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Protonation of Bis(ethylene)(η^5-indenyl)rhodium and (Cyclooctatetraene)(η^5-indenyl)rhodium: A 500-MHz Nuclear Magnetic Resonance Study

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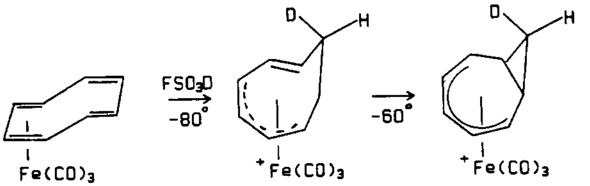
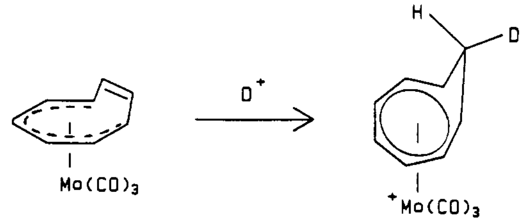
A 500-MHz ^{1}H and 125-MHz ^{13}C NMR spectroscopic study of the protonation of bis(ethylene)(η^5-indenyl)rhodium(I) with trifluoroacetic acid revealed the formation of the bis(ethylene)(η^6-indene)rhodium(I) cation in which the metal has migrated from the 5- to the 6-membered ring. Use of CF_3CO_2D led to the incorporation of deuterium at the 1- and 3-positions of the indene and also into the ethylene ligands; the course of the reaction was monitored by ^{2}H NMR spectroscopy. In contrast, protonation of (cyclooctatetraene)(η^5-indenyl)rhodium yields the (1–3:6,7-η-cyclooctatrienylium)(η^5-indenyl)rhodium(I) cation as the major product and (1–5-η-bicyclooctadienylium)(η^5-indenyl)rhodium(I) trifluoroacetate as the minor product. When CF_3CO_2D is used, deuterium is found only at the 8-endo position of the methylene groups of both products. The mechanisms of these reactions are discussed in terms of initial protonation at the rhodium atom with subsequent migration onto the endo face of the attached ligands.

Introduction

Protonation of metal–polyene complexes can, in principle, occur at a variety of sites;[1] they may even proceed via initial attack at the metal center with subsequent migration of the metal hydride onto the π-complexed alkene. In some cases, the stereochemistry of attack has been unequivocally established by using deuterons rather than protons. Typically, (η^4-cyclooctatetraene)$Fe(CO)_3$ (**1**) reacts with FSO_3H–FSO_2Cl at −80 °C to generate the (1–5-η-cyclooctatrienylium)$Fe(CO)_3$ system **2** which in turn rearranges above −60° to produce the (2–6-η-bicyclo[5.1.0]octadienylium)$Fe(CO)_3$ cation **3**. In this case, protonation occurred by exo attack.[2] In contrast, protonation of (1–6-η-cyclooctatetraene)$Mo(CO)_3$ (**4**) proceeds via endo attack to give the homotropylium species **5**, presumably via the intermediacy of a molybdenum hydride.[3]

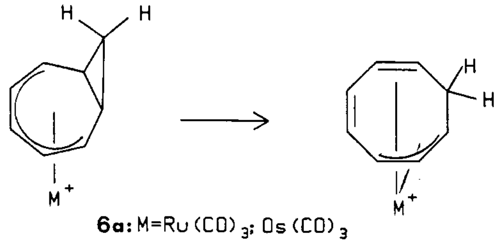


1 **2** **3**



4 **5**

Ruthenium and osmium analogues of **3** are known, but these subsequently ring open to give the corresponding 1–3:6,7-η-cyclooctatrienylium complexes **6**.[4] These studies have been extended to include the protonation of η^4-cyclooctatetraene complexes of the Co, Rh, Ir triad in which the metal also bears a cyclopentadienyl or pentamethylcyclopentadienyl ligand.[5,6]



6a: M=Ru(CO)$_3$; Os(CO)$_3$

6b: M=CpCo; CpRh; CpIr; (C$_5$Me$_5$)Rh; (C$_5$Me$_5$)Ir

In recent years, the chemistry of indenyl–metal complexes has received much attention. Their enormously enhanced reactivity compared to that of their cyclopentadienyl analogues has been rationalized in terms of a slippage from an η^5- to an η^3-bonding mode.[7,8] This interpretation has received convincing support from kinetic studies on ligand replacement reactions,[9] X-ray crystallographic data,[10] decreased barriers to fluxional processes,[11,12]

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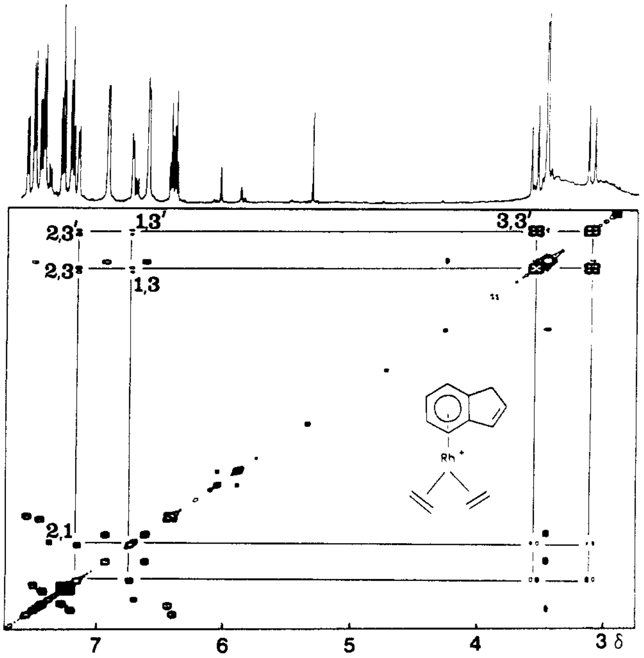

Figure 1. Two-dimensional 500-MHz ^{1}H NMR COSY spectrum of the reaction products from the protonation of (η^5-indenyl)-Rh(C_2H_4)$_2$ with CF_3CO_2H. The correlations indicated are those for the 5-membered ring in **8a**.

and recently the isolation of an η^3-indenyl complex.[13] The ability of organometallic fragments to migrate over the surface of fused ring systems reaches its zenith in naphthalene, fluorenyl, and indenyl systems where one can effect complete transfer of an ML_n unit from one ring to another.[14-17]

The recent report by Salzer[18] that protonation of (η^5-indenyl)-Rh(diene) systems leads to an η^5 to η^6 migration of the metal–diene fragment prompts us to present our own results in this area. In particular, we consider the effect of protonation on bis(alkene)(indenyl)rhodium complexes in which the proton may choose to attack (a) the metal, (b) the indenyl ligand, or (c) coordinated or (d) uncoordinated double bonds in the polyene. Furthermore, deuteronation studies allow one to distinguish between exo and endo attack on the coordinated ligands.

Results and Discussion

The parent molecule of the series bis(alkene)(indenyl)rhodium is, of course, the bis(ethylene) complex **7a**, the molecular dynamics of which we have recently elucidated.[12] In this system it is possible to slow (on the NMR time scale) not only the rotation of the ethylenes about the Rh–C_2H_4 axis but also the rotation of the Rh(C_2H_4)$_2$ unit about the Rh–C_5-ring axis. (The relevance of the fluxional behavior of this complex to its reaction with protons will become apparent.) Our goal was to elucidate the site of attack of protons and to determine whether the rhodium retained its bonding to the 5-membered ring.

Table I. ^{1}H and ^{13}C NMR Data for Indene and for 8a

	indene	[(indene)Rh(C_2H_4)$_2$]$^+$ (**8a**)
H-1	6.63 (d) (J_{1-2} = 5.2 Hz)	6.75 (d) (J_{1-2} = 5.5 Hz)
H-2	6.94 (d)	7.17 (m) ($J_{2-3} \approx$ 1 Hz)
H-3	3.45 (s)	3.09 (d), 3.53 (d) (J_{3-3} = 24 Hz)
H-4	7.52 (d) (J_{4-5} = 7.3 Hz)	7.57 (d) (J_{4-5} = 6.1 Hz)
H-5	7.23 (t) (J_{5-6} = 7.3 Hz)	6.41 (t) (J_{5-6} = 6.0 Hz)
H-6	7.30 (t) (J_{6-7} = 7.4 Hz)	7.45 (t) (J_{6-7} = 6.0 Hz)
H-7	7.44 (d)	7.45 (d)
C_2H_4		2.3 (br), 3.2 (br)
C-1	134.7	127.0
C-2	132.2	146.1
C-3	39.4	38.2
C-4	121.3	105.5
C-5	124.9	99.9
C-6	126.6	102.4
C-7	124.1	102.3
C-8	145.3^a	122.8^a
C-9	144.2^a	120.8^a
C_2H_4		56.0 (J_{Rh-C} = 12.1 Hz)

^{a} Assignments could be reversed.

Accordingly, trifluoroacetic acid was added dropwise to (indenyl)Rh(C_2H_4)$_2$ in CD_2Cl_2 and the 500-MHz ^{1}H NMR spectrum recorded at room temperature. A typical example of the spectra obtained appears in Figure 1. Because of the multitude of peaks which indicated the presence not only of unreacted starting material but also of at least two products, the 2D COSY spectrum[19,20] was obtained. The conventional 1D spectrum, presented as a contour plot, lies along the diagonal while off-diagonal peaks indicate which proton resonances are related via scalar couplings. The network of coupled spins immediately reveals which proton environments must be assignable to the same molecule since all the couplings observed are intramolecular interactions. In Figure 1, we indicate the resonances attributable to the [(η^6-indene)Rh(C_2H_4)$_2$]$^+$ cation **8a** in which protonation of the 5-membered ring has brought about migration of the ML_2 unit onto the 6-membered ring. Precedents for such a process have been cited already. The ^{1}H–^{13}C shift-correlated two-dimensional NMR experiment[19,21] allowed the complete assignment of the ^{13}C spectrum and was in accord with the picture afforded by the ^{1}H NMR data.

Addition of excess acid resulted in formation of free indene (or 1-methylindene when **7b** was protonated). Werner[22] has noted that the protonation of (η^5-indenyl)-Rh(PMe_3)$_2$ in which the metal is a relatively strong Lewis base also results in loss of indene when CO or excess phosphine is added. We had also protonated (η^5-indenyl)(1,5-cyclooctadiene)rhodium (**9**) and found an analogous η^5 to η^6 shift as in **10**, but this observation has since been reported independently by Salzer and Täschler,[18] who also studied the corresponding norbornadiene complex. Since our data are in accord with theirs, we need not discuss them further. Chemical shift and coupling constant data are collected in Table I.

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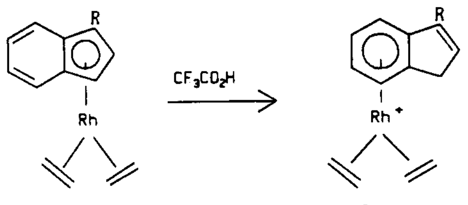
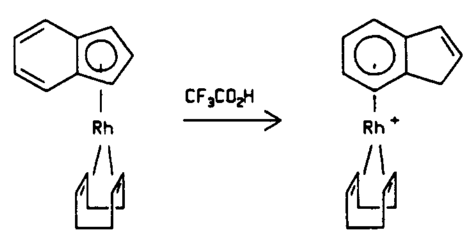


7a R = H **8a**

7b R = Me **8b**



9 **10**

Of more interest to us was the question whether protonation occurred via direct attack on the exo face of the ligand or rather via initial formation of a rhodium hydride with subsequent migration onto the endo face of the indenyl moiety. The methylene protons of **8a** which resonate at δ 3.53 and 3.09 comprise an exo–endo pair; however, attempts to assign them unambiguously via their different nuclear Overhauser interactions with the ethylene protons[23] were inconclusive. Nevertheless, **7a** was treated with CF_3CO_2D to see whether stereospecific deuteronation of only one of the methylene positions was observed. In fact, it turns out that *both* methylene proton resonances at C-3 are diminished in intensity as also is the vinylic peak at C-1. After several hours, the three aforementioned resonances for the protons at C-1 and C-3 have completely disappeared while the former multiplet at δ 7.17 assigned to the vinylic proton at C-2 has become a clean singlet. These observations are confirmed by the ^2H spectrum (see Figure 2) which exhibits sharp resonances at δ 6.8, 3.5, and 3.1 together with a broad resonance at δ 2.8. It is thus apparent that deuterium is incorporated not only at the 1- and 3-positions of the 5-membered ring but also into the ethylene ligands. This latter phenomenon was not obviously detectable in the 500-MHz ^1H NMR spectrum since at this field the ethylene resonances have almost disappeared into the base line as rotation about the Rh–C_2H_4 axis slows on the NMR timescale;[12] the ethylene peak only sharpens up at this field when the temperature is raised. However, in the ^2H spectrum (which is recorded at only 76 MHz on a 500-MHz instrument) the chemical shift difference between the "inside" and "outside" deuterons of the ethylene is reduced by a factor of 6.5 relative to the situation with protons. Thus the ethylene resonance is only slightly broadened in the ^2H spectrum shown in Figure 2 just as it is for protons on an 80-MHz instrument. The occurrence of multiple deuteriation in the 5-membered ring of **8a** requires that the protonation (deuteronation) reaction must be reversible so as to allow the original protons the opportunity to escape from the molecule. This reversibility is also indicated by the observation in the ^2H spectrum of a resonance attributable to deuterons in the 1- and 3-positions of the starting material, viz., (indenyl)Rh$(C_2H_4)_2$ (**7a**).

The observation of deuterium incorporation into the ethylene ligands in **8a** parallels the important result described by Brookhart, Green, and Pardy[24] concerning the fluxional behavior of $(C_5H_4R)Co(C_2H_4)_2$ in acidic solution. In that case, the exchange process

$$[CpM(H)(C_2H_4)_2]^+ \rightleftarrows [CpM(C_2H_4)(C_2H_5)]^+$$

is mediated via an agostic hydrogen;[25] in the present case, an agostic hydrogen interaction between the rhodium atom and an ethylene ligand is an obvious mechanistic possibility and would, in principle, be detectable at low temperature. To this end, **7a** in CD_2Cl_2 was treated with CF_3CO_2H at −90 °C and the ^1H NMR spectra recorded over the range −90 to +30 °C. At no stage did we observe a high-field resonance attributable to a rhodium hydride; indeed, the spectrum changed very little over the temperature range except for the nonequivalence of the ethylene protons brought about by the cessation of Rh–olefin rotation on the NMR timescale. We thus conclude that, unlike $[CpCo(H)(C_2H_4)_2]^+$ which adopts a ground-state geometry possessing an agostic hydrogen, the proton added to (indenyl)Rh$(C_2H_4)_2$ is stored in the 5-membered ring. Clearly, this proton can undertake excursions via rhodium into the ethylene ligands, but the barrier is so high (and the rate of exchange so slow) as to preclude its observation by NMR line-broadening techniques.

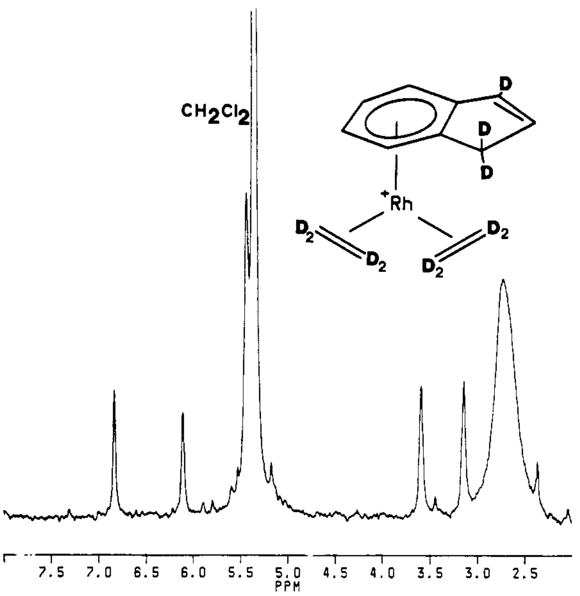
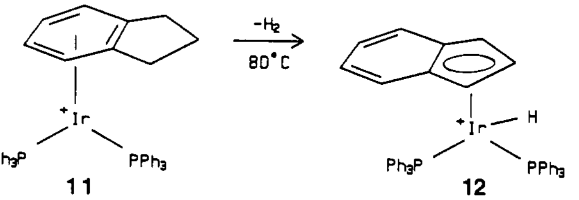


Figure 2. 76-MHz ^2H NMR spectrum of the product of the reaction of (η^5-indenyl)Rh$(C_2H_4)_2$ with CF_3CO_2D; the reaction had been proceeding at 0 °C for 16 h.

Interestingly, Crabtree[14] has noted that $[(\eta^6\text{-indan})Ir(PPh_3)_2]^+$ (**11**) loses hydrogen from the 5-membered ring to generate $[(\eta^5\text{-indenyl})Ir(H)(PPh_3)_2]^+$ (**12**), in which the proton is bonded to the relatively basic iridium atom.



11 **12**

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[23] This technique has been used to differentiate the "inner" and "outer" ethylene protons in $CpNi(C_2H_4)CH_3$: Benn, R. *Org. Magn. Reson.* **1983**, *21*, 723.

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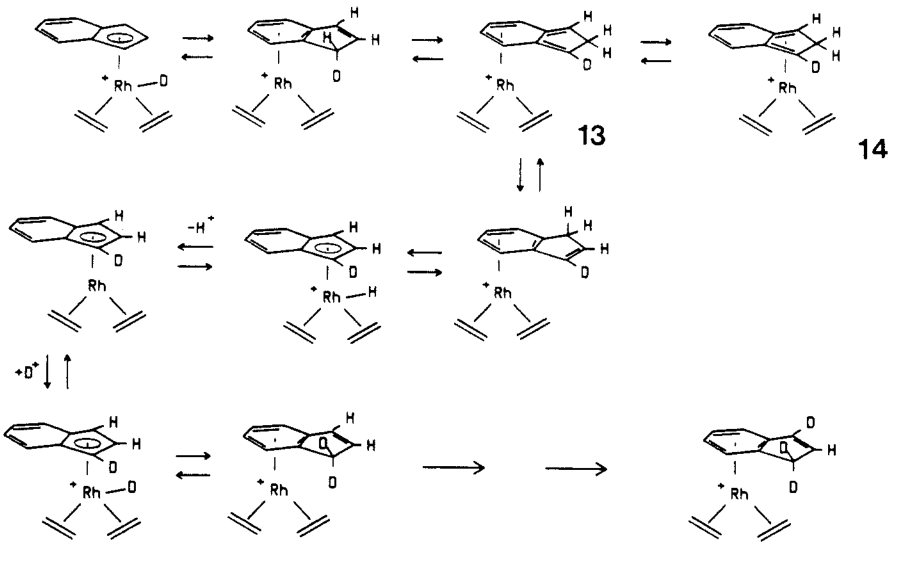
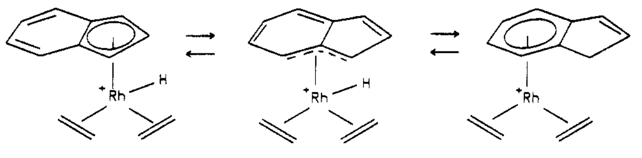
Scheme I. Proposed Mechanism to Incorporate Deuterium Only at Positions C-1 and C-3 in the Indenyl Ring of 8a



Scheme II. Proposed Mode of Migration of Rhodium From the 5- to the 6-Membered Ring



Nevertheless, one fact is clear, protonation of **7a** must occur at the metal center and this implies that initial transfer from rhodium to the indenyl ligand would place deuterium initially in the endo position of the methylene group at C-3. If, for the moment, we discount the possibility of direct exo protonation, then scrambling between the exo and endo positions can be accomplished via a series of symmetry-allowed [1.5] suprafacial sigmatropic shifts[26] as in Scheme I. One would have to assume that the hydrogen migrations occur only on the exo face of the 5-membered ring since the hydrogen atom originally at C-2 never leaves this site. We note that such a mechanism would require the intermediacy of an isoindene complex,[27] such as **13** or **14**. However, recent work by Carpenter[28] casts doubt on the viability of exo migrations, and hence these results are perhaps more readily explained in terms of competitive exo vs. endo (via metal) protonations.

The question of the mechanism of migration of the rhodium fragment from one ring to the other is particularly fascinating, and one must turn to calculations to gain some insight into this problem. Haptotropic migrations have been extensively studied by using extended Hückel methods, and it has been shown[29] that the least motion pathway across the center of the bond shared by two rings is by no means the lowest energy route. The favored transit involves migration via the periphery of the rings, and a tentative proposal adopting such an approach is presented in Scheme II.

We turn now to the case of a molecule, viz., (η^5-indenyl)(1,2:5,6-η-cyclooctatetraene)rhodium (**15**), in which protonation could occur not only at the indenyl ring or the metal atom but also at either the coordinated or uncoordinated double bonds of the polyene. As with the bis(ethylene) complex **7** protonation of **15** with CF_3CO_2H at room temperature yielded a plethora of NMR peaks that were readily assignable to particular molecules by using the ^1H–^1H two-dimensional COSY sequence.[19] As shown in Figure 3, the major product possesses an obvious network of nine connected spins, clearly indicating that protonation has occurred on the COT ligand. It is readily apparent that the (η^5-indenyl)Rh unit is now bonded to a 1–3:6,7-η-cyclooctatrienylium moiety, as in **17**. Furthermore, the minor product of the protonation of **15** was identified as (2–6-η-bicyclo[5.1.0]octadienylium)(η^5-indenyl)rhodium (**16**). This follows the pattern previously

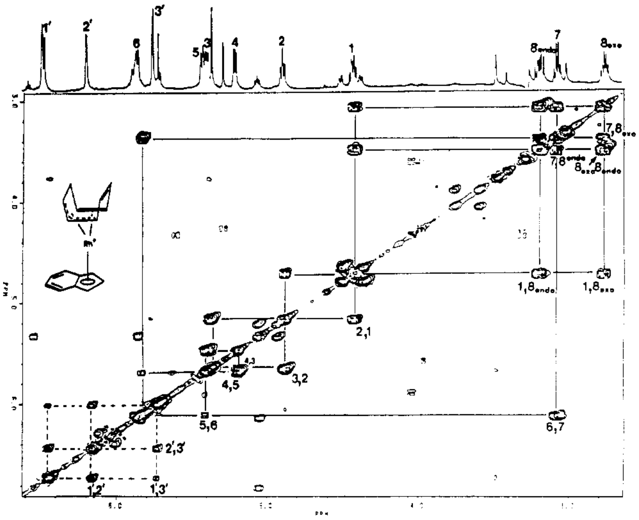
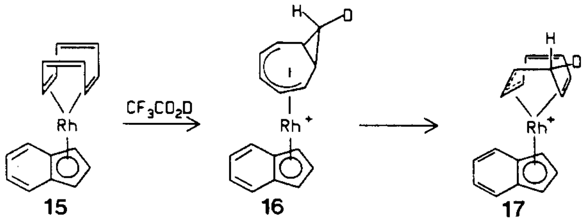


Figure 3. Section of the two-dimensional 500-MHz ^1H COSY spectrum of the reaction products from the protonation of (η^5-indenyl)Rh(COT) with CF_3CO_2H. The correlations indicated are those for the cyclooctatrienylium ligand in 17.



15 **16** **17**

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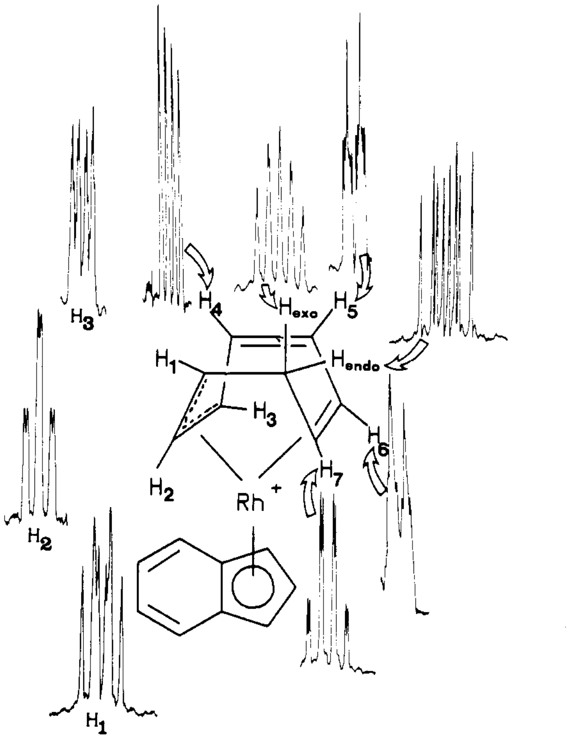


Figure 4. Selected peaks from the 500-MHz ^1H spectrum of **17**; the individual resonances are those of the protons in the cyclooctatrienylium ligand.

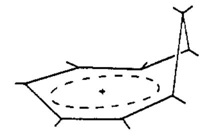
Table II. ^1H NMR Data for Molecules 15, 16, and 17[a]

	15	16	17
H-1	4.18 (d)	2.20 (d,d,t)	44.4 (t,d)
H-2	4.18 (d)	5.98 (m)	4.94 (t,d)
H-3	5.56 (s)	5.12 (d,d,d)	5.46 (d,d,d)
H-4	5.56 (s)	6.71 (t)	5.27 (d,d)
H-5	4.18 (d)	5.12 (d,d,d)	5.49 (d,m)
H-6	4.18 (d)	5.98 (m)	5.97 (d,t)
H-7	5.56 (s)	2.20 (d,d,t)	3.00 (q,d)
H-8_{exo}		1.34 (q)	2.67 (t,d,d)
H-8_{endo}		1.40 (t,d)	3.12 (d,d,d)
H-1′	5.18 (d)	*b*	6.61 (d)
H-2′	6.22 (q)	*b*	6.30 (q)
H-3′	5.18 (d)	*b*	5.84 (d)
H-4′-7′	7.2–7.4	*b*	7.7–7.4

[a] Coupling constants (in Hz): **15**, $J_{1'-Rh} = 1.3$, $J_{1'-2'} = J_{2'-3'} = J_{2'-Rh} = 2.8$; **16**, $J_{1-2} = J_{6-7} = 2.5$, $J_{1-7} = 2.5$, $J_{2-3} = J_{5-6} = 7.5$, $J_{3-5} = 1.1$, $J_{3-4} = J_{4-5} = 6.6$, $J_{1-8exo} = J_{7-8exo} = J_{8exo-8endo} = 5.1$, $J_{1-8endo} = J_{7-8endo} = 8.2$; **17**, $J_{1-2} = 8.1$, $J_{2-3} = 8.1$, $J_{3-4} = 3.8$, $J_{4-5} = 7.6$, $J_{5-6} \approx 1$, $J_{6-7} = 7.5$, $J_{7-8exo} = 7.3$, $J_{7-8endo} = 7.3$, $J_{8exo-8endo} = 13.1$, $J_{8exo-1} = 6.8$, $J_{8exo-2} = 1.2$, $J_{8endo-1} = 9.3$, $J_{3-Rh} = 0.8$, $J_{6-Rh} = 0.9$, $J_{7-Rh} = 0.8$, $J_{2-1} = J_{2-3} = J_{2-Rh} = 2.4$. [b] Peaks not clearly resolved due to overlap.

established for the closely analogous CpRh(COT) system;[5] however, the remarkable chemical shift dispersion available at 500 MHz provides a more detailed picture of the reaction than was previously achievable.

First of all, the asymmetric nature of the C_8H_9 ligand in **17** is indicated by the splitting of the degeneracy of the protons at the 1- and 3-positions in the indenyl group. The individual proton resonances in the 1–3:6,7-η-cyclooctatrienylium fragment of **17** are shown in Figure 4, and the proton-proton coupling constants are readily calculable. Thus the 8-exo and 8-endo protons are easily distinguished by the magnitude of their coupling to the H-1 position. Of particular significance here is the 1.2-Hz coupling constant between 8-exo and H-2. This allylic interaction ($^4J_{H-H}$) is very characteristic[30] of protons oriented at dihedral angles approaching 90° and is completely reversed from the well-known Karplus relationship[31] for vicinally disposed protons which correlates large $^3J_{H-H}$ values with dihedral angles of approximately 0° or 180°. Clear examples of observable $^4J_{H-H}$ couplings are found for H-6–H-4β in ergosterol or for H-14–H-7α in methyl podocarpate.[32] It can be seen from Figure 4 that, while the J_{H-H} values between essentially coplanar H—C=C—H pairs are typical of those for cis olefins ($J_{1,2} = J_{2,3} = 8.1$ Hz; $J_{4,5} = 7.6$ Hz; $J_{6,7} = 7.5$ Hz), the values for $J_{3,4}$ (3.8 Hz) and $J_{5,6}$ (~1 Hz) are markedly reduced relative to their expected values for an almost planar system. Apparently, the noncoordinated double bond between C-4 and C-5 is bent away from the C-1,C-2,C-3 plane and also from the H-6–C-6–C-7–H-7 plane, as indicated in Figure 4. This contrasts with the crystallographic data,[33,34] on the non-complexed homotropylium ion which adopts a shallow boat conformation (of C_s symmetry) in which planes are defined by the C-1, C-2, C-6, and C-7 atoms and by the C-2, C-3, C-5, and C-6 atoms, as in **18**. In this latter molecule, the slight bending of the 7-membered ring is reflected in the small reduction of $J_{1,2}$ and $J_{3,4}$ to ~9 Hz.[33]



18

The ^{13}C NMR spectrum of **17** was assigned by using the two-dimensional ^1H–^{13}C shift-correlated sequence; since the proton network had already been firmly established, the carbon–carbon connectivity could also be unequivocally defined. The ^1H and ^{13}C chemical shift and coupling constant data are collected in Table II. For the most part, the ^{13}C data are in excellent agreement with those proposed[5] for the cyclopentadienyl analogue of **17**, viz., **6b**.

In like manner, complete ^1H NMR assignments for the bicyclo[5.1.0]octadienyl complex **16** were also obtained. The exo and endo methylene protons were distinguished by the magnitude of their couplings to the bridgehead protons at positions 1 and 7. The 8-endo proton exhibits an 8-Hz coupling to $H_{1,7}$ while the corresponding $J_{H_{8exo}-H_7}$ value is 5 Hz. These values are in accord with those in simple cyclopropyl systems.[35] The individual proton peaks are depicted in Figure 5; the resonance for H-2,6 was partially obscured by the H-6 peak of **17**.

Use of CF_3CO_2D led to specific deuterium incorporation in both **16** and **17** only at the endo methylene positions. It therefore seems mandatory to invoke initial protonation at the rhodium atom with subsequent migration onto a coordinated double bond. However, thus far we have been unable to detect a rhodium hydride intermediate even at

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[30] (a) Sternhell, S. *Rev. Pure Appl. Sci.* **1964**, *14*, 15. (b) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon: Oxford, 1969; pp 316–324. (c) R. K. Harris, *Nuclear Magnetic Resonance Spectroscopy*; Pitman: London, 1983; p 223.

[31] (a) Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11. (b) Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870.

[32] Perrier, R. E.; Mailvaganam, B.; Sayer, B. G.; McGlinchey, M. J., manuscript in preparation.

[33] Childs, R. F.; Faggiani, R.; Lock, C. J. L.; Mahendran, M. *J. Am. Chem. Soc.* **1986**, *108*, 3613.

[34] The crystallographic data for the 1-ethoxy derivative closely resemble the structure predicted for the parent cation using MINDO/3: Haddon, R. C. *Tetrahedron Lett.* **1975**, 863.

[35] Graham, J. D.; Rogers, M. T. *J. Am. Chem. Soc.* **1962**, *84*, 2249.

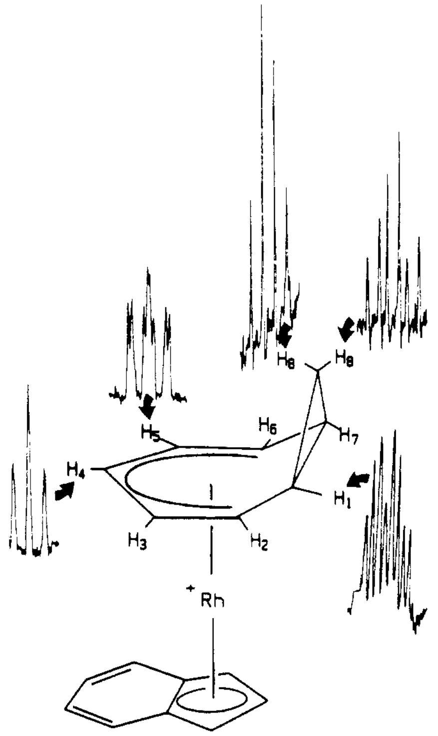
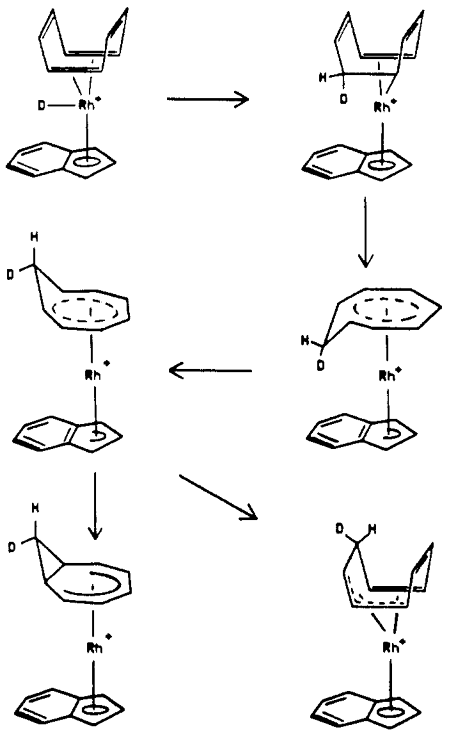


Figure 5. Selected peaks from the 500-MHz ^1H spectrum of **16**; the individual resonances are those of the protons in the bicyclo[5.1.0]octadienylium ligand.

low temperature. It is noteworthy that, unlike the reaction of protons with CpRh(COT) which yields initially the bicyclo[5.1.0]octadienylium complex analogous to **16** and subsequently undergoes electrocyclic ring opening with a barrier of ~30 kcal mol^{-1} to give **6b**, the (indenyl)Rh(COT) complex **15** yields almost exclusively the ring-opened product at room temperature. Interestingly, the low-temperature (-90 °C) protonation of **15** likewise produces very little bicyclo compound **16**, possibly indicating that the transformation of **16** to **17** is a much more facile process when the accompanying ligand on rhodium is indenyl rather than cyclopentadienyl. This is perhaps rationalizable in terms of the increased metal orbital availability for the indenyl molecule. The relatively high entropy of activation for the electrocyclic ring opening in the [CpRh-$(C_8H_9)]^+$ system has been interpreted in terms of the change in coordination of the rhodium atom.[5] The ability of the Rh atom to slide toward an η^3-indenyl mode of complexation is of obvious advantage. However, another observation remains unexplained. Even after several days in solution the reaction mixture still contains approximately the same fraction of bicyclo compound and it is not certain that **16** is the sole precursor of the monocyclic complex **17**. Indeed, one might speculate that these two products are formed independently; such a proposal has been advanced by Maitlis in the case of the (C_5Me_5)Ir-(COT) system.[6]

Some final remarks concerning the overall conformational change undergone by the 8-membered ring are perhaps in order. The proton initially bonded to the rhodium atom must be transferred to a carbon which is itself coordinated to the metal. This olefinic carbon now becomes a methylene carbon and is ultimately (i.e., in **17**) positioned distal with respect to the metal. The proton–proton coupling constants in **17** indicate that the geometry of the 8-membered ring is far from planarity; indeed, one could take the extreme view that the original tub-shaped conformation of the COT ligand in **15** has become inverted in **17**. It was established by Winstein and co-workers[36] that the barrier to bridge flipping in the homotropylium cation is ~22 kcal mol^{-1} and this conformational change was assumed to proceed via the planar cyclooctatrienylium transition state. This inversion process presumably occurs via a relatively flat intermediate so as to maintain the bonding between the rhodium and the 8-membered ring. Indeed, the favored geometry would bind all seven unsaturated carbon centers to the rhodium atom simultaneously as in the [(homotropylium)Mo(CO)$_3$]$^+$ complex **5**. Now, this would require the rhodium atom to adopt a 20-electron configuration unless the accompanying ligand could bind in a tri-hapto fashion. This latter criterion is easily met by the indenyl ligand but not by the cyclopentadienyl group. A tentative mechanism incorporating these concepts is presented as Scheme III.

Scheme III. Proposed Reaction Sequence Showing the Inversion of the Cyclooctatrienylium Ring in 17 via an (η^3-Indenyl)Rh Intermediate



In conclusion, the site of protonation of (indenyl)Rh-$(C_2H_4)_2$ is initially at the metal atom, and subsequently attack occurs on the endo face of the 5-membered ring of the indenyl ligand; concomitantly, the Rh$(C_2H_4)_2$ moiety migrates onto the 6-membered ring. A competitive process involves exchange of the rhodium-bound hydrogen with those in the ethylene ligands; however, an agostic intermediate could not be detected. These processes must be reversible since use of excess CF_3CO_2D leads to complete deuteriation of the ethylenes and also at the 1- and 3-positions of the indene ligand. In contrast, protonation of (indenyl)Rh(COT), which must also proceed via a rhodium hydride, yields (2–6-η-bicyclo[5.1.0]octadienylium)(indenyl)rhodium and (1–3:6,7-η-cyclooctatrienylium)(indenyl)rhodium via endo attack on the COT ligand.

Experimental Section

^1H, ^2H, and ^{13}C NMR spectra were acquired by using a Bruker

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[36] (a) Winstein, S. *Q. Rev., Chem. Soc.* **1969**, *23*, 141. (b) Winstein, S.; Kreiter, C. G.; Brauman, J. I. *J. Am. Chem. Soc.* **1966**, *88*, 2074. (c) Ahlberg, P.; Harris, D. L.; Roberts, M.; Warner, P.; Seidl, P.; Sakai, M.; Cook, D.; Diaz, A.; Dirlam, J. P.; Hamberger, H.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 7063.

AM500 spectrometer operating at 500, 76.75, and 125.72 MHz, respectively. The (indenyl)Rh(diene) complexes (~100 mg) were dissolved in CD_2Cl_2, and the solutions were filtered, degassed, and cooled to -80 °C at which temperature several drops of trifluoroacetic acid were added. The initially yellow solutions became dark amber or red on protonation. To obtain the ^2H NMR spectra, the solvent used was CH_2Cl_2.

Bis(ethylene)(η^5-indenyl)rhodium(I) (**7a**) was synthesized by using the method described by Green et al.[8] Protonation of **7a** was followed by ^1H and ^{13}C NMR spectroscopy which showed the formation of bis(ethylene)(η^6-indene)rhodium(I) trifluoroacetate and, subsequently, of indene itself. The ^1H and ^{13}C NMR data are collected in Table I. Protonation of bis(ethylene)(η^5-1-methylindenyl)rhodium(I) (**7b**), prepared as described elsewhere,[12] yielded as the major product 1-methylindene which exhibited ^1H NMR peaks (in trifluoroacetic acid solution) at δ 7.50 (d, 7.4 Hz) [H-4], 7.39 (d, 7.4 Hz) [H-7], 7.35 (t, 7.4 Hz) [H-6], 7.24 (t, 7.4 Hz) [H-5], 6.27 (m) [H-2], 3.37 (d, 1.3 Hz) [H-3], and 2.12 (d, 1.3 Hz) [Me]; weaker resonances at δ 7.56 (d) [H-4], 7.32 (d) [H-7], 7.11 (t) [H-6], 7.05 (t) [H-5], 6.70 (d) [H-2], 3.43 (d) [H-3], 2.98 (d) [H-3′], and 2.10 (s) [Me] can be attributed to the η^6-complex **8b**. At -90 °C, the ratio of complex to free methylindene was higher, but there was no evidence of a metal hydride intermediate.

(1,2:5,6-η^4-Cyclooctatetraene)(η^5-indenyl)rhodium(I) (**15**), synthesized as described previously,[8] was protonated at -80 °C, and the NMR spectra were recorded over the temperature range -80 to +30 °C. At no stage was there a peak observable at low frequency (high field) attributable to a rhodium-hydride intermediate. The ^1H and ^{13}C NMR data are collected in Table II.

Acknowledgment. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. D.T.C. and M.M. were the recipients of NSERC post-graduate scholarships. We thank our colleague Dr. R. F. Childs for helpful discussions on the concept of homoaromaticity and the reviewers for their incisive comments.

Registry No. **7a**, 63428-46-6; **7b**, 69074-22-2; **8a**, 109584-73-8; **8a**-d_{11}, 109584-74-9; **8b**, 109612-94-4; **15**, 74436-27-4; **16**, 109584-76-1; **17**, 109584-75-0; CF_3CO_2H, 76-05-1; CF_3CO_2D, 599-00-8; indene, 95-13-6; 1-methylindene, 767-59-9.

Electrophile- and Nucleophile-Induced Transformations of μ-Ketene Ligands on Triosmium Clusters

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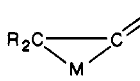
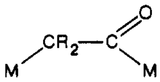
The reaction of [PPN][$Os_3(CO)_{10}(\mu$-I)(μ-CH_2CO)] (**2**, PPN = $(Ph_3P)_2N$) with various electrophilic and nucleophilic reagents is reported. Cluster **2** reacts with MeOH and MeLi to give the enolate clusters [PPN][$Os_3(CO)_{11}(CH_2C\{O\}R)$] (R = OMe (**4**), Me (**6**)). These belong to a relatively rare class of terminal alkyl clusters, and **4** is one of the few to be structurally characterized: $P2_1/c$, a = 19.875 (4) Å, b = 15.056 (4) Å, c = 19.118 (6) Å, β = 115.27 (2)°, V = 5173 (3) Å^3, Z = 4, R = 0.042, R_w = 0.051 for 4982 reflections with $F_o > 4\sigma(F_o)$. The enolate ligand is bound to a single Os atom in an equatorial position and points away from the Os_3 triangle. Electrophilic $CH_3OSO_2CF_3$ alkylates the ketene oxygen in **2** to give the fluxional σ,π-vinyl cluster $Os_3(CO)_{10}(\mu$-I)(μ-C(OCH_3)CH_2) (**7**). A similar reaction of **2** with $HOSO_2CF_3$ gives the acetyl cluster $Os_3(CO)_{10}(\mu$-I)(μ-O=CCH_3) (**5**). This product is proposed to form via initial protonation of the ketene oxygen to yield a hydroxyvinyl ligand which tautomerizes to the acetyl ligand. Cluster **2** also reacts at the ketene oxygen with the Lewis acid $BF_3 \cdot Et_2O$ to give an unstable adduct which rapidly protonates to yield **5**. Both complex **2** and the neutral ketene cluster $Os_3(CO)_{12}(\mu$-CH_2CO) react with amines to yield free amides, although the reactions are highly sensitive to the steric bulk of the amines. The reactivity of **2** is discussed in terms of the contributions of oxycarbene and oxyvinyl resonance forms.

Introduction

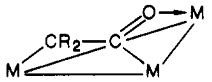
A number of organometallic complexes have been prepared which contain ketene and substituted ketene ligands.[1] These have a variety of different ketene coordination modes with those illustrated in I–VI being most common.[1-7] Type I is an η^2-(C,C) ligand bound to a single metal center typically found for low-valent middle to late transition metals. In type II, a μ_2,η^2-(C,C) ligand bridges



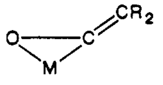
I[2]



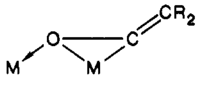
II[3]



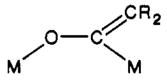
III[4]



IV[5]



V[5b,e,i,6]



VI[5d]

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