Hydrocarbon Complexes of Iron, Ruthenium, and Osmium. Part 15.[1] Stereochemical Non-rigidity of Hexacarbonyldiruthenium Complexes of Monosubstituted Cyclo-octatetraenes

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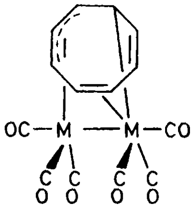
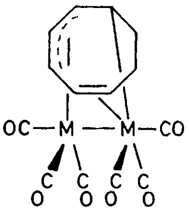
Complexes $[Ru_2(CO)_5(C_8H_7R)]$ are obtained in good yield upon heating $[Ru_3(CO)_{12}]$ with the cyclo-octatetraenes C_8H_7R (R = Me, Ph, $SiMe_3$, $SiMePh_2$, $SiPh_3$, or $GeMe_3$), and are readily carbonylated to give hexacarbonyls $[Ru_2(CO)_6(C_8H_7R)]$. Variable-temperature ^1H and ^{13}C n.m.r. spectra reveal that in the latter the substituent R is attached to an unco-ordinated olefinic bond; however, its presence does not repress stereochemical non-rigidity of the kind established for the parent $[Ru_2(CO)_6(C_8H_8)]$. Each of the complexes $[Ru_2(CO)_6(C_8H_7R)]$ exists at low temperatures as a single isomer, but on warming a ' twitch ' of the $Ru_2(CO)_6$ unit relative to the hydrocarbon occurs to generate another isomer in equilibrium. At ambient temperatures rapid interconversion of the isomers provides time-averaged chemical shifts for the cyclo-octatetraene ring protons.

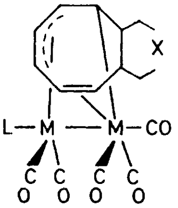
THE fluxional behaviour of $[M_2(CO)_6]$ (M = Fe or Ru) complexes of cyclo-octatetraene and cyclo-octa-1,3,5-triene and its derivatives has attracted much attention.[2-8] *X*-Ray diffraction studies on the complexes (1b),[9] (2a),[10] (3a),[11] (3b),[6], and (3c) [4] have established that a skew η^6 co-ordination is apparently general in the crystalline state, while low-temperature n.m.r. spectra have shown that this asymmetric mode of co-ordination is maintained in solution. However, at ambient temperatures the spectra require the existence of a mirror plane of molecular symmetry. This has been interpreted by Cotton and co-workers [4,9] as arising from a fluxional process which interconverts the two enantiomorphs of (1)—(3), as illustrated (I) for the cyclo-octatetraene complexes (1).



(1a) M = Fe
(1b) M = Ru

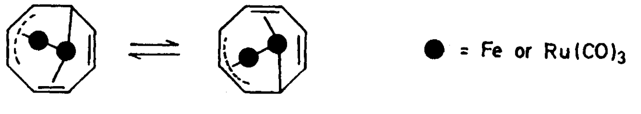


(2a) M = Fe
(2b) M = Ru

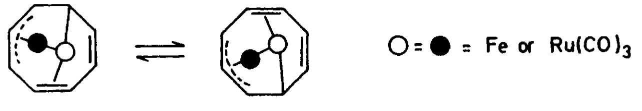


(3a) M = Fe, L = CO, X = CH_2
(3b) M = Fe, L = CO, X = CH_2CH_2
(3c) M = Fe, L = PEt_3, X = CH_2CH_2
(3d) M = Ru, L = CO, X = CH_2CH_2

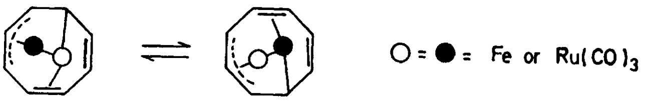
Two possible pathways for this generation of time-averaged mirror symmetry have been recognised, designated as a ' twitch ' (II) or a ' glide ' process (III). Since with the ' twitch ' the metal moieties remain distinct and with the ' glide ' they become equivalent, ^{13}C n.m.r. spectroscopy allows the pathway followed to be distinguished through observations of the carbonyl resonances. This has been achieved through study of complexes (2a),[3] (3a),[8] (3b),[4] and (3d),[7] in none of which do the carbonylmetal groups become equivalent; *i.e.* the ' twitch ' pathway is operative. The same mechanism seems to occur for the related complex $[Rh_2(\eta\text{-}C_5H_5)_2(C_8H_{10})]$ (4) in that ^1H and ^{13}C n.m.r. spectra reveal the existence of a time-averaged mirror plane, yet the two cyclopentadienyl ring signals never coalesce.[12]



(I)

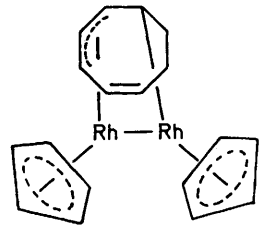


(II)

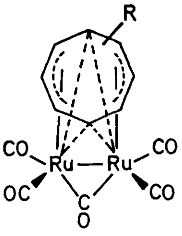


(III)

Substitution of the C_8 rings of (1) or (2) by one or more groups asymmetrically presents an interesting situation, in that the two species inter-related by a ' twitch ' are no longer of equal free energy. The possibility of a degenerate fluxional interconversion of the type described above is thus eliminated, but a non-degenerate interconversion is still permissible, either on the n.m.r. time scale or opposed by a much higher energy barrier. Should the barrier be sufficiently high, the existence of one isomer uniquely or an inconvertible mixture of both



(4)



(5a) R = $SiMe_3$
(5b) R = $SiMePh_2$
(5c) R = $SiPh_3$
(5d) R = $GeMe_3$
(5e) R = Me
(5f) R = Ph

is possible. A few $[M_2(CO)_6]$ complexes of asymmetrically substituted cyclo-octa-1,3,5-trienes have been synthesised, and in each case a single static isomer was obtained.[13-15] We now describe n.m.r. studies of complexes of monosubstituted cyclo-octatetraenes $[Ru_2(CO)_6(C_8H_7R)]$ which show that these exercise a non-degenerate stereochemical non-rigidity comparable to that shown by $[Ru_2(CO)_6(C_8H_8)]$ (1b).

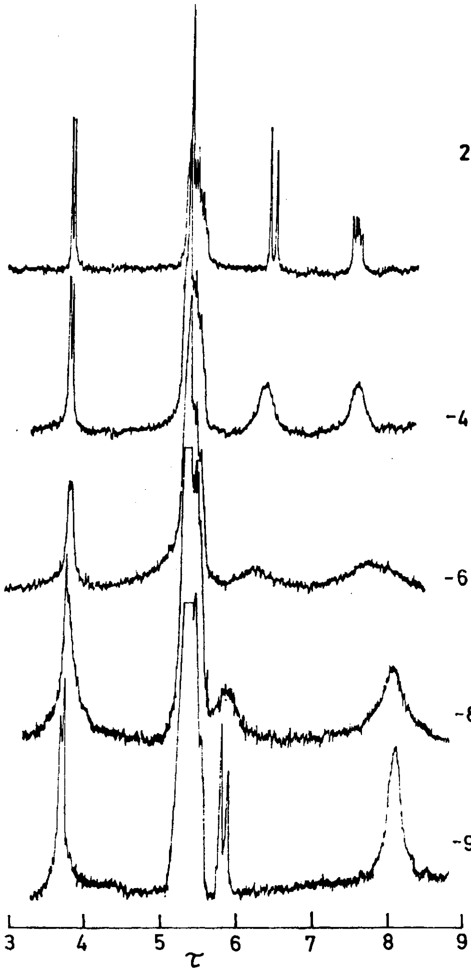
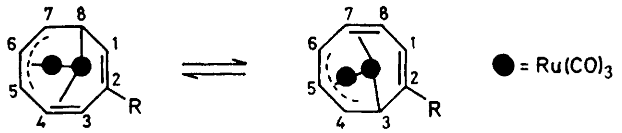


FIGURE 1 ^1H n.m.r. spectrum of $[Ru_2(CO)_6(C_8H_7SiMe_3)]$ (6) in CCl_3F solution



	R	
(6a)	$SiMe_3$	(6b)
(7a)	$SiMePh_2$	(7b)
(8a)	$SiPh_3$	(8b)
(9a)	$GeMe_3$	(9b)
(10a)	Me	(10b)
(11a)	Ph	(11b)

RESULTS AND DISCUSSION

The complexes $[Ru_2(CO)_5(C_8H_7R)]$ (5; R = Me, Ph, $SiMe_3$, $SiMePh_2$, $SiPh_3$, or $GeMe_3$) were prepared in good yield by heating the appropriate cyclo-octatetraene with $[Ru_3(CO)_{12}]$ in heptane. These in turn were readily carbonylated (*ca.* 20 atm) * in acetone to afford the required hexacarbonyl complexes $[Ru_2(CO)_6(C_8H_7R)]$ (6)—(11) in generally good yields. All these complexes

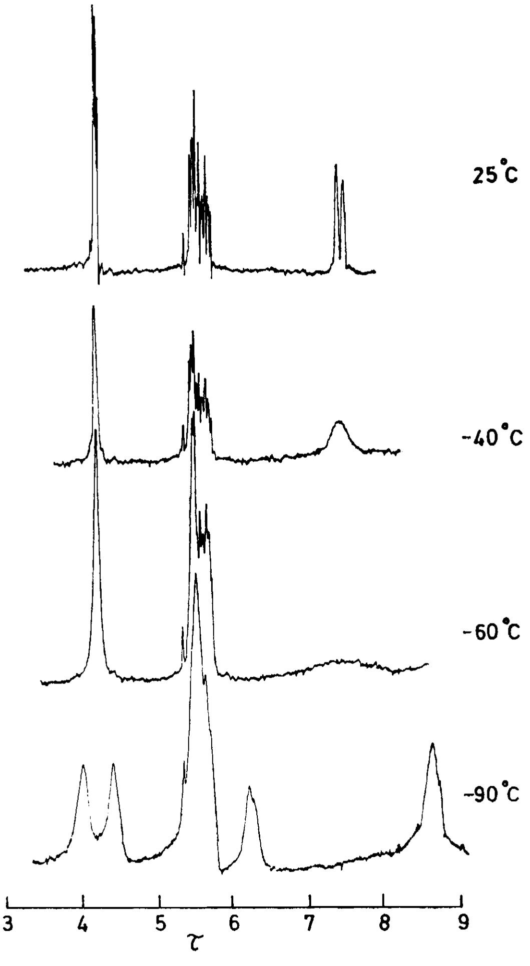


FIGURE 2 ^1H n.m.r. spectrum of $[Ru_2(CO)_6(C_8H_8)]$ (1b) in CCl_3F solution

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* Throughout this paper: 1 atm = 101 325 Pa; 1 mmHg ≈13.6 × 9.8 Pa.

TABLE 1

Physical and analytical data for new complexes

	Complex	M.p. (θc/°C)	Colour	Analysis (%) [a] C	Analysis (%) [a] H	M [a,b]
(5a)	$[Ru_2(CO)_5(C_8H_7SiMe_3)]$	162	Orange	37.5 (37.1)	3.2 (3.1)	519 (519)
(5b)	$[Ru_2(CO)_5(C_8H_7SiMePh_2)]$	164	Orange	47.8 (47.6)	3.1 (3.1)	643 (643)
(5c)	$[Ru_2(CO)_5(C_8H_7SiPh_3)]$	165 (decomp.)	Orange	52.8 (52.8)	3.5 (3.1)	705 (705)
(5d)	$[Ru_2(CO)_5(C_8H_7GeMe_3)]$	168 (decomp.)	Orange	35.1 (34.1)	3.1 (2.8)	564 (564)
(5e)	$[Ru_2(CO)_5(C_8H_7Me)]$	134	Orange	36.5 (36.4)	2.2 (2.2)	461 (461)
(5f)	$[Ru_2(CO)_5(C_8H_7Ph)]$	164	Orange	43.7 (43.7)	2.3 (2.3)	523 (523)
(6)	$[Ru_2(CO)_6(C_8H_7SiMe_3)]$	58	Yellow	37.4 (37.4)	3.1 (2.9)	519 [c] (547)
(7) [d]	$[Ru_2(CO)_6(C_8H_7SiMePh_2)]$	60 [e]	Yellow			643 [c] (671)
(8)	$[Ru_2(CO)_6(C_8H_7SiPh_3)]$	105 (decomp.)	Yellow	52.0 (52.5)	3.2 (3.0)	448 [f] (733)
(9) [d]	$[Ru_2(CO)_6(C_8H_7GeMe_3)]$	40 [e]	Yellow			564 [c] (592)
(10)	$[Ru_2(CO)_6(C_8H_7Me)]$	76	Yellow	36.8 (36.9)	2.0 (2.0)	461 [c] (489)
(11)	$[Ru_2(CO)_6(C_8H_7Ph)]$	106	Yellow	43.9 (43.6)	2.2 (2.2)	523 [c] (551)
(12)	$[Ru_2(CO)_5(C_8H_8CH_2)]$	145—146	Yellow	36.8 (36.4)	2.3 (2.2)	460 [g] (461)
(14)	$[Ru_2(SnMe_2)(CO)_4(C_8H_7SnMe_3)]$	142 (decomp.)	Yellow	28.6 (27.9)	3.2 (3.0)	730 (730)

[a] Calculated values in parentheses. [b] Determined mass spectrometrically. [c] $[M - CO]^+$. [d] Liquid complexes, not obtained analytically pure because of ready CO loss. [e] B.p. (10^{-1} mmHg). [f] Heaviest ion. [g] $[M - H]^+$.

were identified by elemental analyses and the usual spectroscopic methods, the relevant data being presented in Tables 1 and 2. The co-ordination within the complexes $[Ru_2(CO)_5(C_8H_7R)]$ (5) is presumed to be analogous to that established for $[Fe_2(CO)_5(C_8H_8)]$.[16]

The hexacarbonyl complexes display ^1H n.m.r. spectra which are consistent with the substituted cyclo-octatetraenes being co-ordinated to the $[Ru_2(CO)_6]$ unit in a mode identical to that adopted [9] by cyclo-octatetraene itself [see (1b)], but with the substituent attached to the unco-ordinated olefin bond. Thus, the limiting low-temperature ^1H n.m.r. spectrum (Figure 1) of $[Ru_2(CO)_6(C_8H_7SiMe_3)]$ implies the structure (6a). The signal at τ 3.74 (1 H) indicates the presence of a single proton (H^1) on the unco-ordinated olefinic bond and its adjacency to the trimethylsilyl group is confirmed by its doublet character, *i.e.* coupling to H^8. The doublet signal at τ 5.94 (1 H), a shift typical of a co-ordinated

TABLE 2

Spectroscopic data for new complexes

	Complex	Carbonyl bands (cm⁻¹) [a]	^1H n.m.r. (τ) [b]
(5a)	$[Ru_2(CO)_5(C_8H_7SiMe_3)]$	2 037s, 2 011s, 1 971s, 1 821m	Not obtained due to low solubility
(5b)	$[Ru_2(CO)_5(C_8H_7SiMePh_2)]$	2 036s, 2 011s, 1 973s, 1 821m	2.61 (10 H, m), 4.84 (1 H, t, *J* 7.0 Hz), 5.26 (2 H, td, *J* 2.5, 7.0 Hz), 5.52 (4 H, m), 9.22 (3 H, s)
(5c)	$[Ru_2(CO)_5(C_8H_7SiPh_3)]$	2 043s, 2 016s, 1 981s, 1 825m	2.53 (15 H, m), 4.76 (3 H, m), 5.21 (2 H, m), 5.52 (2 H, m)
(5d)	$[Ru_2(CO)_5(C_8H_7GeMe_3)]$	2 036s, 2 009s, 1 970s, 1 822m	4.99 (1 H, t, *J* 7.5 Hz), 5.39 (2 H, t, *J* 6 Hz), 5.61 (4 H, dd, *J* 8.5, 12.0 Hz), 9.81 (9 H, s)
(5e)	$[Ru_2(CO)_5(C_8H_7Me)]$	2 038s, 2 012s, 1 973s, 1 826m	4.84 (1 H, t, *J* 7.5 Hz), 5.29 (4 H, m), 5.75 (2 H, t, *J* 10.0 Hz), 7.84 (3 H, s)
(5f)	$[Ru_2(CO)_5(C_8H_7Ph)]$	2 039s, 2 013s, 1 974s, 1 829m	2.67 (5 H, m), 4.73 (3 H, m), 5.12 (2 H, t, *J* 9.0 Hz), 5.55 (2 H, t, *J* 8.5 Hz)
(6)	$[Ru_2(CO)_6(C_8H_7SiMe_3)]$	2 074s, 2 042s, 2 008s, 2 004s (sh), 1 985m, 1 979w	3.78 (1 H, d, *J* 3.0 Hz), 5.43 (4 H, m), 6.48 (1 H, d, *J* 8.5 Hz), 7.61 (1 H, m), 9.85 (9 H, s) [c,d] 3.74 (1 H, d, *J* 4.0 Hz), 5.44 (4 H, m), 5.94 (1 H, d, *J* 8.5 Hz), 8.24 (1 H, m), 9.86 (9 H, s)
(7)	$[Ru_2(CO)_6(C_8H_7SiMePh_2)]$	2 072s, 2 040s, 2 007s, 2 000s (sh), 1 981m, 1 976w	2.64 (10 H, m), 2.79 (1 H, d, *J* 4.5 Hz), 5.56 (4 H, m), 6.52 (1 H, d, *J* 9.5 Hz), 7.88 (1 H, dd, *J* 4.5, 8.0 Hz), 9.44 (3 H, s) [c,d] 2.64 (10 H, m), 2.79 (1 H, d, *J* 4.0 Hz), 5.56 (4 H, m), 6.00 (1 H, m), 8.45 (1 H, m), 9.44 (3 H, s)
(8)	$[Ru_2(CO)_6(C_8H_7SiPh_3)]$	2 074s, 2 040s, 2 008s, 2 002s (sh), 1 984m, 1 974w	2.65 (15 H, m), 3.63 (1 H, d, *J* 4.5 Hz), 5.48 (3 H, m), 5.82 (1 H, m), 6.26 (1 H, d, *J* 9.0 Hz), 7.88 (1 H, dd, *J* 6.0, 7.0 Hz),[c,d] 2.65 (15 H, m), 3.63 (1 H, m), 5.38 (3 H, m), 5.62 (1 H, m), 5.84 (1 H, m), 8.24 (1 H, m)
(9)	$[Ru_2(CO)_6(C_8H_7GeMe_3)]$	2 073s, 2 040s, 2 007s, 2 003s (sh), 1 986m, 1 973w	3.93 (1 H, d, *J* 3.0 Hz), 5.27 (4 H, m), 6.34 (1 H, d, *J* 6.5 Hz), 7.23 (1 H, m), 9.53 (9 H, s)
(10)	$[Ru_2(CO)_6(C_8H_7Me)]$	2 075s, 2 042s, 2 008s, 2 003s (sh), 1 984m, 1 977w	4.58 (1 H, m), 5.37 (3 H, m), 5.64 (1 H, m), 6.75 (1 H, dd, *J* 1.5, 8.0 Hz), 8.17 (1 H, d, *J* 7.0 Hz), 8.41 (3 H, s); [c,d] 4.58 (1 H, m), 5.31 (3 H, m), 5.54 (1 H, m), 6.06 (1 H, m), 8.41 (3 H, m), 8.66 (1 H, m)
(11)	$[Ru_2(CO)_6(C_8H_7Ph)]$	2 076s, 2 045s, 2 009s, 2 006s (sh), 1 986m, 1 980w	2.82 (5 H, m), 3.83 (1 H, d, *J* 4.5 Hz), 5.40 (4 H, m), 6.85 (1 H, dd, *J* 4.5, 10.5 Hz), 7.32 (1 H, d, *J* 8.0 Hz) [c,d] 2.82 (5 H, m), 3.83 (1 H, d, *J* 8.0 Hz), 5.42 (4 H, m)
(12)	$[Ru_2(C_8H_8CH_2)(CO)_5]$	2 048m, 2 030w (br), 1 998s	5.32 (2 H, m), 5.79 (3 H, dd, *J* 4.5 Hz), 5.96 (1 H, d, *J* 6.5 Hz), 6.01 (1 H, m), 7.41 (1 H, dd, *J* 7.0, 9.0 Hz)
(14)	$[Ru_2(SnMe_2)(CO)_4(C_8H_7SnMe_3)]$	2 007m, 1 987s, 1 947s, 1 939s (sh)	5.16 (1 H, t, *J* 7.5 Hz), 5.72 (2 H, dd, *J* 7.5, 9.0 Hz), 5.90 (1 H, d, *J* 9.5 Hz), 6.13 (2 H, t, *J* 9.0 Hz), 9.74 (6 H, s), 9.99 (9 H, s)

[a] In Hexane. [b] In CCl_3D. [c] At −90 °C. [d] In CCl_3F.

olefinic proton, confirms the position of $SiMe_3$ as adjacent to H^3, which is therefore coupled only to H^4. The complex signal at τ 5.44 (4 H) is assignable to the protons H^{4-7} and that at τ 8.24 (1 H) to proton H^8, which is bonded to an essentially aliphatic carbon atom.

A variable-temperature ^1H n.m.r. spectrum of (1b) of much higher quality than that obtained previously [2] has been recorded during our work (Figure 2). It can be seen that the low-temperature spectra of the structurally characterised (1b) and of (6a) differ only in the number of unco-ordinated olefinic protons present, providing strong evidence for their similar mode of bonding.

FIGURE 3 ^1H n.m.r. spectrum of $[Ru_2(CO)_6(C_8H_7Me)]$ (10) in CCl_3F solution

On warming, the signals of (6a) at τ 5.94 and 8.24 broaden and shift gradually, resharpening at room temperature to signals at τ 6.48 (1 H, d) and 7.61 (1 H, m), respectively (Figure 1). Clearly, a process is occurring in which the olefinic proton H^3 becomes more aliphatic in character, and the aliphatic proton H^8 more olefinic. These changes are consistent with the onset of a dynamic equilibrium between the two isomers (6a) and (6b). At the slow-exchange limit the population of the more stable isomer (6a) is shown by the ^1H n.m.r. spectrum to be effectively exclusive. As the temperature is raised it can be appreciated that a gradually increasing proportion of the less stable isomer (6b), in equilibrium with (6a), will effect an increase in aliphatic character of H^3 and an increase in olefinic character of H^8, on a time-averaged basis. At intermediate temperatures (−80 to −40 °C) the proportion of (6b) is increasing but the rate of (6a) $\rightleftharpoons$ (6b) interconversion is of the order of the n.m.r. time scale, yielding broad signals.

The ^1H n.m.r. spectra of $[Ru_2(CO)_6(C_8H_7R)]$ (R = $SiMe_2Ph$ or $SiPh_3$) vary with temperature in a nearly identical manner to that of (6), establishing the same exclusive population of the isomers (7a) and (8a) at low temperature and an equilibrium at higher temperature. The nature of the groups attached to silicon therefore seems of little consequence. Similar behaviour is expected for $[Ru_2(CO)_6(C_8H_7GeMe_3)]$ (9) on the basis of the similarity of its room-temperature ^1H n.m.r. spectrum with that of $[Ru_2(CO)_6(C_8H_7SiMe_3)]$ (6).

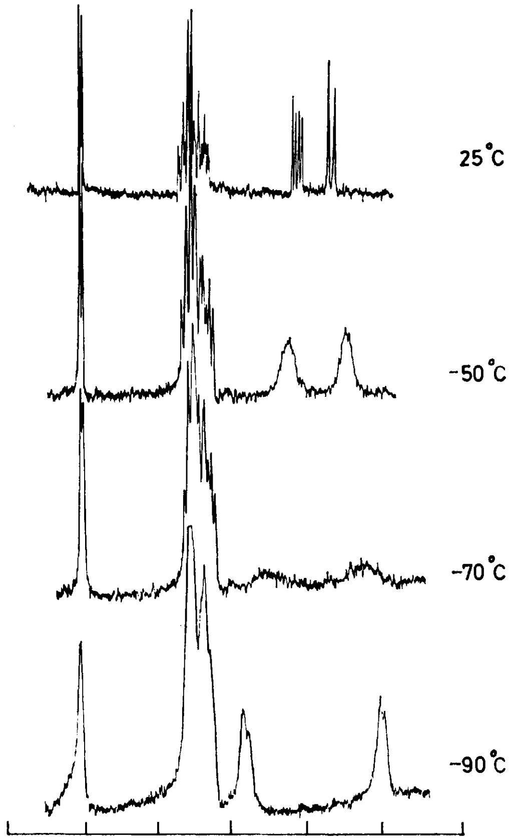


FIGURE 4 ^1H n.m.r. spectrum of $[Ru_2(CO)_6(C_8H_7Ph)]$ (11) in CCl_3F solution

The variable-temperature ^1H n.m.r. spectra (Figures 3 and 4) of $[Ru_2(CO)_6(C_8H_7R)]$ [R = Me (10), Ph (11)] show again the existence of a single isomer at low temperature and an interconversion of two isomers at higher temperatures. The spectra are, however, indicative of the stable isomer now being of the form (10b) and (11b), respectively, for these substituents. Thus, the ring-proton signal at highest field, clearly of aliphatic character, appears as a doublet. This contrasts with the multiplicity of the corresponding signal in the spectra of (6)—(9), and establishes the aliphatic proton as now being adjacent to the methyl or phenyl group in the stable isomer, *i.e.* (b).

In view of the fact that both methyl and phenyl substituents favour isomer (b) over (a), it is evident that electronic factors are not dominant in determining relative stability. The importance of steric effects seems to be signalled by the preference for isomer (a) rather than (b) with a variety of bulky silyl and germyl substituents. Some rationale for this is provided by the determination [9] of the molecular structure of $[Ru_2(CO)_6(C_8H_8)]$, which indicates that carbon C(1) of the (a) isomers is marginally closer to the $\sigma : \eta^2$-bound $Ru(CO)_3$ group than is C(2), so that steric clash should be correspondingly slightly less when bulky groups are attached to C(2) rather than C(1). However, the rapid interconversion of isomers (a) and (b) observed at even quite low temperatures shows that the factors controlling their relative stabilities are finely balanced.

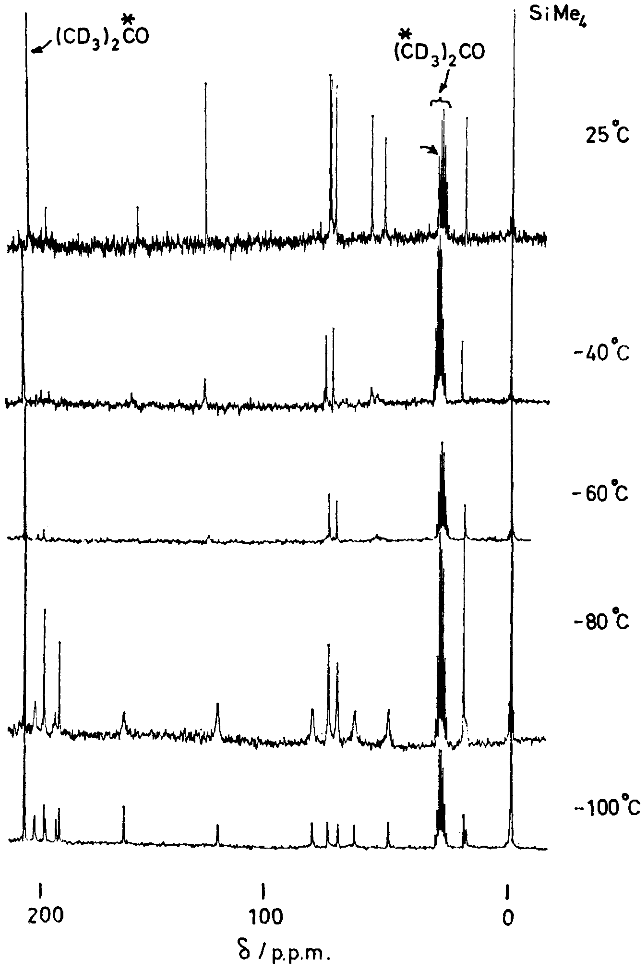


FIGURE 5 $^{13}C-\{^1H\}$ n.m.r. spectrum of $[Ru_2(CO)_6(C_8H_7Me)]$ (10) in $[^2H_6]$acetone solution

The $^{13}C-\{^1H\}$ n.m.r. spectra of the complexes (6) and (10) at various temperatures confirm their structures and the nature of their dynamic behaviour. Spectra of compound (10) are shown in Figure 5. The spectrum at −100 °C displays eight ring-carbon signals at 164.6, 124.4, 84.2, 77.5, 73.3, 66.4, 52.2, and 19.2 p.p.m. (downfield of $SiMe_4$), as expected for the presence of only isomer (10b) with no symmetry. A temperature-invariant signal at 20.4 p.p.m. is readily assigned to the methyl carbon, while the adjacent signal at 19.2 p.p.m. is clearly attributable to the aliphatic carbon C(3). The two lowest-field ring-carbon signals are at shifts typical of unco-ordinated olefinic carbon atoms and are assigned to C(1) and C(2). From the relatively low intensity of the lower-field signal of this pair at 25 °C, it is assumed to be due to C(2), which does not bear a proton. By comparison with the ^{13}C n.m.r. spectrum of (4),[12] which was totally assigned through consideration of Rh–C coupling, proton-decoupled spectra, and double-irradiation experiments, the next lowest-field signal in the spectrum, at 84.2 p.p.m., is attributed to the central carbon C(5) of the allyl unit in (10b). Other data [17] invariably place such central allylic carbons at lower field than the terminal carbons.

The remaining four ring carbons of (10b) cannot be unequivocally assigned without consideration of their variation in shift with temperature. On warming to −60 °C all but two (77.5 and 77.3 p.p.m.) of the ring-carbon signals broaden and collapse, *i.e.* there are two carbons whose chemical shifts are not appreciably different in the isomers (10a) and (10b). The chemical shifts of C(5) and C(6) should vary upon isomerisation, as mentioned earlier, and it seems likely therefore that the unshifted carbons are C(4) and C(7), although individual assignment is not possible. The signal at 52.2 p.p.m. becomes due to C(6). The greatest shift variations are expected for C(3) and C(8). The substantial low field shift (*i.e.* increase in olefinic character) of the 19.2 p.p.m. signal on warming (bringing it just downfield, at 29.8 p.p.m., of the acetone solvent multiplet) thus confirms its assignment as C(3), while the corresponding upfield shift of the 66.4 p.p.m. signal (*i.e.* increase in aliphatic character) characterises this signal as due to C(8).

The variable-temperature $^{13}C-\{^1H\}$ n.m.r. spectrum of $[Ru_2(CO)_6(C_8H_7SiMe_3)]$ (6) is shown in Figure 6, with ring-carbon signals (−100 °C) at 161.5, 144.4, 84.2, 76.6, 72.7, 71.5, 52.7, and 19.1 p.p.m., and $SiMe_3$ at −1.7 p.p.m. The spectrum bears a close resemblance to that of (10), save that in the room-temperature spectrum of (6) the higher-field signal of the two unco-ordinated olefinic carbons now has the lower intensity, *i.e.* this carbon bears the $SiMe_3$ substituent. This accords with the previous conclusion that isomer (a) is most stable for complex (6) and isomer (b) most stable for complex (10). It can be seen in Figure 6 that at −100 °C there is a weak signal just downfield of the $SiMe_3$ signal. This may be the $SiMe_3$ signal of the less stable isomer (6b), present in *ca.* 10% relative abundance.

Each of the complexes (6) and (10) displays six carbonyl carbon signals in the low-temperature n.m.r. spectrum (Figures 5 and 6) as required by the static asymmetric structure. On warming, four of the carbonyl groups become involved in a dynamic process and their signals collapse, while two remain sharp temporarily. On further warming the last signals also collapse, but when room temperature is attained no distinguishable features are yet observable. The initial collapse of only four CO signals is evidence that in the complexes $[Ru_2(CO)_6(C_8H_7R)]$ the ' twitch ' pathway for (a) $\rightleftharpoons$ (b) isomerisation is in operation, with the two axial carbonyls retaining their identity. The further carbonyl-scrambling pathways operative at higher temperatures in such complexes have been well characterised previously.[4]

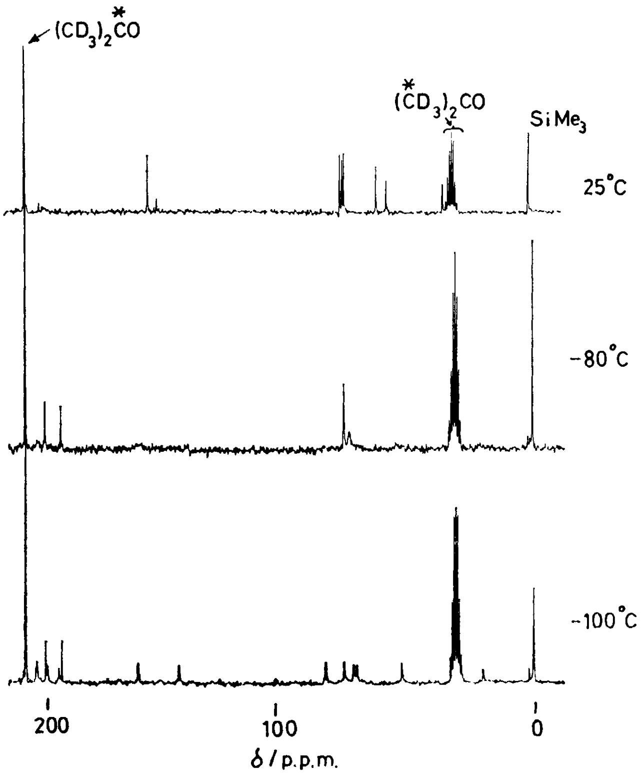
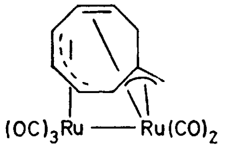


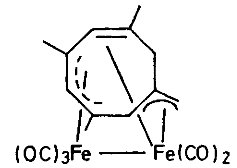
FIGURE 6 $^{13}C-\{^1H\}$ n.m.r. spectrum of $[Ru_2(CO)_6(C_8H_7SiMe_3)]$ (6) in $[^2H_6]$acetone solution

During the preparation of the complex $[Ru_2(CO)_5(C_8H_7Me)]$ (5e) from $[Ru_3(CO)_{12}]$ and methylcyclo-octatetraene a minor (*ca.* 3%) product was isolated, and identified as an isomer of structure (12). A related complex (13), whose structure has been established[18] by *X*-ray diffraction, was obtained from the interaction of 1,3,5,7-tetramethylcyclo-octatetraene with $[Fe_2(CO)_9]$, again as a minor product in company with $[Fe_2(CO)_5(C_8H_4Me_4)]$. A shift of a proton to create an exocyclic methylene is common to both (12) and (13), which have a similar pattern of carbonyl stretching frequencies in the i.r. The mass spectrum of (12) has a heaviest ion corresponding to $[M - H]^+$, but the ^1H n.m.r. spectrum confirms the presence of ten protons, and lack of a methyl group.

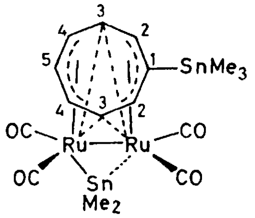
Another interesting complex was obtained from the reaction of trimethylstannylcyclo-octatetraene and $[Ru_3(CO)_{12}]$. This reaction was designed to yield a complex $[Ru_2(CO)_5(C_8H_7SnMe_3)]$ and thence $[Ru_2(CO)_6(C_8H_7SnMe_3)]$, but this objective was not realised. Instead a mixture of low-yield products was formed, one of which was yellow crystalline $[Ru_2(\mu\text{-}SnMe_2)(CO)_4(\eta^8\text{-}C_8H_7SnMe_3)]$ (14). The mass spectrum revealed a molecular ion and other significant ions due to loss of a methyl and two CO groups, each with a distinctive Ru_2Sn_2 isotopic distribution pattern. The ^1H n.m.r. spectrum has two methyltin signals in the intensity ratio 2 : 3, consistent with the presence of a bridging dimethyltin ligand and a carbon-bound $SnMe_3$ group. The remaining four signals, in the intensity ratio 1 : 2 : 2 : 2, correlate with a $C_8H_7SnMe_3$ ring bisected, through the $C(SnMe_3)$ carbon, by a plane of symmetry. The similarity of the i.r. spectrum of (14) and of the complex $[Ru_2(C_8H_9)I(CO)_4]$ (15)[19] suggests the structure illustrated, the co-ordination of the ring being derived from that in the complexes (5). Were the $SnMe_3$ substituent attached to one of the ' bridging ' carbons C(3), a plane of symmetry would still be present in the ring, but the methyl groups on the bridging tin would be inequivalent. It is possible, however, that the plane of symmetry apparent in the n.m.r. spectrum may arise from a fluxional process similar to that observed in complexes $[Ru_2(SiMe_3)_2(CO)_4(\eta^8\text{-}C_8H_7R)]$.[15]



(12)



(13)



(14)

The ^1H n.m.r. spectrum (Table 2) can be completely assigned. The triplet signal at τ 5.16 is readily attributed to H^5 on the basis of its intensity, while protons H^2, coupled substantially to only H^3, are expected as a doublet, *i.e.* the signal at τ 5.90. From a consideration of coupling constants the signal at τ 5.72 is clearly due to protons H^4, and that at τ 6.13 to protons H^3.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 257 instrument and n.m.r. spectra using Varian Associates HA 100 and JEOL PFT-100 spectrometers, the latter operating in the Fourier-transform mode for ^{13}C. All preparations were carried out under nitrogen using solvents dried by distillation from calcium hydride. Substituted cyclo-octatetraenes C_8H_7R (R = $SiMePh_2$, $SiPh_3$, $GeMe_3$, or $SnMe_3$) were prepared by treating cyclo-octatetraenyllithium with the appropriate halide in the manner described for $C_8H_7SiMe_3$.[20]. Methyl-[21] and phenyl-[22] cyclo-octatetraene were prepared by the literature methods. Spectroscopic and physical data for new complexes are collected in Tables 1 and 2.

Preparation of Complexes $[Ru_2(CO)_5(C_8H_7R)]$ (5).—The preparation of (5e) is typical and is described in detail below. For the remainder only essential information is given. In each case several low-yield co-products were formed but no attempt was made to identify these, which were presumed to be derivatives of the complexes obtained from $[Ru_3(CO)_{12}]$ and cyclo-octatetraene.[2,15]

$[Ru_2(CO)_5(C_8H_7Me)]$ (5e). The carbonyl $[Ru_3(CO)_{12}]$ (0.5 g, 0.78 mmol) was heated in heptane (70 cm^3) under reflux with C_8H_7Me (0.5 g, 4.2 mmol) for 26 h, yielding a dark red solution which was concentrated and chromatographed on alumina. Elution with hexane developed a yellow band from which yellow *crystalline* $[Ru_2(C_8H_8CH_2)(CO)_5]$ (12) was obtained (15 mg, 3%). Further elution with dichloromethane–hexane (1 : 1) gave an orange band which yielded 0.27 g (50%) of orange *crystalline* $[Ru_2(CO)_5(C_8H_7Me)]$ (5e) upon crystallisation.

$[Ru_2(CO)_5(C_8H_7Ph)]$ (5f). Heating $[Ru_3(CO)_{12}]$ (1.0 g, 1.56 mmol) and C_8H_7Ph (1.0 g, 5.6 mmol) in heptane (70 cm^3) under reflux for 6 d gave 0.16 g (13%) of (5f).

$[Ru_2(CO)_5(C_8H_7SiMe_3)]$ (5a). Heating $[Ru_3(CO)_{12}]$ (0.5 g, 0.78 mmol) and $C_8H_7SiMe_3$ (0.5 g, 2.18 mmol) in heptane (70 cm^3) under reflux for 23 h provided 0.56 g (92%) of (5a).

$[Ru_2(CO)_5(C_8H_7SiMePh_2)]$ (5b). Heating $[Ru_3(CO)_{12}]$ (0.5 g, 0.78 mmol) and $C_8H_7SiMePh_2$ in heptane (70 cm^3) under reflux for 60 h provided 0.28 g (38%) of (5b).

$[Ru(CO)_5(C_8H_7SiPh_3)]$ (5c). Heating $[Ru_3(CO)_{12}]$ (0.5 g, 0.78 mmol) and $C_8H_7SiPh_3$ (1.5 g, 4.14 mmol) in heptane (70 cm^3) under reflux for 28 h afforded 0.15 g (20%) of (5c).

$[Ru_2(CO)_5(C_8H_7GeMe_3)]$ (5d). Heating $[Ru_3(CO)_{12}]$ (0.5 g, 0.78 mmol) and $C_8H_7GeMe_3$ (0.6 g, 2.71 mmol) in heptane (70 cm^3) under reflux for 23 h provided 0.19 g (30%) of (5d).

Attempted Preparation of $[Ru_2(CO)_5(C_8H_7SnMe_3)]$.—The carbonyl $[Ru_3(CO)_{12}]$ (0.5 g, 0.78 mmol) and $C_8H_7SnMe_3$ (0.6 g, 2.28 mmol) were heated in hexane (70 cm^3) under reflux for 26 h or heptane (70 cm^3) under reflux for 5 h. In each case no $[Ru_2(CO)_5(C_8H_7SnMe_3)]$ was formed, but the complex $[Ru_2(\mu\text{-}SnMe_2)(CO)_4(C_8H_7SnMe_3)]$ (14) was obtained as yellow *crystals* (22 mg, 3%) upon chromatography on alumina with hexane.

Preparation of Complexes $[Ru_2(CO)_6(C_8H_7R)]$.—The preparation of $[Ru_2(CO)_6(C_8H_7Me)]$ (10) is described as being typical.

An acetone (50 cm^3) solution of $[Ru_2(CO)_5(C_8H_7Me)]$ (5e) (0.47 g, 1.1 mmol) was subjected to 20 atm pressure of CO in an autoclave (1 l) for 20 h at 40 °C. The pale yellow solution so formed was evaporated to dryness and the residue chromatographed on a short alumina column. Elution with hexane developed a yellow band which gave rise to 0.45 g (90%) of yellow crystalline $[Ru_2(CO)_6(C_8H_7Me)]$ (10).

In an identical manner the following complexes were obtained in the yields indicated: (6), 31%; (7), 88%; (8), 18%; (9), 54%; and (11), 66%.

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