab. GLC analysis was performed on an Intersmat IGC 121FL instrument. Ru(COD)(COT) was prepared according to published methods.[31]

$[RuH(C_8H_{10})(C_8H_{12})]BF_4$ (1). Ru(COD)(COT) (200 mg, 0.63 mmol) was dissolved in 15 mL of CH_2Cl_2 and cooled to −50 °C. To the resulting yellow solution was added $HBF_4{\cdot}Et_2O$ (145 μL, 0.64 mmol). The solution immediately turned yellow brown and returned slowly to yellow. After 10 min, the volume of the solution was reduced, diethyl ether was added up to floculation, and the solution was finally filtered off, affording at −18 °C yellow crystals of the complex. Yield ca. 80%. Anal. Calcd for $C_{16}H_{23}RuBF_4{\cdot}0.5CH_2Cl_2$: C, 44.46; H, 5.16. Found: C, 44.59; H, 5.63. The presence of CH_2Cl_2 in the crystals was attested by ^{1}H and ^{13}C NMR spectra.

$[RuH(C_8H_{11})_2]BF_4$ (2). The procedure is the same as for **1** but the solution was allowed to warm to room temperature and to react overnight. It was then recrystallized from CH_2Cl_2/Et_2O. Yield ca. 90%. Anal. Calcd for $C_{16}H_{23}RuBF_4$: C, 47.67; H, 5.71. Found: C, 47.34; H, 5.32.

Reaction of Solutions of Ru(COD)(COT) Protonated with NEt_3. Ru(COD)(COT) was protonated as for **1** or **2**, and NEt_3 (1 equiv) was added after 15 min at −50 °C, after 1 h at room temperature, 6 h at room temperature, or 15 h at room temperature. In the first case, the solution was allowed to warm up to ca. −10 °C at which temperature deprotonation occurred. In the other cases, the reaction was immediate. The solutions were then evaporated to dryness, extracted with hexane, and evaporated to dryness again. The residues were analyzed by ^{1}H NMR, showing various spectroscopic yields of Ru(COD)(COT), $Ru(1\text{-}3{:}5\text{-}6\text{-}\eta\text{-}C_8H_{11})(\eta^5\text{-}C_8H_{11})$, and $Ru(\eta^5\text{-}C_8H_{11})_2$.

$[Ru(C_5Me_5)(C_8H_{11})]BF_4$ (7). The procedure was the same as for **2** but C_5Me_5H (100 μL, 0.62 mmol) was added to the solution at −50 °C. The solution then was allowed to react overnight and was recrystallized from $CH_2Cl_2{\cdot}Et_2O$. Yield ca. 80%. Anal. Calcd for $C_{18}H_{27}RuBF_4$: C, 50.25; H, 6.28. Found: C, 50.09; H, 5.75.

$[Ru(C_8H_{11})(PMePh_2)_3]BF_4$ (6). The procedure was the same as for **7** using 480 μL (1.92 mmol) of $PMePh_2$. After stirring for 10 min, the reaction mixture was evaporated in vacuo and recrystallized from CH_2Cl_2/Et_2O. Yield ca. 70%. Anal. Calcd for $C_{47}H_{50}P_3RuBF_4$: C, 63.03; H, 5.58. Found: C, 62.37; H, 5.04.

NMR Observation of $[Ru(C_5H_5)(C_8H_{11})]BF_4$ (9). The procedure was the same as for **7** using 2 mL (excess) of cyclopentene. After 15 h in solution, the reaction mixture was evaporated to dryness and washed with diethyl ether. Attempts of recrystallization failed. No analytical data were obtained. A new compound is observed by NMR for which the title formulation is proposed by comparison with **7**.

$[Ru(C_6Me_6)(C_8H_{11})]BF_4$ (10). The procedure is the same as for **7** using 105 mg (0.65 mmol) of C_6Me_6. The analogous $[Ru(C_6Me_6)(C_8H_{11})]CF_3SO_3$ (**10′**) was prepared similarly from Ru(COD)(COT) (300 mg, 0.95 mmol), CF_3SO_3H (143 mg, 0.95 mmol), and C_6Me_6 (160 mg, 0.97 mmol) and recrystallization from CH_2Cl_2/Et_2O. Yield 80%. Anal. Calcd for $RuC_{21}H_{29}SO_3CF_3$: C, 48.55; H, 5.58. Found: C, 48.88; H, 5.50. The identity of the ^{1}H and ^{13}C NMR spectra of **10** and **10′** was verified.

Catalytic Runs. Hydrogenation. The reactions were performed at room temperature under 1 atm of hydrogen using 5 mL (40 mmol) of 1-hexene, 13 mg of $[RuH(C_8H_{11})_2]BF_4$ (**2**), (0.033 mmol), and 20 mL of CH_2Cl_2 in the case of homogeneous reactions or 20 mL of H_2O in the case of the biphasic reaction (water/hydrocarbon mixture, no added solvent). **2** is totally soluble in water. The reaction was monitored by GLC (3-m × $^1/_8$-in. column filled with 10% SE 30 on gas chrom Q 80/100-mesh, nitrogen flow rate 2.5 mL/min, oven temperature 25 °C).

1-Hexene Isomerization. In a Schlenk tube, **2** (23.8 mg, 0.06 mmol) was dissolved in 10 mL of dichloromethane. 1-Hexene (1 mL) was added at room temperature. The reaction was monitored by GLC analysis under the same conditions as reported above.

Ethylene Dimerization. **2** (100 mg, 0.25 mmol) was dissolved in 20 mL of dichloromethane and transferred to an autoclave. Ethylene was then introduced at a constant pressure of 5 atm while stirring the solution. At the end of the reaction, the autoclave was cooled at −20 °C and depressurized, and the products were collected in a flask of known weight. The conversion of ethylene was determined by weight and the identification of the products by GLC.

Reactions with Norbonene. (a) In Ethanol. A solution of **2** (50 mg, 0.125 mmol) and norbonene (15 g, 160 mmol) in 50 mL of ethanol was stirred for 8 h at room temperature, after which time a white precipitate of polymer formed. The polymer was then filtered and washed with 20 mL of ethanol. Dissolution in benzene followed by precipitation by ethanol afforded the pure polymer characterized by spectroscopic methods (see text). Yield 45%.

(b) In Dichloromethane. The procedure is the same as in (a) above using 53 mg (0.133 mmol) of **2**, 15 g of norbonene, and 50 mL of CH_2Cl_2. The solution became rapidly very viscous. After 8 h, the gel was pumped in vacuo. The polymer was purified as above by dissolution in benzene and precipitation from ethanol. Yield 32%.

X-ray Structure of 2. Collection and Reduction of X-ray Data. The crystals belong to the monoclinic system, space group *C*2/*c*. The selected crystal was glued on a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 25

---

[31] Pertici, P.; Vitulli, G.; Paci, M.; Porri, L. *J. Chem. Soc., Dalton Trans.* **1980**, 1961.

462 *Organometallics* **1991,** *10,* 462–466

reflections in the range $11 < \theta < 14°$. A summary of crystal and intensity collection data is given in Table V. A total of 2465 reflections (*hkl* and *hkl*) were recorded at a 2θ (Mo) maximum of 60° by procedures described elsewhere.[32] Data reduction was then performed.[33] Intensity standards, monitored every 2 h, showed no significant variation. From a ψ scan on four reflections having $\chi > 80°$, empirical absorption corrections[34] were made ($\mu = 9.8$ cm^{-1}, $T_{\min} = 0.91$, $T_{\max} = 1.00$). Equivalent reflections (0*kl* and 0*kl*) were merged ($R_{av} = 0.012$).

Structure Solution and Refinement. The structure was solved by the heavy-atom method. The Ru atom was located. The full-matrix least-squares refinement and difference Fourier processes were achieved with the SHELX76 program[35] with 1722 reflections having $F_o^2 \geq 3\sigma(F_o^2)$. Space group $C2/c$ implies that the B atom is in a special position, the four F atoms being thus disordered. The structure was then refined in the noncentrosymmetric space group Cc. Correlations being greater than 0.9 between parameters of C atoms and the disorder of the BF_4 anion being always present, space group $C2/c$ was then considered as the correct one. The four F atoms were assigned an occupancy factor of 0.5. The BF_4 anion was refined isotropically. Ru and C atoms were refined anisotropically. All H atoms were located on a difference Fourier map except that bonded to Ru atom; they were introduced in calculations in idealized positions (C–H = 0.97 Å) with the isotropic temperature factor $U = 0.09$ Å kept fixed.

The terminal Ru hydride, located on a difference Fourier map at a height of 0.65 e/Å^3, was refined isotropically. Its location is in agreement with molecular mechanic calculations.[36]

The atomic scattering factors used were those proposed by Cromer and Waber[37] with anomalous dispersion effects.[38] Scattering factors for the hydrogen atoms were taken from Stewart et al.[39]

The final full-matrix least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$ converged to $R = 0.031$ and $R_w = 0.033$ with $w = [\sigma^2(F_o) + (0.02F_o)^2]^{-1}$. The error in an observation of unit weight was $S = 1.34$ with 1722 observations and 98 variables. An analysis of variance showed no unusual trends. In the last cycle of refinement, the mean parameter shift was 0.03σ (maximum value being 0.41σ on F parameters). A final difference Fourier map showed a residual electron density of 0.3 e/Å.

All calculations were performed on a VAX-11/730 DEC computer.

The final fractional atomic coordinates are listed in Table VI. An ORTEP plot[40] of the $[RuH(C_8H_{11})_2]$ cation is shown in Figure 1.

Acknowledgment. We thank CNRS for support, Dr. Y. S. Huang for experimental assistance, and Dr. D. Neibecker for helpful discussions.

Supplementary Material Available: Tables listing atomic coordinates, thermal parameters, bond lengths and angles, and least-squares plane equations (5 pages); a table listing observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

---

(32) Mosset, A.; Bonnet, J.-J.; Galy, J. *Acta Crystallogr.* **1977,** *B33,* 2639.

(33) Frenz, B. A. *SDP. Structure Determination Package*; Enraf-Nonius: Delft, Holland, 1082.

(34) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968,** *A24,* 351.

(35) Sheldrick, G. M. SHELX-76. Program for Crystal Structure Determination. University of Cambridge England, 1976.

(36) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980,** 2509.

(37) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.B, pp 99–101.

(38) Cromer, D. T. Reference 37, Table 2.3.1, p 149.

(39) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965,** *42,* 3175.

(40) Johnson, C. K. ORTEP. Report ORNL-3794, 1965; Oak Ridge National Laboratory: Oak Ridge, TN.

Hydrosilylation of Phenylacetylene via an $Os(SiEt_3)(\eta^2\text{-}H_2)$ Intermediate Catalyzed by $OsHCl(CO)(P^iPr_3)_2$

M. A. Esteruelas, L. A. Oro,* and C. Valero

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza—CSIC, 50009 Zaragoza, Spain

Received May 15, 1990

$OsHCl(CO)(P^iPr_3)_2$ is found to be a very active and highly selective catalyst for the addition of triethylsilane to phenylacetylene. *trans*- and *cis*-$PhHC{=}CH(SiEt_3)$ are selectively obtained in high yields depending on the reaction conditions. Although the vinyl compound $Os((E)\text{-}HC{=}CHPh)Cl(CO)(P^iPr_3)_2$ is the main species under hydrosilylation conditions, the catalytic reaction proceeds via the silyl dihydrogen intermediate $Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ according to the following set of reactions: $OsHCl(CO)(P^iPr_3)_2 + HSiEt_3 \rightarrow Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ and $Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2 + PhC_2H \rightarrow OsHCl(CO)(P^iPr_3)_2$ + *trans* and *cis*-$PhHC{=}CH(SiEt_3)$ in which the reaction between $OsHCl(CO)(P^iPr_3)_2$ and triethylsilane is the rate-determining step.

Introduction

The addition of silanes to acetylenes is a reaction of considerable interest in connection with important industrial processes.[1] This reaction is catalyzed by several nickel,[2] palladium,[3] platinum,[4] cobalt,[2] rhodium,[5] iridium,[6] iron,[2] and ruthenium[7] complexes, but to the best of our knowledge, no osmium compounds have been reported

---

(1) Noels, A. F.; Hubert, A. J. In *Industrial Applications of Homogeneous Catalysis*; Mortreux, A., Petit, F., Eds.; D. Reidel Publishing Company: Boston, 1988; Chapter 3.1.3.

(2) Lappert, M. F.; Nile, T. A.; Takahashi, S. *J. Organomet. Chem.* **1974,** *72,* 425.

(3) (a) Kusumoto, T.; Hiyama, T. *Tetrahedron Lett.* **1987,** *28,* 1807. (b) Chatani, N.; Takeyasu, T.; Horiuchi, N.; Hanafusa, T. *J. Org. Chem.* **1988,** *53,* 3539.

(4) (a) Green, M.; Spencer, J. L.; Gordon, F.; Stone, A.; Tsipis, C. A. *J. Chem. Soc., Dalton Trans.* **1977,** 1525. (b) Iovel, I. G.; Goldberg, Y. Sh.; Shymanska, M. V.; Lukevics, E. *Organometallics* **1987,** *6,* 1410. (c) Licchelli, M.; Greco, A. *Tetrahedron Lett.* **1987,** *28,* 3719. (d) Ohshita, J.; Ishikawa, M. *Chem. Express* **1988,** *3,* 179. (e) Caseri, W.; Pregosin, P. S. *Organometallics* **1988,** *7,* 1373.

0276-7333/91/2310-0462$02.50/0