(Grant CHE-8819760) and for the purchase of the Nicolet R3m diffractometer and computing system. K.P. is also grateful to the Deutsche Forschungsgemeinschaft for financial assistance. We also thank E. K. Barefield for helpful discussions.

Registry No. 7, 137365-76-5; 8, 137365-77-6; 9, 137393-39-6; 11, 137365-78-7; CF_3CO_2H, 76-05-1; $Cp_2ZrMe(O_2CCF_3)$, 99494-55-0; ^{t}BuNC, 7188-38-7; $Cp_2Zr(Me)H$, 67659-92-1.

Supplementary Material Available: Lists of complete bond lengths and angles, anisotropic thermal parameters, and H coordinates for 8 and lists of complete bond lengths and angles and anisotropic and isotropic thermal parameters for 9 (26 pages); tables of structure factors for 8 and 9 (51 pages). Ordering information is given on any current masthead page.

Protonation of Diene Complexes of Rhodium, Iridium, Ruthenium, and Osmium: A Fine Balance between Terminal and Agostic Hydrides

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Received February 19, 1991

The structures of the cationic hydrido complexes formed on addition of HPF_6 to (η^5-pentamethylcyclopentadienyl)- and (η^6-arene)metal complexes containing various 1,3-dienes or 1,5-cyclooctadiene have been investigated by IR and NMR (^{1}H, ^{13}C) spectroscopy. The rhodium complexes $[RhH(\eta\text{-}C_5Me_5)(diene)]^+$ (diene = 1,3-cyclohexadiene (1), 2,3-dimethylbutadiene (3)) are highly fluxional η^3-enyl complexes with a M–H–C interaction (agostic hydrides), as shown by their ^{1}H and ^{13}C NMR spectra at −100 °C and by deuteration experiments. As with other compounds of this class, two reversible processes can be observed by variable-temperature NMR spectroscopy: (1) M–H bond cleavage to give a 16e η^3-enyl complex, which leads to exchange of the endo C–H bonds of 1 and exchange of the agostic methyl hydrogen atoms of 3; (2) C–H bond cleavage to give a diene metal hydride, which, in combination with process 1, averages separately the endo and exo protons of 1 and the five dienyl protons of 3. The free energy of activation $\Delta G^\ddagger$ for process 2 is slightly larger than for process 1, the estimated values being about 9.0 and 7.5 kcal/mol in the case of 3. The complexes $[IrH(\eta\text{-}C_5Me_5)(diene)]^+$ (diene = 1,3-cyclohexadiene (2), 2,3-dimethylbutadiene (4)) and $[OsH(\eta\text{-arene})(diene)]^+$ (arene = C_6H_6, diene = 1,3-cyclohexadiene (5), 2,3-dimethylbutadiene (7); arene = 1,3,5-$C_6H_3Me_3$, diene = 1,3-cyclohexadiene (6), 2,3-dimethylbutadiene (8)) are terminal hydrides in which the hydride ligand migrates between metal and diene reversibly and rapidly on the NMR time scale above room temperature ($\Delta G^\ddagger \simeq 12$ kcal/mol for 2 and 4). The coupled ^{13}C NMR spectrum of $[RuH(\eta\text{-}C_6H_6)(C_6H_8)]^+$ (9) at −100 °C suggests that this compound contains an agostic hydride similar to 1 and 3, but the ^{1}H and ^{13}C NMR spectra above −100 °C resemble those expected for a highly fluxional terminal hydrido diene complex, the free energy of activation $\Delta G^\ddagger$ for reversible Ru–H bond cleavage being 8.8 kcal/mol. In contrast to the rhodium complexes and most other agostic hydrides formed from protonation of diene complexes, therefore, $\Delta G^\ddagger$ for C–H bond cleavage (process 2) in 9 is less than that for M–H bond cleavage (process 1) and is probably about 5–6 kcal/mol. The compounds $[RuH(\eta\text{-}C_6Me_6)(C_6H_8)]^+$ (10) and $[RuH(\eta\text{-arene})(1,3\text{-diene})]^+$ (diene = 2,3-dimethylbutadiene, arene = C_6H_6 (11), $C_6H_3Me_3$ (12), C_6Me_6 (13); arene = C_6Me_6, diene = isoprene (14), 2-methyl-1,3-pentadiene (15), 3-methyl-1,3-pentadiene (16)) are also agostic, but in most cases limiting spectra cannot be obtained, even for process 1, at −100 °C. Protonation of M(η-arene)(1,5-COD) gives terminal hydrido diene complexes $[MH(\eta\text{-arene})(1,5\text{-COD})]^+$ (M = Ru, arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6; M = Os, arene = C_6H_6, $C_6H_3Me_3$). The compound obtained from $Ru(\eta\text{-}C_6Me_6)(1,5\text{-COD})$ and DPF_6 incorporates deuterium at the methylene carbon atoms of the coordinated diene, which implies that $[RuH(\eta\text{-}C_6Me_6)(1,5\text{-COD})]^+$ is in equilibrium with η^1,η^2-cyclooctenyl and possibly agostic η^3-cyclooctenyl species. All the protonated diene complexes except $[OsH(\eta\text{-arene})(1,5\text{-COD})]^+$ react with 2e-donor ligands (L) to give nonfluxional 18e complexes of the type $[M(\eta\text{-}C_5Me_5)(\eta^3\text{-enyl})(L)]^+$ (M = Rh, Ir; L = t-BuNC) and $[M'(\eta\text{-arene})(\eta^3\text{-enyl})(L)]^+$ [M' = Ru, Os; L = CO, t-BuNC, $P(OMe)_3$ (not all possible combinations)].

Introduction

Studies of the protonation of (1,3-diene)metal complexes have played an important part in the recognition of M–H–C (agostic) interactions.[1] In 1976 it was shown[2] that the ^{1}H and ^{13}C NMR spectra of protonated $Fe(CO)_3$(1,3-cyclohexadiene) are consistent with the agostic η^3-enyl structure 1; such species are undoubtedly formed on protonation of all (1,3-diene)iron tricarbonyls, though they have never been isolated. Complexes of the type $Fe\{P(OMe)_3\}_3$(1,3-diene) and $[Mn(CO)_3(1,3\text{-diene})]^-$ are more basic than the corresponding $Fe(CO)_3$(1,3-diene) compounds, and their monoprotonated derivatives can be isolated.[3,4] Neutron diffraction studies of the complexes

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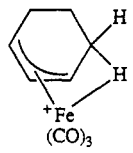

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$[Fe\{P(OMe)_3\}_3(\eta^3\text{-}C_8H_{13})]^+$[5] and $Mn(CO)_3(\eta^3\text{-}C_6H_8CH_3)$[6] have provided precise metrical data for the agostic interactions in these complexes. Dynamic NMR (^1H, ^{13}C) spectroscopic studies have established that there are two independent fluxional processes in which M–H and C–H bonds are separately and reversibly broken. For 3d-element compounds, the activation energy for M–H bond cleavage is less than that for C–H bond cleavage, and studies of a series of ruthenium complexes $[RuL_3(\eta^3\text{-enyl})]^+$ suggest that the same order also holds for these compounds.[7,8] When we started this work in 1978, less was known about the behavior of 1,3-diene complexes of d^8 elements containing η^5-cyclopentadienyl or η^6-arene as coligands. The ^1H NMR spectrum of the η^4-1,3-cyclohexadiene complex $Rh(\eta\text{-}C_5H_5)(C_6H_8)$ in CF_3CO_2H had been interpreted in terms of a fluxional 16e η^3-cyclohexenylrhodium(III) complex $[Rh(\eta\text{-}C_5H_5)(C_6H_9)]^+$ in rapid equilibrium with a (diene)rhodium hydride $[RhH(\eta\text{-}C_5H_5)(C_6H_8)]^+$. The cation, isolated as its PF_6 salt, shows no band due to ν(RhH) in its IR spectrum.[9] We reported briefly similar NMR behavior for the corresponding salt obtained by adding HPF_6 to $Ru(\eta\text{-}C_6Me_6)(C_6H_8)$.[10] The NMR spectrum of $Ir(\eta\text{-}C_5H_5)(C_6H_8)$ in CF_3CO_2H was reported to be consistent with the presence of a (diene)iridium(III) hydride $[IrH(\eta\text{-}C_5H_5)(C_6H_8)]^+$, migration of the hydride ligand between metal and diene occurring rapidly on the NMR time scale only at 80 °C.[9] In contrast, the ^1H NMR spectrum of the butadiene complex $Ir(\eta\text{-}C_5H_5)(C_4H_6)$ in CF_3CO_2H was said to suggest the presence of an (*anti*-1-methallyl)iridium(III) cation, the added proton being transferred rapidly from the metal to the diene.[11] It had also been reported[12] that treatment of the (1,5-cyclooctadiene)iridium(I) complex $Ir(\eta\text{-}C_5H_5)(1,5\text{-}C_8H_{12})$ with CF_3CO_2H or HPF_6 gives a hydrido complex containing 1,3-cyclooctadiene, $[IrH(\eta\text{-}C_5H_5)(1,3\text{-}C_8H_{12})]^+$, though the arguments presented for the isomerization are not persuasive. The behavior of the rhodium(I) complex $Rh(\eta\text{-}C_5H_5)(1,5\text{-}C_8H_{12})$ in CF_3CO_2H is more complex; the species present in equilibrium are believed to be isomeric, (η^3-cyclooctenyl)rhodium(III) cations formed by protonation at one of the coordinated double bonds.[12] In this paper we attempt to identify the species formed on protonation of arene ruthenium and arene osmium complexes of 1,3-cyclohexadiene, acyclic 1,3-dienes, and 1,5-cyclooctadiene. For comparison, we have also examined the protonation of 1,3-cyclohexadiene and 2,3-dimethylbutadiene coordinated to $Rh(\eta\text{-}C_5Me_5)$ and $Ir(\eta\text{-}C_5Me_5)$. When our work was almost complete, a detailed report on the protonation of $M(\eta^5\text{-}C_5R_5)(\eta^4\text{-}1,3\text{-diene})$ complexes (M = Co, Rh, Ir; R = H, Me; 1,3-diene = 1,3-cyclohexadiene, 2,3-dimethylbutadiene) appeared.[13]

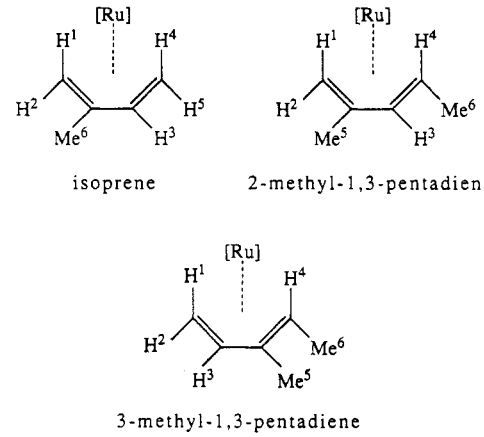

Figure 1. Numbering of protons in 1,3-dienes.

Experimental Section

The following instruments were used for NMR measurements at ANU: Varian HA100 (^1H), JEOL FX60 (^1H; ^{13}C at 15.0 MHz), JEOL FX200 (^1H, ^{13}C at 50.10 MHz), Varian XL200 (^1H; ^{13}C at 50.10 MHz), Bruker HFX 270 (^1H; ^{13}C at 68.0 MHz), Varian XL 300 (^1H), Bruker KR322S (^{31}P at 24.3 MHz) (the internal reference was either $(CH_3)_4Si$ or the residual solvent peak (C_6D_6, CD_2Cl_2)). At UNC, ^1H and ^{13}C NMR spectra were measured on a Varian XL 400 spectrometer. IR spectra were taken on Perkin-Elmer 457 and 683 grating instruments, and mass spectra, on a VG Micromass 7070F instrument at 70 eV.

Microanalyses were performed in the analytical laboratory of the Research School of Chemistry. Analytical and mass spectrometric data are tabulated in the supplementary material.

All reactions were carried out in a nitrogen atmosphere with use of standard inert-atmosphere techniques.

The starting materials $[MCl_2(\eta\text{-}C_5Me_5)]_2$ (M = Rh,[14] Ir[15]), $[RuCl_2(\eta\text{-arene})]_2$ (arene = C_6H_6,[16,17] 1,3,5-$C_6H_3Me_3$,[17] C_6Me_6[18]), $[OsI_2(\eta\text{-}C_6H_6)]_2$,[19] and $[OsCl_2(\eta\text{-}C_6H_3Me_3)]_2$[20] were prepared by literature procedures. The 1,3-cyclohexadiene (C_6H_8) and 2,3-dimethylbutadiene (C_6H_{10}) complexes $M(\eta\text{-}C_5Me_5)$(diene) (M = Rh, Ir) were prepared by heating $[MCl_2(\eta\text{-}C_5Me_5)]_2$ with the diene, 2-propanol, and anhydrous sodium carbonate, as described by Maitlis et al.[21] A similar preparation of $Ru(\eta\text{-}C_6Me_6)(C_6H_8)$ from $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ has been described previously,[18] and the same procedure was used to make all the required (arene)ruthenium

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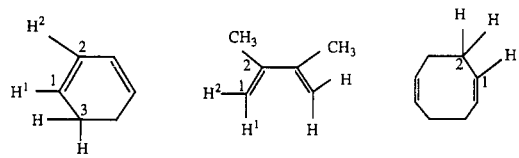
Table I. NMR (^{1}H, ^{13}C) Data (δ) for (Arene)ruthenium(0) and (Arene)osmium(0) Complexes of 1,3-Cyclohexadiene, 2,3-Dimethylbutadiene, and 1,5-Cyclooctadiene[a,b]

	^{1}H		^{13}C	
	arene	diene	arene	diene
Ru(η-C_6H_6)(η^4-1,3-C_6H_8)[c]	4.90 (s)	4.87, 4.84 (dd, H^2), 3.23 (m, H^1), 1.75 (m, H^3)	79.9	75.6 (C^2), 53.8 (C^1), 29.0 (C^3)
Ru(η-C_6Me_6)(η^4-1,3-C_6H_8)[c]	1.98 (s)	4.43 (dd, H^2), 2.40 (m, H^1), 1.80–1.55 (m, H^3)	91.7 (C_6), 17.2 (Me)	76.2 (C^2), 55.3 (C^1), 28.0 (C^3)
Os(η-C_6H_6)(η^4-1,3-C_6H_8)	4.87 (s)	5.25 (dd, H^2, J = 5.0, 2.5 Hz), 3.39 (m, H^1), 1.83 (m, H^3)	71.0	69.5 (C^2), 44.6 (C^1), 29.8 (C^3)
Os(η-$C_6H_3Me_3$)(η^4-1,3-C_6H_8)	4.83 (s, Me), 2.07 (s, C_6H_3)	5.09 (dd, H^2, J = 4.5, 2.5 Hz), 2.76 (m, H^1), 1.96–1.56 (m, H^3)	84.9 (*C*Me), 73.2 (*C*H), 20.7 (Me)	70.6 (C^2), 47.4 (C^1), 29.9 (C^3)
Ru(η-C_6H_6)(η^4-C_6H_{10})	4.79 (s)	2.02 (s, H^3), 1.27 (d, H^2), 0.25 (d, H^1, J = 1 Hz)	nm	nm
Ru(η-$C_6H_3Me_3$)(η^4-C_6H_{10})	4.61 (s, C_6H_3), 1.93 (s, Me)	1.97 (s, H^3), 1.56 (d, H^2, J = 1 Hz), 0.33 (br s, H^1)	93.8 (*C*Me), 82.1 (*C*H), 20.4 (Me)	89.3 (C^2), 39.1 (C^1), 18.3 (C^3)
Ru(η-C_6Me_6)(η^4-C_6H_{10})[d,e]	1.90 (s)	1.76 (s, H^3), 1.22 (s, H^2), 0.16 (s, H^1)	91.4 (C_6), 16.8 (Me)	85.3 (C^2), 38.4 (C^1), 19.4 (C^3)
Os(η-C_6H_6)(η^4-C_6H_{10})	4.67 (s)	2.38 (d, H^2), 2.15 (s, H^3), 0.32 (d, H^1, J = 2 Hz)	71.7	83.6 (C^2), 28.9 (C^1), 21.4 (C^3)
Os(η-$C_6H_3Me_3$)(η^4-C_6H_{10})	4.59 (s, C_6H_3), 2.05 (s, Me)	2.13 (s, H^3), 1.91 (d, H^2), 0.51 (d, H^1, J = 2 Hz)	85.3 (*C*Me), 73.4 (*C*H), 20.5 (Me)	83.6 (C^2), 31.1 (C^1), 20.5 (C^3)
Ru(η-C_6Me_6)(η^4-1,5-C_8H_{12})	1.81 (s)	2.64 (m, H^1), 2.39 (m, H^2)	97.1 (C_6), 14.9 (Me)	65.9 (C^1), 34.3 (C^2)
Os(η-C_6H_6)(η^4-1,5-C_8H_{12})	4.74 (s)	3.72 (m, H^1), 2.35 (m, H^2)	79.3	47.4 (C^1), 35.9 (C^2)
Os(η-$C_6H_3Me_3$)(η^4-1,5-C_8H_{12})	4.65 (s, C_6H_3), 1.78 (s, Me)	3.23 (m, H^1), 2.36 (m, H^2)	91.2 (*C*Me), 82.4 (*C*H), 18.1 (Me)	50.8 (C^1), 36.0 (C^2)

[a] Spectra measured in C_6D_6 at 100 MHz (^{1}H) and 15 MHz (^{13}C), except where indicated otherwise. [b] Numbering of nuclei:



[c] ^{1}H at 200 MHz; ^{13}C at 50.1 MHz. [d] ^{1}H at 300 MHz; ^{13}C at 50.1 MHz. [e] ^{1}H NMR (300 MHz) (CD_2Cl_2): δ 1.67 (s, H^3), 0.90 (s, H^2), −0.47 (s, H^1).

and (arene)osmium diene complexes. They were purified by crystallization from hexane at −78 °C, chromatography on alumina (neutral, activity 1) in hexane or petroleum ether (60–80 °C), or sublimation at ca. 50 °C/10^{-5} mm on to a −10 °C probe; in some cases, a combination of these techniques was necessary. Yields varied from 30 to 70%.

As mentioned in the text, reaction of [$OsCl_2$(η-$C_6H_3Me_3$)]$_2$ with 1,5-cyclooctadiene and 2-propanol in the presence of anhydrous Na_2CO_3 gave an oily product that contained only small amounts of Os(η-$C_6H_3Me_3$)(1,5-COD). The latter was obtained pure by treatment of the oil with HPF_6 (see below) and reaction of the resulting hydride salt [OsH(η-$C_6H_3Me_3$)(1,5-COD)]PF_6 with aqueous Na_2CO_3.

NMR (^{1}H, ^{13}C) spectroscopic data for the (arene)ruthenium(0) and (arene)osmium(0) complexes of 1,3-cyclohexadiene, 2,3-dimethylbutadiene, and 1,5-cyclooctadiene are in Table I. ^{1}H NMR data for the Ru(η-C_6Me_6) complexes of other 1,3-dienes in C_6D_6 solution are given below, protons being numbered as shown in Figure 1. Quoted IR bands refer to M–H stretching frequencies.

Ru(η-C_6Me_6)(η^4-isoprene). ^{1}H NMR: δ 4.16 (dd, J_{34} = 7.5 Hz, J_{35} = 6 Hz), 1.98 (s, C_6Me_6), 1.83 (s, H^6), 1.40 (dd, H^5, J_{35} = 6 Hz, J_{45} = 1.5 Hz), 1.29 (d, H^2, J_{12} = 1 Hz), 0.26 (d, H^1, J_{12} = 1 Hz), 0.18 (dd, H^4, J_{34} = 7.5 Hz, J_{45} = 1.5 Hz).

Ru(η-C_6Me_6)(η^4-2-methyl-1,3-pentadiene). ^{1}H NMR: δ 4.01 (d, H^3, J_{34} = 6.5 Hz), 1.98 (s, C_6Me_6), 1.81 (s, H^5), 1.38 (d, H^6, J_{46} = 6 Hz), 1.22 (d, H^2, J_{12} = 1 Hz), 0.54 (m, H^4), 0.12 (d, H^1, J_{12} = 1 Hz).

Ru(η-C_6Me_6)(η^4-3-methyl-1,3-pentadiene). ^{1}H NMR: δ 4.04 (dd, H^3, J_{23} = 7 Hz, J_{13} = 6 Hz), 1.98 (s, C_6Me_6), 1.82 (s, H^5), 1.35 (d, H^6, J_{46} = 6 Hz), 1.26 (dd, H^2, J_{23} = 6 Hz, J_{12} = 2 Hz), 0.50 (q, H^4, J_{46} = 6 Hz), 0.07 (dd, H^1, J_{13} = 7 Hz).

Protonation Reactions. The same procedure was used in all cases. The neutral complex (ca. 100–300 mg) was dissolved in ether (10–20 mL), and the stirred solution was treated dropwise with an excess of HPF_6 (60% aqueous). The protonated salt precipitated immediately, and one or two drops of the acid were usually enough to complete the reaction. The precipitate was allowed to settle, and the supernatant liquid was removed by syringe. The solid salt was washed well with ether and dried in a vacuum. Yields ranged from 50% to almost quantitative but were generally lower (30–50%) for the Os(η-C_6H_6) derivatives. Spectroscopic data for the complexes derived from 1,3-dienes are given below. Protons and carbon atoms are numbered as shown in the appropriate scheme (see text): **1**, **9**, **10** (Scheme I); **2**, **4–8** (Scheme II); **3**, **11–13** (Scheme III); **14** (Scheme VI); **15** (Scheme VII); **16** (Scheme VIII). Data for complexes derived from 1,5-cyclooctadiene are in Table II.

Deprotonation Reactions. The following procedure is representative. A sample of [RuH(η-C_6Me_6)(1,5-COD)]PF_6 (100 mg) was added to a solution of Na_2CO_3 (0.5 g) in water (5 mL). The mixture was stirred for 30 min and extracted with ether (3 × 10 mL). The extracts were dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The resulting complex was identified as Ru(η-C_6Me_6)(1,5-COD) (57 mg, 80%) by NMR and mass spectroscopy.

[Rh(η-C_5Me_5)(η^3-C_6H_9)]PF_6 (1). ^{1}H NMR: 270 MHz, CD_2Cl_2, −105 °C, δ 5.10 (br m, $H^{2,4}$ (av), H^3), 2.1–1.4 (2 br m, $H^{1,5}$ exo (av), H^6 endo), 1.87 (s, C_5Me_5), 0.6 (H^6 exo), −3.4 (br m, $H^{1,5}$ endo (av)); +20 °C, δ 3.42 (m, $H^{2,3,4}$, $H^{1,5}$ exo), 1.98 (s, C_5Me_5), −1.65 (m, $H^{1,5}$ endo, H^6 endo).

[IrH(η-C_5Me_5)(η^4-1,3-C_6H_8)]PF_6 (2). ^{1}H NMR: 270 MHz, CD_2Cl_2, −60 °C, δ 5.26 (dd, H^2, J = 5.0, 2.4 Hz), 4.13 (m, H^1), 2.16 (s, C_5Me_5), 2.0–1.6 (m, H^3), −14.98 (s, IrH); CD_3NO_2, +120 °C, δ 3.95 (br m, $H^{1,2}$, H^3 exo (av)), 2.16 (s, C_5Me_5), −3.7 (v br, H^3 endo, IrH (av)). ^{13}C{^{1}H} NMR (68 MHz, CD_2Cl_2, −90 °C): δ 101.5 (C_5), 83.2 (br, C^1), 60.6 (br, C^2), 26.5 (br, C^3), 10.2 (C_5*Me*$_5$). IR (Nujol): 2165 cm^{-1} (w).

[Rh(η-C_5Me_5)(η^3-C_6H_{11})]PF_6 (3) (Derived from 2,3-Dimethylbutadiene). ^{1}H NMR: 270 MHz, CD_2Cl_2, −100 °C, δ 2.87 (m, H^5), 2.12 (s, H^6 or H^7), 1.77 (s, C_5Me_5), 1.72 (s, H^7 or H^6), 1.27 (m, H^4), −0.5 (br m, $H^{2,3}$), −7.0 (br m, H^1); CD_2Cl_2, +20 °C, δ 2.04 (s, $H^{6,7}$ (av)), 1.88 (s, C_5*Me*$_5$), −0.36 (m, H^{1-5} (av)). ^{13}C{^{1}H} NMR (50 MHz, CD_2Cl_2, −100 °C): δ 106.5 (C^2 or C^3), 99.9 (C^5, J_{RhC} = 7.5 Hz), 88.4 (C^3 or C^2), 55.7 (C^4), 18.0, 16.9 (C^6, C^7), 9.21 (C_5Me_5), 6.8 (br, C^1).

[IrH(η-C_5Me_5)(η^4-2,3-C_6H_{10})]PF_6 (4). ^{1}H NMR (270 MHz, CD_2Cl_2, −80 °C): δ 2.86 (d, H^2, J_{12} = 3.3 Hz), 2.11 (s, H^3), 2.06 (s, C_5*Me*$_5$), 1.48 (approximate t, H^1), −14.70 (s, IrH). ^{13}C NMR

Table II. NMR (^{1}H, ^{13}C) (δ) and IR Data (cm^{-1}) for Protonated (Arene)ruthenium and (Arene)osmium Complexes of 1,5-Cyclooctadiene[a,b]

complex	temp of NMR measmt, °C	^{1}H NMR			^{13}C NMR			IR
		arene	olefin	MH	arene	olefin	CH_2	ν(MH)
$[RuH(\eta\text{-}C_6H_6)(COD)]PF_6$	−50 (^{1}H), −30 (^{13}C)	6.30 (s)	4.67 (m), 3.71 (m)	−5.30 (br)	96.9	74.1, 68.2	32.1, 31.1	c
$[RuH(\eta\text{-}C_6H_3Me_3)(COD)]PF_6$[d]	27 (^{1}H), 25 (^{13}C)	5.95 (s, C_6H_3), 2.30 (s, Me)	4.05 (m), 3.52 (m)	−6.08 (br)	114.0 (*C*Me), 95.9 (CH, J = 172 Hz), 19.5 (Me, J = 129 Hz)	76.4 (J = 164 Hz), 68.1 (J = 159 Hz)	32.1 (J = 130 Hz), 31.5 (J = 129 Hz)	2080 (w)
$[RuH(\eta\text{-}C_6Me_6)(COD)]PF_6$	27 (^{1}H), 30 (^{13}C)	2.26 (s, Me)	3.28 (m)	−6.32 (br)	109.1 (*C*Me), 16.8 (Me)	78.6, 70.5	31.6, 31.2	2050 (w)
$[OsH(\eta\text{-}C_6H_6)(COD)]PF_6$[e]	−20	6.21 (s)	4.96 (m), 3.77 (m)	−8.92 (t, 2.1 Hz)	nm	nm	nm	2120 (w)
$[OsH(\eta\text{-}C_6H_3Me_3)(COD)]PF_6$[e]	+20	5.94 (s, C_6H_3), 2.45 (s, Me)	4.17 (m), 3.61 (m)	−9.80 (s)	nm	nm	nm	2145 (w)

[a] NMR spectra measured in CD_2Cl_2 at 100 MHz (^{1}H) and 15 MHz (^{13}C), except where indicated otherwise; IR spectra measured in Nujol mulls. [b] CH_2 resonances of all complexes appear as complex multiplets in the range δ 3.0–1.6. [c] Not observed. [d] ^{13}C NMR at 50.1 MHz. [e] ^{1}H NMR at 200 MHz.

(68 MHz, CD_2Cl_2, −60 °C): δ 102.4 (C_5), 94.9 (C^2), 34.4 (C^1, J = 163 Hz), 15.9 (C^3, J = 129 Hz), 9.2 (C_5Me_5, J = 129 Hz). IR (Nujol): 2200 cm^{-1} (w).

$[OsH(\eta\text{-}C_6H_6)(\eta^4\text{-}1,3\text{-}C_6H_8)]PF_6$ (5). ^{1}H NMR (CD_2Cl_2, 200 MHz, −20 °C): δ 6.33 (s, C_6H_6), 5.68 (dd, H^2, J = 5.2, 2.5 Hz), 4.20 (m, H^1), 1.80 (m, H^3), −11.62 (t, OsH, J = 3.6 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 15 MHz, −40 °C): δ 88.2 (C_6H_6), 75.2 (C^2), 53.1 (C^1), 27.4 (C^3). IR (Nujol): 2140 cm^{-1} (w).

$[OsH(\eta\text{-}C_6H_3Me_3)(\eta^4\text{-}1,3\text{-}C_6H_8)]PF_6$ (6). ^{1}H NMR (CD_2Cl_2, 200 MHz, +20 °C): δ 6.18 (s, C_6H_3), 5.32 (br, H^2), 3.98 (br, H^1), 2.48 (s, $C_6H_3Me_3$), 1.79 (m, H^3), −11.99 (s, OsH). ^{13}C NMR (68 MHz, CD_2Cl_2, −30 °C): δ 104.9 (C_3Me), 88.3 (C_3H, J = 177 Hz), 77.1 (C_2, J = 176 Hz), 52.5 (C^1, J = 162 Hz), 27.1 (C^3, J = 131 Hz), 19.7 ($C_6H_3Me_3$, J = 130 Hz). IR (Nujol): 2130 cm^{-1} (w).

$[OsH(\eta\text{-}C_6H_6)(\eta^4\text{-}2,3\text{-}C_6H_{10})]PF_6$ (7). ^{1}H NMR (CD_2Cl_2, 200 MHz, −20 °C): δ 6.22 (s, C_6H_6), 3.28 (d, H^2, J_{12} = 2.5 Hz), 2.39 (s, H^3), 1.32 (t, H^1, J = 2.9 Hz), −11.34 (t, OsH, J <1 Hz). IR (Nujol): 2130 cm^{-1} (w).

$[OsH(\eta\text{-}C_6H_3Me_3)(\eta^4\text{-}2,3\text{-}C_6H_{10})])PF_6$ (8). ^{1}H NMR (CD_2Cl_2, 200 MHz, +20 °C): δ 6.02 (s, C_6H_3), 2.94 (br, H^2), 2.43 (s, $C_6H_3Me_3$), 2.24 (s, H^3), 1.22 (br, H^1), −12.09 (br, OsH). ^{13}C NMR (CD_2Cl_2, 68 MHz, −30 °C): δ 105.4 (C_3Me), 91.4 (C^2), 88.5 (C_3H, J = 177 Hz), 29.0 (C^1, J = 162 Hz), 18.7 ($C_6H_3Me_3$, J = 130 Hz), 18.5 (C^3, J = 129 Hz). IR (Nujol): 2140 cm^{-1} (w).

$[Ru(\eta\text{-}C_6H_6)(\eta^3\text{-}C_6H_9)]PF_6$ (9). ^{1}H NMR: 270 MHz, CD_2Cl_2, −100 °C, δ 6.04 (s, C_6H_6), 5.56 (m, $H^{2,3}$ (av)), 3.53 (m, H^1 exo, H^4 (av)), 1.38 (m), 1.15 (m) (CH_2), −11.05 (m, H^1 endo); +27 °C, δ 5.80 (s, C_6H_6), 3.22 (q, $H^{1,5,6}$ exo, $H^{2,3,4}$ (av)), J = 3 Hz), −2.94 (m, $H^{1,5,6}$ endo (av)). ^{13}C NMR: 15 MHz, CD_2Cl_2, −100 °C, δ 86.9 (C_6H_6, J = 180 Hz), 77.5 ($C^{2,3}$ (av), J = 135 Hz), 46.8 ($C^{1,4}$ (av), J = 159 Hz, 41 Hz), 23.8 ($C^{5,6}$ (av), J = 135 Hz); +25 °C, δ 87.2 (C_6H_6, J = 180 Hz), 49.6 (C^{1-6} (av), J = 165 Hz, 48 Hz).

$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}C_6H_9)]PF_6$ (10). ^{1}H NMR: 100 MHz, $CHClF_2$, −120 °C, δ 2.30 (s, C_6Me_6), −11.03 (br, H^1 endo); CD_2Cl_2, 27 °C, δ 2.30 (s, C_6Me_6), 2.97 (m, $H^{1,5,6}$ exo, $H^{2,3,4}$ (av)), −2.90 (septet, $H^{1,5,6}$ endo (av)). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ 100.1 (*C*Me), 50.4 (C^{1-6} (av)).

$[Ru(\eta\text{-}C_6H_6)(\eta^3\text{-}C_6H_{11})]PF_6$ (11) (Derived from 2,3-Dimethylbutadiene). ^{1}H NMR: 60 MHz, CD_2Cl_2, −95 °C, δ 5.97 (s, C_6H_6), 2.22 (s, $H^{6,7}$ (av)), 1.65 (m, $H^{3,5}$ (av)), −0.48 (m, $H^{2,4}$ (av)), −10.07 (m, H^1); +25 °C, δ 5.93 (s, C_6H_6), 2.22 (s, $H^{6,7}$ (av)), −1.26 (m, H^{1-5} (av)). ^{13}C{^{1}H} NMR (15 MHz, CD_2Cl_2, 25 °C): δ 93.8 ($C^{2,3}$ (av)), 87.5 (C_6H_6), 25.2 ($C^{1,4}$). Resonance at δ 25.2 collapses at −95 °C.

$[Ru(\eta\text{-}C_6H_3Me_3)(\eta^3\text{-}C_6H_{11})]PF_6$ (12) (Derived from 2,3-Dimethylbutadiene). ^{1}H NMR: 100 MHz, CD_2Cl_2, −90 °C, δ 5.53 (s, $C_6H_3Me_3$), 2.27 (s, $C_6H_3Me_3$), 2.11 (s, $H^{6,7}$ (av)), 1.96 (m, $H^{3,5}$ (av)), −0.42 (m, $H^{2,4}$ (av)), −10.33 (m, H^1); +28 °C, δ 5.53 (s, $C_6H_3Me_3$), 2.27 (s, $C_6H_3Me_3$), 2.12 (s, $H^{6,7}$ (av)), −1.43 (m, H^{1-5} (av)). ^{13}C{^{1}H} NMR (15 MHz, CD_2Cl_2, 25 °C): δ 104.0 (C_3Me), 92.8 (C_3H), 86.3 ($C^{2,3}$ (av)), 26.1 ($C^{1,4}$ (av)), 19.9 ($C_6H_3Me_3$).

$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}C_6H_{11})]PF_6$ (13) (Derived from 2,3-Dimethylbutadiene). ^{1}H NMR: 100 MHz, CD_2Cl_2, −90 °C, δ 2.26 (s, C_6Me_6), 1.93 (s, $H^{6,7}$ (av)), 1.64 (m, $H^{3,5}$ (av)), −0.48 (m, $H^{2,4}$ (av)), −10.07 (m, H^1); +28 °C, δ 2.23 (s, C_6Me_6), 1.94 (s, $H^{6,7}$ (av)), −1.66 (m, H^{1-5} av). ^{13}C NMR (15 MHz, CD_2Cl_2, 25 °C): δ 99.2 (C_6Me_6), 90.4 ($C^{2,3}$ (av)), 25.5 ($C^{1,4}$ (av)), J_{av} = 68.4 Hz), 17.9 ($C^{6,7}$ (av), J = 129 Hz), 16.8 (C_6Me_6, J = 129 Hz). Resonance at δ 25.5 collapses at −95 °C.

"$[RuH(\eta\text{-}C_6Me_6)(2\text{-}CH_3C_4H_5)]PF_6$" (14) (Derived from Isoprene). ^{1}H NMR: 100 MHz, CD_2Cl_2, −95 °C, δ 5.01 (m, H^4), 2.27 (s, C_6Me_6), 2.10 (s, H^7), −10.4 (br, H^1), peaks due to $H^{2,3}$ and $H^{5,6}$ collapsed; +27 °C, δ 2.27 (s, C_6Me_6), 2.10 (s, H^7), −1.53 (m, $H^{1,2,3}$, $H^{5,6}$ (av)).

"$[RuH(\eta\text{-}C_6Me_6)(2\text{-}CH_3C_5H_7)]PF_6$" (15) (Derived from 2-Methyl-1,3-pentadiene). ^{1}H NMR: 100 MHz, CD_2Cl_2, −95 °C, δ 4.17 (d, H^4, J_{45} = 7 Hz), 2.03 (s, C_6Me_6), 1.90 (s, H^6), 1.88 (d, H^7, J_{57} = 5 Hz), 0.98 (br, H^3), 0.30 (br, H^5), −1.52 (br, H^2), −11.24 (br, H^1); +27 °C, δ 4.43 (m, H^3), 2.17 (s, C_6Me_6), 2.03 (s, H^6), 1.30 (m, H^7).

"$[RuH(\eta\text{-}C_6Me_6)(3\text{-}CH_3C_5H_7)]PF_6$" (16) (Derived from 3-Methyl-1,3-pentadiene). ^{1}H NMR: 100 MHz, CD_2Cl_2, −95 °C, δ 2.15 (s, C_6Me_6), 1.94 (s, H^7), 1.03 (br), 0.07 (br), −0.95 (br), −11.55 (br, H^1); +27 °C, δ 2.25 (s, C_6Me_6), 2.01 (s, H^7).

Table III. ^{1}H NMR (δ) and IR Spectra (cm^{-1}) of η^3-Allyl Ligand Complexes Derived from 1,3-Diene Complexes[a]

complex	NMR: arene or Cp	NMR: other	IR
$[Rh(\eta\text{-}C_5Me_5)(\eta^3\text{-}C_6H_9)(CN\text{-}t\text{-}Bu)]PF_6$[b]	1.88 (s, Me)	4.56 (t, H^1), 4.26 (t, H^2, J_{12} = 6.5 Hz), 2.41 (m), 1.8–1.1 (m, CH_2), 1.53 (s, *t*-Bu)	2170 [ν(CN)]
$[Ir(\eta\text{-}C_5Me_5)(\eta^3\text{-}C_6H_9)(CN\text{-}t\text{-}Bu)]PF_6$[b]	1.98 (s, Me)	4.34 (t, H^1), 4.16 (t, H^2, J_{12} = 6.4 Hz), 2.74 (m), 1.9–1.7 (m), 1.3–1.0 (m, CH_2), 1.55 (s, *t*-Bu)	2165 [ν(CN)]
$[Os(\eta\text{-}C_6H_6)(\eta^3\text{-}C_6H_9)\{P(OMe)_3\}]PF_6$	6.02 (s, C_6H_6)	4.95 (m, H^1, H^2), 3.66 (d, P(O*Me*)$_3$, J_{PH} = 12.5 Hz), 2.5–1.0 (m, CH_2)	
$[Os(\eta\text{-}C_6H_3Me_3)(\eta^3\text{-}C_6H_9)(CN\text{-}t\text{-}Bu)]PF_6$	5.75 (s, C_6H_3), 2.28 (s, Me)	4.75 (t, H^2), 4.09 (t, H^1, J_{12} = 6.5 Hz), 2.63 (m), 1.2–0.8 (m, CH_2), 1.55 (s, *t*-Bu)	2150 [ν(CN)]
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}C_6H_9)(CN\text{-}t\text{-}Bu)]PF_6$	2.17 (s, Me)	3.92 (m, H^1), 3.50 (t, H^2, J_{12} = 6 Hz), 1.8–1.0 (m, CH_2), 1.47 (s, *t*-Bu)	2140 [ν(CN)]
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}C_6H_9)\{P(OMe)_3\}]PF_6$	2.13 (s, Me)	3.80 (m, H^1), 3.60 (d, P(O*Me*)$_3$, J_{PH} = 12 Hz), 3.44 (t, H^2, J_{12} = 6 Hz), 2.1–1.0 (m, CH_2)	
$[Ru(\eta\text{-}C_6H_6)(\eta^3\text{-}C_6H_9)\{P(OMe)_3\}]PF_6$	6.01 (s, C_6H_6)	4.93 (m, H^1, H^2), 3.71 (d, P(O*Me*)$_3$, J_{PH} = 12 Hz), 2.3–1.1 (m, CH_2)	
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}C_8H_{13})(CO)]PF_6$	2.36 (s, Me)	3.98 (m, H^1), 3.59 (t, H^2, J_{12} = 8 Hz), 2.1–1.5 (m, CH_2)	1970 [ν(CO)]
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}C_8H_{13})(CN\text{-}t\text{-}Bu)]PF_6$	2.18 (s, Me)	3.54 (m, H^1), 3.28 (t, H^2, J_{12} = 8 Hz), 1.6–1.2 (m, CH_2), 1.47 (s, *t*-Bu)	2150 [ν(CN)]
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}C_8H_{13})\{P(OMe)_3\}]PF_6$	2.19 (s, Me)	3.98 (m, H^1), 3.59 (t, H^2, J_{12} = 8 Hz), 3.56 (d, J_{PH} = 12 Hz, P(O*Me*)$_3$)	
$[Ru(\eta\text{-}C_6H_3Me_3)(\eta^3\text{-}C_8H_{13})(CN\text{-}t\text{-}Bu)]PF_6$	5.62 (s, C_6H_3), 2.22 (s, Me)	4.34 (t, H^2, J_{12} = 8 Hz), 3.83 (m, H^1), 2.2–1.2 (m, CH_2), 1.46 (s, *t*-Bu)	2145 [ν(CN)]
$[Ru(\eta\text{-}C_6H_6)(\eta^3\text{-}C_8H_{13})(CN\text{-}t\text{-}Bu)]PF_6$	6.01 (s, C_6H_6)	4.38 (m, H^1, H^2), 2.4–1.2 (m, CH_2), 1.49 (s, *t*-Bu)	2155 [ν(CN)]
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}1,1,2\text{-}C_3H_2Me_3)(CO)]PF_6$	2.31 (s, Me)	2.90 (d, H^2), 2.30 (d, H^1, J_{12} = 3 Hz), 1.87 (s, Me^2 or Me^3), 1.68 (s, Me^3 or Me^2), 1.23 (s, Me^1)	1995 [ν(CO)][c]
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}1,1,2\text{-}C_3H_2Me_3)(CN\text{-}t\text{-}Bu)]PF_6$	2.38 (s, Me)	2.83 (d, H^2), 2.08 (d, H^1, J_{12} = 2.5 Hz), 1.96 (s, Me^2 or Me^3), 1.74 (s, Me^3 or Me^2), 1.64 (s, *t*-Bu), 1.19 (s, Me^1)	2145 [ν(CN)]
$[Ru(\eta\text{-}C_6H_3Me_3)(\eta^3\text{-}1,1,2\text{-}C_3H_2Me_3)(CO)]PF_6$	5.97 (s, C_6H_3), 2.38 (s, Me)	3.31 (d, H^2), 2.52 (d, H^1, J = 3 Hz), 2.06 (s, Me^2 or Me^3), 1.87 (s, Me^3 or Me^2), 1.34 (s, Me^1)	1995 [ν(CO)]
$[Ru(\eta\text{-}C_6H_6)(\eta^3\text{-}1,1,2\text{-}C_3H_2Me_3)(CO)]PF_6$	6.38 (s, C_6H_6)	3.88 (d, H^2), 2.38 (d, H^1, J = 2.5 Hz), 2.11 (s, Me^2 or Me^3), 2.05 (s, Me^3 or Me^2), 1.38 (s, Me^1)	2010 [ν(CO)][c]
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}1,1\text{-}C_3H_3Me_2)(CO)]PF_6$	2.34 (s, Me)	3.57 (dd, H^3, J_{13} = 11.5 Hz), 2.79 (dd, H^2, J_{23} = 7 Hz, J_{12} = 3 Hz), 1.64 (s, Me^2), 1.24 (s, Me^1)	1998 [ν(CO)][c]
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}syn\text{-}1,1,3\text{-}C_3H_2Me_3)(CO)]PF_6$	2.29 (s, Me)	3.62 (d, H^2, J_{12} = 11 Hz), 3.05 (dq, H^1), 1.68 (s, Me^2), 1.62 (d, Me^3, J_{13} = 6 Hz), 1.19 (s, Me^1)	1996 [ν(CO)][c]
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}anti,syn\text{-}1,2,3\text{-}C_3H_2Me_3)(CO)]PF_6$	2.34 (s, Me)	3.66 (q, H^2), 3.18 (q, H^1), 1.84 (s, Me^2), 1.64 [d, Me^3, $J(H^1\text{–}Me^3)$ = 7 Hz], 1.19 [d, Me^1, $J(H^2\text{–}Me^1)$ = 7 Hz]	2000 [ν(CO)][c]

[a] ^{1}H NMR spectra in CD_2Cl_2 at 100 MHz; IR spectra as Nujol mulls, except where indicated otherwise. Protons are numbered as in Schemes IV–VIII. [b] ^{1}H NMR at 200 MHz. [c] In CH_2Cl_2.

Table IV. ^{13}C NMR Spectra (δ) of (Arene)ruthenium(II) η^3-Allyl Ligand Complexes[a]

complex	arene	other
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}C_6H_9)(CN\text{-}t\text{-}Bu)]PF_6$	104.5 (*C*Me), 16.2 (Me)	84.2 (C^2), 60.5 (C^1), 31.0 (*C*Me_3),[b] 28.6, 19.6 (CH_2)
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}C_6H_9)\{P(OMe)_3\}]PF_6$[c]	106.5 (*C*Me), 16.4 (Me)	82.1 (C^2), 57.1 (OMe, J_{PC} = 7.8 Hz), 52.5 (C^1), 26.4 (J_{PC} = 3.9 Hz), 20.4 (CH_2)
$[Ru(\eta\text{-}C_6H_6)(\eta^3\text{-}C_6H_9)(CN\text{-}t\text{-}Bu)]PF_6$	72.8 (CH, 176 Hz)	78.2 (C^2, 168 Hz), 59.0 (C^1, 156 Hz), 30.5 (*C*Me_3, 128 Hz),[b] 27.8 (133 Hz), 18.8 (133 Hz) (CH_2)
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}C_8H_{13})(CO)]PF_6$	110.4 (*C*Me), 16.9 (Me)	200.4 (CO), 86.7 (C^2), 68.2 (C^1), 33.8, 28.7, 24.7 (CH_2)
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}C_8H_{13})(CN\text{-}t\text{-}Bu]PF_6$	104.7 (*C*Me), 16.4 (Me)	84.7 (C^2), 65.5 (*C*Me_3), 63.2 (C^1), 32.9 (CH_2), 30.9 (C*Me*$_3$), 29.3, 25.6 (CH_2)
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}C_8H_{13})\{P(OMe)_3\}]PF_6$[d]	106.7 (*C*Me), 16.6 (Me)	82.1 (C^2), 59.7 (OMe, J_{PC} = 15.8 Hz), 51.6 (C^1), 30.4 (J_{PC} = 3.9 Hz), 28.4, 24.9 (CH_2)
$[Ru(\eta\text{-}C_6H_3Me_3)(\eta^3\text{-}C_6H_{13})(CN\text{-}t\text{-}Bu)]PF_6$	109.9 (*C*Me), 91.4 (CH, 172 Hz), 19.4 (Me, 129 Hz)	78.5 (C^2, 164 Hz), 65.0 (C^1, 152 Hz), 59.9 (*C*Me_3),[e] 32.9 (CH_2, 128 Hz), 30.5 (C*Me*$_3$, 129 Hz), 29.2 (125 Hz), 25.6 (128 Hz) (CH_2)
$[Ru(\eta\text{-}C_6H_6)(\eta^3\text{-}C_8H_{13})(CN\text{-}t\text{-}Bu)]PF_6$	92.8 (CH)	78.1 (C^2), 61.7 (C^1), 60.3 (*C*Me_3),[e] 32.6 (CH_2), 30.4 (C*Me*$_3$), 29.0, 25.5 (CH_2)
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}1,1,2\text{-}C_3H_2Me_3)(CO)]PF_6$	111.4 (*C*Me), 16.8 (Me)	200.0 (CO), 98.6 (C^2), 73.3 (C^1), 40.7 (C^3), 28.5, 26.0, 19.0 (Me)
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}1,1,2\text{-}C_3H_2Me_3)(CN\text{-}t\text{-}Bu)]PF_6$	105.6 (*C*Me), 16.4 (Me)	159.8 (CN), 95.5 (C^2), 65.4 (C^1), 58.4 (*C*Me_3), 41.2 (C^3), 30.7 (C*Me*$_3$), 28.5, 26.1, 19.1 (Me)
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}1,1\text{-}C_3H_3Me_2)(CO)]PF_6$	110.2 (*C*Me), 16.8 (Me)	84.7 (C^2), 40.0 (C^3),[f] 28.7, 25.9 (Me)
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}syn\text{-}1,1,3\text{-}C_3H_2Me_3)(CO)]PF_6$	111.1 (*C*Me), 16.2 (Me)	199.9 (CO), 86.7 (C^2), 78.4 (C^1), 57.4 (C^3), 29.1, 27.2, 18.1 (Me)
$[Ru(\eta\text{-}C_6Me_6)(\eta^3\text{-}anti,syn\text{-}1,2,3\text{-}C_3H_2Me_3)(CO)]PF_6$	110.8 (*C*Me), 16.8 (Me)	198.4 (CO), 99.4 (C^2), 59.0, 55.7 (C^1, C^3),[g] 20.4, 18.3, 15.3 (Me)

[a] Measured at 15.0 MHz in CD_2Cl_2, except where indicated otherwise. Carbon atoms are numbered as in Schemes V–VIII. Numbers in parentheses are J_{CH} values except where indicated otherwise. [b] CN and *C*Me_3 resonances not located. [c] δ(P) = 140.6 ppm to high frequency of external 85% H_3PO_4. [d] δ(P) = 93.4. [e] CN resonance not located. [f] C^1 and CO resonances not located. [g] Measured in $CDCl_3$.

Reactions of Ligands with Protonated Diene Salts. (1) CO. Carbon monoxide was bubbled through a solution of the salt (150–200 mg) in dichloromethane (10 mL) for 1 h. The η^3-enyl salt was precipitated by addition of ether and was purified by recrystallization from dichloromethane/ether. Yields were 70–85%.

(2) *t*-BuNC or P(OMe)$_3$. A solution of the salt (150–200 mg) in dichloromethane (10 mL) was treated with an approximately 1 molar excess of the ligand; this generally caused the color of the solution to lighten. The mixture was stirred for about 1 h at room temperature. The η^3-enyl salt was isolated and purified as above; several recrystallizations were often necessary to obtain samples of analytical purity. Yields were 60% (Rh, Ir), 50–70% (Ru), and 60–100% (Os); the yield of $[Os(\eta\text{-}C_6H_6)(\eta^3\text{-}C_6H_{11})\{P\text{-}$

$(OMe)_3]PF_6$ was only 30%.

NMR spectroscopic data for the complexes are in Table III (^1H) and Table IV (^{13}C).

Results

The new diene complexes of ruthenium(0) and osmium(0) were prepared by heating $[RuCl_2(\eta\text{-arene})]_2$ (arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6) or $[OsX_2(\eta\text{-arene})]_2$ (X = I, arene = C_6H_6; X = Cl, arene = 1,3,5-$C_6H_3Me_3$) with the diene (1,3-cyclohexadiene, 1,5-cyclooctadiene, 2,3-dimethylbutadiene, and other substituted butadienes) in 2-propanol and anhydrous sodium carbonate, following procedures already described (eq 1).[10,15,18,22] Other con-

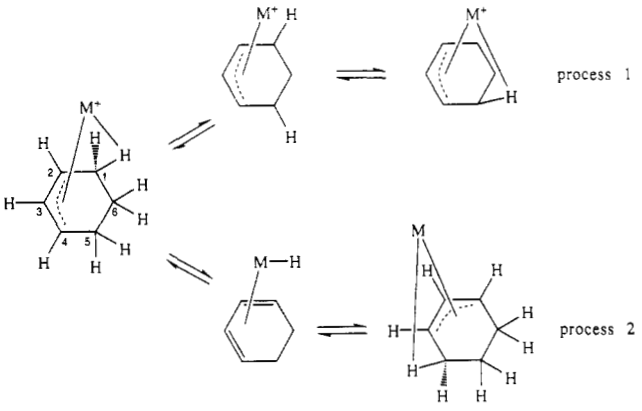
$$[MX_2(\eta\text{-arene})]_2 + (CH_3)_2CHOH + 2Na_2CO_3 + 2\text{diene} \rightarrow 2M(\eta\text{-arene})(\text{diene}) + (CH_3)_2CO + 4NaX + 2H_2O + 2CO_2 \quad (1)$$

venient methods of making $Ru(\eta\text{-}C_6H_6)(1,3\text{-}C_6H_8)$ and $Ru(\eta\text{-arene})(1,5\text{-COD})$ complexes have been reported.[23,24] The new compounds were isolated as pale yellow, air-sensitive solids, generally in yields of 30–60% (Ru) and 50–80% (Os), and were characterized by elemental analysis, by the appearance of parent ion peaks in their mass spectra, and by NMR (^1H, ^{13}C) spectroscopy (Table I). In the NMR spectra of the 1,3-diene complexes, the terminal carbon atoms and the inner protons attached to them are highly shielded (δ_C ca. 20–30 ppm, δ_H ca. 0 ppm).

Although $Os(\eta\text{-}C_6H_6)(1,5\text{-}C_8H_{12})$ was obtained in good yield from the reaction of $[OsI_2(\eta\text{-}C_6H_6)]_2$ with 1,5-cyclooctadiene, 2-propanol, and Na_2CO_3, the corresponding reaction with the mesitylene complex $[OsCl_2(\eta\text{-}C_6H_3Me_3)]_2$ was more complicated. An inseparable mixture of three η-mesitylene complexes in variable proportions was obtained; the least abundant of these compounds was $Os(\eta\text{-}C_6H_3Me_3)(1,5\text{-}C_8H_{12})$, which shows mesitylene resonances at δ 1.78 (Me) and 4.65 (C_6H_3). The major products, which have not been identified, showed mesitylene resonances at δ 1.73, 1.99 (Me) and 4.64, 4.59 (C_6H_3), and the rest of the spectrum was complex. Fortunately, treatment of the crude mixture with HPF_5 gave one product, $[OsH(\eta\text{-}C_6H_3Me_3)(1,5\text{-}C_8H_{12})]PF_6$ (see below), which was deprotonated by aqueous Na_2CO_3 to give pure $Os(\eta\text{-}C_6H_3Me_3)(1,5\text{-}C_8H_{12})$. It is of interest that the reaction of $[MCl_2(\eta\text{-}C_5Me_5)]_2$ (μ-H)(μ-Cl) (M = Rh, Ir) with 1,5- or 1,3-cyclooctadiene gives either the η^3-cyclooctenyl complex $M(\eta\text{-}C_5Me_5)(\eta^3\text{-}C_8H_{13})Cl$ or the 1,5-cyclooctadiene complex $M(\eta\text{-}C_5Me_5)(1,5\text{-}C_8H_{12})$, depending on reaction conditions.[25] The reaction of 1,5-cyclooctadiene with $Fe(CO)_5$, $Ru_3(CO)_{12}$, or $Os_3(CO)_{12}$ also yields various organometallic products.[26]

Protonation Studies. (1) M(η-C_5Me_5)(1,3-diene) (M = Rh, Ir). Treatment of $Rh(\eta\text{-}C_5Me_5)(1,3\text{-}C_6H_8)$ with HPF_6 precipitates an orange solid of empirical formula $[Rh(\eta\text{-}C_5Me_5)(C_6H_9)]PF_6$ (1). The ^1H NMR spectrum of 1 at 20 °C shows a 6 H multiplet at δ 3.42 and a 3 H multiplet at δ −1.65 due to the C_6H_9 protons, in addition to the C_5Me_5 singlet. On cooling, these multiplets collapse and, at -105 °C, five new broad resonances at δ 5.10 (3 H), 2.1–1.4 (3 H), 0.6 (1 H), and −3.4 (2 H) appear; the resonance at δ 2.1–1.4 contains two broad signals that overlap with each other and with the C_5Me_5 singlet. The spectrum resembles that of the agostic complex $Mn(CO)_3(C_6H_9)$ at 0 °C.[4a] By analogy, and in agreement with the conclusions of Salzer et al.,[13] we propose that 1 has an agostic ground state that undergoes the two degenerate modes of isomerization mentioned in the Introduction, viz. the following: (1) reversible Rh–H bond cleavage, leading to alternating coordination of the two *endo* C–H bonds adjacent to the allylic group via a 16e intermediate; (2) reversible C–H bond cleavage leading to 1,2-migration of the $Rh(\eta\text{-}C_5Me_5)$ fragment around the ring via an 18e diene hydride intermediate, $RhH(\eta\text{-}C_5Me_5)(\eta^4\text{-}C_6H_8)$. These are illustrated in Scheme I, which also gives the numbering of protons and carbon atoms. At −105 °C, process 1 is still fast on the NMR time scale, whereas process 2 is slow, so that protons H^2 and H^4, H^1 endo and H^5 endo, and H^1 exo and H^5 exo are separately averaged. The spectrum at −105 °C is assigned as follows: δ 5.10 ($H^{2,4}$ (av), H^3), 2.1–1.4 ($H^{1,5}$ exo (av), H^6 exo), 0.6 (H^6 endo), −3.4 ($H^{1,5}$ endo (av)). At 20 °C the second process is also fast on the NMR time scale, so that, in combination with the first process, $H^{1,5}$ endo and H^6 endo average to give the 3 H multiplet at δ −1.65 and the remaining six protons average to give the 6 H multiplet at δ 3.42. The resonances due to H^6 endo and $H^{1,5}$ endo coalesce at about −60 °C, which gives an approximate value of 9.0 ± 0.5 kcal/mol for the free energy of activation of process 2.

Scheme I. Fluxional Processes in an Agostic η^3-Cyclohexenyl Complex Formed from 1,3-Cyclohexadiene



In contrast to its rhodium analogue, the iridium complex $[Ir(\eta\text{-}C_5Me_5)(C_6H_9)]PF_6$ (2) obtained by addition of HPF_6 to $Ir(\eta\text{-}C_5Me_5)(1,3\text{-}C_6H_8)$ has a diene hydride structure. Its solid-state IR spectrum shows a sharp band at 2165 cm^{-1} due to ν(IrH). The ^1H NMR spectrum at −60 °C shows a 2 H doublet of doublets at δ 5.26 due to the inner diene protons H^2, a 2 H multiplet at δ 4.13 due to the terminal diene protons H^1, a 4 H multiplet at δ ca. 2 due to the methylene protons H^3, and a singlet hydride resonance at δ −14.98. At 20 °C the signals due to the diene and the hydride collapse into the baseline; at 100 °C in $C_6D_5NO_2$ there are two broad resonances at δ 3.95 (6 H) and δ −3.7 (3 H), similar to the spectrum of the rhodium compound at room temperature. The $^{13}C\{^1H\}$ NMR spectrum of 2 is broad even at −90 °C, but there are only three peaks at δ 83.2, 60.6, and 26.5 due to the diene carbon atoms, in agreement with the diene hydride structure. Clearly, the hydride ligand migrates between the metal atom and the diene, possibly via a 16e intermediate $Ir(\eta\text{-}C_5Me_5)(\eta^3\text{-}C_6H_9)$ (Scheme II). A measurement of the line width at half-height ($W_{1/2}$) of the IrH signal at 0 °C and application of the slow-exchange approximation $k = \pi W_{1/2}$ gave a rate

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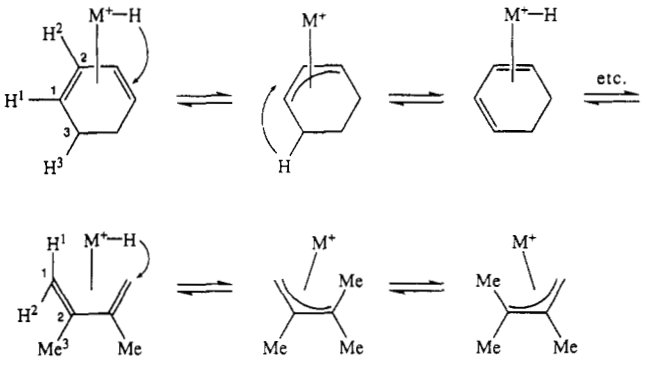
Scheme II. Fluxional Process in Metal Hydrides Containing 1,3-Cyclohexadiene or 2,3-Dimethylbutadiene



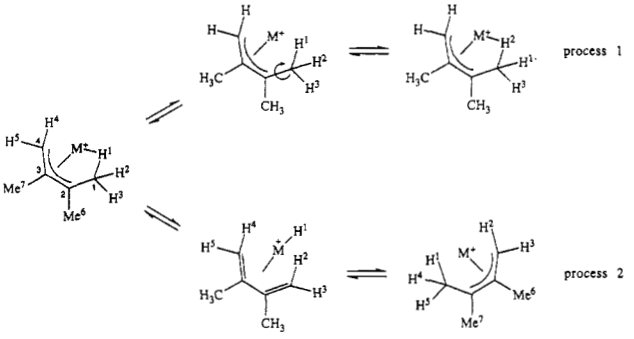
of 628 s^{-1}, corresponding to a free energy of activation $\Delta G^{\ddagger}$ of 12.4 kcal/mol.

Treatment of $Rh(\eta\text{-}C_5Me_5)(C_6H_8)$ with an excess of DPF_6 gives a yellow product whose ^1H NMR spectrum has resonances at δ −1.65, −2.07, and −2.62. The most intense resonance (δ −1.65) is that of the all protio compound, which presumably arises from adventitious HPF_6. The least intense resonance (δ −2.62) is due to the incorporation of two *endo* deuterium atoms. This large equilibrium isotope effect is characteristic of systems that have an agostic ground-state structure.[1] Similarly, the ^1H NMR spectrum at 100 °C of the corresponding iridium compound generated from DPF_6 shows resonances at δ −3.7 (most intense) and −4.8 and −6.5 (least intense), which are assigned to $[IrH(\eta\text{-}C_5Me_5)(1,3\text{-}C_6H_8)]^+$, $[IrH(\eta\text{-}C_5Me_5)(1,3\text{-}C_6H_7\text{-}endo\text{-}D)]^+$, and $[IrH(\eta\text{-}C_5Me_5)(1,3\text{-}C_6H_6\text{-}endo\text{-}D_2)]^+$, respectively. The large equilibrium isotope effect observed here is a consequence of the large zero-point energy differences of C–H relative to Ir–H and the resulting preference for deuterium to occupy the *endo* C–H(D) sites relative to the Ir–H site.

The protonation behavior of the $M(\eta\text{-}C_5Me_5)(C_6H_8)$ and $M(\eta\text{-}C_5H_5)(C_6H_8)$ complexes is clearly similar for each metal (M = Rh, Ir). The limiting spectrum for $[IrH(\eta\text{-}C_5H_5)(C_6H_8)]^+$ in CF_3CO_2H is reached at −20 °C;[9] cf. −60 °C for the C_5Me_5 complex. The species present in solutions of $Rh(\eta\text{-}C_5H_5)(C_6H_8)$ in CF_3CO_2H is probably agostic, analogous to **2**, although surprisingly Lewis et al.[11] do not mention any isotope effect on the ^1H NMR spectrum in CF_3CO_2D.

The 2,3-dimethylbutadiene complexes $M(\eta\text{-}C_5Me_5)(C_6H_{10})$ (M = Rh, Ir) are protonated in the same way as the 1,3-cyclohexadiene complexes. The NMR spectroscopic behavior of the orange complex $[Rh(\eta\text{-}C_5Me_5)(C_6H_{11})]PF_6$ (**3**) is consistent with an agostic η^3-methallyl structure[48] in which the Rh–H and C–H bonds are being reversibly cleaved. This is illustrated in Scheme III, which also gives the numbering of protons and carbon atoms. In the ^1H NMR spectrum at 20 °C there is a singlet at δ 2.04 due to the diene methyl groups and a 5 H multiplet at δ −0.36 arising from averaging of the four dienyl protons and the added proton. On cooling, these resonances collapse and, at −100 °C, the spectrum consists of two 3 H singlets at δ 2.12 and 1.72 due to inequivalent methyl groups ($H^{6,7}$), two 1 H multiplets at δ 2.87 and 1.27 due to the outer and inner terminal protons H^5 and H^4 of a η^3-allyl group, and two very broad resonances at δ −0.5 (2 H) and −7.0 (1 H) due to the terminal and bridging protons, $H^{2,3}$ and H^1, of an agostic methyl group. The $^{13}C\{^1H\}$ NMR spectrum at −100 °C is still fairly broad but clearly shows six separate resonances corresponding to the six inequivalent carbon atoms of the dienyl unit. The

Scheme III. Fluxional Processes in an Agostic η^3-Methallyl Complex Formed from 2,3-Dimethylbutadiene



carbon atom C^1 and the C–H–Rh bridging group appears at δ 6.8, which is typical of the shielding in such environments.[1] Salzer et al.[13] have shown that, in the coupled ^{13}C NMR spectrum of **3**, the J_{CH} values for C^1 are 107 and 89 Hz, the lower value being typical of agostic systems.[1] The NMR spectra resemble those reported for other fluxional protonated 2,3-dimethylbutadiene complexes, e.g. $[Fe(\eta^3\text{-}C_6H_{11})\{P(OMe)_3\}_3]^+$[3] and $[IrH(PPh_3)_2(\eta^3\text{-}C_6H_{11})]^+$.[27] The IR spectrum shows no band assignable to ν(RhH) or ν(CH···Rh) in the region 2700–1500 cm^{-1}.

The free energies of activation for the reversible cleavages of the Rh–H and endo C–H bonds are clearly lower than those for the corresponding processes in $Mn(CO)_3(\eta^3\text{-}C_6H_9)$ [$\Delta G^{\ddagger}$(M–H) = 8.3 kcal/mol; $\Delta G^{\ddagger}$(C–H) = 15.4 kcal/mol].[4a] Their effects on the variable-temperature NMR spectra are less easy to separate than in $Mn(CO)_3(\eta^3\text{-}C_6H_9)$, which implies that the two activation energies do not differ so much. A value for the free energy of activation of Rh–H bond cleavage (process 1) has been estimated from the line width of the peak due to H^1 at −100 °C, measured at 270 MHz, and use of the slow-exchange approximation. This gives a rate of 1373 s^{-1} ($\Delta G^{\ddagger}$ = 7.5 kcal/mol). The ^1H NMR spectrum at −80 °C consists of a pair of broadened resonances at δ −2.17 and +2.90 due to $H^{1,2,3}$ and H^5, respectively, the latter being just resolved from the C_5Me_5 resonance. Assuming that the observed broadening is due only to the onset of process 2, the measured line width ($W_{1/2}$) of the peak at δ −2.17 gives, according to the slow-exchange approximation, a rate of 388 s^{-1}, corresponding to $\Delta G^{\ddagger}$ = 8.8 kcal/mol. Our $\Delta G^{\ddagger}$ values are in good agreement with the more accurate values obtained by line-shape analysis,[13] viz. 6.8 kcal/mol (−119 °C) for Rh–H cleavage and 8.3 kcal/mol (−119 °C) for C–H bond cleavage.

The fast-exchange ^1H NMR spectrum of the compound obtained by treatment of $Rh(\eta\text{-}C_5Me_5)(C_6H_{10})$ with DPF_6 shows, in addition to a weak signal at δ −0.36 due to the monoprotio species, peaks at δ −0.46, −0.57, −0.70, and −0.85 corresponding to the incorporation of one, two, three, and four deuterium atoms, respectively. This observation provides more evidence for an agostic structure. We have assumed in Scheme III that a 16e species $Rh(\eta\text{-}C_5Me_5)(\eta^3\text{-}C_6H_{11})$ is an intermediate in the low-energy process, but an "in-place" rotation[28] is also possible.

Treatment of $Ir(\eta\text{-}C_5Me_5)(C_6H_{10})$ with HPF_6 gives the diene hydride $[IrH(\eta\text{-}C_5Me_5)(C_6H_{11})]PF_6$ (**4**) as a white solid, whose IR spectrum shows a ν(IrH) band at 2200 cm^{-1}. At −80 °C the ^1H NMR spectrum shows a 6 H singlet due to the equivalent diene methyl groups H^3, a doublet at δ

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2.86 due to the outer diene protons H^2, and an asymmetric triplet at δ 1.48 due to the inner diene protons H^1. The latter appear to be weakly coupled to the hydride proton, which appears as a broadened singlet at δ −14.70. At room temperature, the peaks due to H^1, H^2, and IrH collapse into the baseline owing to reversible hydride migration between metal and diene, (Scheme II). The $^{13}C\{^1H\}$ NMR spectrum of **4** at −60 °C (see Experimental Section) supports the structural assignment as a diene hydride. The C^1 signal shows no coupling to IrH, and its chemical shift (δ 34) is consistent with a η^4-diene formulation with no Ir–H–C bridging interaction. A measurement of $W_{1/2}$ for the IrH resonance at −20 °C gave a rate of hydride migration of 505 s^{-1}, corresponding to $\Delta G^\ddagger$ = 11.6 kcal/mol, similar to the value found for **2**.

(2) M(η-arene)(1,3-diene) (M = Ru, Arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6; M = Os, Arene = C_6H_6, 1,3,5-$C_6H_3Me_3$). The (arene)osmium complexes behave similarly to the Ir(η-C_5Me_5) complexes on protonation with HPF_6, though the products are more sensitive to air and heat than are their iridium analogues. The cream-colored solids [OsH(η-arene)(1,3-diene)]PF_6 (arene = C_6H_6, diene = 1,3-cyclohexadiene (**5**), 2,3-dimethylbutadiene (**6**); arene = 1,3,5-$C_6H_3Me_3$, diene = 1,3-cyclohexadiene (**7**), 2,3-dimethylbutadiene (**8**)) show weak, sharp bands at 2130–2140 cm^{-1} due to ν(OsH) in their IR spectra. The ^1H NMR spectra of the complexes at −20 °C resemble those of the corresponding Ir(η-C_5Me_5) complexes at −60 °C, except that the hydride resonances appear as triplets, probably owing to coupling with the terminal protons of the diene (J = 3.6 Hz for 1,3-cyclohexadiene and ca. 1 Hz for 2,3-dimethylbutadiene). The ^1H NMR spectra do not change on cooling below −20 °C but they broaden at +20 °C, probably owing to reversible hydride migration (Scheme II). At higher temperatures, the complexes decompose. In the ^{13}C NMR spectra, no coupling is observed between OsH and the terminal carbon atoms of the diene units, which also is consistent with a terminal hydride formulation.

Protonation of Ru(η-arene)(1,3-C_6H_8) with HPF_6 precipitates pale yellow salts [Ru(η-arene)(C_6H_9)]PF_6 (arene = C_6H_6 (**9**), $C_6H_3Me_3$ (**10**)). Similar salts are obtained on treatment of Ru(η-C_6Me_6)(C_6H_8) with HBF_4 or BF_3·H_2O. The ^1H NMR spectra of the C_6H_9 fragment at room temperature are similar to those of **1** and can be assigned similarly. Thus, the benzene complex **9** shows, in addition to a C_6H_6 resonance at δ 5.80, a 6 H multiplet at δ 3.22 due to the exo protons and a 3 H multiplet at δ −2.94 due to the endo protons. On cooling, these multiplets broaden and collapse and, at −60 °C, only the C_6H_6 singlet is visible. At −95 °C there are four new resonances at δ 5.56 (m, 2 H), 3.53 (m, 2 H), 1.26 (m, 4 H), and −11.05 (m, 1 H). The spectrum of the hexamethylbenzene complex **10** at −95 °C shows only the C_6Me_6 singlet; at −120 °C a broad resonance at δ −11.0 is visible. The ^1H NMR spectrum of **9** at −95 °C clearly resembles those of the diene hydrides [IrH(η-C_5Me_5)(C_6H_8)]PF_6 (**4**) at −60 °C and [OsH(η-arene)(C_6H_8)]PF_6 (**7**) at −20 °C and differs from that of the agostic η^3-cyclohexenyl [Rh(η-C_5Me_5)(C_6H_9)]PF_6 (**1**) at −100 °C. At first sight, this appears to be consistent with the presence of a diene hydride, the peaks being assigned as follows: δ 5.56 (H^2), 3.53 (H^1), 1.26 (H^3), −11.05 (RuH). Clearly the hydride is migrating rapidly between the metal atom and the diene. By careful measurement of the broadening of the RuH resonance at 400 MHz in the temperature range −108 to −84 °C and application of the slow-exchange approximation ($k = \pi W_{1/2}$), the rate at −94 °C has been calculated as 88 s^{-1}, corresponding to a free energy of activation $\Delta G^\ddagger$ of 8.8 kcal/mol.

The $^{13}C\{^1H\}$ NMR spectrum of **9** at room temperature shows a singlet at δ 49.6 due to the carbon atoms of the C_6H_9 group. In the ^1H-coupled spectrum this appears as a doublet of doublets, the average coupling to RuH, H^5 endo, and H^6 endo being 47.7 Hz and to the exo protons being 165.2 Hz. At −60 °C the resonance collapses, and at −95 °C three new resonances appear at δ 77.0, 46.5, and 23.5, which, on the basis of the diene hydride structure, could be assigned to C^2, C^1, and C^3.

An alternative and, we believe, more plausible explanation of the results is that the [Ru(η-arene)(C_6H_9)]PF_6 compounds have an agostic structure but that, in contrast to [Rh(η-C_5Me_5)(C_6H_9)]PF_6, reversible C–H bond cleavage via a diene hydride intermediate (process 2 in Scheme I) is fast on the NMR time scale at −100 °C and reversible M–H bond cleavage via a 16e η^3-enyl intermediate (process 1) is slow. If this idea is correct, the ^{13}C resonances should broaden further below −100 °C and eventually separate into six distinct signals due to the inequivalent carbon atoms of the agostic structure. In fact, below −90 °C, the band at δ 46.5 assigned to C^1, C^4(av) in the agostic structure shows pronounced broadening, while the bands at δ 77.0 and 23.5 broaden only slightly. The initial rate of broadening due to process 2 will be greatest for the signal due to those carbon atoms that differ most in chemical shift. This is likely to be the signal due to C^1 and C^4 in the agostic η^3-C_6H_9 structure, e.g. in $Mn(CO)_3(\eta^3$-$C_6H_9)$ $\delta(C^4) - \delta(C^1)$ = 58 or 53 ppm (depending on the assignment of C^4), $\delta(C^3) - \delta(C^2)$ = 21 or 26 ppm (depending on the assignment of C^2), and $\delta(C^5) - \delta(C^6)$ = 10 ppm.[4a] This argument, therefore, supports the hypothesis of an agostic ground-state structure for [Ru(η-C_6H_6)(C_6H_9)]PF_6 (**9**) and suggests that the value of $\Delta G^\ddagger$ for reversible C–H bond breaking must be close to the limit obtainable by NMR spectroscopy, viz. ca. 6 kcal/mol. The $\Delta G^\ddagger$ values for breaking Ru–H and C–H bonds in [Ru(η-C_6Me_6)(C_6H_9)]PF_6 (**10**) must be even closer together than those for **9**. Salzer et al.[13] have noted that the free energies of activation for breaking the M–H bonds (process 1) in [M(η-C_5H_5)(η^3-C_6H_9)]$^+$ (M = Co, Rh) are ca. 1 kcal/mol higher than those for the same process in the corresponding C_5Me_5 complexes; the same probably holds in the (arene)ruthenium complexes when C_6H_6 is replaced by C_6Me_6.

The signal due to $C^{1,4}$ in the coupled ^{13}C NMR spectrum of **9** at −100 °C is broad when measured at 50 or 100 MHz, but at 15 MHz it appears as a doublet of doublets (J_{CH} = 159, 41 Hz). Presumably, at the higher field strengths the resonance starts broadening because of the slowing down of process 2 before it completely sharpens from the freezing out of process 1. The smaller coupling must represent half the magnitude of $J_{CH^1(endo)}$, which, accordingly, is ca. 82 Hz. This is typical of agostic systems[1] and thus provides strong evidence for the formulation of **9**, and of the other protonated (arene)ruthenium diene complexes, as agostic η^3-enyl complexes rather than as diene hydrides, despite the first impression gained from their ^1H NMR spectra at low temperature. This conclusion has been confirmed by an X-ray structure determination of the PF_6 salt formed by protonation of Ru(η-$C_6H_3Me_3$)($C_{18}H_{15}$) ($C_{18}H_{15}$ = 2,3-dimethylene-5,6:7,8-dibenzobicyclo[2.2.2]octane.[29]

It should be noted that the ^{13}C NMR spectra of [Ir(η-C_5Me_5)(C_6H_9)]PF_6 (**2**) and [Os(η-arene)(C_6H_9)]PF_6 (**5**) do not show the differential broadening described above, consistent with the formulation of these species as normal diene hydrides. Also, in contrast to the iridium and os-

(29) Bennett, M. A.; Pelling, S.; Robertson, G. B.; Wickramasinghe, W. A. *Organometallics* **1991**, *10*, 2166.

mium complexes, the ruthenium compounds show no absorption in their IR spectra assignable to a M–H stretching frequency; the spectra are otherwise uninformative.

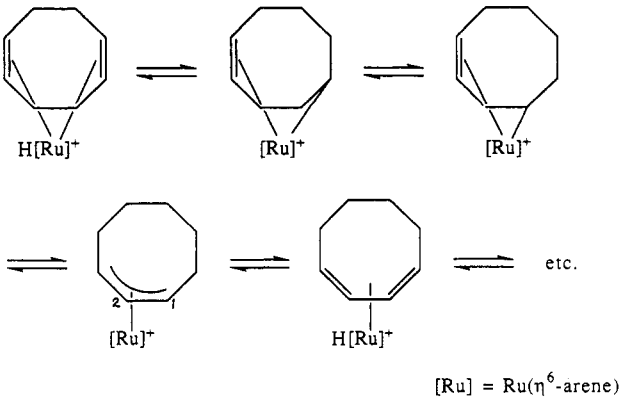
Addition of aqueous HPF_6 to ether solutions of Ru(η-arene)(2,3-dimethylbutadiene) (arene = C_6H_6 (**11**), $C_6H_3Me_3$ (**12**), C_6Me_6 (**13**)) precipitates pale yellow salts [Ru(η-arene)(C_6H_{11})]PF_6. The C_6Me_6 compound is air stable as a solid but decomposes slowly in solution even under nitrogen. The benzene and mesitylene complexes are much less stable and could not be recrystallized without decomposition. They can, however, be characterized via the η^3-allyl complexes formed by reaction with ligands (see below).

The ^1H NMR spectrum of [Ru(η-C_6Me_6)(C_6H_{11})]PF_6 (**13**) at 28 °C is very similar to that of [Rh(η-C_5Me_5)(C_6H_{11})]PF_6 (**1**). In addition to a C_6Me_6 singlet at δ 2.23, there is a singlet at δ 1.94 due to the diene methyl groups and a 5 H multiplet at δ –1.66 due to the remaining protons. Cooling causes the last of these signals to collapse. Eventually, at –90 °C, two 2 H multiplets appear at δ 1.64 and 0.55 together with a broad 1 H multiplet (an approximate triplet) at δ –10.28; the singlets at δ 1.94 and 2.23 are unaffected. The $^{13}C\{^1H\}$ NMR spectrum at room temperature shows resonances at δ 90.4 ($C^{2,3}$), 25.5 ($C^{1,4}$), and 17.9 (CH_3 of diene); on cooling, the signal due to $C^{1,4}$ collapses, but no new peaks are observed, even at –95 °C. Clearly, the low-temperature NMR spectra of the Rh(η-C_5Me_5) and Ru(η-C_6Me_6) complexes of 2,3-dimethylbutadiene differ in the same way as do the spectra of the corresponding 1,3-cyclohexadiene complexes, and we offer a similar interpretation, viz. an agostic η^3-methallyl ground-state structure which is in rapid equilibrium with a diene hydride, even at the lowest accessible temperature.

The Ru(η-C_6Me_6) complexes of isoprene, 2-methyl-1,3-pentadiene, and 3-methyl-1,3-pentadiene also react with HPF_6 to give yellow, air-sensitive, monoprotonated salts. These could not be recrystallized owing to decomposition. Their fluxional ^1H NMR spectra resemble that of the 2,3-dimethylbutadiene complex can be interpreted similarly in terms of isomeric agostic η^3-methallyl complexes which are in rapid equilibrium with a diene hydride.

(3) M(η-arene)(1,5-cyclooctadiene) (M = Ru, Arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6; M = Os, Arene = 1,3,5-$C_6H_3Me_3$). Treatment of Ru(η-arene)(1,5-COD) with HPF_6 gives pale yellow monoprotonated salts [RuH(η-arene)(COD)]PF_6, whose thermal stability increases in the order $C_6H_6 < C_6H_3Me_3 < C_6Me_6$. The IR spectra of the C_6Me_6 and $C_6H_3Me_3$ complexes each show a weak band at ca. 2050 cm^{-1} assignable to ν(RuH), but the corresponding band could not be observed in the spectrum of the C_6H_6 complex. The colorless osmium complex [OsH(η-C_6H_6)(COD)]PF_6, made from Os(η-C_6H_6)(1,5-COD) and HPF_6, is thermally more stable than its ruthenium analogue and shows a ν(OsH) band at 2120 cm^{-1}. As already mentioned, the (mesitylene)osmium compound is obtained as a buff solid by protonation of the crude yellow oil isolated from the reaction of $[OsCl_2(\eta\text{-}C_6H_3Me_3)]_2$, 1,5-cyclooctadiene, and Na_2CO_3 in 2-propanol. The ^1H NMR spectrum of [OsH(η-C_6H_6)(COD)]PF_6 at 28 °C shows two multiplets due to the diene protons at δ 4.96 and 3.77 and a hydride resonance at δ –8.92, which is a triplet (J = 2 Hz) owing to coupling with a pair of diene protons. The spectrum is invariant to –20 °C; at temperatures above ca. 30 °C decomposition occurs. The spectra of the other members of the series are similar except that the hydride resonances appear as slightly broad singlets. The ^1H NMR spectrum of [RuH(η-$C_6H_3Me_3$)(COD)]PF_6 does not change from room temperature to –95 °C; that of the benzene analogue can only be observed at low temperature because of rapid decomposition. The diene resonances of [RuH(η-C_6Me_6)(COD)]PF_6 seem to be slightly broadened by exchange at room temperature and sharpen on cooling to –95 °C. The results are apparently consistent with a diene hydride formulation for the COD complexes but do not resolve the question of whether the eight-membered ring is present as 1,5-COD or 1,3-COD. The ^1H-coupled ^{13}C NMR spectrum of [RuH(η-$C_6H_3Me_3$)(COD)]PF_6 shows four COD resonances at δ 76.4 (d, J_{CH} = 164 Hz), 68.1 (d, J_{CH} = 154 Hz), 32.1 (t, J_{CH} = 130 Hz), and 31.5 (t, J_{CH} = 129 Hz). The inner and outer diene carbon atoms of Fe{P(OMe)$_3$}$_3$(1,3-COD) appear at δ 86.2 and 50.7;[30] i.e., they differ in chemical shift by over 30 ppm. The difference of only 8 ppm for the diene carbon atoms in [RuH(η-$C_6H_3Me_3$)(COD)]PF_6 suggests that they are in fairly similar environments and is consistent with the presence of 1,5-COD.[49] The monodeuterio salt obtained by treatment of Ru(η-C_6Me_6)(1,5-COD) with DPF_6 shows a hydride resonance in its ^1H NMR spectrum corresponding to less than one proton, and the IR spectrum shows a residual ν(RuH) band at 2050 cm^{-1}. The ^2H NMR spectrum of the salt shows two broad peaks at δ 2.2 and –6.4, confirming that deuterium exchanges between the metal atom and the methylene carbon atoms. Treatment of [RuH(η-C_6Me_6)(COD)]PF_6 with Na_2CO_3/D_2O incorporates up to four deuterium atoms into the methylene positions; similar observations have been made with [IrH(η-C_5H_5)(COD)]PF_6 and [Fe{P(OMe)$_3$}$_3$(η^3-C_8H_{13})]BPh_4.[3] Surprisingly, however, there was no evidence for H/D exchange in [OsH(η-C_6H_6)(COD)]$^+$.

Scheme IV. Hydride Migration in a Hydrido 1,5-Cyclooctadiene Complex



As shown in Scheme IV, the exchange is assumed to take place by reversible hydride migration between the metal and the double bonds via (η^1,η^2-cyclooctenyl)-, (η^3-cyclooctenyl)-, and (1,3-cyclooctadiene)hydridoruthenium(II) intermediates. The process is clearly slower than that occurring in the 1,3-diene systems, but it may be responsible for the broadening observed in the ^1H NMR spectrum of [RuH(η-C_6Me_6)(COD)]PF_6. The η^3-cyclooctenyl intermediate can be intercepted by treatment of [RuH(η-arene)(COD)]PF_6 with ligands such as CO, *t*-BuNC, and $P(OMe)_3$ (see below). In contrast to [RuH(η-arene)(COD)]$^+$ the closely related complexes RuH(1,5-COD)L_3 (L = various tertiary phosphines or arsines) isomerize irreversibly to agostic η^3-cyclooctenyl complexes RuL_3(η^3-C_8H_{13}).[7,31]

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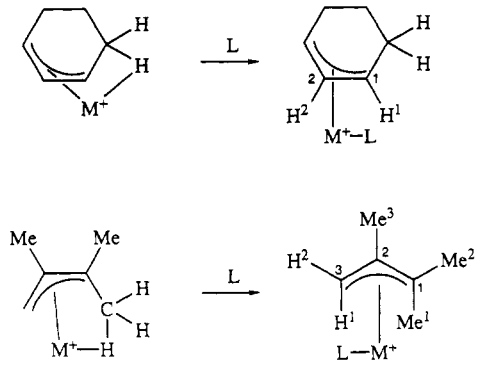
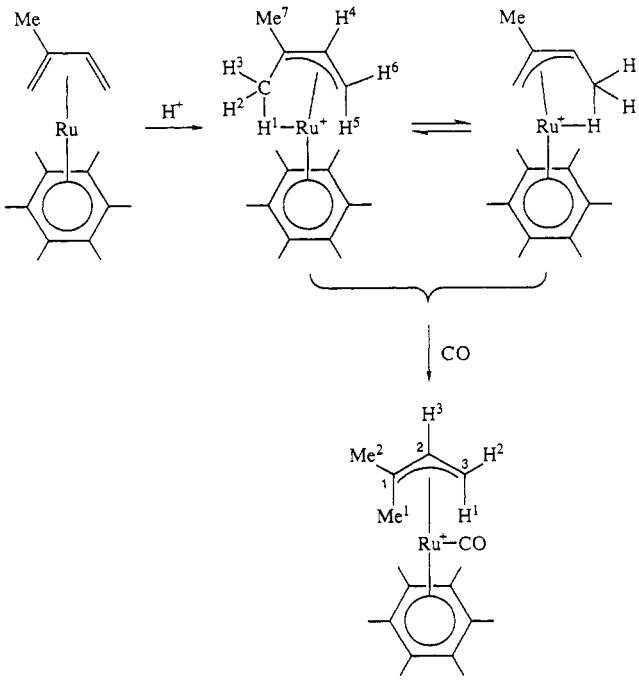
Scheme V. Addition of Ligands to Agostic η^3-Cyclohexenyl Complexes and to Agostic η^3-1,1,2-Trimethylallyl Complexes



Scheme VI. Addition of CO to the Protonated Salt of Ru(η-C_6Me_6)(η^4-isoprene)



(Arene)ruthenium and (Arene)osmium η^3-Allyl Complexes. The coordinatively unsaturated, 16e η^3-allyl complexes that are likely intermediates in the fluxional processes of protonated 1,3-diene complexes can often be intercepted by reaction with 2e donors.[1-3,4b,13,32] The complexes formed by protonation of 1,3-dienes react with CO, *t*-BuNC, and $P(OMe)_3$ to give yellow, air-stable solids of general formula $[M(\eta\text{-arene})(\eta^3\text{-allyl})L]^+$ (M = Ru, Os) or $[M(\eta\text{-}C_5Me_5)(\eta^3\text{-allyl})L]^+$ (M = Rh, Ir), which are readily characterized by elemental analyses and by NMR (^1H, ^{13}C) spectroscopy (Tables III and IV). They are not fluxional and show no tendency to lose the added ligand. The ^1H NMR spectra of the η^3-cyclohexenyl complexes show a pair of triplets in a 2:1 ratio in the region δ 3.5–4.5 due to the terminal and inner allylic protons H^1 and H^2, respectively, in addition to the methylene resonances (Scheme V). Addition of ligands (CO, *t*-BuNC, $P(OMe)_3$) to the protonated 2,3-dimethylbutadiene complexes gives η^3-1,1,2-trimethylallyl complexes that show in their ^1H NMR spectra three methyl singlets and a pair of 1 H doublets (J_{HH} ca. 3 Hz) in the region δ 2–3 due to the terminal allylic protons.

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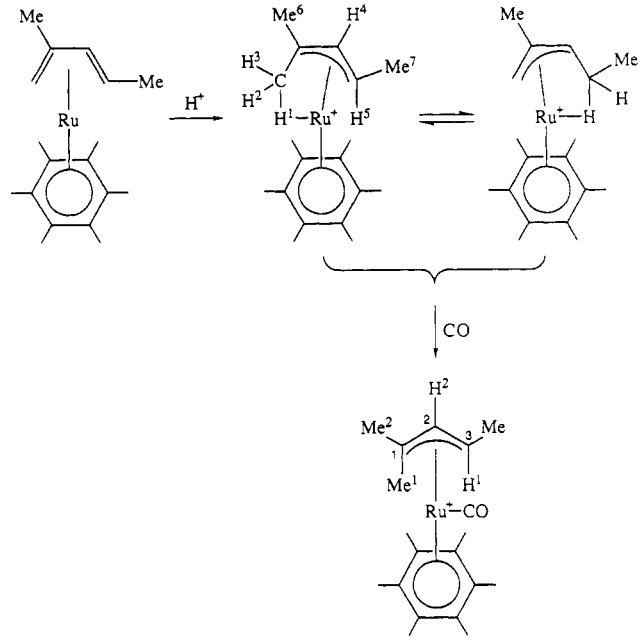
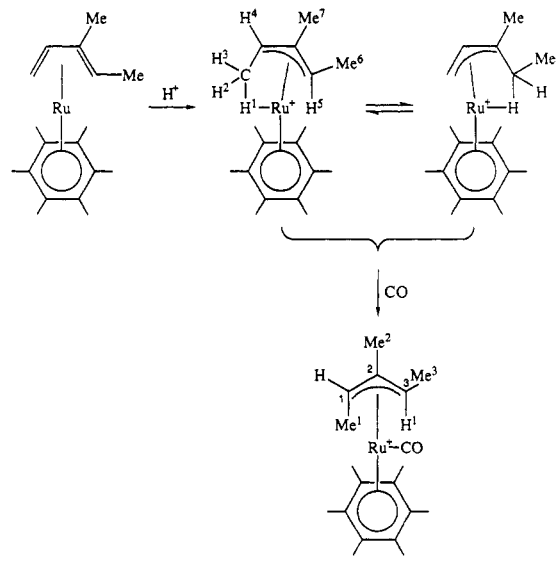
Scheme VII. Addition of CO to the Protonated Salt of Ru(η-C_6Me_6)(η^4-2-methyl-1,3-pentadiene)



Scheme VIII. Addition of CO to the Protonated Salt of Ru(η-C_6Me_6)(η^4-3-methyl-1,3-pentadiene)



The reaction of ligands with the protonation product of Ru(η-C_6Me_6)(isoprene) could give two isomers, viz. the 1,1-dimethyl-η^3-allyl complex and the *anti*-1,2-dimethyl-η^3-allyl complex (Scheme VI). The ^1H NMR spectrum of the carbonyl cation indicates the former to be the exclusive product; there are two singlets due to the inequivalent methyl groups and a pair of doublets of doublets at δ 3.57 and 2.79 due to the central proton H^3 and the syn-terminal proton H^2 (J_{13} = 11.5 Hz, J_{23} = 7 Hz, J_{12} = 3 Hz); the resonance due to the anti-terminal proton H^1 is obscured by the C_6Me_6 singlet.

Addition of CO to the complexes formed by protonation of Ru(η-C_6Me_6)(2-methyl-1,3-pentadiene) and Ru(η-C_6Me_6)(3-methyl-1,3-pentadiene) causes the proton to migrate exclusively to the unsubstituted diene carbon atom to give, respectively, the η^3-*syn*-1,1,3-trimethylallyl and η^3-*anti,syn*-1,2,3-trimethylallyl complexes (Schemes VII and VIII). The latter does not undergo anti–syn isomerization, either at room temperature or at 80 °C. The

closely related η^3-allyl complexes $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)L$ (L = CO, PPh_3) have been reported to exist in solution as conformational isomers in which the allyl group is either endo or exo with respect to the $\eta\text{-}C_5H_5$ group.[33-35] There was no evidence for isomers of this type in the arene complexes, and we assume that the η^3-allyl ligand is in the more stable exo conformation.

The ^{13}C NMR spectra of the arene η^3-allyl complexes are similar to those reported for other η^3-allyl complexes.[36] The resonance due to the central carbon atom appears at δ ca. 85 when the carbon atom carries only a hydrogen atom and at δ ca. 75 when it bears a methyl group. Unsubstituted terminal allylic carbon atoms resonate at δ ca. 40; those bearing one or two methyl groups appear at δ ca. 55 and 65–80, respectively. Similar substituent effects have been observed in the ^{13}C NMR spectra of a series of $[(\eta^3\text{-allyl})Fe(CO)_4]^+$ complexes.[37]

Addition of ligands to $[RuH(COD)(\eta\text{-arene})]PF_6$ gives cationic η^3-cyclooctenyl complexes $[Ru(\eta\text{-arene})(\eta^3\text{-}C_8H_{13})L]PF_6$ (L = CO, *t*-BuNC, $P(OMe)_3$) whose spectroscopic properties are similar to those of the cyclohexenyl complexes. This observation provides further evidence that the 16e species $[Ru(\eta\text{-arene})(\eta\text{-}C_8H_{13})]^+$ is in equilibrium with $[RuH(COD)(\eta\text{-arene})]^+$ (Scheme IV). Similar behavior has been noted for the neutral hydrido complex $RuH(\eta\text{-}C_5Me_5)(1,5\text{-COD})$, which reacts with ligands to give $[Ru(\eta\text{-}C_5Me_5)(\eta^3\text{-}C_8H_{13})L$ (L = PPh_3, *p*-xylyl(NC)).[38] The osmium complex $[OsH(\eta\text{-}C_6H_6)(COD)]PF_6$ does not react with ligands, consistent with its failure to incorporate deuterium in the presence of D_2O (see above).

Discussion

The results illustrate the well-recognized trend that terminal alkene- or diene–hydride structures are preferred over agostic structures for third-row transition elements such as iridium and osmium. For example, protonation of $M(\eta\text{-arene})(C_2H_4)_2$ generates the agostic species $[M(CH_2CH_2\text{-}\mu\text{-}H)(C_2H_4)(\eta\text{-arene})]^+$ for M = Ru and arene = C_6Me_6 and the terminal hydride $[MH(C_2H_4)_2(\eta\text{-arene})]^+$ for M = Os and arene = $C_6H_3Me_3$.[39] Not surprisingly, the free energy of activation for M–H bond cleavage in the terminal hydrido 1,3-diene complexes of iridium (Scheme II) is 3–4 kcal/mol higher than in the agostic η^3-enyl complexes of rhodium and ruthenium (process 1, Schemes I and III). For second-row elements, however, the free energy difference between the two isomeric forms is small [<3.7 kcal/mol for the protonation product of $Rh(\eta\text{-}C_5Me_5)(C_2H_4)_2$, which is agostic in the ground state].[40] This feature undoubtedly accounts for the highly fluxional nature of the protonated $Rh(\eta\text{-}C_5Me_5)$(1,3-diene) and $Ru(\eta\text{-arene})$(1,3-diene) systems. Another consequence is that the ground-state structure varies according to the nature of the ancillary ligands. Thus, the complexes $[RhH(\eta\text{-}C_5R_5)(C_2H_4)(L)]^+$ (R = H, L = PMe_3;[41] R = Me, L = PPh_3,[42] PMe_3,[42] $P(OMe)_2Ph$,[42] $P(OMe)_3$[43]) are terminal hydrides, whereas $[RhH(\eta\text{-}C_5Me_5)(C_2H_4)_2]^+$ is agostic.[40] Similarly, $[RuH(\eta\text{-}C_6Me_6)(C_2H_4)(PPh_3)]^+$ is a terminal hydride,[44] whereas $[RuH(\eta\text{-}C_6Me_6)(C_2H_4)_2]^+$ is agostic.[39] This fine balance becomes even more evident in the behavior of $[RuH(\eta\text{-arene})(1,3\text{-diene})]^+$. Although these probably adopt an agostic structure in the solid state,[29] the interaction between the metal atom and the C–H bond is so strong, and the C–H bond is presumably so weakened, that the C–H bond breaks more easily than the M–H bond in the fluxional process, which is the reverse of the normal order. At the lowest accessible temperature (ca. −100 °C), therefore, the ^1H NMR spectra resemble those expected for terminal hydrido diene complexes. The closely related agostic (η^5-2,4-dimethylpentadienyl)ruthenium(IV) complexes $[RuH(\eta^5\text{-}C_7H_{11})_2]^+$,[45] $[RuH(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_7H_{11})]^+$,[46] and $[RuH(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_7H_{11})]^+$,[46] which were reported during the preparation of this manuscript, belong in the same category, the $\Delta G^\ddagger$ values in kcal/mol for reversible M–H and C–H bond cleavage being respectively 11.1 (M–H), 9.3 (C–H); 12.6 (M–H), <7.2 (C–H); and 11.3 (M–H), <7.2 (C–H). In surprising contrast, the (η^5-cyclooctadienyl)ruthenium(IV) complex $[RuH(\eta^5\text{-}C_8H_{11})_2]^+$ is a terminal hydride.[47] The only other case of which we are aware where the normal order for the activation energies of M–H and C–H bond cleavage is reversed (or, at least, the two become equal within experimental error) is $[Rh(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_6H_{11})]^+$ [values of $\Delta G^\ddagger$ at −117 °C: 7.7 ± 0.2 kcal/mol (process 1), 7.5 ± 0.2 kcal/mol (process 2).[13]

The fluxional behavior of the protonated $RuL_3(\eta^3\text{-}1,3\text{-diene})$ complexes (L = various tertiary phosphines) seems to be normal, i.e. M–H bond cleavage precedes C–H bond cleavage.[7,8] Because 1,3-dienes are probably better π acceptors than tertiary phosphines, the agostic M–H–C interaction in the tertiary phosphine complexes may be weaker (i.e. the C–H bond may be stronger) than in $[RuH(\eta\text{-arene})(1,3\text{-diene})]^+$ because of the greater electrophilicity of the metal center in the latter. However, steric effects may also be important, and it would be of obvious interest to examine the protonation behavior of $Ru(CO)_3$(diene) complexes.

The 1,5-cyclooctadiene complexes clearly prefer to form terminal hydrides on protonation, even for ruthenium, although an agostic η^3-enyl species is a likely intermediate in the reversible hydride transfer between ruthenium and diene. This process appears not to occur readily for the corresponding complexes of osmium and iridium, in line with their greater tendency of these third-row elements to form terminal hydrides.

Acknowledgments. We thank the National Science Foundation for Grant CHE-8705534 (to M.B.) and Johnson-Matthey (U.K.) for generous loans of $RuCl_3$ and OsO_4 (to M.A.B.).

Registry No. 1, 137202-56-3; 2, 137202-58-5; 3, 137202-59-6; 4, 137202-61-0; 5, 137202-63-2; 6, 137202-65-4; 7, 137259-16-6; 8,

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Supplementary Material Available: Tables of elemental analyses and parent ions in mass spectra of (arene)ruthenium diene and (arene)osmium diene complexes and elemental analyses and decomposition points of protonated diene complexes and of their ligand derivatives (4 pages). Ordering information is given on any current masthead page.

Selective Hydrogenation of 1-Alkynes to Alkenes Catalyzed by an Iron(II) *cis*-Hydride η^2-Dihydrogen Complex. A Case of Intramolecular Reaction between η^2-H_2 and σ-Vinyl Ligands

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Received June 17, 1991

The reactions of the *cis*-hydride η^2-dihydrogen complex [$(PP_3)Fe(H)(H_2)$]BPh_4 (1) and of the dinitrogen derivative [$(PP_3)Fe(H)(N_2)$]BPh_4 (2) with a variety of 1-alkynes have been investigated. From this study, it is apparent that the insertion of the alkyne across the Fe–H bond in 1 to give a σ-alkenyl intermediate proceeds via decoordination of a phosphine arm of PP_3 rather than via H_2 decoordination. Terminal alkynes are selectively and catalytically hydrogenated to alkenes by 1 in tetrahydrofuran or 1,2-dichloroethane solutions under mild conditions. A kinetic study on the hydrogenation reaction of HC≡CPh to H_2C=CHPh has shown that the reduction is first order in catalyst and alkyne concentrations and zero order in hydrogen pressure. Incorporation of a large body of experimental data leads to the conclusion that (i) the dihydrogen ligand does not leave the metal prior to alkyne coordination and (ii) the reduction of the substrate most likely occurs via an intramolecular acid/base reaction involving η^2-H_2 and σ-vinyl ligands mutually cis disposed.

Introduction

In 1984 an X-ray analysis revealed the presence of an intact H_2 ligand in Kubas' complex [$W(\eta^2$-$H_2)(CO)_3(PCy_3)_2$].[1] Since then, essentially due to the development of improved diagnostic tools for distinguishing classical from nonclassical metal polyhydrides,[2] more than 100 η^2-H_2 complexes have appeared in the literature.[3,4] Most d-block metals, in various oxidation states, can form a stable dihydrogen adduct when assisted by an appropriate ligand set. It is therefore quite reasonable to state that (dihydrogen)metal complexes now constitute a class of compounds.

In comparison with the abundance and variety of compounds, what is known of the chemical properties of coordinated dihydrogen (the H_2 ligand may behave as a good leaving group[5] and may exhibit remarkable acidic char-

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