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Formation of η^3-Cyclooctenyl Complexes from Hydride Transfer Reactions in Hydrido(cycloocta-1,5-diene)tris(ligand)ruthenium(II) Cations: The Dominant Role of Steric Effects

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The hydrido diene complexes $[RuH(cod)L_3][PF_6]$ [1, cod = cycloocta-1,5-diene, L = $P(OMe)_2Ph$, PMe_3, PMe_2Ph, $P(OMe)Ph_2$, and $PMePh_2$, and $L_3 = CH_3C(CH_2PPh_2)_3$] convert irreversibly in dichloromethane or nitromethane solution to the η^3-cyclooctenyl complexes $[Ru(\eta^3\text{-}C_8H_{13})L_3][PF_6]$, **2**, in the temperature range 273–363 K. The ease of conversion of **1** to **2** may be correlated with increasing size of L. NMR studies of **2** show a bonding interaction between the metal and an endo C–H bond adjacent to the η^3-allylic group. Two fluxional processes govern the appearance of the NMR spectra of **2**: one process involves the mutual exchange of the three phosphorus donor ligands, whereas the other process involves the endo hydrogen atoms on the two carbon atoms adjacent to the allylic functionality. Other hydrido diene complexes [**1**, L = $P(OMe)_3$, $AsMe_3$, $AsMe_2Ph$, and $AsMePh_2$] do not isomerize to **2** in detectable amounts (by ^{1}H NMR) up to temperatures at which decomposition occurs. All the new compounds were isolated as analytically pure solids and were characterized by IR and ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy.

Introduction

The preliminary reports on the formation[1] and structure[2] of the cation $[Fe(\eta^3\text{-}C_8H_{13})\{P(OMe)_3\}_3]^+$ contained the first description of a bonding interaction between a metal atom and the endo hydrogen atom adjacent to an allylic functional group (Figure 1, M = Fe). This M···H–C interaction, which has been described as approaching a two-electron, three-center bond (with the hydrogen atom occupying a bridging position), apparently arises so that the metal can approach a complete 18-electron configuration. These species are members of a more general class of compounds,[3] those which contain an interaction between the metal center and a proximal CH bond of a ligand. The term agostic has been proposed[4] to describe this type of bonding interaction. The study of complexes containing agostic ligands is attracting increasing interest[5] especially in the context of C–H bond activation and aliphatic C–H bond fission.

Other systems containing an agostic η^3-allylic ligand have since been characterized, including $[Fe(\eta^3\text{-enyl})\{P(OMe)_3\}_3]^+$ (enyl = butenyl, cyclohexenyl, and cycloheptenyl),[6] $[Ir(H)(\eta^3\text{-2,3-dimethylbutenyl})(PPh_3)_2]^+$,[7] $[Mn(\eta^3\text{-cyclohexenyl})(CO)_3]$,[8] and $[Ru(\eta^3\text{-cyclohexenyl})(C_6Me_6)]^+$.[9] These species have a number of interesting chemical and spectroscopic properties in common including (1) a high-field resonance in the ^{1}H NMR spectra due to coordination to the metal of an endo hydrogen atom and (2) fluxional processes including intramolecular ligand exchange, exchange between coordinated and noncoordinated endo hydrogen atoms, and reversible hydrogen transfer between the metal and the hydrocarbon moiety.

In a preliminary communication, we reported[10] the conversion of a range of hydrido cycloocta-1,5-diene complexes of ruthenium(II) into the corresponding η^3-enyl complexes $[Ru(\eta^3\text{-}C_8H_{13})L_3]^+$ (Figure 1, M = Ru). These complexes are of interest for two reasons: first they are analogues of the complex $[Fe(\eta^3\text{-}C_8H_{13})\{P(OMe)_3\}_3]^+$ and second, access to a range of complexes provides the first opportunity of studying how changes in the steric and electronic properties of the ligands L affect the M···H–C interaction. This paper contains the preparation and spectroscopic characterization of the various η^3-cyclooctenyl complexes and a discussion of their formation from new and previously isolated[11] hydrido diene complexes. These studies have shown that the conversion of the hydrido 1,5-diene complex into an η^3-allyl species is clearly influenced by the size of the ligand L.

Results

Preparation of Hydrido Cycloocta-1,5-diene Complexes $[RuH(cod)L_3][PF_6]$ (1). By slightly modifying our previously published procedure[11] for the preparation of hydrido diene complexes $[RuH(cod)L_3][PF_6]$ (1, cod = cycloocta-1,5-diene), we have succeeded in isolating these salts for a greater range of ligands. Thus, in one modification, the reaction of $[RuH(cod)(NH_2NMe_2)_3][PF_6]$[12] with phosphorus donor ligands in MeOH in the temperature range of −10 to 0 °C gave high yields of the salts 1 [L =

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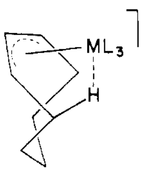
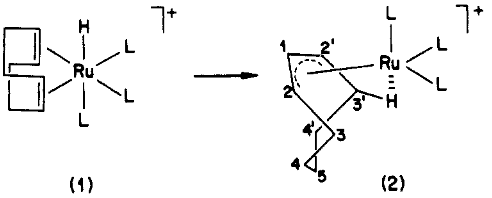


Figure 1. Coordination geometry of the cations $[M(\eta^3\text{-}C_8H_{13})L_3]^+$ (M = Fe, Ru).



(1) (2)

Figure 2. Coordination geometry of the hydrido cycloocta-1,5-diene complex 1 and the atom numbering of the η^3-cyclooctenyl ligand in 2.

P(OMe)$_2$Ph, P(OMe)Ph$_2$, and PMePh$_2$; L_3 = $CH_3C(CH_2PPh_2)_3$] as white, cream, or pale yellow microcrystalline precipitates, whereas the tertiary arsine complexes 1 (L = AsMe$_3$, AsMe$_2$Ph, and AsMePh$_2$) were obtained by carrying out the appropriate reaction in acetone under reflux[13] or, with L = AsMePh$_2$, at room temperature. The compounds decomposed in air, slowly in the solid state and more rapidly (within ca. 30 min) in solution. They could be stored indefinitely under dinitrogen at −20 °C; at higher temperatures, however, most[14] of the complexes, even in the solid state, eventually converted to the η^3-cyclooctenyl species 2. All the IR spectra (Nujol mulls) of the complexes 1 contained an absorption in the region 1965–2090 cm^{-1}, assigned to the Ru-H stretching frequency. These data[15] together with melting points, microanalytical results, and NMR data from ^{1}H, ^{13}C, and ^{31}P studies are given in Tables I, II, and III, respectively.

Preparation of the η^3-Cyclooctenyl Complexes $[Ru(\eta^3\text{-}C_8H_{13})L_3][PF_6]$ (2). On warming solutions of 1 [L = P(OMe)$_2$Ph, PMe$_2$Ph, P(OMe)Ph$_2$, and PMePh$_2$; L_3 = $CH_3C(CH_2PPh_2)_3$] between 0 and 60 °C or by reacting 3 molar equiv of L with $[RuH(cod)(NH_2NMe_2)_3][PF_6]$ in acetone under reflux, rapid hydride transfer occurred to give the corresponding η^3-cyclooctenyl species 2 (Figure 2). For 1, (L = PMe$_3$) conversion to 2 occurred only on heating nitromethane solutions of the complex at ca. 70 °C. None of these hydride transfer processes was observed to be reversible on cooling the solutions down to −90 °C. The η^3-cyclooctenyl species 2 were isolated by precipitation from cold ethanol. Relevant data for the complexes are given in Tables I–III.

Attempts to obtain the corresponding η^3-cyclooctenyl complexes by heating 1 [L = P(OMe)$_3$, AsMe$_3$, AsMe$_2$Ph, and AsMePh$_2$] in dichloromethane, acetone, nitromethane, and dimethyl sulfoxide led either to recovery of the starting material, decomposition, or, in the case of the arsine ligands, conversion to uncharacterized species with liberation of cycloocta-1,3-diene.

NMR Studies of the Complexes 1 and 2. The complexes exhibited three separate processes that governed the appearance of the NMR spectra. The first was the irreversible change from the hydrido diene isomer 1 to the η^3-cyclooctenyl isomer 2. Thus, the history of the solution was important; spectra of 1 were obtained from material dissolved and studied at a temperature low enough to prevent conversion to the η^3-cyclooctenyl species. When the solution was allowed to warm, signals for either 2, or both 1 and 2 simultaneously, were observed depending on the rate of the isomerization process and the length of time that the solution was at the higher temperature. The second process was the mutual exchange of the three phosphorus nuclei of 2 rendering them equivalent on the NMR time scale and giving rise to an A_3 spin system. There was also evidence from one complex (vide infra ^{31}P NMR) that such a process might occur in the hydrido diene isomers as well. Upon cooling, the exchange of phosphorus nuclei was slowed so that ^{31}P spectra of an AB_2 spin system were obtained. The equivalence of two of the phosphorus nuclei arose from the third isomerization process that exchanged bridged and unbridged endo hydrogen atoms H_3 and H_3' (Figure 2). At still lower temperatures this process was slowed, giving an ABC spin system indicating that one of the endo hydrogen atoms occupied the sixth coordination site for a time which was long on the pertinent time scale.

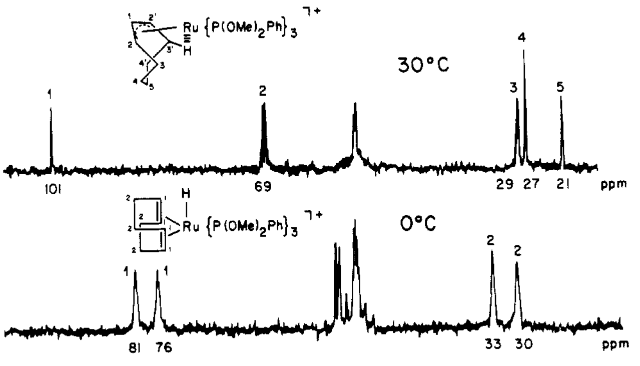


Figure 3. ^{13}C NMR spectra of the isomers 1 and 2 [L = P(OMe)$_2$Ph].

The two reversible exchange processes have been discussed in detail by Ittel et al.[6] and Brookhart et al.,[8] who have used ^{1}H, ^{13}C, and ^{31}P NMR to investigate the M···H–C bonding. In view of their work such detailed investigations on our systems were unnecessary and we restricted our studies to (1) obtaining characteristic data for the complexes, (2) establishing trends along the series, and (3) comparing the properties of the ruthenium species described here with the $[Fe(\eta^3\text{-cyclooctenyl})\{P(OMe)_3\}_3]^+$ complex.

^{1}H NMR Spectra of 1 and 2. The ^{1}H NMR spectra of 1 each contained olefinic proton resonances typical[12,16-18] of a coordinated cycloocta-1,5-diene ligand and a high-field signal (−5 to −9 ppm), confirming the presence of a metal hydride group. For the complexes with phosphorus donor ligands the hydride resonance comprised a doublet (J_{Trans} = 80 Hz) of triplets (J_{cis} = 20 Hz), establishing the ligand configuration to be as shown for 1 in Figure 2. The ^{1}H NMR spectra of 2 in CD_2Cl_2 at normal temperatures show characteristic allylic resonances (ca. 5 (t, 1 H), ca. 4 ppm (q, 2 H)), a complex aliphatic resonance (1.2–1.8 ppm (8 H)), and a high-field signal (ca. −2 ppm (2 H)). The high-field signal is due to the exchange average of the two endo hydrogen atoms of C_3 and C_3' alternating between

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[13] At room temperature incomplete substitution of the dimethylhydrazine ligands occurred; these hydrazine-containing complexes will be described in a separate publication.

[14] The complexes (1, L = P(OMe)$_3$, PMe$_3$, AsMe$_3$, and AsMe$_2$Ph) are stable for several months, at 20 °C under nitrogen.

[15] The complexes (1, L = P(OMe)$_3$, $P(OCH_2)_3Me$, and PMe$_2$Ph) have been characterized previously.[11]. The spectroscopic data reported previously[10] for [1, L = PMePh$_2$ and P(OMe)Ph$_2$] are actually those of the cyclooctenyl isomers.

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Table I. Color, Melting Point, Analyses, Infrared, and ^{1}H NMR Data of the Complexes

ligand	isomer	color	mp,[a] °C	analyses[b] C	analyses[b] H	infrared,[c] cm^{-1} (Ru-H)	solv and temp, °C	^{1}H NMR[d]
$P(OMe)_2Ph$	1	white	e	44.01 (44.40)	5.21 (5.36)	1980	CD_2Cl_2, −20	3.6–3.7 (br m, OMe, 18 H), 1.1–5.0 (br, cod, 12 H), −5.62 (dt, J_{trans} = 71, J_{cis} = 21, RuH)
	2	yellow	125–127	44.17 (44.40)	5.32 (5.36)		CD_2Cl_2, 34	4.8 (t, C_1H, 1 H), 4.00 (q, C_2H, 2 H), 3.47 (t,[f] J = 11.4,[g] OMe, 18 H), 1.9–0.9 (br m, C_4H and C_5H, 6 H), −1.85 (br m, endo C_3H, 2 H)
PMe_3	1	white	e	35.1 (35.00)	7.18 (6.91)	1990	CD_3NO_2, 34	3.07–3.93 (br m, =CH, 4 H), 1.95–2.67 (br m, CH_2, 8 H), 1.70 (d, J = 6.6, Me, 9 H), 1.42 (t, J = 8.7, Me, 18 H), −6.00 (dt, J_{trans} = 54, J_{cis} = 30, RuH)
	2	yellow	>130[h]	35.03 (35.00)	6.80 (6.91)		CD_3NO_2[i]	4.90 (t, C_1H, 1 H), 4.08 (q, C_2H, 2 H), 1.0–2.6 (br m, exo C_3H, C_4H, C_5H, and Me, 33 H), −1.73 (br m, endo C_3H)
PMe_2Ph	1	cream	e	50.27 (49.94)	5.99 (6.02)	1985	CD_2Cl_2, −20	2.3–4.3 (br, cod, 12 H), 2.2–1.3 (br, Me, 18 H), −8.6 (dt, J_{trans} = 60, J_{cis} = 30, RuH)
	2		132–134				CD_2Cl_2, 34	5.10 (t, C_1H, 1 H), 3.95 (q, C_2H, 2 H), 1.0–2.3 (br, endo C_3H, 2 H)
$P(OMe)Ph_2$	1	white	e	j			CD_2Cl_2, −10	3.8 (br s, =CH, 2 H), 3.3 (d, J_{PH} = 10, OMe, 3 H), 3.1 (br s, OMe, 6 H), 3.2–1.1 (br, =CH and CH_2, 10 H), −5.36 (dt, J_{trans} = 62, J_{cis} = 25, RuH)
	2	yellow	168–169	k			CD_2Cl_2, 34	4.65 (t, C_1H, 1 H), 3.75 (q, C_2H, 2 H), 3.1–3.9 (br m, OMe, 9 H), 1.0–1.5 (br m, exo C_3H, C_4H, and C_5H, 6 H), −1.80 (br, endo C_3H, 2 H)
$PMePh_2$	1	white	e	j		2070	CD_2Cl_2, −20	1.6–4.2 (s and br m, cod and Me, 21 H), −5.16 (dt, J_{trans} = 52, J_{cis} = 26, RuH)
	2	orange	154–156	k			CD_2Cl_2	7.0–7.9 (br m, Ph, 30 H), 3.6–5.3 and 1.2–2.4 (s and br m, C_1–C_5H and Me, 20 H), −2.45 (br, endo C_3H, 2 H)
$CH_3C(CH_2PPh_2)_3$	1	cream	e	59.75 (60.05)	5.45 (5.35)	2090	CD_2Cl_2, 34	3.40 (br s, =CH, 2 H), 2.95 (br s, =CH, 2 H), 2.75–2.0 (CH_2, 14 H), 1.70 (s, CH_3, 3 H), −5.0 (dt, J_{trans} = 50, J_{cis} = 20, RuH)
	2	orange	164	59.50 (60.05)	5.25 (5.35)		CD_2Cl_2, 34	5.58 (t, C_1H, 1 H), 4.53 (q, C_2H, 2 H), 2.8–2.2 (br), 2.25 (m), 1.95 (m), 1.78 (m), 1.45 (m, CH_2 and exo C_3H, 14 H), 1.53 (s, CH_3, 3 H), −1.4 (s, endo C_3H, 2 H)
$P(OCH_2\text{-}t\text{-}Bu)_3$	2	white		51.70 (51.65)	9.25 (9.15)		$(CD_3)_2CO$, 34	5.58 (t, C_1H, 1 H), 4.90 (q, C_2H, 2 H), 4.05 (s, OCH_2, 6 H), 3.90 (s, OCH_2, 12 H), 4.5–1.2 (br, exo C_3H, C_4H, and C_5H, 8 H), 1.1 (br, t-Bu, 81 H), −1.9 (br, endo C_3H, 2 H)
$AsMe_3$	1	beige	>120[h]	28.73 (28.55)	5.67 (5.64)	1990	CD_2Cl_2, 34	3.4–3.73 (br m, =CH, 2 H), 1.82–2.97 (br m, CH_2, 8 H), 1.60 (s, Me, 9 H), 1.30 (s, Me, 18 H), −6.07 (s, RuH)
$AsMePh_2$	1	beige	>130[h]	51.88 (51.90)	4.83 (4.82)	2080	CD_2Cl_2, 34	1.5–4.2 (br m, Me and cod, 21 H), −5.24 (s, RuH)
$AsMe_2Ph$	1	beige	145–148	42.41 (42.63)	5.33 (5.14)	2020 sh, 1980 s	CD_2Cl_2, 34	3.63–4.00 (br m, =CH, 2 H), 1.67–2.75 (br m, CH_2, 8 H), 1.88 (s, Me, 6 H), 1.50 (s, Me, 6 H), 1.33 (s, Me, 6 H), −5.53 (s, RuH)

[a] In air, melting points corrected. [b] Calculated values are in parentheses. [c] Nujol mulls, sh = shoulder, s = strong. [d] Values in ppm; J in Hz; s = singlet, d = doublet, t = triplet, q = quartet, br = broad, br m = broad multiplet, dt = doublet of triplets. Phenyl proton resonances omitted. [e] Hydride converts to allyl before melting. [f] Virtual coupled triplet. [g] Separation of outer peaks. [h] Decomposition without melting. [i] Sample heated to 70 °C, spectrum run at 34 °C. [j] Rapid conversion to allyl precludes analysis. [k] Reference 11.

Table II. Selected ^{13}C NMR Data for Complexes 1 and 2

		$P(OMe)_3$	$P(OCH_2$-t-$Bu)_3$	$P(OMe)_2Ph$	PMe_3	PMe_2Ph	$P(OMe)Ph_2$	$AsMe_3$	$AsMe_2Ph$	$AsMePh_2$
1	CH	88.8, 85.1[a]		88.1, 84.6	80.8, 76.1[b]	81.8, 77.5[a]	85.8, 81.6[b]	73.6, 69.7[e]	76.2, 72.9[c]	74.0, 69.3[a]
	CH_2	32.4, 28.6[a]		32.4, 28.6	32.9, 30.4[b]	32.1, 28.4[a]	31.6, 28.6[b]	32.3, 29.0[e]	32.0, 29.1[c]	27.9, 25.2[a]
2	C_1		99.1[e]	101.1[a]	98.5[d]	97.0[a]	99.1[a]			
	C_2		66.6[e]	68.9[a]	64.0[d]	65.9[a]	68.8[a]			
	C_3		27.2[e]	27.4[a]	29.5[d]	29.1[a]	28.5[a]			
	C_4		28.3[e]	28.6[a]	28.0[d]	28.7[a]	28.5[a]			
	C_5		21.7[e]	21.7[a]	22.5[d]	21.7[a]	21.6[a]			

[a] CD_2Cl_2, 30 °C. [b] CD_2Cl_2, 0 °C. [c] $(CD_3)_2SO$, 30 °C. [d] CD_3NO_2, 30 °C after heating to 70 °C. [e] CD_2Cl_2, −40 °C.

Table III. ^{31}P NMR Data[a] for Complexes 1 and 2

	isomer 1				isomer 2			
L	T[b]	P_A	P_B	J	T[b]	P_A	P_B	J
$P(OMe)_3$[c]	273	143.5	140.4	55				
$P(OMe)_2Ph$[c]	253	168.8	164.7	41	193	173.6	170.9	52
PMe_3	303	−22.8	−10.9	34	253	40.0	−7.6	36
PMe_2Ph	233	−9.2	1.2	31	233	46.5	5.2	34
$P(OMe)Ph_2$[c]	193	136.9	132.5	37	253	155	138	
$PMePh_2$	253	−2.6	16.4	27	223	48.3	15.0	30
$CH_3C(CH_2PPh_2)_3$	223	6.4	23.9	32	223	67.1	26.7	40

[a] For solutions in CD_2Cl_2 except L = PMe_3 (CD_3NO_2). δ from external H_3PO_4 positive downfield; J in Hz. P_A is the unique phosphorus of the AB_2 systems. [b] Temperature of solution in degrees Kelvin. [c] Values from second-order analysis.

a coordination site at the ruthenium atom and a position removed from the metal (i.e., between a bridged and unbridged form). For 2 [L = $P(OMe)Ph_2$] the slow-exchange spectrum was obtained at 203 K by using a 500-MHz instrument; signals at 0.15 (1 H) and −5.62 ppm (1 H) attributable to unbridged and bridged H_3 endo protons, respectively, were observed. However, the complex with the less bulky ligand, L = $P(OMe)_2Ph$, did not give slow-exchange spectra even at 183 K. When acetone-d_6 was used in place of CD_2Cl_2, the spectra of 2 at 30 °C contained additional resonances characteristic of uncoordinated cycloocta-1,3-diene.

^{13}C NMR Spectra of 1 and 2. As described in our preliminary communication, the ^{13}C NMR spectra afforded a direct method of distinguishing between the hydrido diene species 1 and the η^3-cyclooctenyl species 2 (Figure 3). The coordinated cyclooctadiene gave rise to four resonances (1:1:1:1, 2CH + $2CH_2$) in the ^{13}C NMR spectra of 1, whereas the isomer 2 showed five resonances (1:2:2:2:1, 2CH + $3CH_2$) for the η^3-cyclooctenyl ring. Moreover, with the ^{31}P-containing ligands, each isomer contained resonances where ^{31}P–^{13}C couplings were resolved: for 1 these consisted of a second-order multiplet due to an [AA′MX] spin system, whereas for 2 these signals appeared as a binomial quartet due to an $[A_3X]$ spin system. The twofold symmetry in the η^3-cyclooctenyl ring arises because of exchange between the C–H endo protons of the two C_3 carbons (see Figure 3) one of which interacts at any one time with the metal atom. The extreme low-temperature forms of 2 (AB_2 and ABC ^{31}P spin systems) were not attained with ^{13}C NMR. Assignments for the cyclooctenyl ligand can be made from the chemical shifts, relative intensities, and sford multiplicities except for distinction between C_3 and C_4 both of which give signals in the region 27.4 to 29.4 ppm. Selective $^{13}C\{^1H\}$ decoupling at the ^1H frequency of H_3 endo gave the assignment of Table IV for 2 [L = $P(OMe)_2Ph$]. Otherwise, the assignments were made by assigning C_4 to the constant signal at 28.6 ± 0.1 ppm in CD_2Cl_2 solutions.

^{31}P NMR Spectra of 1 and 2. The ^{31}P NMR spectra of 1 [L = PMe_3, PMe_2Ph, and $PMePh_2$; L_3 = $CH_3C(CH_2PPh_2)_3$] consist of a doublet (2 P) and a triplet (1 P) for, respectively, two equivalent ^{31}P nuclei trans to the cyclooctadiene ligand and a unique ^{31}P nucleus trans to the hydride ligand. The spectra of the phosphite complexes showed little difference between the chemical shifts of the nonequivalent phosphorus nuclei. For L = $P(OMe)Ph_2$ an exchange broadened signal was obtained at 263 K that separated and sharpened on cooling to give at 193 K the slow-exchange spectrum of the hydrido diene species. The latter observation indicated that ligand interchange might occur when complexes 1 contained bulky ligands.

Table IV. Assignment[a] of Chemical Shift Values to the η^3-Cyclooctenyl Protons of Complex 2 [L = $P(OMe)_2Ph$]

carbon atom	^1H	^{13}C
1	4.89 (t)	101.1
2	4.12 (q)	68.9
3	−1.89 (12 peaks, endo H), 1.84 (m, exo H)	27.4
4	1.24–1.76 (m overlapping with m of H(5))	28.6
5	1.24–1.70 (m overlapping with m of H(4))	21.7

[a] Selective $^{13}C\{^1H\}$ using the above proton frequencies at 125 MHz (Bruker WM-500); CD_2Cl_2 solution. Chemical shifts in ppm.

The conversion of the phosphine complexes 1 into 2 [L = PMe_3, PMe_2Ph, and $PMePh_2$; L_3 = $CH_3C(CH_2PPh_2)_3$] produced a large change (ca. 55 ppm) in the chemical shift of the unique phosphorus nucleus P_A with the change in position from trans to hydride to trans to the endo CH bond (Table III). The spectra of the phosphite complexes showed little difference in the chemical shifts of the two sets of nonequivalent phosphorus nuclei, and the shift of the resonance of the P_A nucleus with the isomerization was much smaller. The complex 2 [L = $P(OMe)Ph_2$] was studied at lower temperatures and gave the series of spectra of Figure 4 that demonstrated the changes involved as the spin system varied from A_3 through A_2M to AMX. The final low-temperature limiting spectrum consisted of three pseudotriplets at 153.9, 145.4, and 129.3 ppm with the three coupling constants in the range 37–42 Hz.

Discussion

Hydride transfer from a metal atom to a coordinated alkene, together with the reverse process "β-hydride

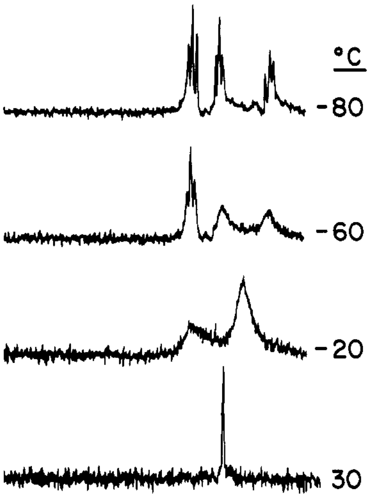


Figure 4. Variable-temperature ^{31}P NMR spectra of 2 [L = P(OMe)Ph$_2$].

elimination", has been implicated[17] in a number of catalytic reactions, including hydrogenation, isomerization, and hydroformylation. As a consequence of the relative ease of this intramolecular hydride migration reaction hydrido alkene complexes are rare. Migration of a hydride to a 1,3-diene ligand is equally facile as demonstrated by the protonation of [Fe(η^4-diene)L$_3$] complexes[6] and of [Mn(η^4-cyclohexadiene)(CO)$_3$][8] and the reaction of the hydride complex [Ir(H)$_2$(PPh$_3$)$_2$(OCMe$_2$)$_2$]$^+$ with 2,3-dimethylbutadiene,[7] all of which are proposed to occur through unstable hydrido diene intermediates. There are, however, a few examples of isolated hydrido alkene complexes and, in particular, of hydrido-1,3-diene complexes that are relatively stable, e.g., [IrH(η^5-C$_5$H$_5$)(1,3-cod)]$^+$,[18] [IrH(C$_4$H$_6$)(P-i-Pr$_3$)$_2$],[19] and [CoH(2,3-dimethyl-1,3-butadiene)(PPh$_3$)$_2$.][20]

So far, there is only one report of direct spectroscopic evidence for an equilibrium between hydrido diene and η^3-enyl forms; in an NMR study a number of hydridobis(η^4-diene)iridium complexes were shown[21] to be favored at low temperatures, whereas the corresponding η^3-enyl species predominated at higher temperatures. The question that necessarily arises from these observations is: what determines the relative stability of the two forms?

The formation of the η^3-cyclooctenyl species 2 was irreversible for all the reactions investigated in this study. Once conversion to 2 had occurred this process was not reversed by recooling the solution. Thus, the species 2 were thermodynamically stable with respect to the hydrido diene form 1 in the temperature range -90 to +90 °C.

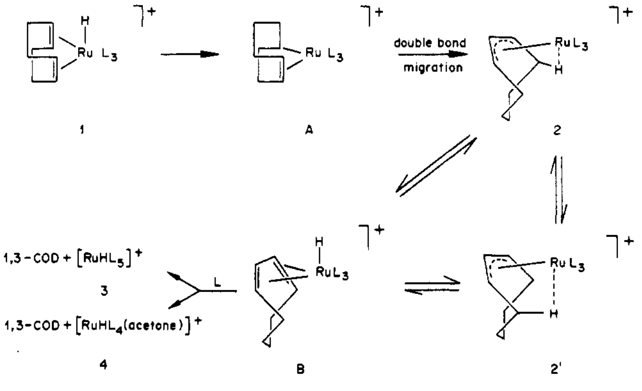
The kinetic stability of the hydrido cycloocta-1,5-diene cations 1 with respect to conversion to the cyclooctenyl species 2 varied considerably throughout the range of ligands used in this study. The reaction rate was influenced markedly by the size of the ligands L in 1. An increase in ligand size, within a class of ligands with similar electronic properties, led to increasing rates of reaction. The half-lives of the reaction at 30 °C are given in Table V for a number of the ligands used in this study. The ligands have been placed into groups containing electronically similar donor atoms. Within each group the reaction rate increases with increasing size of ligand and the influence of steric size is especially marked for the two pairs of ligands, CH$_3$C(CH$_2$PPh$_2$)$_3$, slower than PMePh$_2$, and P(OMe)$_3$, no reaction, and P(OCH$_2$-t-Bu)$_3$, very fast, where electronic differences between the ligands of each pair are minimal. In fact, even with the limited data, a rough plot of the observed rate constants vs. Tolman's cone angles and electronic parameters shows[22] a nice potential energy surface with strong steric and electronic contributions; however, an analytical description of the surface requires a larger data set that we are presently attempting to obtain.

Table V. Half-Lives of the Conversion[a] of [RuH(cod)L$_3$]$^+$ to [Ru(η^3-C$_8$H$_{13}$)L$_3$]$^+$

ligands L			
group 1	group 2	group 3	$t_{1/2}$, min
AsMe$_3$			no reaction
AsMe$_2$Ph		P(OMe)$_3$	no reaction
AsMePh$_2$	PMe$_3$		>60
		P(OMe)$_2$Ph	24.8
	CH$_3$C(CH$_2$PPh$_2$)$_3$		12.0
	PMe$_2$Ph		7.2
	PMePh$_2$	P(OMe)Ph$_2$	<1
		P(OCH$_2$-t-Bu)$_3$	too fast to allow isolation of 1

[a] The kinetics of the conversion of cations 1 to the cyclooctenyl species 2 were studied by conventional UV-visible spectrophotometry by monitoring the increase in optical density at λ = 375 nm in CH$_2$Cl$_2$ at a constant temperature of 309 K. Excellent linear plots of ln (OD$_\infty$ - OD$_t$) vs. reaction time were obtained for more than 90% of the reaction confirming a first-order process as expected for an intramolecular conversion of species 1 into species 2. The half-life of the reaction was read from the graph of ln (OD$_\infty$ - OD$_t$) vs. reaction time.

Scheme I



Our conclusion that the rate of formation of the η^3-cyclooctenyl species was increased by increasing ligand size is in apparent contradiction with observations made earlier[23] concerning the conversion of [CoH(2,3-dimethyl-1,3-butadiene)(PPh$_3$)$_2$] to [Co(η^3-1,1-dimethyl-2-methylallyl)(PF$_3$)$_3$] on reaction of the former compound with PF$_3$. The rationale given for the formation of a η^3-allyl on replacement of two PPh$_3$ ligands by three PF$_3$ groups was that "the lowering of steric constraints induces rapid diene insertion into the cobalt-hydrogen bond". It is not clear, however, that this rationale is valid; three PF$_3$ ligands may in fact cause greater steric crowding at the metal than two PPh$_3$ ligands (cone angle[22a] of PF$_3$ is 101° and of PPh$_3$

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145°). In addition, electronic effects cannot be discounted in this reaction as the donor/acceptor properties of PPh_3 and PF_3 are significantly different.

A plausible reaction pathway for the conversion of 1 into 2 is given in Scheme I. The first step is most likely a hydride transfer from the metal to an olefin group to form the coordinatively unsaturated species A of Scheme I. It is worth noting that the ligand configuration deduced for 1 (see ^1H NMR of Results) is that which contains a coplanar Ru(C=C)H system, thus allowing[24] rapid hydride transfer to occur. Evidence in support of an initial hydride transfer step came from the isolation of the complex $[Ru(1\text{-}\sigma, 4,5\text{-}\eta\text{-}C_8H_{13})(CNR)_4]^+$ from reactions of $[RuH(cod)(NH_2NMe_2)_3][PF_6]$ with isocyanide ligands.[26] In this case the intermediate A was "trapped" by coordination of an additional isocyanide ligand. The enyl ligand of A has been identified previously in several organometallic complexes, including $[Rh(\eta^5\text{-}C_5H_5)(1\text{-}\sigma,4,5\text{-}\eta\text{-}C_8H_{13})]^+$,[18] $[Pt(1\text{-}\sigma,4,5\text{-}\eta\text{-}C_8H_{13})L_2]$ (L_2 = acac, hfacac, and tfacac),[27] $[Pt(1\text{-}\sigma,4,5\text{-}\eta\text{-}C_8H_{13})cod]^+$,[27] and $[Co(1\text{-}\sigma,4,5\text{-}\eta\text{-}C_8H_{13})(cod)]$.[28] The latter complex is in labile equilibrium with a hydrido form $[CoH(cod)_2]$. Interestingly, an isomeric species $[Co(\eta^3\text{-}C_8H_{13})(cod)]$, which is not in equilibrium with the 1-σ-4,5-η-enyl form, has also been characterized.[16] Both species, however, react with CO or phosphines to give the same coordinatively saturated η^3-cyclooctenyl complexes $[Co(\eta^3\text{-}C_8H_{13})(cod)L]$ (L = CO, PR_3). Thus, in the cobalt system the σ-enyl form exists as a coordinatively unsaturated species, whereas in the ruthenium–isocyanide system the opposite is found.

Following the initial hydride transfer step, the resultant $1\text{-}\sigma,4,5\text{-}\eta\text{-}C_8H_{13}$ ligand can undergo successive addition–elimination reactions of β-hydrogen atoms (i.e., double-bond migration) until the η^3-cyclooctenyl species 2 are obtained. We favor this route over the alternative route, isomerization of 1,5- to 1,3-cod through suprafacial 1,3-hydrogen shifts,[29] since the reaction is affected by ligand size that would have a negligible influence on the latter route.

The interconversion between 2 and 2′ of Scheme I has been identified from the NMR studies in CD_2Cl_2 presented earlier in this paper. Under conditions of fast exchange, this dynamic process gives the η^3-cyclooctenyl species effective mirror symmetry. There is possibly a second dynamic process, however, that is inferred from the detection of uncoordinated cycloocta-1,3-diene in acetone-d_6 solutions of 2. This involves the formation of the hydrido 1,3-diene species B that may be in slow exchange with the two forms 2 and 2′ on the route to the species $[RuHL_5]^+$ (3) and $[RuHL_4]^+$ (4) in Scheme I.

The hydrocarbon ligand is readily displaced (as cycloocta-1,3-diene) on treating acetone solutions of either 1 or 2, heated under reflux, with excess ligand. In this way, the cations $[RuHL_5]^+$ [3, L = $AsMe_3$, $AsMe_2Ph$,[30] PMe_3,[11,31] $P(OMe)_2Ph$,[32] and PMe_2Ph[33]] were isolated as PF_6^- salts and for bulkier ligands the solvated species $[RuHL_4(acetone)]^+$ [4, L = $AsMePh_2$, $P(OMe)Ph_2$, and $PMePh_2$] were detected[30] in solution together with excess ligand.

The ease with which displacement of the hydrocarbon ligand occurs from complexes 1 in the above reactions parallels the ease with which 2 is formed from 1. For example 1 [L = $P(OMe)_3$], which does not form 2 and which contains the smallest ligand used, is inert toward substitution, whereas the hydrido diene complexes with the small arsine ligands $AsMe_3$ and $AsMe_2Ph$ react very slowly with excess of the respective ligands in refluxing acetone solutions. In the case of $AsMe_3$ a 1:1 mixture of 1 and $[RuH(AsMe_3)_5]^+$ is obtained after 3 days, and in the case of $AsMe_2Ph$ a relatively faster reaction occurs to give complete conversion to $[RuH(AsMe_2Ph)_5]^+$ after 20 h. Complex 1 (L = PMe_3) reacts slowly with excess PMe_3 at 56 °C, the temperature at which 2 (L = PMe_3) is detected to give $[RuH(PMe_3)_5]^+$ over a period of 12 h. The formation of $[RuHL_5]^+$ [L = $P(OMe)_2Ph$ and PMe_2Ph] and the solvated species $[RuHL_4(acetone)]^+$ [L = $AsMePh_2$, $P(OMe)Ph_2$, and $PMePh_2$] from the appropriate precursor 1 and excess ligand all occur rapidly (within 30 min) in refluxing acetone solutions.

We infer from the detection of cycloocta-1,3-diene and the trend of increasing reaction rates with steric size that the species 2 are also intermediates in the above substitution reactions of the arsine complexes.

Comparison of the reactivity of 2 toward substitution with that reported for the analogous iron complex $[Fe(\eta^3\text{-cyclooctenyl})\{P(OMe)_3\}_3]^+$ suggests that the η^3-cyclooctenyl group is more strongly bonded in the iron system as the iron complex was found to be inert toward substitution reactions except for the small ligands CO and *t*-BuNC. These ligands gave mixed $[Fe(enyl)L_4]^+$ species in which only the endo H coordination of the cyclooctenyl group was displaced.

Evidence for the relative strength of the Ru···H–C interaction comes from consideration of exchange averaged ^1H and ^{13}C chemical shifts. The preferred indication,[5] the value of $^1J(CH)$ at stopped exchange, seems inaccessible in both iron– and ruthenium–η^3-cyclooctenyl systems, and only in the case of complex 2 [L = $P(OMe)Ph_2$] could the slow-exchange ^1H spectrum be attained at 500 MHz. The ^{13}C spectrum of this solution gave only broad resonances, indicating that at 125 MHz the system was still at intermediate exchange at 183 K. If we take as the unperturbed value of $\delta(C_3)$ (32 ppm), the chemical shift reported for stable 16-electron Pd^+[27] and Pt^+[34] η^3-cyclooctenyl complexes, then the value for the Fe complex[6] (21 ppm) is substantially shielded, whereas the values for the Ru complexes (28 ppm) show less pronounced shielding. Inspection of $\delta(C_3)$ values (Table II) gives the trend $PMe_3 > PMe_2Ph > P(OMe)Ph_2 > P(OMe)_2Ph$, suggesting that the shielding responds to the basicity of L, the more basic ligands decreasing the electron deficiency at the metal and hence the degree of Ru···H–C interaction.

Conclusions

The hydrido diene species 1 convert, presumably through hydride migration followed by double-bond migration in the resultant 1-σ,4,5-η-cyclooctenyl ligand, to the thermodynamically more stable η^3-cyclooctenyl species 2 and the rate of conversion is determined by the size of L when the electronic contribution is kept close to con-

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[24] Crabtree[25] has pointed out that the isomer of $[IrH_2(cod)L_2]^+$, which contains M—H bonds orthogonal to the M(C=C) unit, does not undergo hydride insertion readily.

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stant. In some cases involving the smallest ligands the conversion does not occur at least up to temperatures where decomposition takes place. Displacement of 1,3-cod is observed when **1** or **2** are treated with excess ligand at 60 °C and either $[RuHL_5]^+$ or, for more bulky ligands, $[RuHL_4(acetone)]^+$ are obtained. A comparison of the analogous iron complex with the ruthenium systems suggests that the cyclooctenyl group is more strongly bound to iron than to ruthenium.

Experimental Section

General Data. Solvents were dried and distilled under nitrogen before use. Reactions and recrystallizations were performed under nitrogen and filtrations of the crude products were carried out in air. Melting points were determined on a Kofler hot-stage apparatus and are corrected. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer. NMR spectra were recorded on Varian EM-390 (^{1}H), Bruker WM500 (^{1}H and ^{13}C), and Varian CFT-20 (^{31}P) instruments. Elemental analyses were carried out at NCRL, CSIR, Pretoria.

The complex $[RuH(cod)(NH_2NMe_2)_3][PF_6]$ was prepared according to the literature method.[12] The ligands were obtained commercially (Strem) and were not purified further.

Preparation of the Hydrido Diene Complexes $[RuH(cod)L_3][PF_6]$. $[RuH(cod)\{P(OMe)_2Ph\}_3][PF_6]$. Dimethoxyphenylphosphine (0.53 g, 3.1 mmol) was added to a stirred solution of $[RuH(cod)(NH_2NMe_2)_3][PF_6]$ (0.54 g, 1 mmol) in dry, degassed methanol (20 mL) that gave a white precipitate almost immediately. The precipitate was filtered off and washed with ethanol and diethyl ether; yield 0.77 g (89%).

$[RuH(cod)\{P(OMe)Ph_2\}_3][PF_6]$. Methoxydiphenylphosphine (0.67 g, 3.1 mmol) was added to a solution of $[RuH(cod)(NH_2NMe_2)_3][PF_6]$ (0.54 g, 1 mmol) in dry, degassed methanol (20 mL) at −10 °C that gave a cream precipitate almost immediately. The precipitate was filtered off and washed with diethyl ether; yield 0.4 g (40%).

$[RuH(cod)(PMePh_2)_3][PF_6]$. Methyldiphenylphosphine (0.62 g, 3.1 mmol) was added to a stirred solution of $[RuH(cod)(NH_2NMe_2)_3][PF_6]$ (0.54 g, 1 mmol) in dry, degassed methanol at −10 °C that gave a cream precipitate almost immediately. The precipitate was filtered off and washed with diethyl ether; yield 0.9 g (94%).

$[RuH(cod)\{CH_3C(CH_2PPh_2)_3\}][PF_6]$. 1,1,1-Tris(diphenylphosphinomethyl)ethane (0.63 g, 1 mmol) in dichloromethane (15 mL) was added dropwise over a 15-min period to a solution of $[RuH(cod)(NH_2NMe_2)_3][PF_6]$ (0.54 g, 1 mmol) in methanol (20 mL) at 0 °C. After 1 h, the reaction solution was concentrated by using reduced pressure and the resultant pale yellow precipitate filtered and washed (0°C) with methanol and diethyl ether; yield 0.5 g (51%).

$[RuH(cod)(AsMe_3)_3][PF_6]$. Trimethylarsine (0.38 g, 3.1 mmol) was added to a stirred solution of $[RuH(cod)(NH_2NMe_2)_3][PF_6]$ (0.54 g, 1 mmol) in acetone (20 mL) and the solution refluxed for 2 h. Saturation with diethyl ether gave the compound as a beige solid that was recrystallized from acetone–ethanol; yield 0.68 g (95%).

$[RuH(cod)(AsMe_2Ph)_3][PF_6]$. Dimethylphenylarsine (0.56 g, 3.1 mmol) was added to a stirred solution of $[RuH(cod)(NH_2NMe_2)_3][PF_6]$ (0.54 g, 1 mmol) in acetone (20 mL) and the solution refluxed for 2.5 h. Saturation with diethyl ether gave the compound as a beige solid that was recrystallized from acetone–ethanol; yield 0.45 g (50%).

$[RuH(cod)(AsMePh_2)_3][PF_6]$. Methyldiphenylarsine (0.76 g, 3.1 mmol) was added to a stirred solution of $[RuH(cod)(NH_2NMe_2)_3][PF_6]$ (0.54 g, 1 mmol) in methanol (20 mL). Within ca. 5 min a beige solid separated from solution. This was filtered off and recrystallized from acetone–ethanol; yield 0.82 g (75%).

Preparation of the η^3-Cyclooctenyl Complexes. $[Ru(\eta^3\text{-}C_8H_{13})(PMe_3)_3][PF_6]$. $[RuH(cod)(PMe_3)_3][PF_6]$ (0.3 g, 0.5 mmol) was suspended in ethanol (20 mL) and cycloocta-1,5-diene (0.6 mL, excess) added. The stirred suspension was heated under reflux, giving an orange solution after ca. 0.5 h. On cooling (0 °C) the product precipitated as a yellow powder; yield 0.25 g (83%).

$[Ru(\eta^3\text{-}C_8H_{13})(PMe_2Ph)_3][PF_6]$. $[RuH(cod)(PMe_2Ph)_3][PF_6]$ (0.4 g, 0.5 mmol) was suspended in ethanol (20 ml) and the stirred suspension was heated under reflux (15 min) until a dark red solution had formed. On slow cooling (to room temperature and then to 0°C) the product crystallized as orange-red prisms. Yield 0.3g (75%).

$[Ru(\eta^3\text{-}C_8H_{13})\{P(OMe)_2Ph\}_3][PF_6]$. $[RuH(cod)\{P(OMe)_2Ph\}_3][PF_6]$ (0.5 g, 0.6 mmol) was dissolved in methanol (20 mL) and the solution heated gently for ca. 10 min. The solution was reduced to half volume under a reduced pressure. The yellow solid was filtered off and washed with diethyl ether; yield 0.4 g (77%).

$[Ru(\eta^3\text{-}C_8H_{13})\{P(OMe)Ph_2\}_3][PF_6]$, $[Ru(\eta^3\text{-}C_8H_{13})\{PMePh_2\}_3][PF_6]$, and $[Ru(\eta^3\text{-}C_8H_{13})\{CH_3C(CH_2PPh_2)_3\}][PF_6]$ were obtained in the following three ways: (a) from $[RuH(cod)(NH_2NMe_2)_3][PF_6]$, as for the corresponding hydrido diene species except the reaction temperature was 25 °C (yield ca. 80%), (b) by heating methanol suspensions of the corresponding hydrido diene complexes for ca. 10 min at 50 °C (yield ca. 90%), and (c) by allowing the corresponding hydrido diene complex to stand at room temperature in the solid state for ca. 1 day (quantitative conversion).

$[Ru(\eta^3\text{-}C_8H_{13})\{P(OCH_2\text{-}t\text{-}Bu)_3\}_3][PF_6]$. Trineopentyl phosphite (0.9 g, 3 mmol) was added to a solution of $[RuH(cod)(NH_2NMe_2)_3][PF_6]$ in methanol (30 mL) at 0 °C. After the solution had been stirred for 1 h at 0 °C, the solvent was removed in vacuo and ether (5 mL) added. Dropwise addition of pentane gave a white precipitate, which was identified as the η^3-cyclooctenyl species; yield 0.4 g (33%).

Registry No. 1 (L = $P(OMe)_2Ph$), 82648-15-5; 1 (L = PMe_3), 68811-85-8; 1 (L = PMe_2Ph), 61003-34-7; 1 (L = $P(OMe)Ph_2$), 61003-57-4; 1 (L = $PMePh_2$), 61003-59-6; 1 (L_3 = $CH_3C(CH_2PPh_2)_3$), 91127-96-7; 1 (L = $AsMe_3$), 82648-17-7; 1 (L = $AsMePh_2$), 91127-98-9; 1 (L = $AsMe_2Ph$), 91156-98-8; 1 (L = $P(OMe)_3$, 61024-44-0; 2 (L = $P(OMe)_2Ph$), 82641-00-7; 2 (L = PMe_3), 82640-96-8; 2 (L = PMe_2Ph), 82640-98-0; 2 (L = $P(OMe)Ph_2$), 82641-02-9; 2 (L = $PMePh_2$), 91156-94-4; 2 (L_3 = $CH_3C(CH_2PPh_2)_3$), 91156-96-6; 2 (L = $P(OCH_2\text{-}t\text{-}Bu)_3$, 82641-04-1; $[RuH(Cod)(NH_2NMe_2)_3][PF_6]$, 64772-25-4.