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REACTIONS OF HYDRIDO(CYCLOOCTA-1,5-DIENE)TRIS(PHOSPHINE)RUTHENIUM(II) CATIONS WITH 1,3-DIENES: FORMATION OF AGOSTIC η^3-ENYL SPECIES [Ru(η^3-enyl)L_3]$^+$

TERENCE V. ASHWORTH, ANTHONY A. CHALMERS, ELSIE MEINTJIES,
HESTER OOSTHUIZEN and ERIC SINGLETON *

National Chemical Research Laboratory, Council for Scientific and Industrial Research, Pretoria 0001 (Republic of South Africa)

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Summary

Treatment of either the hydrido-diene complexes [RuH(cod)L_3][PF_6] (cod = cycloocta-1,5-diene, L = PMe_3, PMe_2Ph, $P(OMe)_2Ph$, $P(OMe)Ph_2$) or the isomeric cyclooctenyl species [Ru(η^3-C_8H_{13})L_3][PF_6] with 1,3-dienes gives the corresponding η^3-enyl cations [Ru(η^3-heptenyl)L_3]$^+$, [Ru(η^3-hexenyl)L_3]$^+$ and [Ru(η^3-butenyl)(PMe_2Ph)$_3$]$^+$. The products contain an aliphatic C–H $\cdots$ Ru interaction and exhibit four distinct fluxional processes as revealed by variable temperature NMR studies: mutual exchange of the phosphorus donor ligands; a 1,2-metal migration around the *endo* face of the carbocyclic ring; an exchange involving C–H interaction at the metal, and in the case of the butenyl complex, methyl group rotation. Whereas the first two processes are of relatively high energy and can be frozen out at low temperatures, the remaining processes are still rapid at the lowest temperature investigated (183 K), except for the complex [Ru(η^3-cycloheptenyl)-{$P(OMe)_2Ph$}$_3$]$^+$ which gave a slow-exchange ^{1}H NMR spectrum at 500 MHz.

Introduction

We have recently shown [1] that the hydrido-diene complexes [RuH(cod)L_3][PF_6] (**1**) convert into the corresponding η^3-enyl species [Ru(η^3-C_8H_{13})L_3][PF_6] (**2**) at a rate which is clearly influenced by the size of the ligand L. These results prompted us to reinvestigate the structures of the products of **1** with 1,3-dienes which had been assigned earlier [2] as having a hydrido-diene configuration based on an X-ray diffraction study of the product of the reaction of **1** with 1,3-butadiene. The variable temperature NMR studies reported herein show that these products are η^3-enyl species in which an aliphatic C–H $\cdots$ Ru interaction exists. A preliminary account of this work has been published [3].

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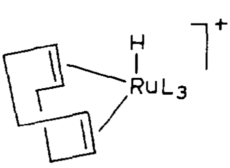

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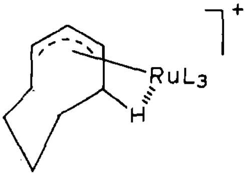

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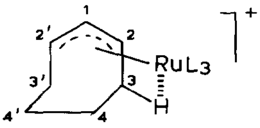
Results and discussion

Preparation of the complexes

The complexes **3** and **4** were prepared, as described previously [2], by addition of an excess of the appropriate 1,3-diene to a suspension of either **1** or **2** in methanol under reflux. The products precipitated from the resultant solutions in yields ranging from 50 to 85%, except for **4b** which required evaporation of the solvent and precipitation from dichloromethane/ethanol mixtures. The formation of **3a** was accompanied by formation of the cycloheptadienyl complex $[Ru(\eta^5\text{-}C_7H_9)(PMe_2Ph)_3]^+$ and the mixture proved impossible to separate. Compound **5** was made by warming a suspension of **1a** or **2a** in methanol under an atmosphere of 1,3-butadiene.



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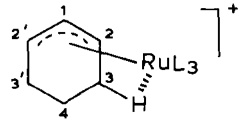

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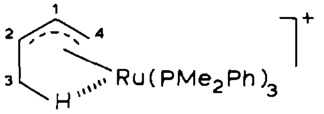
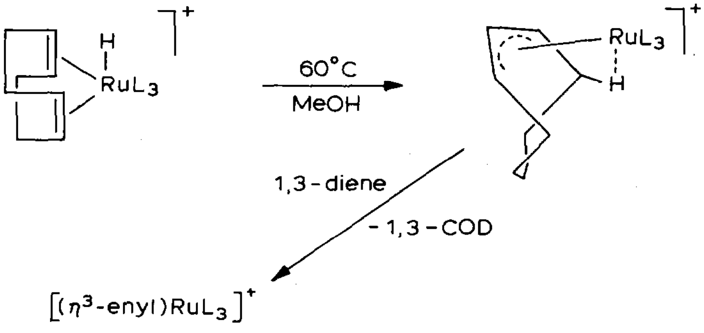


(**5a**: L = PMe_2Ph;
5b: L = PMe_3;
5c: L = $P(OMe)_2Ph$;
5d: L = $P(OMe)Ph_2$)

The reaction solutions contained only the 1,3-isomer of cyclooctadiene suggesting the following reaction pathway:



The compounds are stable indefinitely under a nitrogen atmosphere but decompose in the presence of oxygen, slowly in the solid state (over a period of weeks) and more rapidly in solution (over a period of hours). The microanalytical results, colour and melting point of each compound are given in Table 1.

NMR Studies of the complexes 3–5

The complexes exhibited four separate fluxional processes detectable by variable temperature NMR techniques: (i) The mutual exchange of the three phosphorus nuclei, a relatively high energy process, which is most readily appreciated from a study of the variable temperature ^{31}P spectra although it is also manifested in changes in ^{1}H and ^{13}C resonances.

(ii) A 1,2-metal migration [4] around the *endo* face of the carbocyclic ring which occurs in a similar temperature region to the phosphorus scrambling process and proceeds through a 1,3-diene hydride intermediate. The outcome is a series of very characteristically averaged ^{1}H spectra as well as exchange broadened ^{13}C spectra.

(iii) An interchange of the aliphatic moiety participating in the C–H ··· Ru interaction [5] which, in the cycloalkenyl complexes, involves simple interchange between the ruthenium centre and each of the two C(3)–H *endo* units adjacent to the allyl functional group, but in the butenyl complex requires the exchange of a proton between the methyl and the terminal methylene group.

(iv) Methyl group rotation [5] in the butenyl complex **5**.

The last two processes are of relatively low activation energy and, except in one case, were found to be rapid at the lowest temperatures investigated (183 K).

^{31}P NMR spectra

The ^{31}P spectra of the complex **4d** (Fig. 1) typify the changes which may be

TABLE 1

EXPERIMENTAL ANALYSIS

Compound	Colour	Melting Point (°C)	Analysis (Found (calcd) (%))	
			C	H
$[Ru(C_6H_9)\{P(OMe)_2Ph\}_3][PF_6]$	Yellow	172–174	42.90 (43.02)	5.00 (5.05)
$[Ru(C_6H_9)(PMe_3)_3][PF_6]$ [a]	Yellow	Decomposition without melting >170	32.72 (32.44)	6.49 (6.53)
$[Ru(C_6H_9)\{P(OMe)Ph_2\}_3][PF_6]$	Yellow	146–148	55.47 (55.39)	5.13 (4.96)
$[Ru(C_7H_{11})\{P(OMe)_2Ph\}_3][PF_6]$	Yellow	171–174	43.52 (43.72)	5.08 (5.21)
$[Ru(C_7H_{11})(PMe_3)_3][PF_6]$	Yellow	Decomposition without melting >150	33.95 (33.75)	6.48 (6.73)
$[Ru(C_7H_{11})\{P(OMe)Ph_2\}_3][PF_6]$	Yellow	160–162	55.69 (55.82)	4.94 (5.09)
$[Ru(C_7H_{11})(PMePh_2)_3][PF_6]$ [b]	Yellow	Decomposition without melting >150	58.44 (58.66)	5.02 (5.35)

[a] Compound decomposes in air. [b] Compound insoluble in dichloromethane, acetone, diethyl ether, methanol.

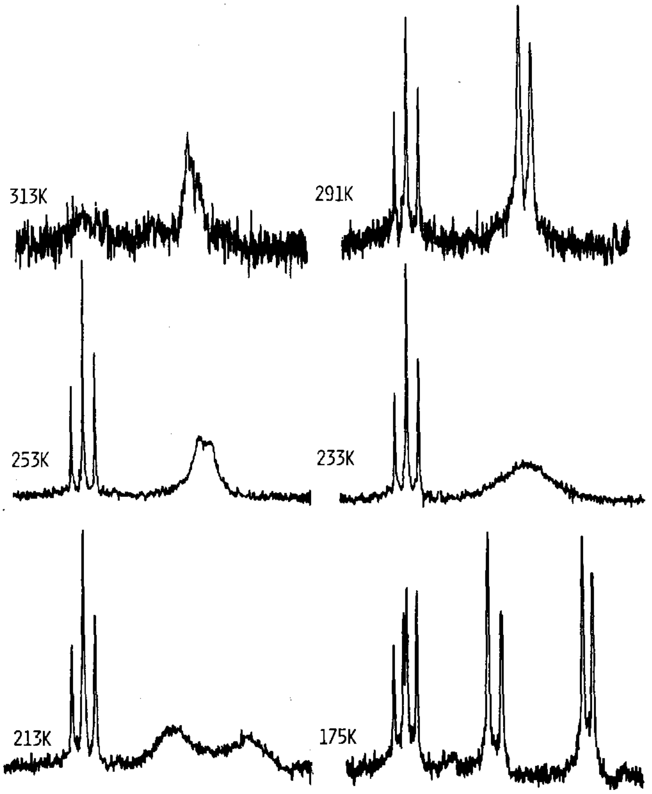


Fig. 1. The 32.2 MHz ^{31}P spectra of compound **4d** at various temperatures.

observed. At normal temperatures the phosphorus exchange process i is of a rate which results in detectable though broadened resonances. (The complexes decomposed in higher boiling solvents, CD_3NO_2, $(CD_3)_2SO$, when attempts were made to reach the single line of the fast exchange region.) Slight cooling slows the exchange sufficiently to give AB_2 spectra and the ^{31}P (δ_A, δ_B and J_{AB}) parameters of Table 2 are for these species. With further cooling the B_2 doublet coalesces and collapses but the A triplet remains sharp. Next, two separate signals appear for the P_B nuclei and ultimately a fully developed ABC spectrum is observed at the lowest temperature. The full low temperature limiting ABC spectrum was only given by the butenyl complex **5** and **4d** (Fig. 1), both show a small value for the coupling between P_B and P_C contrasting with the normal value reported previously in the η^3-cyclooctenyl analogue [1]. The phosphine and phosphite derivatives differ in that the latter have rather small chemical shift differences between P_A and P_B necessitating second-order calculation of the NMR parameters.

^{13}C NMR spectra

In general we find that ^{13}C NMR does not provide such a direct means of characterization of these complexes as for the previously reported η^3-cyclooctenyl analogues [1]. The latter gave rise to an easily recognisable 1/2/2/2/1 pattern of resonances over a wide temperature range, whereas the complexes reported here gave

TABLE 2

^{13}C, ^{31}P AND ^{1}H DATA FOR THE COMPLEXES

(^{1}H and ^{13}C chemical shifts in ppm from internal TMS. ^{31}P chemical shifts for AB_2 systems in ppm from external H_3PO_4. Temperatures in degrees Kelvin. a = *anti*, s = *syn*, x = *exo*, n = *endo*.)

Compound	C(1)	C(2)	C(3)	C(4)	*T*(K)	P_A	P_B	J_{AB}	*T*(K)	H(1)	H(2)	H(3)	H(4)	*T*(K)
5a	94.9	67.2	2.8	41.2	253	38.9	−3.2	27	293	5.25	4.85	−3.25	0.65a, 2.05s	223
4a	90.5	64.9	24.0	17.6	202	34.3	3.5	36	303	5.05	4.05	1.65x, −4.25n	0.75, 0.90	213
4b	91.5	62.2	23.1	17.7	193	27.6	−4.6	39	303	4.72	3.96	1.78x, −4.30n	0.90	193
4c	95.2	66.9	23.5	16.3	193	171.8	169.9	47	213	5.01	4.37	0.93x	1.1, 0.5	193
4d	94.7	68.5	25.2	16.8	230	148.2	136.0	40	281	4.76	3.91	1.73x,		260
3a	91.7	62.6	20.6	22.5	223					4.80	3.80	1.35x, −3.85n	1.00, 1.20	223
3b	92.7	60.1	20.1	22.7	193	29.6	−6.2	36	303	4.46	3.80	1.37x, −3.45n		223
3c	96.3	63.5	19.4	22.6	193					4.74	4.06	1.55x, −3.30n		193
3d	95.0	64.9	18.1	21.8	253	149.0	137.7	43	281	4.66	4.00	1.56x, −3.37n	1.18, 1.29	253

exchange broadened spectra at most accessible temperatures. At room temperature the 1,2-shift process ii is occurring at an intermediate rate so that all alkenyl carbon signals are difficult to detect and at the lower temperatures where this process has slowed the *endo* C–H exchange, process iii has become of intermediate rate. Consequently, in the spectra reported (Table 2) for the cyclohexenyl and cycloheptenyl complexes the resonances assigned to C(2) and C(3) were markedly broadened. The slow exchange limiting spectrum was not reached for any of the complexes at the low temperature extreme of our instrument (183 K) so no values of ^1J(CH) for the agostic unit C–H ··· Ru could be measured [6]. The low temperature ^{1}H-coupled spectra of the cycloalkenyl and butenyl complexes display triplet and quartet signals, respectively, for the C(3) resonance with unexceptional (~ 125 Hz) values for the averaged ^1J(CH).

^1H *NMR spectra*

The ^{1}H NMR signals for all three η^3-enyl species are exchange broadened at normal temperatures and cooling is required before the distinct resonances of Table 2 can be observed. The spectrum of the η^3-butenyl complex conforms with that of the Fe[P(OMe)$_3$]$_3$ analogue [5] in showing a separate 1H signal for each of the allyl protons and a 3H high field signal for the methyl protons; the latter broadens to 60 Hz halfwidth at 193 K but does not separate into the three signals expected [5] for slowing of the methyl rotation process iv. The room temperature spectrum of **4a** consists of the expected PMe$_2$Ph signals and two broad resonances at 3.1 ppm (6H) and −2.6 ppm (3H) account for the protons of the C_6H_9 moiety. Comparison with the elegant investigations by Brookhart et al. [4] of [Mn(η^3-C_6H_9)(CO)$_3$] and derivatives shows that the averaging is due to the 1,2-metal shift process ii and allows the assignment of the low field signal to (H(1), H(2), H(2′), H(3x), H(3′x), H(4x)) and the high field signal to (H(3n), H(3′n), H(4n)). The changes in the spectrum with cooling are also substantially the same as the changes shown by the Mn complex and at 213 K the 1,2-metal shift process ii is slowed sufficiently that the six resonances of the η^3-cyclohexenyl ring are observed (Table 2). Further cooling brings into play the process iii with broadening of the signals for H(2,2′), H(3x,3′x) and H(3n,3′n) the latter collapses into the baseline at 183 K but the barrier to exchange is apparently too small for the observation of a separate H(3n) signal at very high field which is the herald of the stopped exchange region in the Fe analogues [5]. The η^3-cycloheptenyl complexes show similar behaviour although at room temperature the protons of C_7H_{11} already give four broad signals which further resolve with only slight cooling into the seven signals expected (Fig. 2). The assignments follow from the general principles established from the η^3-cyclohexenyl spectra, further cooling broadens the signals in the order H(3n,3′n) > H(2,2′) > H(3x,3′x) > H(4n,4′n) > H(4x,4′x) as the rate of the exchange process iii is slowed until at 193 K the signal for H(3n,3′n) has collapsed. At 183 K the complex with L = P(OMe)$_2$Ph showed a high field resonance (−8.2 ppm) attributable to the agostic proton C–H(3n) ··· Ru. Its exchange partner H(3′n) is presumably lost among the bulk of the aliphatic resonances at ~ 1.5 ppm.

Because the low temperatures necessary to reach the slow exchange region were either beyond or at the limit of the present range of our instrument, it was not possible to obtain a quantitative value for the exchange barrier of the agostic C–H ··· Ru interaction. Ittel and co-workers obtained evidence to suggest that the

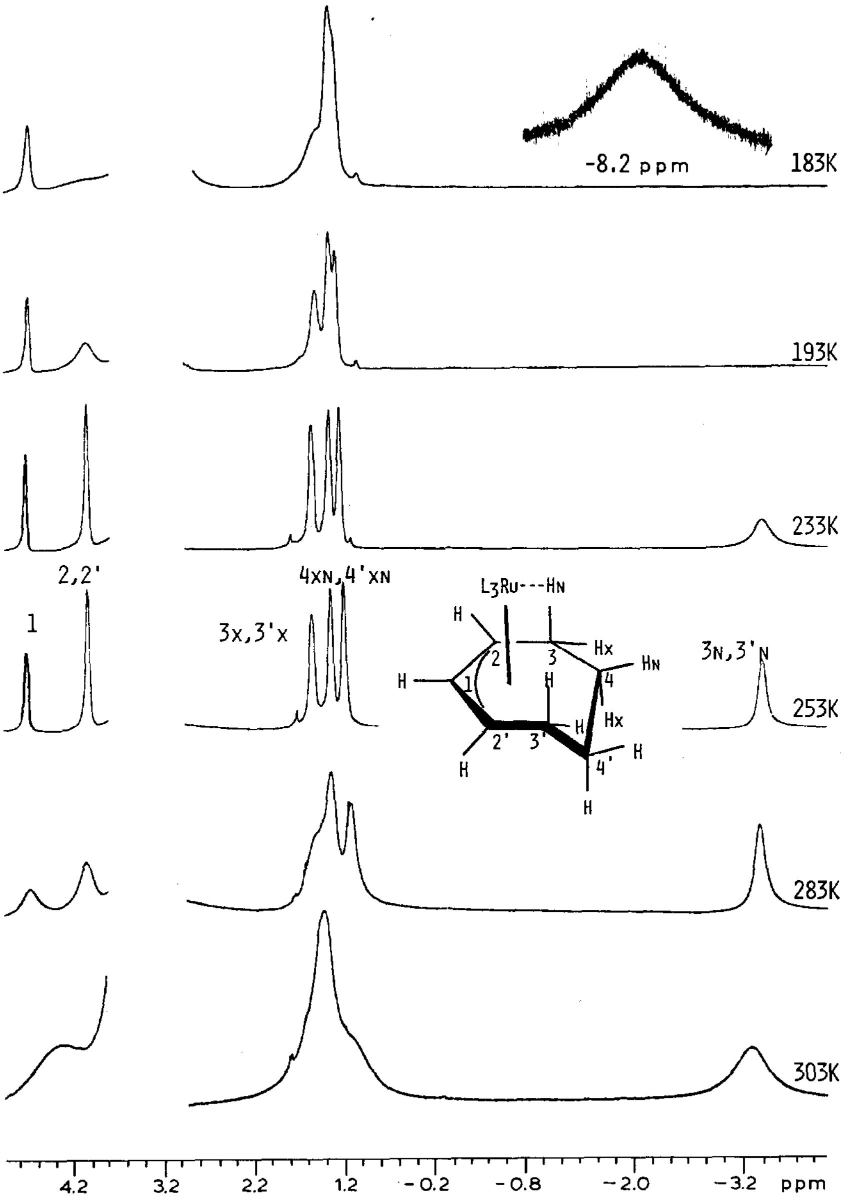


Fig. 2. The 500 MHz ^1H spectra of compound **3d** at various temperatures. For clarity the OMe group signals at ~ 3.5 ppm have been removed.

exchange barriers in the cycloalkenyliron complexes were a function of ring size, with an increase in activation energy with ring contraction. Our studies of the cyclooctenyl complexes of ruthenium suggested that the cyclooctenyl ligand was more weakly bound to ruthenium than to iron. We observed, however, a limiting ^1H NMR spectrum with the complex $[Ru(\eta^3\text{-}C_8H_{13})\{P(OMe)Ph_2\}_3]^+$. It was of interest, therefore, to determine whether there was an increase in the activation energy with the corresponding cycloheptenyl and cyclohexenyl complexes. Because of the above mentioned experimental difficulties such a correlation could not be conclusively shown although the ^{31}P NMR spectra of the cyclohexenyl **4d** reached the limiting ABC pattern at 175 K whereas the cycloheptenyl **3d** still showed exchange at this temperature.

The 1,2-metal migration around the carbocyclic ring (a process not observed in cyclooctenyl complexes [1,5]) requires a much lower activation energy in the ruthenium compounds of this study as compared to the manganese complexes investigated by Brookhart et al. at elevated temperatures. The mechanism is not explicitly discussed by Ittel et al. for the Fe system but the reported distinct (though exchange broadened) ^1H resonances for $[Fe(cycloheptenyl)\{P(OMe)_3\}_3]^+$ at 295 K suggests that the barrier is also somewhat higher than for the Ru complexes. Apparently, the complex $[IrH(\eta^3\text{-2,3-dimethylbutenyl})(PPh_3)_2]^+$ shows [7] exchange processes occurring at more or less the same temperatures as ours.

The establishment of the solution structure of the compounds brings into question the assignment of the hydrido-diene configuration in the solid state as originally described in the report [2] of the X-ray structure determination of **5**. Although the positions of the butadiene moiety were not determined with the desired precision, a reexamination of the positional parameters reveals that they are consistent only with an agostic butenyl ligand. This can best be appreciated by examining Fig. 3.

All four carbon atoms are within bonding distance of the ruthenium ion, (hence the original interpretation of a coordinated butadiene group); the Ru–C(1) distance (2.38 Å) is, however, much longer than the range of distances found previously in enyl systems (2.13–2.31 Å). Atom C(1) is positioned close to the coordination site on the ruthenium atom *trans* to P(3). A hydrogen atom in the calculated [9] position shown in Fig. 3 yields a Ru ··· H distance of 1.84 Å and a P(3)–Ru ··· H angle of 175.6°. Whereas these parameters are entirely consistent with the presence of an agostic butenyl ligand, they are inconsistent with the presence of separate butadiene and hydride ligands since a hydride ligand, which would be required to occupy a

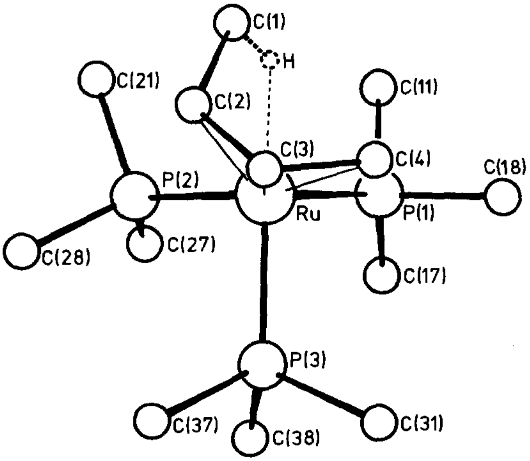


Fig. 3. A view of the cation of **5** showing the coordination about the ruthenium atom. The positional parameters were obtained from ref 2. The hydrogen atom position was calculated as discussed in the text [9].

TABLE 3

METAL–CARBON BOND DISTANCES (Å) OF AGOSTIC η^3-ENYL MOIETIES

Compound	Ref.	C(1) [a]	C(2)	C(3)	C(4)
5	2	2.38(2)	2.14(2)	2.17(2)	2.26(2)
$[Ru(\eta^3\text{-}C_8H_{13})\{P(OMe)Ph_2\}_3]^+$	8	2.592(9)	2.197(8)	2.216(8)	2.246(7)
$[Fe(\eta^3\text{-}C_8H_{13})\{P(OMe)_3\}_3]^+$	10	2.362(2)	2.053(5)	2.081(5)	2.170(5)
$[Mn(\eta^3\text{-}C_7H_{11})(CO)_3]$	4	2.301(2)	2.053(3)	2.092(2)	2.168(3)

[a] The carbon atoms have been re-labelled so that C(1) refers to the carbon of the M ··· H–C interaction as shown in Figure 3.

position approximately the same as that of the calculated one, would be unacceptably close to C(1).

The positions of the other carbon atoms of the C(4) ligand are also in keeping with an agostic η^3-enyl ligand. Atom C(3) lies close to the plane which bisects the P(1)–Ru–P(2) angle as expected for the central carbon atom of an η^3-enyl moiety. The atoms C(2)–C(4) lie above the plane defined by P(1), Ru and P(2) and are unsymmetrically bound to the ruthenium atom so that C(2) has the largest deviation from the plane. This unsymmetrical coordination has been observed previously in $[Fe(\eta^3\text{-}C_8H_{13})\{P(OMe)_3\}_3]^+$ [5], $[Mn(\eta^3\text{-}C_7H_{11})(CO)_3]$ [4] and $[Ru(\eta^3\text{-}C_8H_{13})\{P(OMe)Ph_2\}_3]^+$ [8] and is a consequence of the M ··· H–C interaction. The metal–carbon bond distances in the above three structures show clear trends reflecting this unsymmetric coordination and this trend is also present in the relevant distances of **5** as shown in Table 3.

Experimental

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. NMR spectra were recorded on Varian EM-390 (^1H), Bruker WM500 (^1H and ^{13}C) and Varian CFT-20 (^{31}P) instruments. Elemental analyses were carried out at NCRL, CSIR, Pretoria. The ruthenium starting materials were prepared by previously described methods [2,3]. In the following experiments the enyl species $[Ru(\eta^3\text{-}C_8H_{13})L_3][PF_6]$ may be used in place of the hydride complexes $[RuH(C_8H_{12})L_3][PF_6]$.

$[Ru(C_6H_9)\{P(OMe)_2Ph\}_3][PF_6]$

1,3-Cyclohexadiene (0.25 ml) was added to a solution of $[RuH(cod)\{P(OMe)_2Ph\}_3][PF_6]$ (0.5 g, 0.58 mmol) in methanol (15 ml) and refluxed for ca. 2 h. The pale yellow solid which separated from solution was recrystallized from dichloromethane/diethyl ether. Yield 0.4 g (82%).

$[Ru(C_6H_9)(PMe_3)_3][PF_6]$

1,3-Cyclohexadiene (0.25 ml) was added to a solution of $[RuH(cod)(PMe_3)_3][PF_6]$ (0.5 g, 0.86 mmol) in methanol (15 ml) and refluxed for ca. 2 h. The resultant orange solution was taken to dryness and the oil recrystallized from dichloromethane/ethanol to give the pale yellow solid. Yield 0.25 g (53%).

$[Ru(C_6H_9)\{P(OMe)Ph_2\}_3][PF_6]$

1,3-Cyclohexadiene (0.25 ml) was added to a suspension of $[Ru(\eta^3\text{-}C_8H_{13})\{P(OMe)Ph_2\}_3][PF_6]$ (0.5 g, 0.50 mmol) in methanol (20 ml) and the mixture refluxed for ca. 2 h. The pale yellow solid which separated from solution was recrystallized from dichloromethane/ethanol. Yield 0.3 g (62%).

$[Ru(C_7H_{11})\{P(OMe)_2Ph\}_3][PF_6]$

1,3-Cycloheptadiene (0.25 ml) was added to a solution of $[RuH(cod)\{P(OMe)_2\text{-}Ph\}_3][PF_6]$ (0.5 g, 0.58 mmol) in methanol (20 ml) and refluxed for ca. 2 h. The yellow solution was reduced to half volume and the solid obtained recrystallized from dichloromethane/ethanol. Yield. 0.3 g (61%).

$[Ru(C_7H_{11})(PMe_3)_3][PF_6]$

1,3-Cycloheptadiene (0.25 ml) was added to a solution of $[RuH(cod)(PMe_3)_3][PF_6]$ (0.5 g, 0.86 mmol) in methanol (20 ml) and refluxed for ca. 2 h. The orange solution was reduced in volume and the yellow solid obtained recrystallized from dichloromethane/ethanol. Yield 0.3 g (61%).

$[Ru(C_7H_{11})\{P(OMe)Ph_2\}_3][PF_6]$

1,3-Cycloheptadiene (0.25 ml) was added to a suspension of $[Ru(\eta^3\text{-}C_8H_{13})\{P(OMe)Ph_2\}_3][PF_6]$ (0.5 g, 0.50 mmol) in methanol (20 ml) and the mixture refluxed for ca. 2 h. The yellow solid which separated from solution was recrystallized from dichloromethane/ethanol. Yield 0.35 g (71%).

$[Ru(C_7H_{11})(PMePh_2)_3][PF_6]$

1,3-Cycloheptadiene (0.25 ml) was added to a suspension of $[Ru(\eta^3\text{-}C_8H_{13})(PMePh_2)_3][PF_6]$ (0.5 g, 0.52 mmol) in methanol (20 ml) and the mixture refluxed for ca. 2 h. The yellow solid which separated from solution was isolated, washed with ether and dried. Yield 0.4 g (82%).

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9 Assuming a regular tetrahedral angle for C(2)–C(1)–H of 109.5° and a C(1)–H bond length of 1.08 Å, then rotation of such a C(1)–H bond about the C(1)–C(2) vector to give the closest approach of H to Ru (i.e. H lies in the Ru, C(1), C(2) plane) gives a H position of 0.2372, −0.0250, 0.1739.

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