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SYNTHESIS AND ^{31}P NMR SPECTRA OF SOME DIENE COMPLEXES OF IRON(0) AND RUTHENIUM(0) CONTAINING PHOSPHINE LIGANDS

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Summary

The preparation of the η^4-butadiene complexes of zerovalent iron and ruthenium $Ru(\eta^4\text{-}C_4H_6)(PPh_3)(L)_2$, ($L = P(OCH_2)_3CMe, P(OMe)_3, PF_2NMe_2, PF_3$); $Fe(\eta^4\text{-}C_4H_6)(CO)(L)_2$, ($L = P(OMe)_3, P(OCH_2)_3CMe$), and the cyclohexadiene complexes $Ru(\eta^4\text{-}C_6H_8)L_3$ ($L = P(OMe)_3, P(OCH_2)_3CMe$ and PF_3,) is described and some variable temperature ^{31}P NMR studies are reported.

Introduction

There have been several reports of the synthesis and fluxional behaviour of η^4-diene complexes of the type $M(\eta^4\text{-diene})L_3$ (M = Fe, Ru) [1—19]. In this paper we describe new synthetic routes and NMR spectroscopic studies for a number of diene complexes of zerovalent iron and ruthenium containing phosphine, phosphite and fluorophosphine ligands.

Results and discussion

Treatment of the bis(butadiene)ruthenium(0) complex $Ru(\eta^4\text{-}C_4H_6)_2(PPh_3)$ [14] with an excess of $P(OMe)_3$, $P(OCH_2)_3CMe$ or PF_2NMe_2 results in displacement of one butadiene molecule and formation of complexes of the type $Ru(\eta^4\text{-}C_4H_6)(PPh_2)(L)_2$ (I, $L = P(OMe)_3$; II, $L = P(OCH_2)_3CMe$; III, $L = PF_2NMe_2$).

$$Ru(\eta^4\text{-}C_4H_6)_2(PPh_3) \xrightarrow{2L} \underset{\text{(I—III)}}{Ru(\eta^4\text{-}C_4H_6)(PPh_3)\,L_2} + C_4H_6$$

The corresponding reaction with PF_3 at 90°C results in formation of $Ru(\eta^4\text{-}C_4H_6)(PPh_3)(PF_3)_2$ (IV) as a minor product, since under the reaction conditions some further displacement of butadiene also occurs to give $Ru(PF_3)_4(PPh_3)$ as the major product. The latter complex was characterised by comparison of its ^{19}F and ^{31}P NMR spectra with those of a known sample formed by treating $RuH(CO_2Me)(PPh_3)_3$ with PF_3 [20].

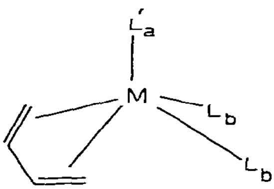
The bis(butadiene)iron complex Fe(η^4-C_4H_6)$_2$(CO) [21] also undergoes displacement of only one butadiene ligand when treated with the phosphites P(OCH_2)$_3$CMe and P(OMe)$_3$ in refluxing toluene to yield Fe(η^4-C_4H_6)(CO)(P(OCH_2)$_3$CMe)$_2$ (V) and Fe(η^4-C_4H_6)(CO)(P(OMe)$_3$)$_2$ (VI), respectively. The infrared spectra of V and VI both show a single strong broad carbonyl stretching band (at 1915 and 1920 cm^{-1}, respectively) whereas the analogous PF_3 derivative [1] exhibits a strong band at 2001 and a weaker band at 1956 cm^{-1}.

Another useful precursor for 1,3-cyclohexadiene complexes of ruthenium(0) is 1,3-cyclohexadiene(benzene)ruthenium(0) Ru(η^4-C_6H_8)(η^6-C_6H_6) [22] which is readily prepared directly from $RuCl_3$ by treatment with 1,3-cyclohexadiene in the presence of zinc. The benzene is readily displaced by P(OMe)$_3$ or P(OCH_2)$_3$CMe to give Ru(η^4-C_6H_8)(P(OMe)$_3$)$_3$ (VII) and Ru(η^4-C_6H_8)(P(OCH_2)$_3$CMe)$_3$ (VIII), respectively.

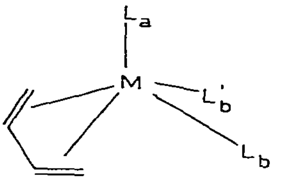
$$RuCl_3 \xrightarrow[Zn]{C_6H_8} Ru(\eta^4\text{-}C_6H_8)(\eta^6\text{-}C_6H_6) \xrightarrow{3L} \underset{(VII—IX)}{Ru(\eta^4\text{-}C_6H_8)\,L_3} + C_6H_6$$

Trifluorophosphine reacts with Ru(η^4-C_6H_8)(η^6-C_6H_6) in a sealed tube at 90°C to give a mixture of Ru(η^4-C_6H_8)(PF_3)$_3$, (IX) and Ru(PF_3)$_5$ which were subsequently separated by careful trap to trap fractionation in the high vacuum line.

X-ray crystallographic studies on complexes of this structural type [16—18] suggest that they adopt a 'square pyramid' geometry with the diene occupying two of the basal sites. This indicates that complexes I—VI can exist as isomeric structures C and D shown below, while complexes VII—IX most likely adopt structure E (a = axial, b = basal).



(C)



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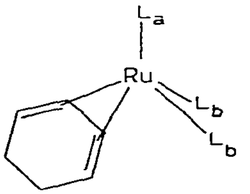
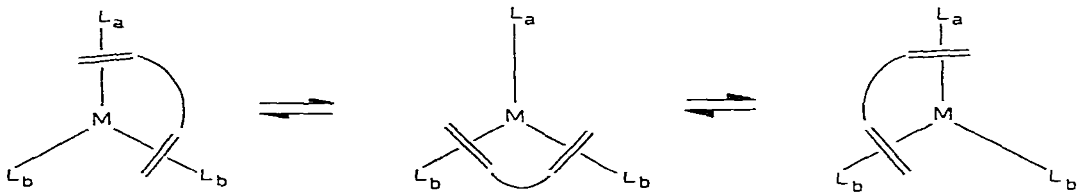


(E)

As mentioned earlier, this type of complex can undergo 'dynamic' or fluxional behaviour in which the phosphine ligands exchange intramolecularly between axial and basal positions. The mechanism is probably best described as a diene rotation, [19], which is indistinguishable on the NMR timescale from successive rearrangements of the Berry "pseudo-rotation" type [23].



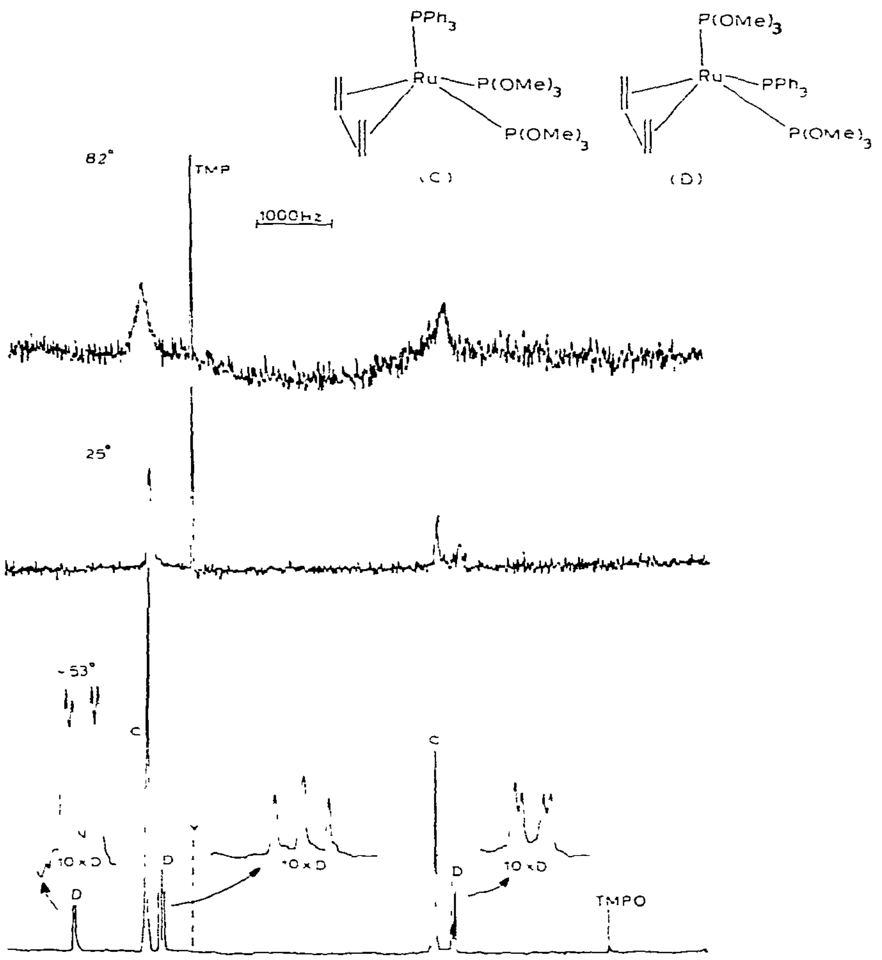
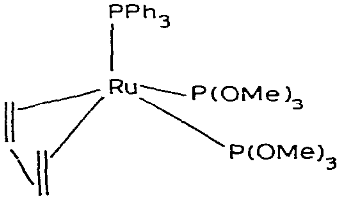
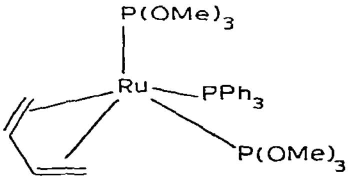


Fig. 1. Variable temperature ^{31}P NMR spectra of Ru(η^4-C_4H_6)(PPh_3)[P$(OMe)_3$]$_2$ (I) (Y = calculated TMP chemical shift).

Not surprisingly therefore, the NMR spectra of complexes I—IX are temperature dependent. Fig. 1 shows the variable temperature ^{31}P{^{1}H} NMR spectra of I which is typical for the Ru(η^4-C_4H_6)(PPh_3)$(L)_2$ and Fe(η^4-C_4H_6)(CO)$(L)_2$ complexes. Chemical shift and coupling constant data for complexes I—VI are listed in Table 1 together with ^{19}F NMR data where relevant, while Table 2 summarises the ^{1}H NMR spectroscopic data. Interestingly, in the latter spectra the diene resonances were often very broad and poorly resolved.



(I C)



(I D)

TABLE 1

^{19}F AND ^{31}P NMR CHEMICAL SHIFT AND COUPLING CONSTANTS DATA FOR M(DIENE)(L)(L')$_2$ COMPLEXES [a]

Complex	$\phi(F)$ [b]	Temperature (°C)	$\delta(P)$ [c]	$\delta(PPh_3)$ [c]	$^2J(PMP)$ [d]	$[^1J(PF) + n^3J(PF)]$ [d]
$Ru(\eta^4\text{-}C_4H_6)(PPh_3)[P(OMe)_3]_2$ (I)	—	25	−13.8	80.4, isomer C 87.9, isomer D	—	
		82 [e]	−16.3	83.5 [b]	—	
		−53	−14.2	80.3, isomer C	19.5	
			−37.8, −9.0	86.7, isomer D [f]	39.1, 9.7	
$Ru(\eta^4\text{-}C_4H_6)(PPh_3)[P(OCH_2)_3CMe]_2$ (II)	—	25	6.4	78.7, isomer C	—	
			−8.9	87.2, isomer D	—	
$Ru(\eta^4\text{-}C_4H_6)(PPh_3)(PF_2NMe_2)_2$ (III)	29.0, 32.2	25 [g]	−33.4	84.2, isomer C	—	1109 [i]
			−42.2	90.2, isomer D	—	1099 [i]
		93 [e]	−35.4	87.1	—	
		−30	−33.5	83.7, isomer C	—	
			−50.0	90.2, isomer D	—	
$Ru(\eta^4\text{-}C_4H_6)(PPh_3)(PF_3)_2$ (IV)	3.2	25 [g]	3.4, −17.3	90.3	—	1307 [i]
$Ru(\eta^4\text{-}C_6H_8)[P(OMe)_3]_3$ (VII)	—	25	−26.5	—	—	
		−22	−38.5, −21.5	—	—	—
		−54	−30.9, −21.2	—	31.7 [h]	
$Ru(\eta^4\text{-}C_6H_8)[P(OCH_2)_3CMe]_3$ (VIII)	—	25	1.3	—	—	—
$Ru(\eta^4\text{-}C_6H_8)(PF_3)_3$ (IX)	3.5	25 [e]	−0.2	—		1309 [j]
		−93	−12.7, −3.4	—	28.3 [h,k]	
$Fe(\eta^4\text{-}C_4H_6)(CO)[P(OCH_2)_3CMe]_2$ (V)	—	25	−23.4	—	—	
		−80	−18.3, −29.6	—	24.5 [h]	
$Fe(\eta^4\text{-}C_4H_6)(CO)[P(OMe)_3]_2$ (VI)	—	25	−51.7	—	—	

[a] In CH_2Cl_2 solutions unless otherwise stated. [b] ppm relative to $CFCl_3$. [c] ppm relative to TMP. [d] Hz. [e] Toluene solution. [f] $[^2J(P'_aRuP'_b) = 34.1$ Hz]. [g] Benzene solution. [h] Coupling between P' ligands. [i] $n = 1$. [j] $n = 2$. [k] $^3J(PRuPF) = 10.3$ Hz.

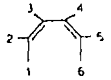
TABLE 2

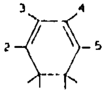
^{1}H NMR CHEMICAL SHIFT DATA FOR COMPLEXES OF THE TYPE M(DIENE)(L)(L$'$)$_2$

Complex	Solvent	Olefin resonances [a,d]			Other resonances [a]
		H(3, 4)	H(2, 5)	H(1, 6)	
Ru(η^4-C_4H_6)(PPh_3)[P(OMe)$_3$]$_2$ (I)	C_6D_6	5.4(br)	8.9(br)	11.1(br)	2.3(m), 3.5(m, PPh_3) 7.3(t, P(OMe)$_3$)
Ru(η^4-C_4H_6)(PPh_3)[P(OCH$_2$)$_3$CMe]$_2$ (II)	CD_2Cl_2	5.4(br)	8.7(br)	10.6(br)	2.2—2.8(m, PPh_3) 6.1(s, P(OCH_2)$_3$CMe), 9.3(s, P(OCH$_2$)$_3$CMe)
Ru(η^4-C_4H_6)(PPh_3)(PF_2NMe_2)$_2$ [a] (III)	C_6D_6	5.5(br)	8.8(br)	—	2.8—3.7(m, PPh_3) 8.2(d, t, PF$_2$NMe_2)
Ru(η^4-C_4H_6)(PPh_3)(PF_3)$_2$ (IV)	C_6D_6	n.o.	n.o.	n.o.	2.7—3.6(m, PPh_3) [c]
Ru(η^4-C_6H_8)[P(OMe)$_3$]$_3$ (VII)	$CDCl_3$	4.8(br)	6.9(br)	—	8.1(br) [b], 5.9(m, P(OMe)$_3$)
Ru(η^4-C_8H_8)[P(OCH$_2$)$_3$CMe]$_3$ (VIII)	$CDCl_3$	4.9(br)	7.2(br)	—	8.3(br) [b], 5.8(s, P(OCH_2)$_3$CMe), 9.3(s, P(OCH$_2$)$_3$CMo)
Ru(η^4-C_6H_8)(PF_3)$_3$ (IX)	C_7H_8	5.6(m)	7.5(m)	—	9.1(m) [b]
Fe(η^4-C_4H_6)(CO)[P(OCH$_2$)$_3$CMe]$_2$ (V)	$CDCl_3$	4.9(br)	8.6(br)	10.5(br)	5.8(s, P(OCH_2)$_3$CMe), 9.2(s, P(OCH$_2$)$_3$CMe)
Fe(η^4-C_4H_6)(CO)[P(OMe)$_2$]$_2$ (VI)	$CDCl_3$	5.2(br)	8.7(br)	10.0(br)	6.6(t, P(OMe)$_3$)

[a] Relative to TMS. [b] Methylene protons of 1,3-cyclohexadiene. [c] ^3J(PNCH) = 10 Hz, ^4J(FPNCH) = 3 Hz.

[d]





A line at 3.4 τ was unassigned, n.o. = not observed.

The limiting low temperature $^{31}P\{^1H\}$ NMR spectrum of I at −53°C shows the presence of both isomers IC and ID. The most intense doublet at low field is assigned to the trimethylphosphite resonance in isomer IC, arising from coupling to the axial triphenylphosphine ligand ($^2J(PRuP')$). The corresponding resonance for the axial PPh_3 in isomer IC occurs at high field as a 1 : 2 : 1 triplet pattern from coupling to the two magnetically equivalent $P(OMe)_3$ ligands. The resonances of $P(OMe)_3$ ligands in ID occur at lowest field as two sets of doublets of doublets, the one at higher chemical shift appearing as a triplet because of fortuitous overlapping of lines.

In cyclic diene and dienyl complexes of the type M(diene/dienyl)$(CO)_x$-$[P(OCH_2)_3CEt]_{3-x}$, it has been reported [7] that ^{31}P resonance for the basal phosphite ligand occurs at higher field than the apical phosphite. On the basis of this observation we have assigned the higher field resonance in our spectrum of ID to the basal trimethylphosphite.

The resonance for the basal triphenylphosphine in isomer D appears as a doublet ($^2J(P_b'RuP_b)$ = 39.1 Hz) of doublets ($^2J(P_a'RuP_b)$ = 9.7 Hz) arising from coupling to the two magnetically non-equivalent trimethylphosphite ligands. In

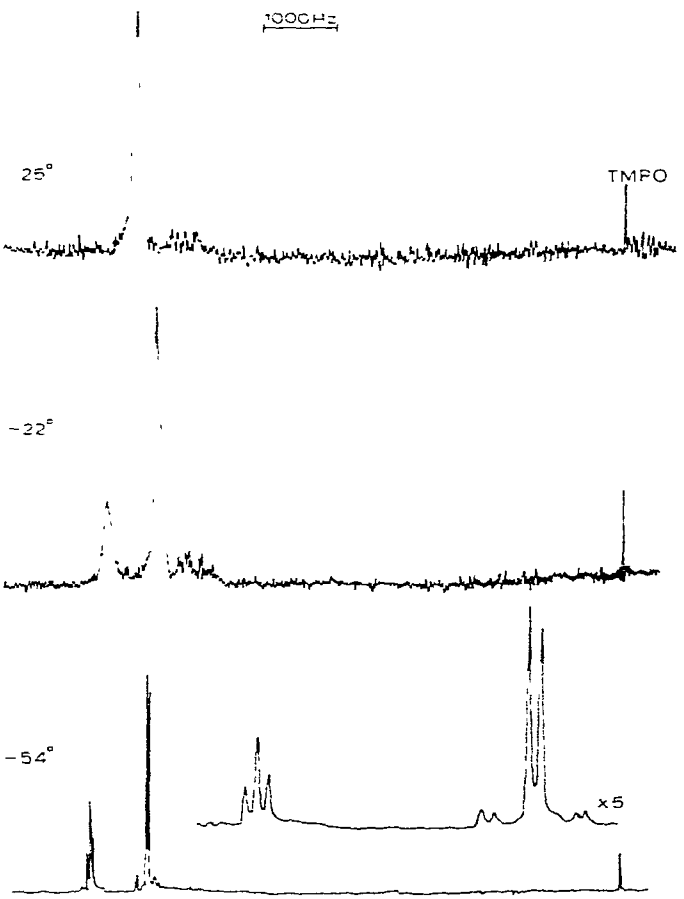
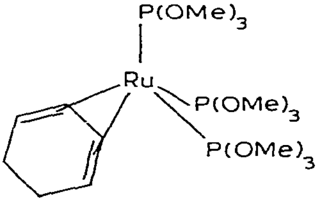


Fig. 2. Variable temperature ^{31}P NMR spectra of $Ru(\eta^4\text{-}C_6H_8)[P(OMe)_3]_3$.

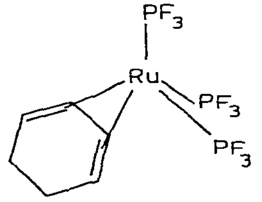
the complex Ru(η^4-C_4H_6)(PPh_3)$_3$ [14] which has a trigonal bipyramidal geometry, the coupling constant between the axial and equatorial phosphine is small (^2J(PP') = 4.8 Hz), and on this basis we assign the smaller coupling in isomer D to the apical trimethylphosphite—basal triphenylphosphine interaction within a square pyramid.

The two isomers of I interconvert as the temperature is raised, and at 82°C complete averaging of the triphenylphosphine and P(OMe)$_3$ resonances occurs.

The ^{31}P{^{1}H} NMR spectrum of Ru(η^4-C_6H_8)(P(OMe)$_3$)$_3$ (VII) is temperature-dependent, as shown in Fig. 2, indicating that it too is fluxional. At room temperature the proton decoupled ^{31}P NMR spectrum exhibits a single, slightly broad peak for the apparently equivalent three P(OMe)$_3$ ligands. On cooling the sample to —22°C, a new broad resonance at lower field begins to emerge, while the original resonance is shifted slightly to higher field. The limiting approximately [AX_2] spectrum, which is reached at —54°C shows the expected two resonances, in a ratio of 2 : 1 for the basal and apical P(OMe)$_3$ groups, respectively. The lower field resonance (intensity 1) which appears as a triplet, is readily assigned to the unique apical P(OMe)$_3$ group. The two basal P(OMe)$_3$ ligands resonance occurs at higher field as a 1 : 1 doublet (^2J(L_aRuL_b) = 31.7 Hz) (see Table 1). The magnitude of this coupling constant is similar to that of the analogous ruthenium complex Ru(η^4-C_6H_8) [P(OCH_2)$_3$CEt]$_3$ (^2J(L_aRuL_b) = 38.1 Hz) reported by Whitesides [7] and synthesised in only 11% yield by a different route involving displacement of CO from Ru(η^4-C_6H_8)(CO)$_3$. In the latter complex, the chemical shift differences between the apical and basal resonances is reported to be 10.1 ppm, while in complex VII it is slightly larger (18.2 ppm).



(VII)



(XI)

The room temperature ^{19}F NMR spectrum of Ru(η^4-C_6H_8)(PF_3)$_3$ (IX) (Fig. 3) exhibits the expected mirror image doublet of multiplets typical of an [AX_3]$_3$ spin system [A = phosphorus X = fluorine] [24] indicative of the equivalence of the three PF_3 ligands. A similar spectrum was reported previously [2] for the iron analogue but the limiting spectrum could not be reached even at —100°C.

The energy barrier for intramolecular ligand exchange in IX however, is found to be larger than that of the iron complex as illustrated by the variable temperature ^{31}P{^{1}H} NMR spectrum of Ru(η^4-C_6H_8)(PF_3)$_3$ (See Fig. 4).

The ^{31}P{^{1}H} NMR spectrum at room temperature exhibits a basic 1 : 3 : 3 : 1 quartet pattern [^1J(P—F)] showing further complicated fine structure expected for the A part of an [AX_3]$_3$ spin system (A = phosphorus, X = fluorine). At —48°C the original pattern of lines becomes broad and by —58°C a second, weaker 1 : 3 : 3 : 1 quartet begins to appear. The limiting spectrum is obtained at —93°C and shows two overlapping quartet patterns in the ratio 1 : 2 with much further fine structure evident. Further spin coupling between the two

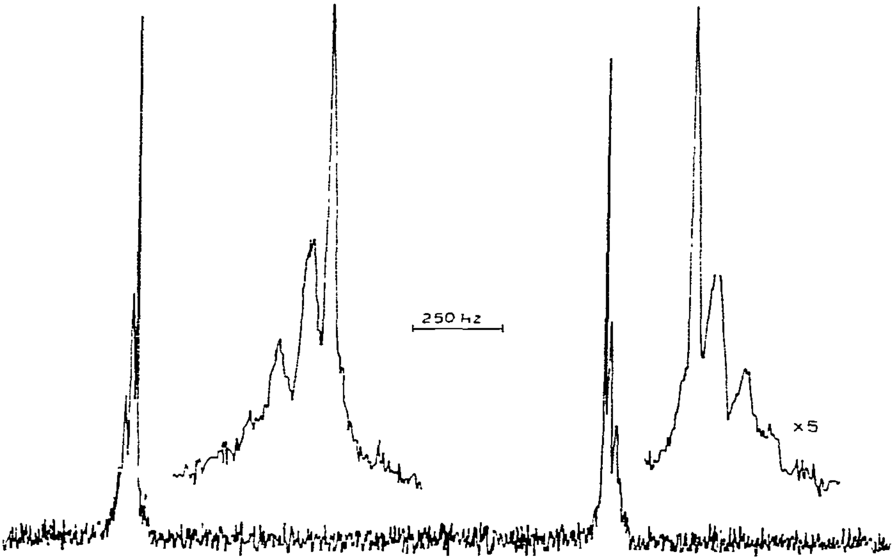


Fig. 3. ^{19}F NMR spectrum of Ru(η^4-C_6H_8)(PF_3)$_3$ (IX) (25°C).

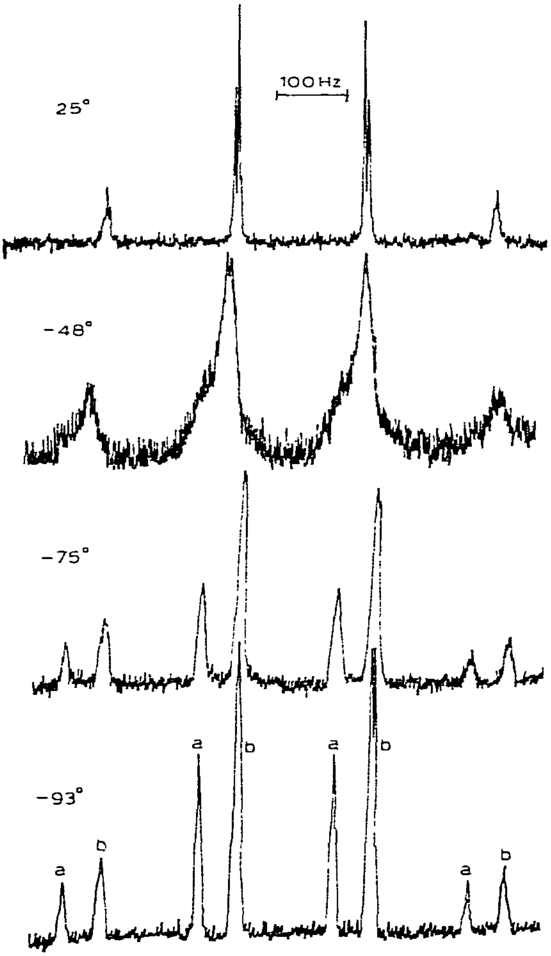


Fig. 4. Variable temperature ^{31}P NMR spectra of Ru(η^4-C_6H_8)(PF_3)$_3$, (IX).

$[AX_3]$ and $[AX_3]_2$ spin systems is possible and precludes a full analysis of the complex NMR spectrum but some approximate coupling constant data are listed in Table 1. No ^{31}P NMR data are available for $Fe(\eta^4-C_6H_8)(PF_3)_3$.

The coalescence temperature (*Tc*) for $Ru(\eta^4-C_6H_8)(PF_3)_3$, is found to be about —48°C and this value can be compared with $Tc = 15°C$ for $Ru(\eta^4-C_6H_8)[P(CH_2O)_3CEt]_3$ and $Tc = -21°C$ for $Ru(\eta^4-C_6H_8)(CO)_3$ [7].

Coalescence temperatures *Tc* and/or activation energies for several fluxional five-coordinate Fe^0 and Ru^0 complexes have been determined. It is interesting to note that the barrier for ligand exchange is found to be higher for Fe than Ru for ML_5 complexes ($L = PF_3$, $P(OMe)_3$) [25—27] whereas data for diene complexes of the type $M(\eta^4-C_6H_8)(CO)L_2$ and $M(\eta^4-C_7H_{10})(CO)L_2$ (M = Fe, Ru; $L = P(OCH_2)_3CEt$) [7] are in the opposite order in agreement with our observation of $Tc = -48°C$ for $Ru(\eta^4-C_6H_8)(PF_3)_3$ compared with $Tc = < -100°C$ for $Fe(\eta^4-C_6H_8)(PF_3)_3$ [2].

Experimental

All reactions were carried out under argon or dry nitrogen or in sealed evacuated tubes. Solvents were carefully dried before use. ^1H NMR spectra were recorded on a Varian A60 spectrometer and ^{31}P NMR spectra on a Jeol FT spectrometer operating at 40.25 MHz, with capillaries of $P(OMe)_3$ or $OP(OMe)_3$ as internal standards.

Preparation of $RuH_4(PPh_3)_3$. $RuCl_2(PPh_3)_3$ (1.5 g, 1.56 mmol) was dissolved in hydrogen-saturated benzene (60 cm^3) and methanol (100 cm^3). Solid sodium borohydride was added until the originally deep red solution had changed to light orange. Rapid stirring of this solution for a few minutes at room temperature produced the reddish-white product. This was collected, washed several times with degassed methanol and stored under argon (1.165 g, 1.31 mmol; 83.6%). Control of the temperature of the reaction of $RuCl_2(PPh_3)_3$ and $NaBH_4$ in ethanol is important since at 50°C abstraction of CO from the solvent occurs with formation of $RuH_2(CO)(PPh_3)_3$ which does not react with buta-1,3-diene to give $Ru(\eta^4-C_4H_6)(PPh_3)_3$ (see below).

Preparation of $Ru(\eta^4-C_4H_6)_2(PPh_3)$. Buta-1,3-diene was bubbled through a suspension of $RuH_4(PPh_3)_3$ (1.10 g, 1.23 mmol) in toluene (20 cm^3) for 20 min at room temperature, during which time the initial reddish solution changed to a brown-yellow colour. The solution was reduced in volume (3 cm^3) and petroleum ether (20 cm^3) was added with vigorous stirring. The expected pale yellow solid of $Ru(\eta^4-C_4H_6)(PPh_3)_3$ was not formed [14], but a small amount of greenish decomposition product was obtained. Filtration and evaporation of solvent gave a brownish-yellow oil whose ^{31}P NMR spectrum showed a singlet which is unambiguously assigned to the complex $Ru(\eta^4-C_4H_6)_2(PPh_3)$.

Preparation of $Ru(\eta^4-C_4H_6)(PPh_3)[P(OMe)_3]_2$ *(I)*. A mixture of $Ru(\eta^4-C_4H_6)_2(PPh_3)$ (0.254 g, 0.538 mmol) in toluene (20 cm^3) and an excess of trimethylphosphite (0.278 g, 2.24 mmol) was heated under reflux for $4\frac{1}{2}$ h. The colour of the solution changed from brown-yellow to colourless. Solvent and excess trimethylphosphite were pumped off, leaving an oil which on washing with hexane (2 × 10 cm^3), followed by recrystallisation from dichloromethane/hexane, gave colourless crystals of (η^4-buta-1,3-diene)bis(trimethylphosphite)(triphenylphosphine)ruthenium(0) (0.320 g, 0.481 mmol; 89.4%; m.p. 140—142°C;) (Found: C, 50.9; H, 5.8. $C_{28}H_{39}O_3P_3Ru$ calcd.: C, 50.52; H, 5.87%). IR spectrum: 3062vw (sh), 3050w, 1630w, 1305vw (br), 1290vw (sh), 1265vw (br), 1170m (br), 1250w (sh), 1080m (sh), 1045s (br), 1014s, 918vw, 870vw, 842vw, 780m (sh), 745s, 730 (sh), 713m, 698s, 692s, 658w, 610vw (br), 522ms, 508ms, 495ms, 475vw, 450m, 437w, 423m, 360vw, 317vw, 282w (br) cm^{-1} (Nujol mull).

Preparation of $Ru(\eta^4\text{-}C_4H_6)(PPh_3)P(OCH_2)_3CMe]_2$ *(II).* Similarly, a solution of $Ru(\eta^4\text{-}C_4H_6)_2(PPh_3)$ (0.35 g, 0.742 mmol) in benzene (25 cm^{-3}) and an excess of $P(OCH_2)_3CMe$ (0.54 g, 3.64 mmol) was refluxed for 3½ h, during which the colour changed from brown-yellow to yellow. After solvent removal, the resulting yellow oil was scratched and washed with hexane (2 × 10 cm^3) to give the yellow solid product (η^4-buta-1,3-diene)bis(4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)(triphenylphosphine)ruthenium(0) (0.44 g, 0.616 mmol; 83%) (Found: C, 53.5; H, 5.8. $C_{32}H_{39}O_6P_3Ru$ calcd.: C, 53.85; H, 5.51%). IR spectrum: 3040w, 1583w, 1568vw (sh), 1300vw (sh), 1275w (br), 1182ms, 1173ms, 1154w (sh), 1113vw, 1081w, 1065w (sh), 1036vs, 1015vs, 968m, 959m, 921ms, 868m (sh), 856s, 776s, 768s, 749vs, 740vs, 728vs, 693s, 680w (sh), 657s, 645s, 618vw, 531ms, 517s, 498ms, 477w, 453m, 432ms, 415m, 376w (sh), 368m, 342vw, 270vw, 254w cm^{-1} (Nujol mull).

Preparation of $Ru(\eta^4\text{-}C_4H_6)(PPh_3)(PF_2NMe_2)_2$ *(III).* An excess of PF_2NMe_2 (0.2 g, 1.77 mmol) was condensed into a solution of $Ru(\eta^4\text{-}C_4H_6)_2(PPh_3)$ (0.233 g, 0.494 mmol) in benzene (12 cm^3) in an evacuated tube, and the contents sealed off. No reaction was observed at room temperature, but on heating the mixture at 90°C overnight, a change in colour from brown-yellow to yellowish occurred. The tube was opened under dry nitrogen gas and the excess volatile ligand and solvent were pumped away. The resulting oily product was formulated as a mixture of two isomers of (η^4-buta-1,3-diene)bis(dimethylaminodifluorophosphine)(triphenylphosphine)ruthenium(0) on the basis of its ^1H, ^{19}F and variable temperature ^{31}P NMR spectra.

Reaction of $Ru(\eta^4\text{-}C_4H_6)_2(PPh_3)$ *with trifluorophosphine.* In a similar fashion to that described above, $Ru(\eta^4\text{-}C_4H_6)_2(PPh_3)$ (0.200 g, 0.424 mmol) in benzene (15 cm^3) and an excess of PF_3 (0.38 g, 4.32 mmol) gave a pale-yellow oily product identified as a mixture of two isomers of $Ru(\eta^4\text{-}C_4H_6)(PPh_3)(PF_3)_2$ (IV) and $Ru(PF_3)_4(PPh_3)$ on the basis of their ^{19}F and ^{31}P NMR spectra.

Preparation of $Fe(\eta^4\text{-}C_4H_6)(CO)[P(OCH_2)_3CMe]_2$ *(V).* A mixture of $Fe(\eta^4\text{-}C_4H_6)_2(CO)$ * (0.120 g, 0.625 mmol) and an excess of $P(OCH_2)_3CMe$ (0.522 g, 3.52 mmol) in toluene (15 cm^3) was heated under reflux for 6 h, during which time a change in colour from orange to pale-yellow occurred. On cooling the solution, a pale-yellow, microcrystalline product was obtained, which was filtered and washed with hexane (10 cm^3). The pale-yellow solid was characterised as (η^4-buta-1,3-diene)bis(4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane)carbonyliron(0) (0.118 g, 0.271 mmol; 43.5%) (Found: C, 42.4; H, 5.8. $C_{15}H_{24}FeO_7P_2$ calcd.: C, 41.5; H, 5.57%). IR spectrum: 3050vw, 1920s (br), 1350vw, 1329w, 1310vw (sh) 1292vw, 1185m (sh), 1177ms, 1150vw (sh),

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1040s (br), 966m, 957 (sh), 931ms, 882vw, 866ms, 781s, 763s (br), 740s (br), 663ms, 652s 597m (sh), 591ms, 562m, 521m, 496vw, 461vw, 415w, 402vw, 380w, 345m, 270w cm^{-1} (Nujol mull). Further amounts of V contaminated with $P(OCH_2)_3CMe$ were obtained form the filtrate by evaporation.

Preparation of $Fe(\eta^4\text{-}C_4H_6)(CO)[P(OMe)_3]_2$ (VI). In a similar fashion to that described above, a mixture of an excess of trimethylphosphite (2.13 g, 17.2 mmol) and $Fe(\eta^4\text{-}C_4H_6)_2(CO)$ in toluene (15 cm^3) gave (η^4-buta-1,3-diene)bis(trimethylphosphite)carbonyliron(0) as a yellow oil. The formulation is based on its ^1H and ^{31}P NMR spectra. IR spectrum: 3050m, 3010ms, 2970s, 2928m (sh), 2880ms, 1915s (br), 1867m (sh), 1785w (br), 1493w (sh), 1456ms (br), 1445m (sh), 1372w, 1290vw, 1176ms, 1035s (br), 955vw (sh), 918vw, 885w, 850vw, 765s (br), 738s, 718s (br), 675w, 596ms, 564ms, 532ms, 495vw, 473vw, 454w, 430vw, 400m, 375vw, 330w (sh), 315m (br), 294vw (sh), 280vw cm^{-1} (neat).

Preparation of $Ru(\eta^4\text{-}C_6H_8)[P(OMe)_3]_3$ (VII). $Ru(\eta^4\text{-}C_6H_8)(\eta^6\text{-}C_6H_6)$ (0.12 g, 0.462 mmol) in benzene (15 cm^3) was heated under reflux with a large excess of trimethylphosphite (3 cm^3) for 5 h. The colour of the solution changed from yellow to pale yellow and removal of solvent and excess of $P(OMe)_3$ under high vacuum left an oily product, which was extracted with hexane (15 cm^3). Removal of hexane gave a pale yellow oil formulated as (η^4-1,3-cyclohexadiene)-tris(trimethylphosphite)ruthenium(0) on the basis of its ^1H and variable temperature ^{31}P NMR spectra (see text).

Preparation of $Ru(\eta^4\text{-}C_6H_8)[P(OCH_2)_3CMe]_3$ (VIII). $Ru(\eta^4\text{-}C_6H_8)(\eta^6\text{-}C_6H_6)$ (0.34 g, 1.31 mmol) in benzene (30 cm^3) was stirred with $P(OCH_2)_3CMe$ (0.585 g, 3.95 mmol) at room temperature for 2 h. No reaction was observed, but after heating the reaction mixture for 4 h, an oily product was given off after removal of solvent, which after stirring in hexane (30 cm^3) overnight gave the off-white solid complex (η^4-1,3-cyclohexadiene)tris(4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)ruthenium(0) (0.135 g, 0.216 mmol; 17%) (Found: C, 38.7; H, 5.1 $C_{21}H_{35}O_9P_3Ru$ Calcd.: C, 40.32; H, 5.64%). IR spectrum: 3060vw, 1705w, 1614vw, 1320w, 1305vw, 1272m, 1245vw, 1220vw, 1170s (br), 1115vw, 1090vw (sh), 1045vs, 1015vs (br), 960m, 927s, 890vw, 863vs, 842w (sh), 812m (sh), 787vs, 748vs, 730vs (br), 695w, 660s, 646vs, 515s, 500w (sh), 458vw, 446m, 415ms, 380m, 343vw, 284vw (sh), 270w, 255vw (sh) cm^{-1} (Nujol mull).

Reaction of $Ru(\eta^4\text{-}C_6H_8)(\eta^6\text{-}C_6H_6)$ with trifluorophosphine. A mixture of $Ru(\eta^4\text{-}C_6H_8)(\eta^6\text{-}C_6H_6)$ (0.411 g, 1.59 mmol) and an excess of PF_3 (2.13 g, 24.2 mmol) was sealed in an ampoule and left for 50 h at room temperature. No reaction was observed, but after heating the ampoule at 90°C for 3 h, an oily liquid was formed. High vacuum fractionation of the volatiles afforded PF_3 at −196°C and a colourless mixture of $Ru(PF_3)_5$ in benzene (0.109 g) at −78°C. An off-white glassy solid was collected at the −24°C trap and identified as (1,3-cyclohexadiene)tris(trifluorophosphine)ruthenium(0) (IX) (0.207 g, 0.46 mmol; 29.4%) by ^1H, ^{19}F and ^{31}P NMR spectroscopy (see text). IR spectrum: 3058vw (sh), 3018w, 1334w, 1260vw, 1240vw, 1186w, 1113vw, 1005vw, 955w, 928s, 885ms, 874m (sh) 855s, 810vw (sh), 772vw (br), 638w, 541w, 520m, 503vw (sh), 452w cm^{-1} (gas cell).

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