Reaction of Ethylene with $[Ru_3(CO)_{12}]$ and the Dynamic Processes of $[Ru_3H_2(CO)_9(C_2R_2)]$ (R = H, Me, and Et)

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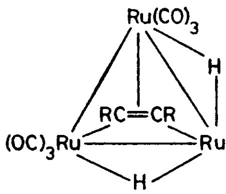
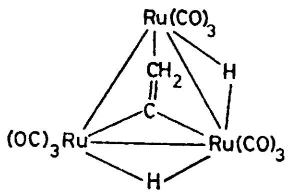
$[Ru(CO)_4(H_2C{=}CH_2)]$ is rapidly formed during the reaction of $[Ru_3(CO)_{12}]$ with ethylene. However, prolonged reflux yielded a mixture of products of which $[Ru_3H_2(CO)_9(C_2R_2)]$ [(1), R = H; (2), R = Me; (3), R = Et], $[Ru_3H(CO)_9(RCCHCEt)]$ [(4), R = Me; (5), R = Et], and $[Ru_4(CO)_{12}(MeC{\equiv}CMe)]$ (6) have been identified. Complexes (1), (2), and (3) are all stereochemically non-rigid. Generation of an apparent symmetry plane by a hydride migration is observed for all three complexes (mechanism 1). The hydride sites are equivalenced in (2) and (3), and the hexyne complex (3) was found to undergo hydride site exchange (mechanism 2) and alkyne oscillation (mechanism 3), probably independently. Increasing the acetylene alkyl group size also increases the rates of the exchange processes.

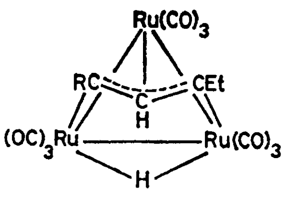
The reaction of dodecacarbonyltriruthenium with ethylene at atmospheric pressure has been reported to give rise to an ethyne complex, $[Ru_3H_2(CO)_9(HC{\equiv}CH)]$ (1a) and the isomeric vinylidene, $[Ru_3H_2(CO)_9(C{=}CH_2)]$ (1b).[1] However, at higher pressures and temperatures, higher nuclearity products $[Ru_6C(CO)_{17}]$,[2] $[Ru_4(CO)_{12}(MeC{\equiv}CMe)]$,[3] and $[Ru_6C(CO)_{15}(MeCH{=}CHCH{=}CHMe)]$ [3] have been identified. We were particularly interested in synthesising the two trinuclear clusters as part of a project to obtain vibrational and carbon-13 n.m.r. spectral parameters of C_2 hydrocarbon fragments on metal clusters. Since the alternative route to these complexes of $Na[BH_4]$ reduction of $[Ru_3(CO)_{12}]$ [4] gives a very low yield, we repeated the reaction between $[Ru_3(CO)_{12}]$ and ethylene under mild conditions to try to isolate the trinuclear isomers. However, we report that this reaction is complicated giving tri- and tetra-nuclear clusters and oligomerised ethylene moieties as ligands.



(1a) R = H
(2) R = Me
(3) R = Et
(7) $R_2 = (CH_2)_6$



(1b)



(4) R = Me
(5) R = Et

RESULTS AND DISCUSSION

Reaction Products.—Under the conditions used of refluxing n-heptane under 1 atm † of ethylene, a complex reaction mixture is formed. However, on introducing ethylene at room temperature, new ν(CO) bands were observed at 2 104m, 2 023s, and 1 977m cm^{-1} consistent with $[Ru(CO)_4(H_2C{=}CH_2)]$.[5] These were still present after *ca.* 30 min heating but were lost thereafter. Nevertheless, this suggests that the observed products could be formed *via* cluster breakdown.

Isolation of the products was attempted by t.l.c., but this was only partially successful. Three fractions were studied, the first two being mixtures of trinuclear complexes. The t.l.c. band of highest R_f value evidently contains two similar products. The identity of one of these, $[Ru_3H_2(CO)_9(EtC{\equiv}CEt)]$ (3), was evident from the mass spectral and i.r. data. Its i.r. spectrum (1 900—2 150 cm^{-1}) is very similar to that reported for $[Ru_3H_2(CO)_9(C_8H_{12})]$ (7).[6] However, the ^1H n.m.r. spectrum revealed a second complex which must have an almost indistinguishable i.r. spectrum. The n.m.r. data indicate that this second species is $[Ru_3H_2(CO)_9(MeC{\equiv}CMe)]$ (2). Since (2) is lighter than (3) by 28 atomic mass units (a.m.u.), it would be difficult to identify in the presence of the heavier complex.

The second t.l.c. band contains three species. One of these has a similar ν(CO) pattern in its i.r. spectrum to (2) and (3), and the spectral data are consistent with those previously reported for $[Ru_3H_2(CO)_9(HC{\equiv}CH)]$.[4] The i.r. spectra of the osmium analogues of (1a) and (1b) are very similar, but the hydrocarbon protons possess quite different chemical shifts.[7] Structure (1b) is favoured on that criterion. The second major species has an i.r. spectrum (2 094m, 2 065vs, 2 041vs, 2 023vs, 2 012s, 2 006s, and 1 994m cm^{-1}) similar to that of the allyl complex $[Ru_3H(CO)_9(C_8H_{11})]$.[6] Its mass spectral and ^1H n.m.r. data are consistent with that reported for $[Ru_3H(CO)_9(MeCCHCEt)]$ (4).[8] A third component exhibits a hydridic proton resonance at δ −20.25 p.p.m. very similar to that of (4). The mass spectrum of this

† Throughout this paper: 1 atm = 101 325 Pa.

mixture contains a weak Ru_3 isotope pattern centred at *m/e* 653, 14 a.m.u. higher than that of (4). We tentatively propose structure (5) for this component.

The last product was identified as [$Ru_4(CO)_{12}(MeC{\equiv}CMe)$] (6) on the basis of its mass spectrum. Its i.r. spectrum is similar to that reported for [$Ru_4(CO)_{12}(PhC{\equiv}CMe)$].[9] This complex has recently been reported in a high-pressure ethylene reaction.[4]

All these products contain known bonding patterns to clusters and some, *e.g.* [$Ru_3H(CO)_9(MeCCHCEt)$] (4), have been reported before. However, (4) was first synthesised from hexa-2,4-diene. The most notable aspect of these reactions is the ready di- and tri-merisation of ethylene on trinuclear clusters. In addition, formation of (5) would require cleavage of a carbon–carbon bond if generated from ethylene. However, we can not rule out its formation from an impurity in the n-heptane solvent.

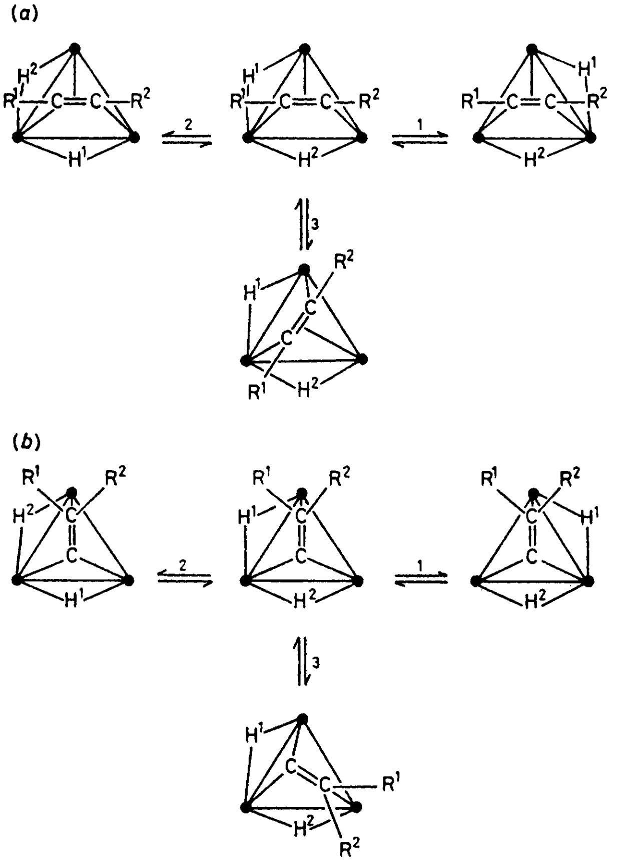


FIGURE 1 The three exchange processes of (*a*) [$Ru_3H_2(CO)_9(RC{\equiv}CR)$] and (*b*) [$Ru_3H_2(CO)_9(C{=}CH_2)$]. Carbonyl groups are omitted for clarity

*Variable-temperature Hydrogen-*1 *N.M.R. Studies.*—The ^1H n.m.r. spectra of (1b), (2), and (3) were all temperature dependent. The two hydride resonances of (1b) at δ −15.66 and −19.73 p.p.m. were invariant between −50 and 31 °C. However, the two acetylene protons are separate (δ 5.24 and 4.88 p.p.m.) at −10 °C, broaden at 10 °C, and have coalesced by 15 °C. Three possible degenerate exchange processes are detailed in Figure 1. Of these only mode 1 (see Table), in which a pseudoplane of symmetry is generated by the motion of hydride H^1, equivalences R^1 and R^2, without also equivalencing H^1 and H^2.

The two methyl resonances in (2) are separate (δ 1.65 and 1.15 p.p.m.) at −80 °C in CD_2Cl_2 solution. Broadening occurs at −60 °C and an average resonance is discernible at −30 °C so that at room temperature they exhibit a sharp singlet at δ 1.4 p.p.m. The hydride resonances of the mixture of (2) and (3) are shown in Figure 2. On comparison of the spectra of mixtures of varying proportions of (2) and (3) we assign the hydride resonances of (2) as those at δ −19.45 p.p.m. and part of that at δ −15.88 p.p.m. These two components are broadened at −10 °C, so that at 30 °C they are sufficiently broad as to be difficult to detect. Evidently, the $\Delta G^{\ddagger}$ of process 1 is lowered compared to that of complex (1). In addition there is now a second type of exchange which interchanges the hydride environment H^1 and H^2. This could be either process 2, involving hydride migration, or mechanism 3 in which the alkyne oscillation averages the two hydride sites.

The hex-3-yne complex (3) also exhibits hydride exchange; even at as low as −50 °C its two resonances at δ −15.92 and −20.40 p.p.m. are broadened and then yield an averaged signal at 30 °C. Again, this is consistent with either of the two exchange processes. However, the resonances of the ethyl group give further evidence. The shift of the methyl resonances in (3) is unaltered between −80 and 30 °C. This suggests that process 1 is already rapid by −80 °C, as has been observed for [$Ru_3H_2(CO)_9(C_8H_{12})$](7).[10] However, as shown in Figure 2, the methylene groups give rise to two multiplets at δ 3.2 and 2.3 p.p.m. If the two ends of the hexyne ligand in (3) are rendered equivalent by process 1, there are two methylene-proton environments because the two protons of each CH_2 moiety are diastereotopic, by virtue of their proximity to the chiral centre of the co-ordinated acetylenic carbon. At 30 °C, these two sites have averaged to one, observed at δ 2.8 p.p.m. This requires racemisation at the co-ordinated C atoms which can be achieved by the acetylene oscillation process 3. What remains in doubt is whether the hydride averaging is due to process 2 or 3. Both processes have similar coalescence temperatures (T_c) and at that temperature the exchange rate constant is estimated to be *ca.* 10^3 s^{-1} for hydride exchange and *ca.* 2×10^2 s^{-1} for methylene exchange, so as observed for [$Os_3H_2(CO)_9(C_9H_6)$],[11] hydride site exchange (process 2) is probably independent of, and more rapid than, alkyne oscillation.

Estimated $\Delta G^{\ddagger}_{T_c}$ values of (1b), (2), (3), and (7) are given in the Table. It is evident that increasing the alkyl-group bulk lowers the energy barrier to mechanisms 1 and probably 2. In addition, while mechanism 1 is slow for [$Os_3H_2(CO)_9(C{=}CH_2)$] at room temperature ($\Delta H^{\ddagger} = 82.4$ kJ mol^{-1} and $\Delta S^{\ddagger} = 32.4$ J K^{-1} mol^{-1}

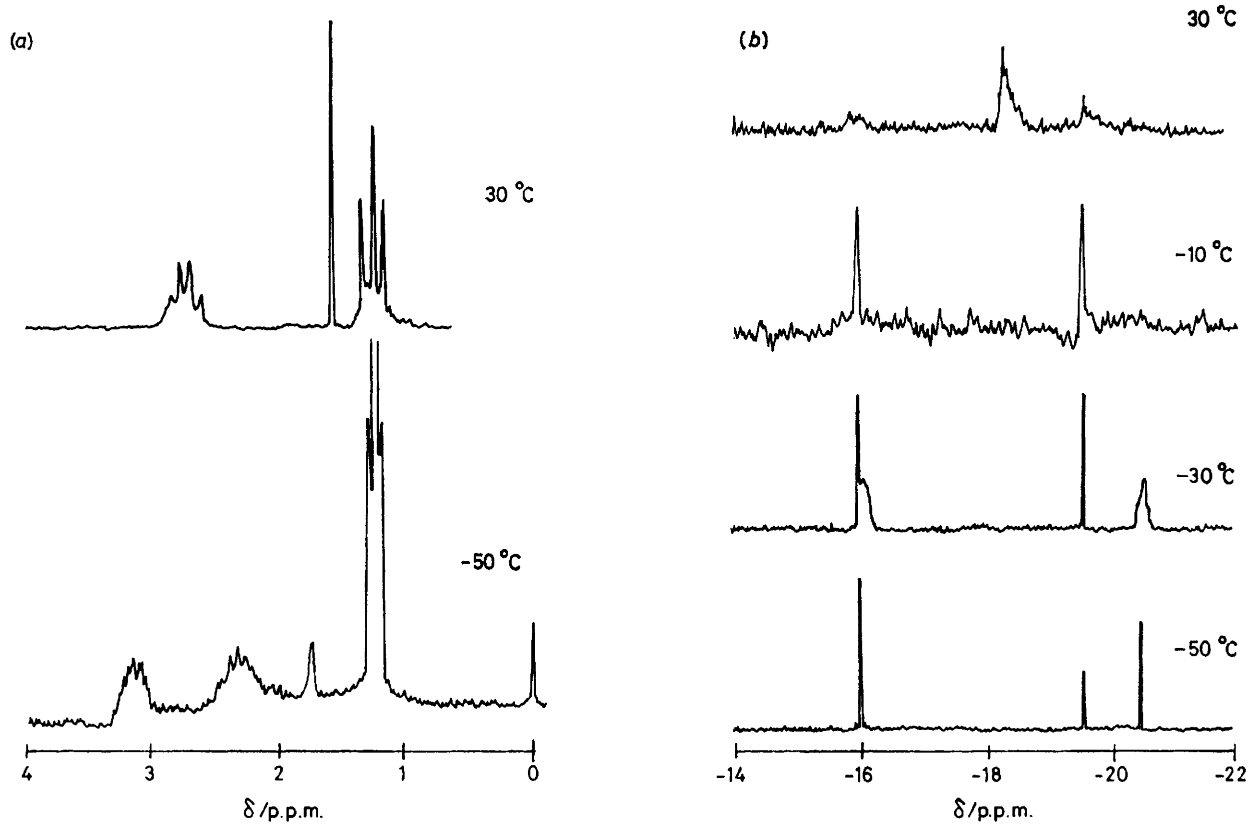


FIGURE 2 Hydrogen-1 n.m.r. spectra of the mixture of (2) and (3) in $CDCl_3$, showing (*a*) the alkyl and (*b*) the hydride regions

$\Delta G^{\ddagger}_{T_c}$ (kJ mol^{-1}) and T_c for the alkyne complexes

	Mechanisms		
Complex	1	2	3
(1)	61.3, 294 K		
(2)	47.4, 233 K	57.7, 313 K [a]	
(3)	low, <193 K	49.0, 263 K	52.5, 263 K
(7) [b]	low, <173 K	49.3, 264 K	65.3, 319 K

[a] Not clear whether mechanism 2 or 3 is operating. [b] Data from refs. 6 and 10.

its two hydride resonances only begin to broaden at 97 °C,[12] mechanism 1 is fast for $[Os_3H_2(CO)_9\{C{=}C(Me)CH_2Pr^i\}]$ at −80 °C [9] and hydride exchange has $T_c = -27$ °C [13] ($\Delta H^{\ddagger} = 49.8$ kJ mol^{-1} and $\Delta S^{\ddagger} = 17$ J K^{-1} mol^{-1}).[14] Thus, alkyl substitution decreases the energy barriers in both types of complex.

EXPERIMENTAL

The i.r., ^1H n.m.r., and mass spectra were recorded on Perkin-Elmer 580B, Varian XL-100, and AEI MS12 spectrometers respectively.

Reaction of $[Ru_3(CO)_{12}]$ *with Ethylene.*—The complex (50 mg) was dissolved in n-heptane (35 cm^3) and ethylene bubbled through the solution. This was heated to reflux for 17 h, allowed to cool, and the solvent removed under reduced pressure. In two further runs, 100 mg of $[Ru_3(CO)_{12}]$ were heated in n-heptane (40 cm^3) as above, and 500 mg refluxed in n-heptane (100 cm^3) for 22 h. The products were separated on silica thin-layer chromatography plates using hexane as solvent. In addition to an orange-brown band of unreacted $[Ru_3(CO)_{12}]$, several bands were obtained which were found to be mixtures on the basis of their i.r. spectra in the ν(CO) region. These were each rechromatographed. While this altered the proportions of the components, it did not effect total separation.

First band (*yellow*). I.r. (cyclohexane): 2 103m, 2 075vs, 2 052vs, 2 038vs, 2 025s, 2 016s (sh), 2 012vs, 2 005s, 1 986m cm^{-1}. Mass spectrum: M^+ 641 (based on $Ru_3 = 305$) with 10 (or 11) apparent losses of 28 a.m.u. ^1H N.m.r., at 31 °C ($CDCl_3$): δ 2.8 (quartet, *J* 7.6), 1.53 (s), 1.3 (t, *J* 7.6 Hz), −18.11 p.p.m. (br); at −80 °C (CD_2Cl_2) δ 3.2 (m), 2.3 (m), 1.65 (d), 1.15 (m), −15.88 (d, *J* 2), −19.45 (d, *J* 2), and −20.35 p.p.m. (d, *J* 2 Hz). Mixture of $[Ru_3H_2(CO)_9(EtC{\equiv}CEt)]$ (3) and $[Ru_3H_2(CO)_9(MeC{\equiv}CMe)]$ (2), total yield 12%.

Second band (*yellow*). I.r. (cyclohexane): 2 104vw, 2 094w, 2 078s, 2 067m, 2 057vs, 2 041vs, 2 023m, 2 020s, 2 012m, 2 006m, and 1 994m cm^{-1}. Mass spectrum: M^+ 585 (based on $Ru_3 = 305$), with nine losses of 28 a.m.u.; 639, with nine losses of 28 a.m.u.; and a weaker ion at 653. ^1H N.m.r., at 31 °C ($CDCl_3$): δ 6.63 (asym, quartet), 5.04 (s, br), 2.9 (m), 2.86 (s), 1.65—0.9 (complex), −15.66 (s, br), −15.88 (weak), −17.77 (weak), −19.44 (weak), −19.73 (d, *J* 3), −20.18 (d, *J* 3 Hz), −20.25 (d, *J* 3 Hz), −20.84 p.p.m. (v. weak); at −50 °C, as above except δ 5.04 resonance replaced by δ 5.24 (s) and δ 4.88 p.p.m. (s). Mixture of $[Ru_3H_2(CO)_9(HC{\equiv}CH)$ (1), $[Ru_3H(CO)_9(MeCCHCEt)]$ (4), and possibly $[Ru_3H(CO)_9(EtCCHCEt)]$ (5), total yield 9%.

Third band (*red-purple*). I.r. (cyclohexane): 2 087w, 2 066m, 2 042vs, 2 035vs, 2 018m, 2 012m, 2 008 (sh), 1 976vw cm^{-1}. Mass spectrum: M^+ 796 (based on Ru_4 as 406). ^1H N.m.r. ($CDCl_3$), at 31 °C: δ 2.83 p.p.m. (s). $[Ru_4(CO)_{12}(MeC{\equiv}CMe)]$ (7), yield 3%.

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