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THE STRUCTURE AND DYNAMICS OF RHODIUM(I) ACETYLACETONATE COMPLEXES OF MONOSUBSTITUTED OLEFINS. A CARBON-13 NMR STUDY

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Summary

A range of monosubstituted olefin rhodium acetylacetonate complexes has been prepared and their solution equilibria and dynamics studied by carbon-13 nuclear magnetic resonance between 188 and 320 K. Vinylcyclohexane forms two diastereomeric bis-olefin complexes which do not interconvert, whereas distyrenerhodium acetylacetonate possesses one major rotamer which interconverts rapidly with its isomers at room temperature.

para-Methoxy- and *para*-nitrostyrene analogues show similar behaviour, and the complexes of these substituted styrenes with rhodium hexafluoroacetylacetonate show enhanced rates of associative olefin exchange. Bis-olefin complexes of *ortho*-methoxystyrene are static in solution with coordination of one of the aryl ether oxygens inhibiting fluxional behaviour. Methyl propenoate forms a bis-olefin complex exhibiting a complex, dynamic ^{13}C NMR spectrum, demonstrating the presence of all possible rotamers of both diastereomers at low temperatures. Vinyl acetate displaces one or two moles of ethylene from diethylenerhodium(I) acetylacetonate. The mixed olefin complex shows rapid independent rotation of its ethylene ligand, whilst bis(vinyl acetate)rhodium(I) acetylacetonate reveals two dynamic processes with different activation energies. The mechanisms of these interconversions are discussed.

Asymmetric hydrogenation is carried out most successfully with chelating phosphinerhodium complexes catalysing the reduction of olefins carrying polar substituents and capable of bidentate coordination [1]. Recent work has provided information on the structure of intermediates in these reactions [2] and on the asymmetric deuteration of monosubstituted olefins [3], but work on simple model systems is also desirable. We have therefore examined the carbon-13 NMR spectra of a number of stable rhodium acetylacetonate complexes of monosubstituted olefins which demonstrate a surprising versatility of structural and dynamic behaviour.

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The square-planar coordinatively unsaturated complex diethylenerhodium(I) acetylacetonate was first prepared by Cramer [4] and affords a simple route to further bis-olefin complexes by displacement of ethylene. It was demonstrated [4,5] that ethylene exchange between free and complexed olefin occurs rapidly on the NMR time scale by an associative mechanism [5] and that rotation of the olefin about its coordination axis surmounts an activation barrier of circa 40 kJ mol^{-1} [6]. More recently, some carbon-13 NMR spectra of substituted olefin-rhodium complexes have been reported [7] and extensive ^{1}H NMR studies made of the dynamic behaviour of methoxyethylenerhodium(I) acetylacetonates [8].

A monosubstituted olefin may form two diastereomeric rhodium acetylacetonates, and each of these may exist in three rotameric forms (Fig. 1). Since two of the three have an axis or plane of symmetry but the third does not, the number of possible signals for each carbon atom of the coordinated olefin is quite large in the slow exchange limit. Rapid rotation will cause simplification as $A_1 \rightleftharpoons A_2 \rightleftharpoons A_3$ and $B_1 \rightleftharpoons B_2 \rightleftharpoons B_3$; intermolecular exchange, or any process which alters the face of olefin coordination from re to si or vice versa will lead to a single line spectrum with loss of rhodium–carbon coupling. The study of such dynamic processes by ^{13}C NMR is much simpler than by ^{1}H NMR because of the absence of complex spin multiplets [8].

Results and discussion

The preparation of complexes was straightforward involving displacement of ethylene from the diethylene complexes of rhodium(I) acetylacetonate [4] and rhodium(I) hexafluoroacetylacetonate [9]. Carbon-13 NMR spectra were recorded as approximately 0.2 *M* solutions in CD_2Cl_2 or $(CD_3)_2CO$ in which the complexes were highly soluble over the temperature range studied, and stable under an argon atmosphere. The solvent resonance obscured the bound-olefinic CH_2 resonance in certain cases.

(a) Divinylcyclohexanerhodium(I) acetylacetonate (**1a**). This was chosen as a mono-substituted alkene complex in which the substituent cannot interact with the metal. Its carbon-13 NMR spectrum is invariant over the temperature range 208 to 300 K and unchanged by addition of a molar equivalent of vinylcyclohexane. Two

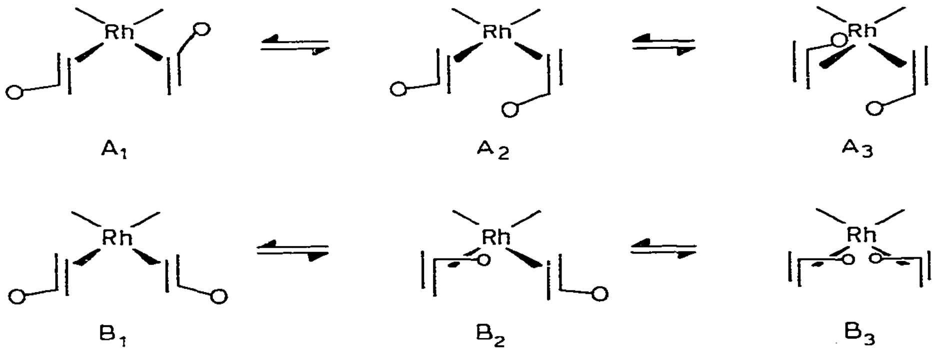
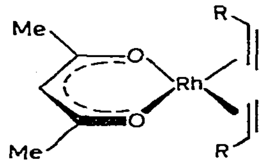
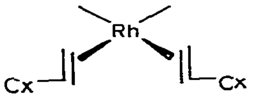


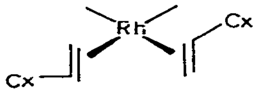
Fig. 1. Rotamers of a monosubstituted bis-olefin complex.



(1a, R = cyclohexyl; 1e, R = o-OMePh
1b, R = Ph; 1f, R = CO_2H;
1c, R = p-OMePh; 1g, R = CO_2Me;
1d, R = p-NO_2Ph; 1h, R = OAc)



(2a)



(2b)

distinct vinyl CH resonances are observed and in view of their non-interconversion at room temperature correspond to the diastereomeric species **2a** and **2b** in ratio 3/1. *endo*-Rotameric forms are presumed to be disfavoured for steric reasons and were below the limit of experimental detection (< 5%).

(b) Distyrenerhodium(I) acetylacetonate (**1b**). This complex has recently been prepared [7], and its carbon-13 NMR spectrum recorded although no information

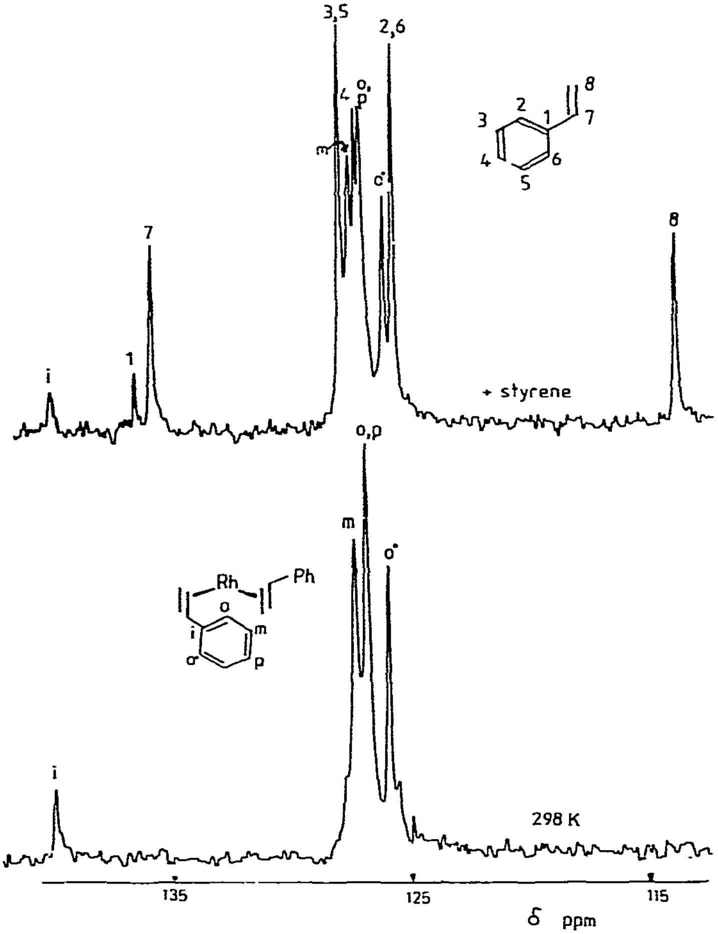
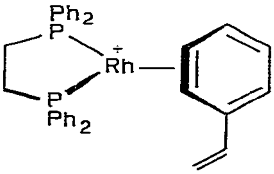


Fig. 2. Aromatic resonances of distyrenerhodium(I) acetylacetonate; upper spectrum plus free styrene.

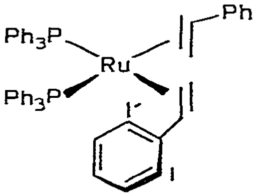
on dynamic processes was presented. The behaviour of **1b** in solution is quite different to that of **1a**. At low temperature (< 263 K) one predominant rotamer exists and up to three minor species are apparent. On raising the temperature the C(2) resonance broadens, coalesces at about 283 K and sharpens somewhat at higher temperatures. The exchange process is intramolecular since addition of a molar excess of styrene to the solution at 298 K causes little or no effect demonstrating that intermolecular exchange is slow (Fig. 2). Similar behaviour was observed for the *para*-methoxy- and *para*-nitro-styrene complexes (**1c** and **1d**). In the aromatic region of all three of these complexes one of the *ortho* carbon atoms of the major isomer resonated ~ 4.5 ppm downfield of its position in free styrene, and the *meta* carbon atoms were ~ 0.7 ppm upfield of their position in free styrene. In the complex *ortho* and *meta* carbon resonances due to minor isomers occurred at about the same chemical shift as in free styrene.

These results are interpreted as the consequence of olefin rotation [6] with an energy barrier of about 50 kJ mol^{-1} at 283 K. This implies that *endo*-rotamers are present at equilibrium here, unlike the case of **1a**. A number of examples are known where styrene coordinates partly or completely by the aromatic ring. Thus diphenylphosphinoethanerhodium(I)-(methanol)$_n$ cations react reversibly with a variety of arenes, and the equilibrium constant for styrene complexation is sufficiently close to that of other alkylbenzenes to suggest structure **3** for the complex, with little double-bond participation, [10]. The X-ray crystal structure of distyrenebis(triphenylphospine)ruthenium(0) has been reported and in this complex (**4**) one of the arenes is canted towards the metal so that a Ru–C(1) distance of 2.75 Å is observed [11]. On this basis, it seem likely that *endo*-rotamers of **1b** are stabilized relative to those of **1a** by a weak interaction between the rhodium atom and *ipso* and *ortho* atoms of the aromatic ring. The stereospecificity in complexation is interesting although the evidence does not distinguish between (*RR*) and (*RS*) diastereomers.

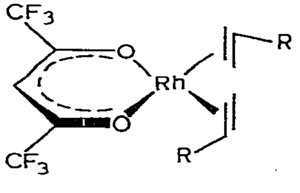
(c) Distyrenerhodium(I) hexafluoroacetylacetonate and related complexes. Perfluoro substitution of an acetylacetonate ligand renders it far more π-acidic, enhancing the facility of oxidative addition to the square planar state. Only one set of rhodium-coupled olefinic resonances can be observed in the low temperature limiting spec-



(3)



(4)



(5a, R = Ph
5b, R = *p*-OMePh
5c, R = *p*-NO$_2$Ph
5d, R = *p*-BrPh
5e, R = *o*-OMePh)

trum of **5a** below 233 K. Addition of free styrene causes significant line broadening ($\omega_{1/2}$C(1) ~ 30 Hz at 233 K), so that the ^{13}C and ^{1}H olefinic resonances are too broad to observe above 260 K. Similar behaviour was shown by *para*-methoxy (**5b**), *para*-nitro (**5c**) and *para*-bromostyrene (**5d**) complexes. Observations of the onset of exchange broadening, and measurements of linewidths of common resonances for addition of molar equivalents of free olefin at a given temperature permit the construction of the following order for the rate of associative olefin exchange: p-NO$_2$ > p-Br > p-H > p-OMe. This order reflects the increasing withdrawal of electron density from the metal into the olefin π^* orbital from methoxy- to nitro-substituted styrenes, stabilising the putative 18e intermediate.

The corresponding complex with *ortho*-methoxystyrene (**5e**) gave static ^{13}C and ^{1}H NMR spectra over the temperature range 200 to 300 K, and addition of up to ten molar equivalents of free olefin had no observable effect on the NMR spectra. This behaviour was also shown with the acetylacetonate complex **1e**, and both complexes were a pale yellow colour in solution (the other complexes were typically deep orange or red). Such behaviour is consistent with increased coordination about rhodium involving coordination of one of the aryl ether oxygens to the metal [12].

(d) Bis(acrylic acid)rhodium(I) acetylacetonate (**1f**). This complex was readily formed but proved to be too insoluble in CD$_2$Cl$_2$ for NMR studies. In dilute chloroform solution the C=O stretch of the acid was 1710 cm^{-1} unchanged from that of the free ligand. The KBr disc spectrum of **1f** showed a shift to 1680 cm^{-1} which may indicate intermolecular coordination of one carbonyl group to the rhodium atom of another molecule in the solid state [13].

(e) Bis(methyl acrylate)rhodium(I) acetylacetonate (**1g**). Unlike the acid **1f**, the solution and KBr disc infrared spectra of ester **1g** were identical, ν 1730 cm^{-1}. In the ^{13}C NMR spectrum the C(1) and C(2) resonances are quite close, δ 78.3 and 74.9 (centred) ppm. At low temperatures the spectrum of the olefinic region is quite

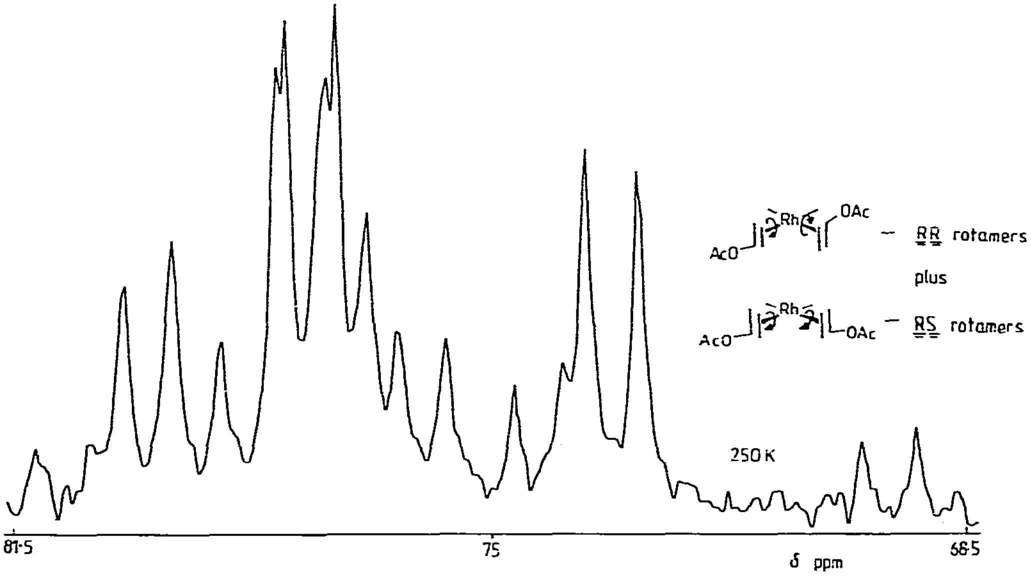


Fig. 3. Olefinic resonances of rotamers of bis(methyl acrylate)rhodium(I) acetylacetonate.

complex (Fig. 3) and shows that both *endo* and *exo* rotamers of both diastereomers must be present. This is reminiscent of the multiplicity of isomers observed in the proton NMR spectrum of bis(methoxyethylene)rhodium(I) acetylacetonate by Herberhold and co-workers [8]. At least ten rhodium coupled signals are observed, compared to a maximum of sixteen if all possible rotamers were present (Fig. 1). Since the two *endo-endo* isomers will show substantial non-bonded interactions it is unlikely that these are present in observable concentration. Nevertheless, this spectrum implies that the *exo-exo* and *exo-endo* rotamers are of comparable energy.

(f) Bis(vinyl acetate)rhodium (I) acetylacetonate. Reaction of diethylenerhodium(I) acetylacetonate with one mole of vinyl acetate gives a statistical mixture of mono- and di-vinyl acetate complexes together with starting material. The ^{13}C NMR spectrum at 301 K reveals both the diethylene complex at 59.5 ppm (olefinic resonances) and the divinyl acetate complex (**Ih**) at 42.9 (C(1)), together with the mixed complex with coordinated ethylene at 61.4 ppm and coordinated vinyl acetate (C(1)) at 42.6 ppm. On cooling, the ethylene carbon resonance of the mixed complex broadens to a coalescence point at 223 K, becoming two sharp doublets at 193 K

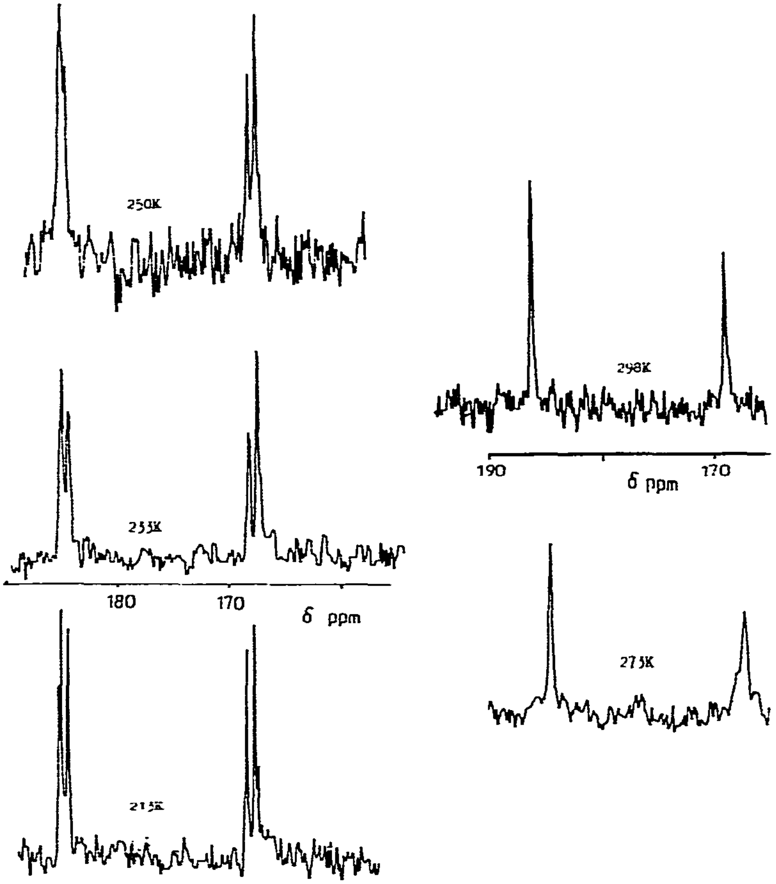
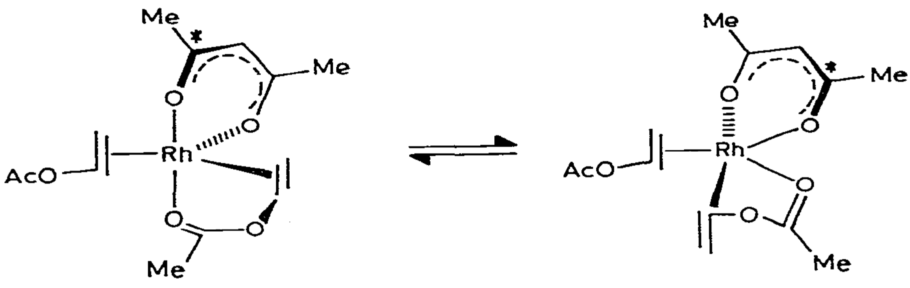


Fig. 4. Carbonyl region of bis(vinyl acetate)rhodium(I) acetylacetonate.



(6a) (6b)

[14]. Evidently, the olefin is rotating rapidly at room temperature, but slowly on an NMR time scale at low temperatures with $\Delta G^{\ddagger}_{223} \approx 40$ kJ mol^{-1}.

The carbon-13 NMR spectrum of the C(1) region of the divinyl acetate complex (**1h**) shows that three major species are present at low temperatures. As the temperature is raised, the two upfield signals broaden and coalesce at circa 245 K, but coalescence of the resulting major and minor species occurs only above 300 K. This duality of behaviour is mirrored in the carbonyl region of the spectrum. The separate acetylacetonate resonances coalesce below 250 K, but the separate acetate resonances only at 270 K (Fig. 4). It is known that vinyl acetate functions as a bidentate ligand towards cationic rhodium biphosphines [15]. Since exchange with free vinyl acetate does not cause dynamic broadening in the temperature range studied it is tempting to speculate that the dynamic process involved at low temperatures is isomerisation without dissociation but at higher temperatures olefin rotation also occurs. A possible mechanism for this isomerisation involves the oxygen coordinated species **6a** in which the acetylacetonate carbons may be equivalenced by pseudorotation (**6a** ⇌ **6b**) [16].

Conclusions

A considerable diversity of dynamic and structural behaviour is exhibited by substituted alkenerhodium(I) complexes. With a simple bulky alkyl group, *exo*-geometry of the substituent is preferred and there is only slow exchange of coordinated and free olefin. With a carbomethoxy group there is a greatly increased proportion of *endo*-rotamers but there is no evidence for carbonyl coordination to the metal. With an *O*-acetyl substituent there is some evidence for an intramolecular isomerisation via an oxygen-coordinated intermediate. With styrene and substituted styrene complexes there may be weak phenyl coordination increasing the population of *endo* rotameric forms. *ortho*-Methoxy-substituted styrene complexes show static behaviour in solution with one of the *o*-OMe groups binding to the metal. Selective asymmetric catalysis depends on the proper orientation of functional groups both in the olefinic substrate and counter ligands. These studies show that subtle factors are involved and both steric and electronic effects, the latter requiring weak coordination to the metal are important.

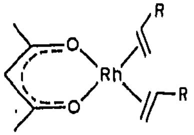
Experimental

Solvents and reagents were purified by conventional methods [17]. All manipulations involving air-sensitive compounds were performed on a vacuum-line using

(Continued on p. 92)

TABLE I

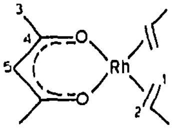
ANALYTICAL DATA FOR acacRh(olefin)$_2$ AND hfacacRh(olefin)$_2$



Olefin R	acacRh(olefin)$_2$			hfacacRh(olefin)$_2$			
	m.p. (°C)	Analysis (Found (calcd.) (%))		m.p. (°C)	Analysis (Found (calcd.) (%))		
		C	H		C	H	F
Cyclohexyl	200 (dec)	59.9(60.0)	7.67(7.86)	-	--	--	--
C_6H_5	106–107	61.8(61.7)	5.68(5.64)	45–46	49.8(49.8)	3.51(320)	21.9(22.0)
p-$OMeC_6H_4$	oil	58.5(58.7)	5.59(5.74)	129–130	47.7(47.8)	3.67(3.64)	19.8(19.6)
p-$NO_2C_6H_4$	74–76	50.6(50.4)	4.48(4.26)	174–175	41.5(41.4)	2.47(2.48)	18.6(18.7)
o-$OMeC_6H_4$	185	58.7(58.7)	5.83(5.74)	132–134	47.7(47.8)	3.61(3.64)	19.5(19.6)
CO_2H	> 150(dec)	38.2(38.2)	4.53(4.38)	-	--	--	--
CO_2Me	86–87	41.8(41.8)	5.15(5.12)	-	--	--	--
OAc	110–120	42.1(41.8)	5.20(5.12)	-	--	--	--
p-BrC_6H_4	-	--	--	136–137	37.5(37.3)	2.35(2.22)	16.6(16.7)

TABLE 2 [19]

SPECTROSCOPIC DATA FOR acacRh(olefin)$_2$ AND hfacacRh(olefin)$_2$ [c,e]



Olefin R	acacRh(olefin)$_2$ [b]						hfacacRh(olefin)$_2$ [a]					
	δ(C(1))	δ(C(2))	Δδ mean [d]	δ(C(3))	δ(C(4))	δ(C(5))	δ(C(1))	δ(C(2))	Δδ mean [d]	δ(C(3))	δ(C(4))	δ(C(5))
Cyclohexyl	60.0	88.0	46.0	26.1	185.9	98.5	-	-	-	-	-	-
C_6H_5	56.2	73.1	59.4	27.2	186.2	98.7	55.9	76.6	59.4	116.8	172.8	89.7
p-MOeC_6H_5	54.9	73.1	60.7	27.0	186.0	98.6	54.3	75.5	59.9	116.4	173.1	89.8
p-$NO_2C_6H_4$	57.7	71.3	61.5	27.1	186.3	99.1	58.2	72.9	60.7	116.6	172.9	90.2
o-OMeC_6H_4	54.6	65.6	63.0	26.8	186.5	98.4	55.3	69.2	60.8	116.2	173.3	90.1
CO_2Me [f]	54.9	58.3	72.7	27.7	188.2	100.4	-	-	-	-	-	-
OAc	42.9	98.7	48.3	27.2	187.1	99.4	-	-	-	-	-	-
p-BrC_6H_4	-	-	-	-	-	-	56.2	74.2	60.3	116.2	173.2	90.0

[a] Typically J(CF) 285 Hz, J(CCF) 36 Hz. [b] Typically J(Rh–C) ~ 13 Hz. [c] Chemical shifts in ppm relative to TMS. [d] $\Delta\delta_{\text{mean}} = 1/2[(\delta(C(1)\text{free}) - \delta(C(1)\text{complex})) + (\delta(C(2)\text{free}) - \delta(C(2)\text{complex}))]$. [e] Recorded in CD_2Cl_2. [f] Recorded in $(CD_3)_2CO$.

standard Schlenk-tube techniques. Proton NMR spectra were recorded at 90 MHz on a Perkin–Elmer R32 and at 200 MHz on a Bruker SY200. Carbon NMR spectra were recorded on a Bruker SY200 and a Bruker WH90 with independent temperature calibration for which we thank Dr. M.J.T. Robinson. Spectra were recorded typically on the accumulation of 1200 transients stored in disc mode and processed with 1.5 Hz line broadening. Free energies of activation for the exchange processes were estimated at the coalescence temperature according to the equation [18] $\Delta G_c^{\neq} = -RT \ln(\frac{h}{kT})(\frac{\pi\Delta\nu}{\sqrt{2}})$. Infrared spectra were recorded as KBr discs or as solutions in the stated solvent using a Perkin–Elmer 297 spectrophotometer. Combustion analyses were performed by Dr. F.B. Strauss (University of Oxford) and Mrs. M. Cocks (University of Durham).

Di-η^2-styrene-2,4-pentanedionato-O,O′-rhodium(I) (**1b**). To di-η^2-ethene-2,4-pentanedionato-*O,O′*-rhodium(I) (0.216 g, 0.84 mmol) in dry ether (5 cm^3) was added styrene (0.195 cm^3, 1.70 mmol) by syringe and the solution stirred for 15 min. Under a stream of argon, the colour darkened from orange to red and solvent was removed in vacuo to give a dark-red oil which crystallised from pentane ether (2/1, −30°C) to give an orange solid, m.p. 106°C (0.34 g, 98%). Physical, spectroscopic and analytical data are recorded in Tables 1 and 2. Other complexes were prepared by minor modifications to this method.

Acknowledgements

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19 The insensitivity of the mean coordination shift to changes in the *para*-substituent of the styrene complexes (with the concomitant changes to the olefin π^* orbital energy), suggest that this is not a reliable parameter for evaluating the strength of the olefinic bond or the relative importance of σ and π contributions to metal–olefin bond strength, and suggests that steric requirements may be more important in determining the degree of σ and π metal–olefin bonding.