Stereochemical Non-rigidity in Rhodium–Triruthenium Clusters studied by Nuclear Magnetic Resonance Spectroscopy

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Variable-temperature (v.t.) ^1H and ^{13}C n.m.r. studies on tetranuclear clusters $[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(\eta\text{-}C_5H_5)]$ (**1**), $[RhRu_3(\mu\text{-}H)_2(\eta\text{-}CO)(CO)_9(\eta\text{-}C_5Me_5)]$ (**2**), and $[RhRu_3(\mu\text{-}H)_4(CO)_9(\eta\text{-}C_5Me_5)]$ (**3**) establish various types of stereochemical non-rigidity in solution. Cluster (**1**) exhibits at least three distinct CO exchange processes: the lowest-energy intramolecular interchange, with $\Delta G^{\ddagger}_{195} = 35.2 \pm 0.3$ kJ mol^{-1}, monitored by v.t. ^1H and ^{13}C n.m.r., including $^{13}C\text{-}\{^1H\}$ two-dimensional exchange correlated spectra at 163 K (NOESY sequence), involves a pairwise exchange of eight CO groups resulting from a 'rocking motion' of CO ligands around a single $RhRu_2$ triangular face. Three isomers of cluster (**2**) are in dynamic equilibrium in solution: one isomer is relatively rigid stereochemically whereas the other two are fluxional and undergo rapid interconversion at all but the lowest temperatures [*e.g.* 146 K ^1H (200 MHz)]. Two distinct exchange processes are observed for cluster (**3**): localised site exchange of CO ligands at $Ru(CO)_3$ centres, with $\Delta G^{\ddagger}_{223} = 47.5 \pm 1.5$ kJ mol^{-1}, and μ-H mobility, with $\Delta G^{\ddagger}_{164} = 29.4 \pm 0.2$ kJ mol^{-1}. Reactions of (**1**) with phosphines produce clusters $[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_{9-n}(\eta\text{-}C_5H_5)(PPh_3)_n]$ [$n = 1$ (**4**) or 2 (**5**)] and $[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)(dppe)]$ (**6**) (dppe = $Ph_2PCH_2CH_2PPh_2$), accompanied by cleavage products including $[Ru_3(CO)_8(dppe)_2]$. Variable-temperature ^1H, ^{13}C, and ^{31}P n.m.r. studies indicate that (**4**) exists in solution in two isomeric forms undergoing slow interconversion at low temperatures: the major isomer is more fluxional with a lowest-energy exchange related to that in (**1**) with $\Delta G^{\ddagger}_{203} = 38.0 \pm 0.3$ kJ mol^{-1}. Clusters (**5**) and (**6**) show n.m.r. spectra of stereochemically rigid species in solution at ambient temperature and structures of these complexes are discussed.

Recently we have reported the syntheses and characterisation of the rhodium–triruthenium clusters $[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(\eta\text{-}C_5H_5)]$ (**1**), $[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(\eta\text{-}C_5Me_5)]$ (**2**), and $[RhRu_3(\mu\text{-}H)_4(CO)_9(\eta\text{-}C_5Me_5)]$ (**3**).[1] These clusters are prepared from $[Rh(CO)_2(\eta\text{-}C_5R_5)]$ (R = H or Me) and $[Ru_3(CO)_{12}]$ with H_2 and undergo facile reversible cleavage reactions with CO. Ambient-temperature ^1H n.m.r. spectra indicated that (**1**) and (**3**) were fluxional and both ^1H n.m.r. and i.r. spectra of cluster (**2**) suggested the presence of isomeric forms in solution. In this paper we present some variable-temperature (v.t.) ^1H and ^{13}C n.m.r. studies of these species including two-dimensional exchange correlated ^{13}C n.m.r. spectra (NOESY sequence) of (**1**), which elucidate stereochemical changes. Also, phosphine substituted derivatives of (**1**) have been synthesised and characterised; stereochemical aspects of these have been studied by ^1H, ^{13}C, and ^{31}P n.m.r. spectroscopy.

Previous work on tetranuclear clusters of particular relevance to these investigations includes studies of the stereochemical non-rigidity of the homonuclear ruthenium clusters $[Ru_4(\mu\text{-}H)_4(CO)_{10}(dppe)]$ (two isomers) (dppe = $Ph_2PCH_2CH_2PPh_2$)[2] and $[Ru_4(\mu\text{-}H)_4(CO)_9\{\mu_3\text{-}(PPh_2)_3CH\}]$,[3] and of the heteronuclear triruthenium cluster $[FeRu_3(\mu\text{-}H)_2(CO)_{13}]$ and its substitution products with phosphorus ligands.[4–6] The more robust triosmium clusters, structurally related to (**1**) and (**3**), *i.e.* $[MOs_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(\eta\text{-}C_5H_5)]$ (M = Co[7] or Rh[8]) and $[MOs_3(\mu\text{-}H)_4(CO)_9(\eta\text{-}C_5R_5)]$ (R = H, M = Co;[9] R = Me, M = Rh[10]) are fluxional, although full analyses of v.t. n.m.r. spectra have not been reported. The existence of isomeric forms of $[CoOs_3(\mu\text{-}H)_2(CO)_{10}(\eta\text{-}C_5Me_4Et)]$, related to (**2**), are similarly supported by i.r. spectra in solution.[11]

N.m.r. studies on the Rh-containing tetranuclear clusters $[Ru_2Rh_2(\mu\text{-}H)_2(CO)_{12}]$[12] and $[Co_2Rh_2(\mu\text{-}CO)_3(CO)_{9-n}(PEt_3)_n]$ (n = 1 or 2)[13] have recently been described.

Experimental

All reactions were performed using Schlenk techniques under an atmosphere of purified dinitrogen. Solvents were commercial reagent grade and were dried and redistilled under dinitrogen. Clusters (**1**), (**2**), and (**3**) were prepared as previously described;[1] ^{13}CO-enriched clusters were obtained from $[Ru_3(^*CO)_{12}]$ (30—40% ^{13}CO) which was produced by slow exchange between $[Ru_3(^{12}CO)_{12}]$, in tetrahydrofuran solution, and ^{13}CO (99%, Amersham International) kept in a sealed vessel under normal laboratory illumination for 3—4 d. The degree of enrichment of $[Ru_3(^*CO)_{12}]$ was monitored by i.r. and mass spectrometry.

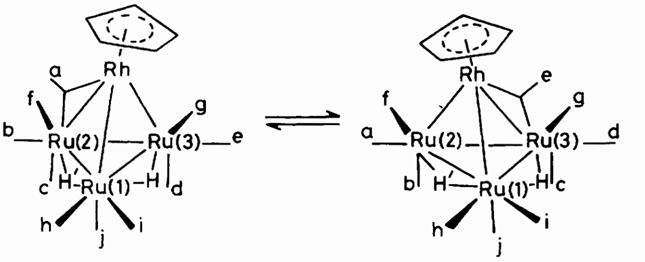
^1H N.m.r. spectra were recorded at 200 MHz on a Bruker WP 200 SY instrument and also, for cluster (**1**), at 500 MHz on a Bruker WM 500 instrument at the Southern Californian Regional N.M.R. Facility (CalTech). Phosphorus-31 and ^{13}C n.m.r. spectra were recorded on a Bruker WP 200 SY spectrometer at 81.0 and 50.3 MHz, respectively. Additionally, ^{13}C n.m.r. spectra were obtained for complexes (**2**) and (**3**) at 90.56 MHz, using a Bruker WH 360 instrument at the University of Edinburgh. Most samples for ^{13}C n.m.r. analysis were 0.05 mol dm^{-3} in $[Cr(acac)_3]$ (acac = acetylacetonate). Selected n.m.r. spectral data are recorded in the Table. I.r. spectra were recorded on a Perkin-Elmer 580 spectrometer.

Reaction of $[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(\eta\text{-}C_5H_5)]$ (**1**) *with Triphenylphosphine.*—Cluster (**1**) (0.091 g, 0.12 mmol) and PPh_3 (0.044 g, 0.17 mmol) were stirred in tetrahydrofuran (thf) (5 cm^3) for 20 h at ambient temperature (*ca.* 20 °C). The reaction mixture was then chromatographed on a silica gel

Table. Selected n.m.r. data for tetranuclear $RhRu_3$ clusters

Cluster	N.m.r.	Frequency (MHz)	Temp. (°C)	Solvent	Resonances[a] ^{1}H:hydride, ^{13}C:CO ligand, or ^{31}P:phosphine ligand	Comments
(1)	^{1}H	500	25	$C_6D_5CD_3$	−17.15 (2 H)	Fast exchange
(1)	^{1}H	500	−88	$C_6D_5CD_3$	−16.50 (1 H), −17.84 (1 H)	Slow exchange ($\Delta\nu_{\frac{1}{2}}$ *ca.* 160 Hz)
(1)	^{13}C-{^{1}H}	50.3	30	CD_2Cl_2–$CFCl_3$	196.2 (10 CO)	Fast exchange ($\Delta\nu_{\frac{1}{2}}$ *ca.* 40 Hz)
(1)	^{13}C-{^{1}H}	50.3	−115	CD_2Cl_2–$CFCl_3$	231.9 (d, J_{Rh-C} 55.3, 1 μ-CO), 199.9 (1 CO), 194.0 (2 CO), 192.9 (1 CO), 191.7 (1 CO), 189.7 (1 CO), 188.9 (1 CO), 188.3 (1 CO), 184.8 (1 CO)	Slow exchange
(2)	^{1}H	200	20	CD_2Cl_2	(*i*) −13.22 (1 H), 20.61 (1 H)	Slow exchange, isomer (**IV**), 20%
					(*ii*) −17.24 (d, J_{Rh-H} 8.7, 2 H)	Fast exchange, isomers (**III**)/(**V**), 80%
(2)	^{1}H	200	−127	CD_2Cl_2–$CFCl_3$	(*i*) −13.33 (1 H), −20.61 (1 H)	Slow exchange, isomer (**IV**), *ca.* 23%
					(*ii*) −16.71 (2 H)	Fast exchange, isomer (**III**), *ca.* 68%
					(*iii*) *ca.* −17.9 (1 H), −19.15 (d, J_{Rh-H} 32, 1 H)	Slow exchange, isomer (**V**), *ca.* 9%
(2)	^{13}C-{^{1}H}	50.3	20	CD_2Cl_2–$CFCl_3$	199.95 (10 CO)[b]	Fast exchange
(2)	^{13}C-{^{1}H}	50.3	−90	CD_2Cl_2–$CFCl_3$	(*i*) 244.0 (d, J_{Rh-C} 33, 1 μ-CO), 198.8 (1 CO), 198.1 (1 CO), 196.8 (1 CO), 194.9 (1 CO), 193.6 (1 CO), 193.0 (1 CO), 192.6 (1 CO), 188.3 (1 CO), 187.5 (1 CO)	Isomer (**IV**)
					(*ii*) *ca.* 194	Broad band ($\Delta\nu_{\frac{1}{2}}$ *ca.* 175 Hz)
(2)	^{13}C-{^{1}H}	90.56	−125	CD_2Cl_2–$CFCl_3$	(*i*) 244.8 (d, J_{Rh-C} 32, 1 μ-CO), 198.5 (1 CO), 197.8 (1 CO), 196.6 (1 CO), 196.4 (1 CO),[c] 192.2 (1 CO), 187.9 (1 CO), 187.1 (1 CO)	Isomer (**IV**) (*ca.* 20%)
					(*ii*) *ca.* 218 (v broad, 2 CO?), 201.5 (1 CO), 195.7 (2 CO?), 193.3 (2 CO), 192.7 (2 CO), 185.3 (1 CO)	Non-rigid species (*ca.* 80%)
(3)	^{1}H	200	20	CD_2Cl_2–$CFCl_3$	−15.99 (d, J_{Rh-H} 13.8, 4 H)	Fast exchange
(3)	^{1}H	200	−125	CD_2Cl_2–$CFCl_3$	−14.31 (2 H),[d] −17.70 (2 H)[e]	Slow exchange
(3)	^{13}C-{^{1}H}	50.3	20	CD_2Cl_2–$CFCl_3$	193.4 (9 CO)	Fast exchange
(3)	^{13}C-{^{1}H}	90.56	−125	CD_2Cl_2–$CFCl_3$	196.0,[f] 192.8, 189.6	Broad bands, not a limiting spectrum
(4)	^{1}H	200	20	CD_2Cl_2	−16.21 (d, J_{P-H} *ca.* 8)	Intermediate exchange between (**VII**) and (**VIII**)
(4)	^{1}H	200	−90	CD_2Cl_2	(*i*) −15.67 (1 H), −17.24 (1 H)	Isomer (**VII**), *ca.* 83% ($\Delta\nu_{\frac{1}{2}}$ *ca.* 35 Hz)
					(*ii*) −16.18 (dd, J_{P-H} 1.6, J_{H-H} 3.0, 1 H), −17.70 (dd, J_{P-H} 10.4, J_{H-H} 3.0, 1 H)	Isomer (**VIII**), *ca.* 17%
(4)	^{31}P-{^{1}H}	81.0	25	$CDCl_3$	39.0	Non-rigid ($\Delta\nu_{\frac{1}{2}}$ *ca.* 30 Hz)
(4)	^{31}P-{^{1}H}	81.0	−90	CD_2Cl_2	(*i*) 47.3 (d, J_{Rh-P} 17.2)	Isomer (**VIII**)
					(*ii*) 40.3 (d, J_{Rh-P} 1.8)	Isomer (**VII**)
(4)	^{13}C-{^{1}H}	50.3	25	CD_2Cl_2	*ca.* 212, 197.0, 194.7	Broad bands
(4)	^{13}C-{^{1}H}	50.3	−110	CD_2Cl_2–$CFCl_3$	232.9 (d, J_{Rh-C} 59.6, 1 μ-CO), 199.6 (1 CO), 198.3 (1 CO), 196.2 (1 CO), 195.8 (1 CO), 193.3(sh) (1 CO), 193.0 (1 CO), 190.8 (2 CO)	Isomer (**VII**)[g]
(5)	^{1}H	200	20	CD_2Cl_2	−15.07 (ddd, J_{P-H} 13.6 and *ca.* 2, $J_{H-H'}$ 2.6, 1 H), −16.48 (ddd, $J_{P-H'}$ 7.0 and *ca.* 9, $J_{H-H'}$ 2.6, 1 H)	Slow exchange
(5)	^{31}P-{^{1}H}	81.0	25	$CDCl_3$	45.25 (d, $J_{Rh-P'}$ 18.1; 1 P), 31.66 (d, J_{Rh-P} 3.7, 1 P)	
(5)	^{13}C-{^{1}H}	50.3	25	CD_2Cl_2	245.3 (d, J_{Rh-C} 46, 1 μ-CO), 207.2 (1 CO), 200.2 (1 CO), 199.3 (1 CO), 196.5 (2 CO), 194.9 (1 CO), 191.0 (1 CO)	Slight variation in shifts with samples[h]
(6)	^{1}H	200	20	$CDCl_3$	−15.59 (J_{P-H} 11.8 and *ca.* 2, $J_{H-H'}$ *ca.* 2, 1 H), −17.06 (J_{P-H} *ca.* 8, $J_{H-H'}$ *ca.* 2, 1 H)[i]	

[a] Chemical shifts, in p.p.m., relative to $SiMe_4$ (^{1}H and ^{13}C-{^{1}H}) or 85% H_3PO_4 (^{31}P-{^{1}H}); *J* in Hz. Resonances are singlets or unresolved single bands unless otherwise indicated. [b] Accompanied by broad, weak bands between 200 and 188 p.p.m. [c] Bands around 193 p.p.m. obscured by resonances of major species. [d] $\Delta\nu_{\frac{1}{2}}$ *ca.* 70 Hz (unresolved doublet coupling to ^{103}Rh). [e] $\Delta\nu_{\frac{1}{2}}$ *ca.* 40 Hz. [f] Asymmetric band with poorly resolved shoulders. [g] Bands of isomer (**VIII**) are weak and obscured. [h] In one sample a weak, broad band at 214 p.p.m. was observed. [i] See text for discussion and also for ^{31}P-{^{1}H} spectrum.



(I) (II)

Scheme 1.

(60—200 mesh) column. Hexane eluted bands of $[Rh(CO)_2(\eta\text{-}C_5H_5)]$ and unreacted (1). Hexane–dichloromethane (5:1) eluted $[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)(PPh_3)]$ (4) as a light brown band and, subsequently, hexane–dichloromethane (1:1) eluted $[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)(PPh_3)_2]$ (5) as a red-brown band. Finally dichloromethane–acetone (1:1) removed an orange band (a phosphinated ruthenium–carbonyl species), leaving some material on the column.

Cluster (4) is sparingly soluble in hexane and was crystallised from dichloromethane–hexane to give deep brown prisms (*ca.* 20 mg) (Found: C, 38.4; H, 2.1. $C_{32}H_{22}O_9PRhRu_3$ requires C, 38.9; H, 2.2%); i.r. (hexane–dichloromethane, 5:1) 2 067s, 2 048m, 2 036vs, 2 022s, 2 002s, 1 993m, 1 978m, and 1 821wm br cm^{-1}.

Cluster (5) was rechromatographed and crystallised from hexane at 20 °C as dark brown prisms (*ca.* 15 mg) (Found: C, 48.5; H, 3.1. $C_{49}H_{37}O_8P_2RhRu_3$ requires C, 48.2; H, 3.1%); i.r. (hexane) 2 047s, 2 011m, 1 995m, 1 984m, 1 967m, and 1 780m cm^{-1}.

Reactions of $[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(\eta\text{-}C_5H_5)]$ (1) *with Bis(diphenylphosphino)ethane (dppe)*.—(*a*) Cluster (1) (0.102 g, 0.14 mmol) and dppe (0.061 g, 0.15 mmol) were stirred in thf (10 cm^3) for 18 h at ambient temperature. The reaction mixture was then evaporated to dryness and chromatographed on silica gel. Hexane–dichloromethane (9:1) eluted some unreacted (1) and also some $[Rh(CO)_2(\eta\text{-}C_5H_5)]$. Dichloromethane eluted a red-orange band which gave, after crystallisation from hexane–dichloromethane, $[Ru_3(CO)_8(dppe)_2]$, identified by spectroscopy and elemental analysis (Found: C, 53.8; H, 3.9. $C_{60}H_{48}O_8P_4Ru_3$ requires C, 54.4; H, 3.6%) (also, see below and ref. 14).

Dichloromethane–acetone (4:1) eluted an orange band, which gave a red-brown solid, (7) (Found: C, 49.0; H, 3.6%); i.r. (CH_2Cl_2) 2 040w, 1 988vs, and 1 966vs cm^{-1}. N.m.r. (CD_2Cl_2, 26 °C): ^1H, δ 7.4 (br, C_6H_5), 5.54 (s, C_5H_5), and 2.6—2.1 p.p.m. (complex, CH_2); $^{31}P\text{-}\{^1H\}$, δ 38.7 (s) and 30.9 p.p.m. (s); $^{13}CO\text{-}\{^1H\}$, δ 211.7 (s) and 206.1 p.p.m. (s). Subsequently, dichloromethane–acetone (1:1) afforded a brown band which yielded a brown solid, $[RhRu_3(\mu\text{-}H)_2(CO)_8(\eta\text{-}C_5H_5)(dppe)]$ (6) (Found: C, 42.9; H, 3.2. $C_{39}H_{31}O_8P_2RhRu_3$ requires C, 42.8; H, 2.9%); i.r. (CH_2Cl_2) 2 045s, 1 997(sh), 1 985vs, 1 926(sh), and 1 766m cm^{-1}. Finally, ethanol removed a small band, leaving appreciable material on the column.

(*b*) Cluster (1) (0.097 g, 0.13 mmol) and dppe (0.133 g, 0.33 mmol) were stirred in thf (10 cm^3) for 18 h at ambient temperature. Chromatography as above gave only one major product, eluted with dichloromethane as an orange band, and identified as $[Ru_3(CO)_8(dppe)_2]$, which crystallised as orange-red crystals (*ca.* 50 mg) from hexane–dichloromethane (Found: C, 55.0; H, 3.8; P, 9.4. $C_{60}H_{48}O_8P_4Ru_3$ requires C, 54.4; H, 3.6; P, 9.4%); i.r. (CH_2Cl_2) 2 035s, 1 980s, 1 954vs br, and 1 924(sh) cm^{-1}. N.m.r. (26 °C): $^{31}P\text{-}\{^1H\}$ ($CDCl_3$), δ 39.9 (s, br) and 39.7 p.p.m. (s, br); $^{13}CO\text{-}\{^1H\}$ (CD_2Cl_2), δ 225.5 (t, J_{P-C} 9.9 Hz, 2 CO), 220.7 (s, 4 CO), and 199.3 p.p.m. (s, 2 CO).

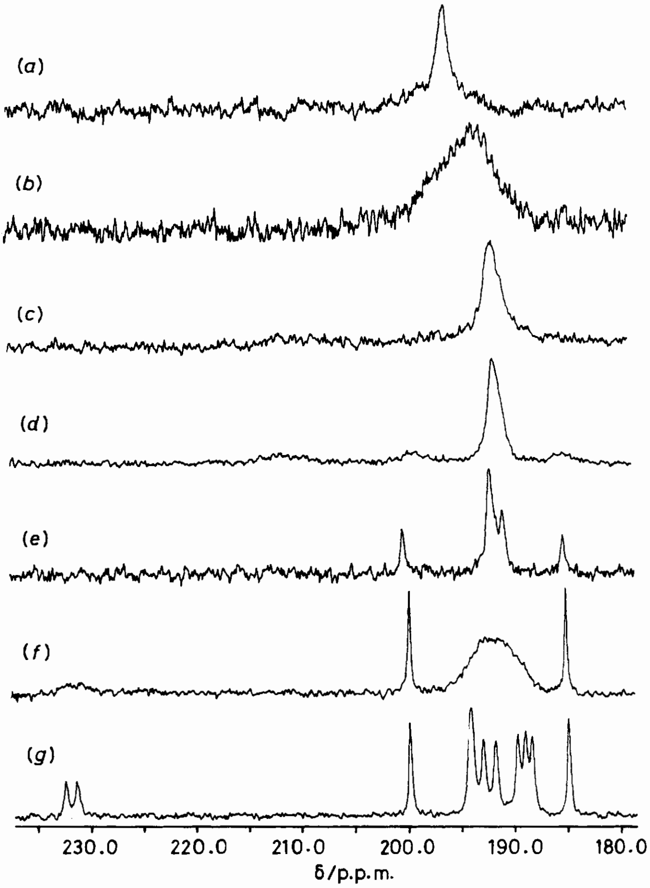


Figure 1. $^{13}C\text{-}\{^1H\}$ N.m.r. spectra of CO ligands in cluster (1) at 50.3 MHz in $CD_2Cl_2\text{–}CFCl_3$: at (*a*) 30, (*b*) 0, (*c*) −30, (*d*) −50, (*e*) −70, (*f*) −90, and (*g*) −110 °C

Results and Discussion

$[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(\eta\text{-}C_5H_5)]$ (1).—The solid-state structure of cluster (1), established by *X*-ray diffraction,[1] is depicted by (I) in Scheme 1. The single, asymmetrically bridging carbonyl group, a, lies almost in the plane Rh–Ru(2)–Ru(3) [Rh–C(a)–Ru(2)/Rh–Ru(2)–Ru(3) = 169.5°], and the bridging H-atoms lie below the Ru_3 plane (exterior interplanar angles, Ru(2)–H′–Ru(1)/Ru(1)–Ru(2)–Ru(3) and Ru(1)–H–Ru(3)/Ru(1)–Ru(2)–Ru(3), = 125—127°). The molecule is completely asymmetric so that all ten CO ligands (labelled a—j) are inequivalent; the two hydride ligands H and H′ are also inequivalent.

The ^1H n.m.r. spectrum of cluster (1) at ambient temperature shows a single bridging hydride resonance at δ −17.15 p.p.m. ($C_6D_5CD_3$) but cooling of this solution causes separation into two resonances undergoing slow exchange, with coalescence at −78 ± 1 °C at 500 MHz; the individual resonances are broadened so that no spin–spin coupling (*e.g.* J_{H-H}) is resolved. At coalescence,[15] $\Delta G^\ddagger$ is 35.2 ± 0.3 kJ mol^{-1} for the exchange process.

At room temperature (r.t.) the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum shows a single ^{13}CO resonance ($\Delta\nu_{\frac{1}{2}}$ *ca.* 50 Hz) and although this sharpens somewhat on raising the temperature ($\Delta\nu_{\frac{1}{2}}$ *ca.* 15 Hz, 80 °C, $C_6D_5CD_3$) no coupling becomes evident. At or below −110 °C ($CD_2Cl_2\text{–}CFCl_3$, 1:1; 50.3 MHz) the ^{13}C n.m.r. of a stereochemically rigid system is observed with nine distinct resonances (two CO ligands being accidentally equivalent) and at intermediate temperatures several exchange processes occur (see Figure 1). In the limiting spectrum, the bridging CO [a in (I)] at 231.9 p.p.m., is a doublet (J_{Rh-C} 55 Hz) but all the other

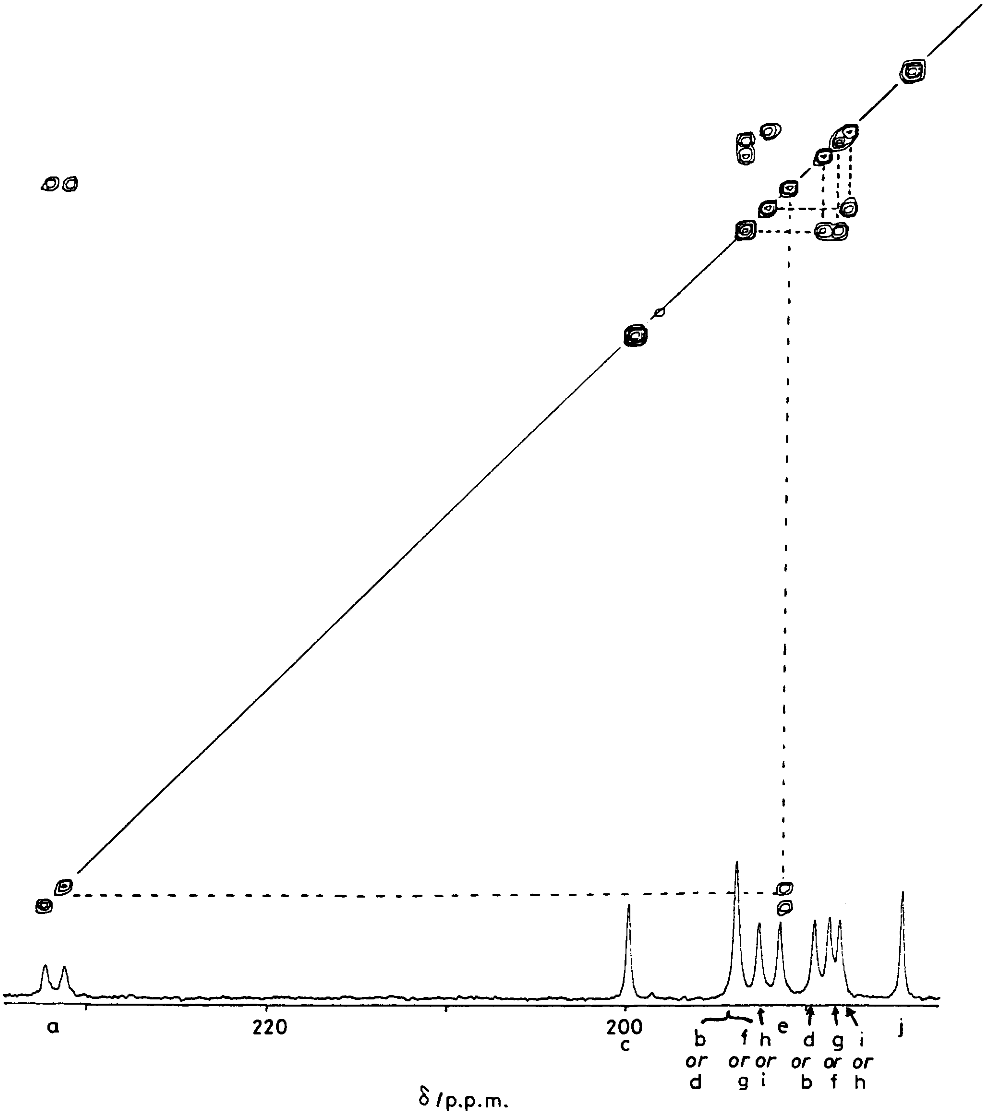


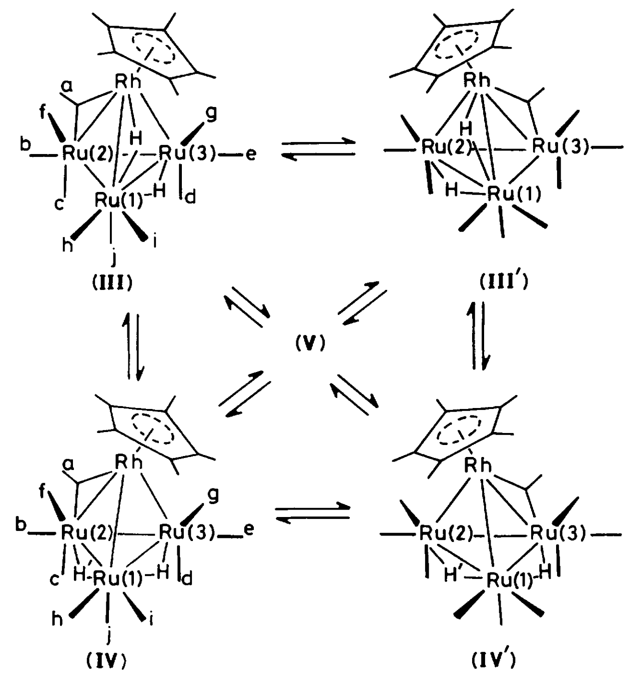
Figure 2. ^{13}C-{^{1}H} Two-dimensional exchange n.m.r. spectrum (NOESY sequence) of cluster (**1**) at −110 °C in CD_2Cl_2–$CFCl_3$; mixing time 100 ms

CO resonances are singlets; thus a mean coupling of *ca.* 5 Hz might be expected for a species executing fast intramolecular exchange above r.t. and this small coupling will be obscured by the linewidths observed. Below −110 °C, non-^{1}H-decoupled spectra do not show clear ^{13}C–^{1}H couplings to the hydride ligands but from decoupling difference spectra it can be established that five terminal CO resonances are broadened by interaction with these hydrogens; these may be assigned to CO groups f—i, all *trans* to H, and probably also j [in (**I**)] which is *cis* to two H ligands.

A ^{13}C-{^{1}H} two-dimensional exchange spectrum (NOESY sequence)[16,17] of (**1**) was recorded at −110 °C (Figure 2) and this established that the lowest-energy exchange process which can be monitored at this temperature involves specific pairwise interchange between four sets of CO ligands leaving two CO groups unchanged. These two unique CO resonances remain sharp in v.t. spectra until above −70 °C (Figure 1), whereas exchange processes broaden all the other bands above −110 °C.

On the basis of the two-dimensional and decoupling experiments we assign the CO resonances [structure (**I**)] as indicated in Figure 2; this is based on the lowest-energy exchange process being the interconversion (**I**) $\rightleftharpoons$ (**II**) for which c and j remain unchanged and interchanges a/e, b/d, f/g, and h/i occur; the high-frequency resonance is attributed to c, *trans* to μ-CO, which is consistent with j, the lowest-frequency resonance, showing detectable attenuation in the non-decoupled spectrum. The b/d pair is assigned on the absence of hydrogen interaction whereas h and i show the greatest interaction and, although it is not possible to assign unequivocally specific resonances to each CO group of these b/d, f/g, and h/i pairs, it may be tentatively proposed that b and f, which are attached to Ru(2) bearing a μ-CO ligand, give the lower-field bands. This assignment bears similarity to those proposed[7,8] for the less fluxional Os clusters $[MOs_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(\eta\text{-}C_5H_5)]$ (M = Co or Rh) but with some differences.

The proposed lowest-energy exchange process (**I**) $\rightleftharpoons$ (**II**) involves a rocking motion of CO groups a—e around the Rh–Ru(2)–Ru(3) plane: this leaves c unchanged but interchanges H and H′ as well as f/g and h/i. This must also be the process causing coalescence of ^{1}H resonances and, although it is not possible to determine precise coalescence temperatures for



Scheme 2.

the pairwise exchange of CO ligands, these occur around -90 °C for the terminal pairs with $\Delta G^{\ddagger}$ *ca.* 34—35 kJ mol^{-1}, not inconsistent with the value obtained at -78 °C from ^{1}H spectra. The exchange between μ-CO (a) and e, with a larger separation of resonances (2 023 Hz), will coalesce at higher temperatures giving rise to the broad band at *ca.* 212 p.p.m. observed above -60 °C with a similar calculated approximate $\Delta G^{\ddagger}$.

A second exchange process sets in above -90 °C in which terminal CO groups b, d, e, f, g, as well as bridging a, are interchanged: this gives rise to the spectra observed at *ca.* -70 to -60 °C in which resonances for c, j and pair i/h are still distinct. Thus, this process does not involve site exchange at Ru(1) nor of b, c, f at Ru(2) in (**I**). Localised site exchange of d, e, g on Ru(3) is the most likely explanation, this being more facile as the Ru atom bears only one μ-hydride ligand.[18]

At higher temperatures, the observed complete interchange of CO ligands which cannot be mechanistically defined but probably involves site exchange at all three Ru centres, may involve motion of the H ligands and, possibly multi-site exchanges of CO. It should be noted that the asymmetry of the resonance that occurs at *ca.* 0 °C arises from the final coalescence of bridging CO (a) with the exchanging terminal CO groups. It is also possible that rapid exchange with other isomeric forms may be proceeding in the fast-exchange regime [*cf.* clusters (**2**) and (**4**) discussed below].

$[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(\eta\text{-}C_5Me_5)]$ (**2**).—The structure[1] of the crystalline form of (**2**) is depicted by (**III**) in Scheme 2. The μ-CO group symmetrically bridges Rh–Ru(2) and is virtually perpendicular (87.9°) to the Rh–Ru(1)–Ru(2) plane. The hydride ligand bridging Rh–Ru(1) is essentially in the Rh–Ru(1)–Ru(2) plane [Rh–H–Ru(1)/Rh–Ru(1)–Ru(2) = 171.6°] whereas the other μ-H ligand lies below the Ru_3 plane. The i.r. spectrum of solid (**2**) is consistent with the crystal structure, exhibiting only one ν(μ-CO) band (1 790 cm^{-1}, KBr); however, in solution three low-frequency ν(CO) bands are observed [1 831, 1 812, and 1 800 cm^{-1}, light petroleum (b.p. 40—60 °C)]. Therefore, it may be concluded that isomers, probably three with single μ-CO groups, are present in solution.

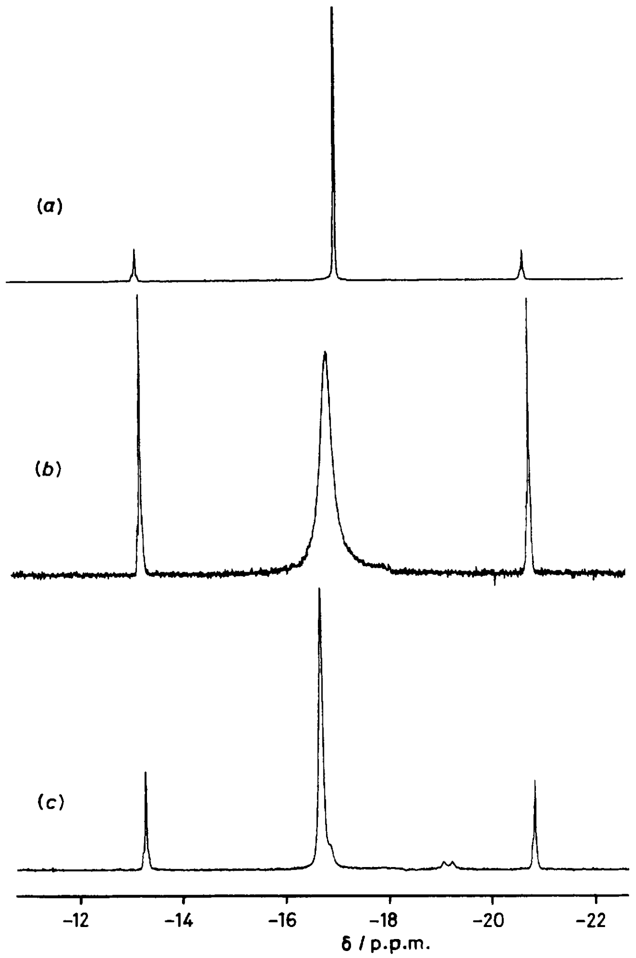


Figure 3. ^{1}H N.m.r. spectra of hydride ligands in cluster (**2**) at 200 MHz in CD_2Cl_2–$CFCl_3$: at (*a*) -50, (*b*) -100, and (*c*) -127 °C

Ambient-temperature ^{1}H n.m.r. spectra of (**2**) may be assigned to two species present in concentrations *ca.* 4:1, and variable-temperature studies between -127 and 25 °C (CD_2Cl_2–$CFCl_3$) show that the minor species (20—23%) is stereochemically rigid on the n.m.r. time-scale throughout this range. The isomer contains two non-equivalent μ-H ligands, giving resonances with small but not clearly resolved mutual H–H coupling and, possibly, ^{103}Rh–H coupling. Thus, neither hydrogen is directly attached to Rh and this isomer can be assigned structure (**IV**), analogous to (**I**). The major species in solution at r.t., with a one doublet μ-H resonance (J_{H-H} 8.7 Hz) is undergoing rapid exchange; at low temperature this resonance broadens to obscure any coupling (*e.g.* at -100 °C, see Figure 3). At the lowest obtainable temperature (-127 °C, CD_2Cl_2–$CFCl_3$) this band resolves into a singlet (-16.71 p.p.m., $\Delta\nu_{\frac{1}{2}} \sim 20$ Hz) accounting for *ca.* 68% of the sample and also a small doublet (-19.15 p.p.m., J_{Rh-H} 32 Hz) accompanied by a small shoulder on the major singlet; these two small resonances may be assigned to a third isomer, *ca.* 9%. The latter spectrum is consistent with a cluster containing one hydrogen bridging Rh–Ru and the second bridging Ru–Ru, as found in (**III**). However, it seems unlikely that this minor component is isomer (**III**) and these bands can be attributed to a third isomer, (**V**), for which a unique structure cannot be established in the light of data available. The major, apparent singlet may be assigned to (**III**) which is still fluxional at -127 °C (Scheme 2); the expected doublet coupling in this resonance (predicted J_{Rh-H} *ca.* 7.7 Hz) is obscured by the linewidth of the signal.

Variable-temperature ^{13}C-{^{1}H} n.m.r. spectra of (**2**) are consistent with the above analysis (see Figure 4). At room temperature (r.t.) the major singlet arises from the rapid exchange of all CO ligands within and between isomers (**III**) and (**V**); smaller broadened resonances, also present, are assignable to the more rigid isomer (**IV**) (*ca.* 20%), undergoing an intermediate rate of exchange. At lower temperatures (CD_2Cl_2–$CFCl_3$), the major singlet collapses and the resonances of (**IV**) become more distinct showing some similarity to those of cluster (**I**), *e.g. at* −90 °C a doublet at 244.0 p.p.m. (J_{Rh-C} 33 Hz), assignable to μ-CO, and nine singlets in the range 187.5—198.8 p.p.m., assignable to terminal CO groups. Spectra below −100 °C exhibit new resonances attributable to (**III**)/(**V**) undergoing slower exchange: five terminal CO bands are apparent (broadened singlets at 201.5, 195.7, 193.3, 192.7, 185.3 p.p.m. at −120 °C) and a broad band (Δν *ca.* 150 Hz) at 218.6 p.p.m. which is somewhat sharper at −110 °C; at −125 °C and 90.56 MHz the latter is much broader whereas the other singlets are essentially unchanged. An explanation for these observations, consistent with other spectroscopic data, is that interchange between isomers (**III**) and (**III′**) is occurring by motion of CO groups a, b, c, d, and e about the Rh–Ru(2)–Ru(3) plane, as in cluster (**1**), with the concomitant interchange of H ligands [additional exchange with the 9% of (**V**) may also make a minor contribution at this stage]. Exchange (**III**) $\rightleftharpoons$ (**III′**) will leave c and j unchanged and average the pairs a/e, b/d, f/g, and h/i giving rise, at the fast-exchange limit, to five resonances in the terminal CO range and one midway between the bridging and terminal regions. This latter band with a larger frequency separation of averaged resonances, should also exhibit coalescence at higher temperatures as found for the band at 218.6 p.p.m., a mean of μ-CO, at *ca.* 240 p.p.m. [*cf.* isomer (**IV**)], and terminal CO, at *ca.* 200 p.p.m.

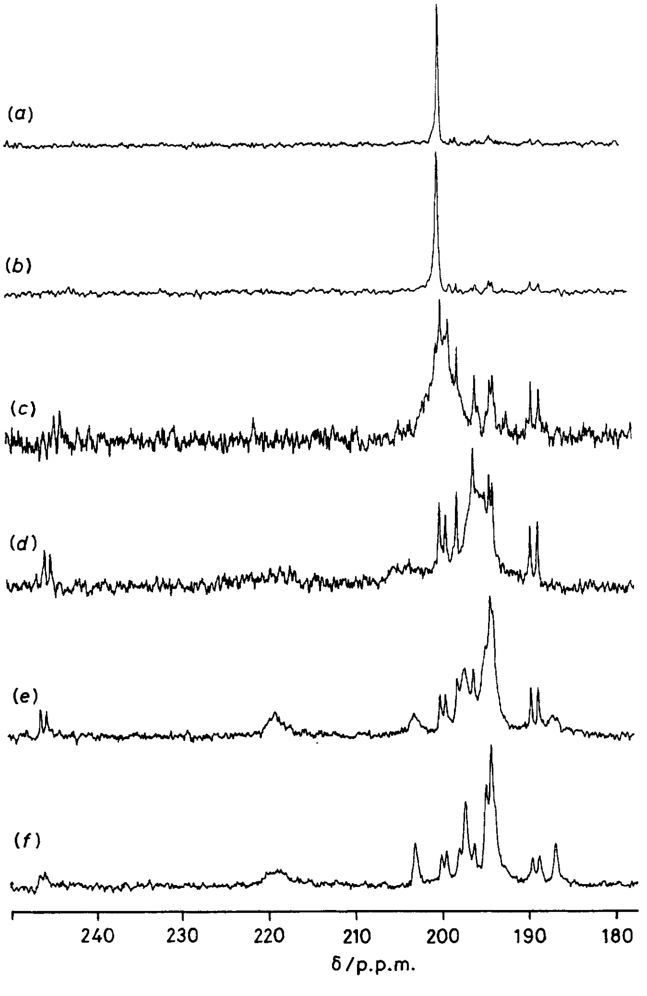


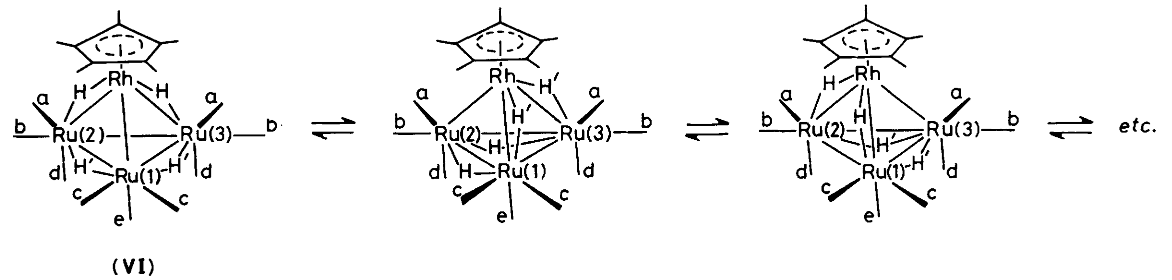
Figure 4. ^{13}C-{^{1}H} N.m.r. spectra of CO ligands in cluster (**2**) at 50.3 MHz in CD_2Cl_2–$CFCl_3$ at (*a*) 20, (*b*) −20, (*c*) −60, (*d*) −90, (*e*) −110, and (*f*) −120 °C

Thus, these studies establish the existence of three isomers for cluster (**2**), (**III**), (**IV**), and (**V**), with concentrations in solution of 68, 23, and 9%, respectively, at −127 °C. Slow exchange on the n.m.r. time-scale takes place between (**IV**) and (**III**)/(**V**) below 25 °C (Scheme 2); (**IV**) is also relatively stereochemically rigid, contrasting with the greater fluxionality of cluster (**1**) with related structure (**I**), and this must be due to the effects of the fully methylated cyclopentadienyl ring in (**2**): it may be noted that there is a much larger separation in chemical shifts of H and H′ in (**IV**) than in (**I**). At temperatures around −120 °C, although the exchange (**III**) $\rightleftharpoons$ (**V**) is relatively slow, isomer (**III**) is still fluxional and a process analogous to the lowest-energy exchange of (**1**) probably occurs (Scheme 1).

[$RhRu_3(\mu$-$H)_4(CO)_9(\eta$-$C_5Me_5)$] (**3**).—The crystal structure[1] of (**3**), depicted by (**VI**) in Scheme 3, establishes the presence of terminal CO groups only. Two hydrogen ligands bridge the Rh–Ru atoms and both lie close to the Rh–Ru(2)–Ru(3) plane (interplanar angles 168—177°). The other two hydrogens bridge Ru–Ru atoms and lie below the Ru_3 plane.

N.m.r. studies are consistent with a similar, unique but fluxional structure existing in solution. ^{1}H N.m.r. spectra at 20 °C show a doublet (−15.99 p.p.m., J_{Rh-H} 13.8 Hz, in CD_2Cl_2–$CFCl_3$) assignable to completely interchanging hydrides. At lower temperatures this signal resolves into the expected two resonances, *e.g.* at −125 °C (200 MHz) a singlet at −17.70 p.p.m. and a broadened resonance at −14.31 p.p.m. ($\Delta\nu_{\frac{1}{2}}$ *ca.* 70 Hz), which presumably includes a doublet coupling to ^{103}Rh, assignable to H′ and H, respectively. Coalescence at −109 °C gives $\Delta G^{\ddagger} = 29.4 \pm 0.2$ kJ mol^{-1} for this hydrogen exchange.

The ^{13}C-{^{1}H} n.m.r. spectrum of CO ligands in (**3**) at 20 °C is a singlet, resulting from complete and rapid interchange, but on



(**VI**)

Scheme 3.

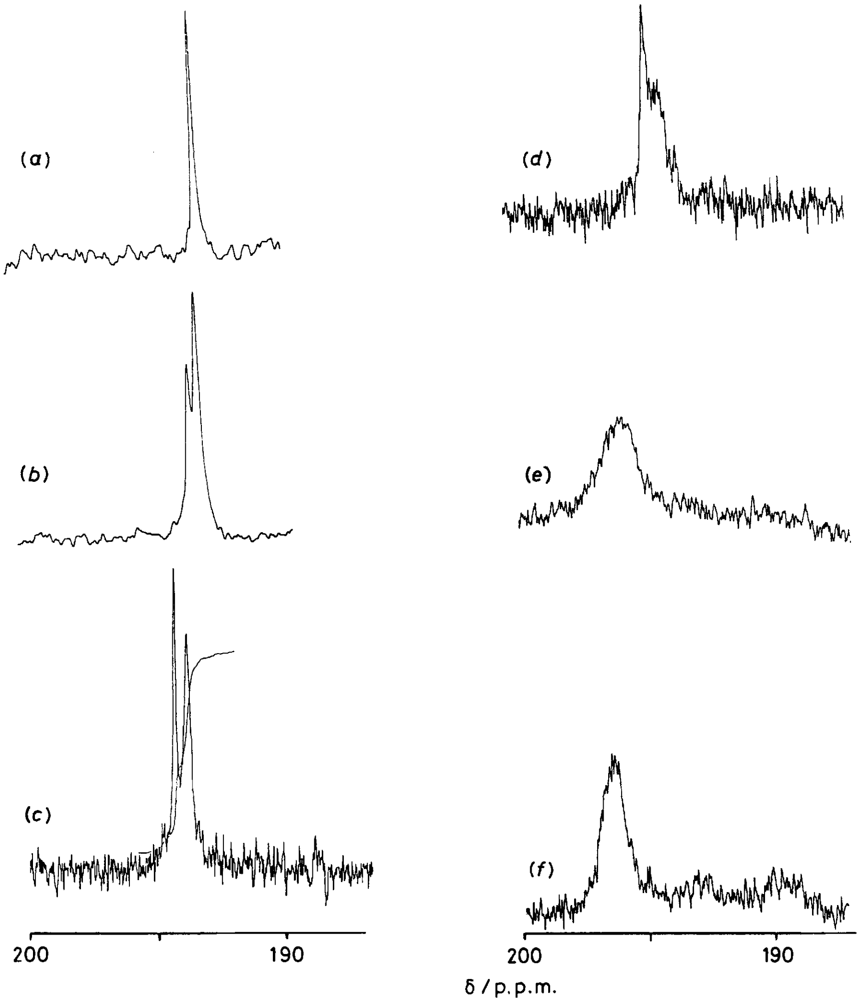


Figure 5. ^{13}C-{^{1}H} N.m.r. spectra of CO ligands in cluster (**3**) in CD_2Cl_2–$CFCl_3$: at (*a*) 20 (50.3), (*b*) −81 (50.3), (*c*) −90 (90.56), (*d*) −100 (90.56), (*e*) −120 (90.56) and (*f*) −125 °C (90.56 MHz)

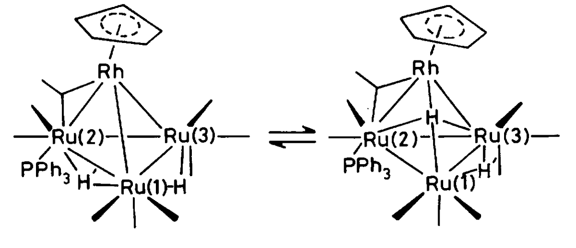
cooling this initially resolves into two singlets of relative intensity 2:1, assignable to equatorial and axial CO groups a/b/c and d/e, respectively (see Figure 5): coalescence of these two unequally populated singlets occurs between −55 and −45 °C (50.3 MHz) giving an approximate value[15,19] of $\Delta G^{\ddagger} = 47.5 \pm 1.5$ kJ mol^{-1} which is associated with localised site exchange between three CO groups at a Ru centre (note that each Ru atom is also bound to two μ-H ligands). At lower temperatures these two singlets undergo secondary broadening and, although a sharp limiting spectrum is not obtained, at −125 °C (90.56 MHz) at least four broad bands can be distinguished which may be assigned to the inequivalent CO groups a, b, c, d, and e in (**VI**).

The exchange process which is observed between −125 and −90 °C in the ^{13}C n.m.r. (90.56 MHz) spectrum is most probably related to that monitored by ^{1}H n.m.r., *i.e.* a process which renders both sets of hydrogen ligands equivalent as well as interchanging all equatorial CO groups and, separately, all axial CO groups. One possible mechanism is shown in Scheme 3 but a more random exchange of hydrogens, *e.g. via* a higher symmetry (C_{3v}) intermediate, cannot be ruled out. The intimate mechanism for H/H′ interchange may involve either edge–face–edge or edge–terminal–edge motions of the hydrogens.

Phosphine Derivatives of $[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(\eta\text{-}C_5H_5)]$ (**1**).—(*a*) *Triphenylphosphine derivatives.* Reaction of (**1**) with PPh_3 in thf at r.t. affords the mono- and bi-substituted clusters $[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_{9-n}(\eta\text{-}C_5H_5)(PPh_3)_n]$ [n = 1 (**4**) or 2 (**5**)] as well as some cleavage products, including $[Rh(CO)_2(\eta\text{-}C_5H_5)]$ and uncharacterised, non-crystalline ruthenium–phosphine derivatives. Reaction between (**1**) and PPh_3 in hexane at r.t. leads only to orange solids which are insoluble in hydrocarbon solvents and are analogous to the ruthenium by-products of reactions in thf.

N.m.r. studies of cluster (**4**) support structure (**VII**) for the dominant isomeric form. However, v.t. ^{1}H and ^{31}P n.m.r. spectra in CD_2Cl_2 establish that a minor isomer is also present in solution and exchange between isomers is slow at low temperatures. Thus, the ^{1}H n.m.r. at −90 °C (see Table) shows isomer (**VII**) (*ca.* 83%) with two broad hydride resonances ($\Delta\nu_{\frac{1}{2}}$ *ca.* 35 Hz), incorporating unresolved coupling, and isomer (**VIII**) (*ca.* 17%) with two equal intensity hydride resonances (doublet of doublets) at −16.18 (H; $^{3}J_{P-H}$ 1.6, J_{H-H} 3.0 Hz) and −17.70 p.p.m. (H′; $^{2}J_{P-H}$ 10.4, J_{H-H} 3.0 Hz); no change in the spectrum was observed on cooling to −115 °C. ^{31}P-{^{1}H} N.m.r. in CD_2Cl_2 at −90 °C also shows two resonances corresponding to (**VII**) and (**VIII**) at 40.3 (d, J_{Rh-P} 1.8 Hz) and 47.3 p.p.m. (d, J_{Rh-P} 17.2 Hz), respectively. The relatively large difference in $^{2}J_{Rh-P}$ values for (**VII**) and (**VIII**) is of interest and must reflect the presence of a μ-CO group spanning the Rh–Ru bond in (**VIII**) and may also arise from a difference in orientations of the Ru–PPh_3 bond to the Rh–Ru vector in these

(VII) **(VII′)**



(VIII) **(VIII′)**

isomers. At r.t. the ^{31}P-{^1H} n.m.r. spectrum in $CDCl_3$ is a broad singlet, at 39.0 p.p.m., so that interchange of isomers is taking place.

Coalescence of the hydride resonances of isomer (**VII**) occurs at *ca.* −70 °C with $\Delta G^\ddagger = 38.0 \pm 0.3$ kJ mol^{-1}, producing a sharp doublet at higher temperatures, *e.g.* −16.28 p.p.m. (J 9.7 Hz; −10 °C). The resonances assigned to isomer (**VIII**) broaden at −10 °C, with loss of resolvable coupling above 0 °C; the coalescence temperature of these resonances is difficult to determine precisely but is *ca.* 20 °C (with corresponding $\Delta G^\ddagger$ *ca.* 56 kJ mol^{-1}). However, at this temperature interchange of isomers (**VII**) and (**VIII**) is apparent from the n.m.r. spectrum and the main doublet of (**VII**) broadens to a singlet on warming and subsequently sharpens to an averaged doublet at 60 °C in $CDCl_3$ (−16.20 p.p.m., J_{P-H} 9.1 Hz).

The more facile fluxionality of isomer (**VII**) can be readily rationalised in terms of the CO exchange proposed for cluster (**1**) since the PPh_3 ligand is not bonded to the Ru atoms bearing the μ-CO ligand [*i.e.* (**VII**) $\rightleftharpoons$ (**VII′**)]. A similar CO interchange on (**VIII**) will cause isomerisation and a process involving H migration [*e.g.* (**VIII**) $\rightleftharpoons$ (**VIII′**)] must occur at the higher temperatures. Interchange of isomers (**VII**) and (**VIII**) must involve both H and CO mobility.

The ^{13}C-{^1H} n.m.r. spectrum of (**4**) at r.t. shows three broad ^{13}CO bands; a spectrum exhibiting slow exchange is obtained at −110 °C in CD_2Cl_2–$CFCl_3$ (Figure 6) but only resonances attributable to the major isomer (**VII**) can be clearly identified [weaker resonances of (**VIII**) are obscured]. Seven singlets between 190 and 200 p.p.m. are assignable to the eight terminal CO groups, with two accidentally degenerate and giving rise to a double intensity band (see Table); a doublet at 232.9 p.p.m. (J_{Rh-C} 59.6 Hz) is assignable to the bridging CO of (**VII**). On warming to −80 °C, only one terminal CO resonance remains sharp (199.6 p.p.m.) consistent with the proposed lowest-energy interchange involving rocking of groups a, b, c, d, and e about the Rh–Ru(2)–Ru(3) face [(**VII**) $\rightleftharpoons$ (**VII′**)], leaving only *c* unchanged. At r.t. the three broad ^{13}C resonances result from additional localised site exchanges at Ru(2) and Ru(3); the three bands may be assigned to average resonances of a/e (*ca.* 212 p.p.m.), h/i (197.0 p.p.m.), and b/c/d/f/e/g (194.7 p.p.m.). In the assignments of Figure 6 it may be noted that PPh_3 substitution at a Ru centre causes low-field shifts of co-ordinated CO, whereas other CO chemical shifts correspond closely to those of cluster (**1**). No obvious resolvable ^{31}P–^{13}C couplings could be assigned in these spectra.

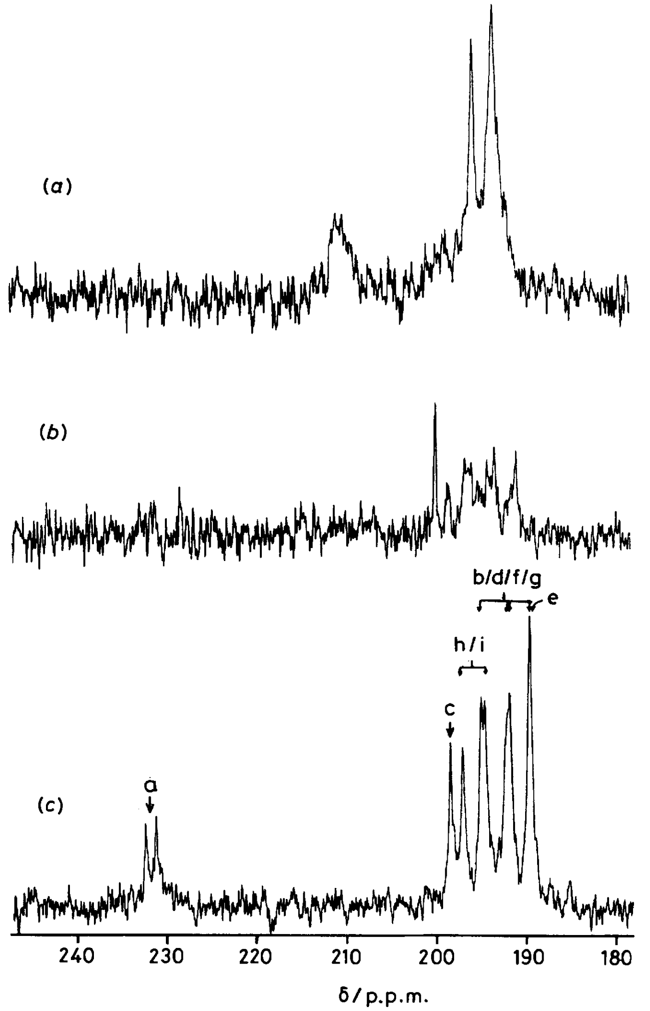
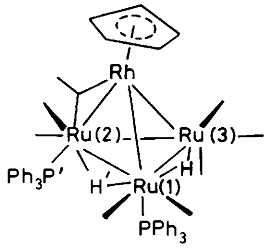
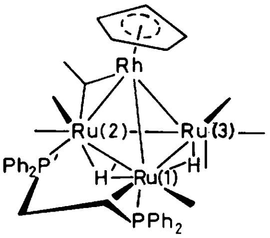


Figure 6. ^{13}C-{^1H} N.m.r. spectra of CO ligands in cluster (**4**) at 50.3 MHz: at (*a*) 25 (CD_2Cl_2), (*b*) −80 (CD_2Cl_2–$CFCl_3$), and (*c*) −110 °C (CD_2Cl_2–$CFCl_3$)

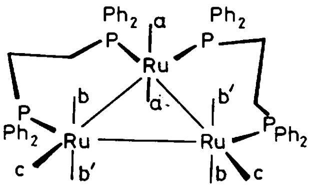
Cluster (**5**) is rigid on the n.m.r. time-scale at ambient temperatures and spectra support structure (**IX**) for the principal isomeric form. The two PPh_3 ligands are probably both in axial co-ordination sites as found in $[NiOs_3(\mu\text{-}H)_3(CO)_7(PMe_2Ph)_2]$.[20] The ^{31}P-{^1H} n.m.r. spectrum exhibits two equal-intensity doublets at 31.66 (J_{P-Rh} 3.7 Hz) and 45.25 p.p.m. ($J_{P'-Rh}$ 18.1 Hz) assignable to P and P′, respectively [again note the difference in coupling constants, consistent with the assignments for (**VII**) and (**VIII**)]. The two multiplet resonances of H and H′ in the ^1H n.m.r. (CD_2Cl_2) spectrum are, respectively, at −15.07 (ddd, J_{P-H} 13.6, $J_{P'-H}$ 2, $J_{H-H'}$ 2.6 Hz) and −16.48 p.p.m. (ddd, $J_{P-H'}$ 7.0, $J_{P'-H'}$ 9, $J_{H'-H}$ 2.6 Hz) which were analysed by selective ^{31}P-decoupling of P and P′; there is no significant change in this spectrum at −90 °C. The ^{13}C-{^1H} n.m.r. spectrum at r.t. (Table) shows six singlet resonances, one of double intensity, for the seven terminal CO groups and a bridging CO resonance as a poorly resolved doublet at 245.3 p.p.m. (J_{Rh-C} *ca.* 49 Hz): a weak, broad resonance at 214 p.p.m. observed in one sample may arise from an isomer or an impurity. The co-ordination of PPh_3 to Ru again causes a shift to higher frequency of ^{13}CO resonances relative to those of cluster (**1**), including that of the μ-CO group (*cf.* refs. 5 and 6). The lower ν(CO) frequency of cluster (**5**) [1 780



(IX)



(X)



(XI)

cm^{-1} (hexane)] is also consistent with structure (**IX**). The broadened μ-CO band at 1 821 cm^{-1} in the i.r. spectrum of (**4**), principally isomer (**VII**), shows evidence for a weak shoulder at lower frequencies which may arise from isomer (**VIII**).

(*b*) *Bis(diphenylphosphino)ethane* (*dppe*) *derivatives*. Cluster (**1**) and dppe in thf at r.t. give several products: using excess dppe [*i.e.* dppe:(**1**) = 2.5:1], the major isolated product is the cleavage species $[Ru_3(CO)_8(dppe)_2]$ (*cf.* ref. 12) accompanied by $[Rh(CO)_2(\eta\text{-}C_5H_5)]$ and other phosphinated ruthenium species which could not be eluted from a silica gel column. By reacting an equimolar ratio of dppe and (**1**) in thf the range of products includes $[Ru_3(CO)_8(dppe)_2]$, a small amount of the monosubstituted $[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)(dppe)]$ (**6**), a red-brown non-hydrido cluster (**7**) of possible composition $[RhRu_4(CO)_9(\eta\text{-}C_5H_5)(dppe)_2]$, which has not been conclusively characterised, and other phosphinated ruthenium species.

Cluster (**6**) shows an ambient-temperature ^1H n.m.r. spectrum (in $CDCl_3$) analogous to that of (**5**) so that structure (**X**) may be assigned: a complex doublet at −15.59 p.p.m. (H; ddd, J_{P-H} 11.8, $J_{P'-H} \sim J_{H-H'}$ *ca.* 2 Hz) and a complex triplet at −17.06 p.p.m. (H′; ddd, $J_{P-H'} \sim J_{P'-H}$ *ca.* 8, $J_{H-H'}$ *ca.* 2 Hz), with the phosphorus interactions being established by broad-band ^{31}P decoupling. The $^{31}P\text{-}\{^1H\}$ n.m.r. (in $CDCl_3$) spectrum of (**6**) at r.t. is more complex than expected for a single structure (**X**) and at least two isomeric forms are present in solution; the spectrum may be analysed in terms of four, approximately equally intense resonances: +37.9 (dd, 44.6 and 17.5 Hz), +32.31 (d, 44.8 Hz), +32.0 (d, 47.2 Hz), and +27.7 p.p.m. (d, 46.7 Hz). These chemical shifts are consistent with bidentate, bridging dppe ligands.[2b,21] Coupling constants of *ca.* 44.7 and *ca.* 47 Hz may be mutual P–P′ interactions of a single bridging dppe ligand in two different isomers but are rather large (N.B. for monodentate dppe, a $J_{P-P'}$ value of 49.5 Hz has been reported[22]). The isomerism may arise from phosphorus co-ordination at differing axial–equatorial sites of Ru(1) and Ru(2) or may be related to the conformations of the methylene groups in the six-membered Ru_2PC_2P ring system;[2b] this has not yet been established. Recently, the latter explanation has been proposed to account for isomers detected in n.m.r. spectra of $[Ir_4(\mu\text{-}CO)_3(CO)_7(\mu\text{-}dppe)]$ whereas an axial–equatorial co-ordination of the longer bridging diphosphine was proposed for $[Ir_4(\mu\text{-}CO)_3(CO)_7\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}]$.[23]

The principal isomeric form of $[Ru_3(CO)_8(dppe)_2]$ is (**XI**), as indicated by $^{31}P\text{-}\{^1H\}$ and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra at ambient temperature. ^{13}CO Resonances of ligands b(b′) and c show no resolvable ^{31}P-coupling whereas carbonyl groups a appear as a triplet (J_{P-C} 9.9 Hz). The $^{31}P\text{-}\{^1H\}$ (81.0 MHz) n.m.r. spectrum shows two singlet resonances in $CDCl_3$, separated by only 14 Hz, which may be assigned to inequivalent ^{31}P atoms with no observable coupling; however, if P–P coupling is large (*i.e.* > 14 Hz) the resonances will be subject to second-order effects and the weaker components of a coupled AA′BB′ system may be unobserved. It is of interest that on changing the solvent to CD_2Cl_2 only a singlet ^{31}P resonance at +39.3 p.p.m. is resolvable ($\Delta\nu_{\frac{1}{2}}$ *ca.* 10 Hz).

Acknowledgements

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