The Chemistry of Polynuclear Compounds. Part 28.[1] The Question of Isomerism in Tridecacarbonyldihydrido- and Dodecacarbonyltetrahydrido-tetraruthenium

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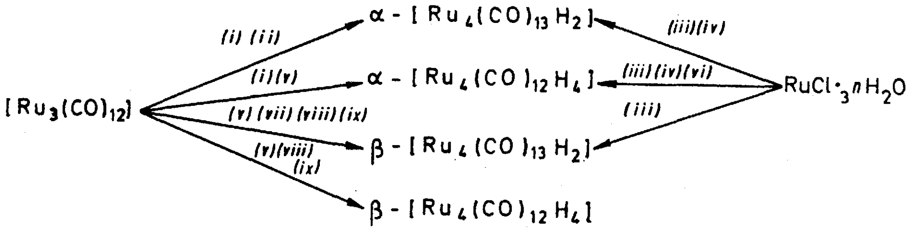
Synthetic routes to the α and β isomers of $[Ru_4(CO)_{13}H_2]$ and $[Ru_4(CO)_{12}H_4]$ have been reinvestigated and the products examined using ^1H Fourier-transform n.m.r. spectroscopy. Whilst a number of these routes, notably the reaction of $Na[BH_4]$ with $[Ru_3(CO)_{12}]$ and the carbonylation of methanolic and ethanolic solutions of $RuCl_3$, have led to the characterisation of hydridoruthenium clusters, *e.g.* $[Ru_3(CMe)(CO)_9H_3]$ and $[Ru_3(C_2H_2)(CO)_9H_2]$, no evidence has been found to support the existence of the β isomers.

A NUMBER of routes have been reported[1-7] for the preparation of the tetranuclear ruthenium carbonyl hydrides, α-$[Ru_4(CO)_{12}H_4]$, [β-$Ru_4(CO)_{12}H_4$], α-$[Ru_4(CO)_{13}H_2]$, and β-$[Ru_4(CO)_{13}H_2]$ most of which are outlined in Scheme 1. Kaesz and his co-workers [8] showed that the reaction of $[Ru_3(CO)_{12}]$ with hydrogen in n-octane at 90 °C leads to the formation in good yields of α-$[Ru_4(CO)_{12}H_4]$. They, like other workers,[9] questioned the existence of β-$[Ru_4(CO)_{12}H_4]$ and doubt must be cast on the isomeric nature of the corresponding $[Ru_4(CO)_{13}H_2]$ clusters. Whereas the infrared spectra in the carbonyl-stretching region of the α and β isomers show only minor differences, our previously reported hydride chemical-shift positions in their proton n.m.r. spectra are quite dissimilar (Table 1). The availability of the ^1H Fourier-transform n.m.r. technique provides a better way of examining these four hydride clusters. This approach, not surprisingly, has led to the appearance of other unassigned hydride resonances. In confirming that these extra hydride resonances were not associated with the tetranuclear ruthenium hydrides, specific compounds producing these resonances were chromatographically isolated and characterised by n.m.r., i.r., and mass spectroscopy. Thus the $Na[BH_4]$ route [Scheme 1(*viii*)] gave rise



SCHEME 1 Reported synthetic routes to the α and β isomers of $[Ru_4(CO)_{12}H_4]$ and $[Ru_4(CO)_{13}H_2]$. (*i*) Refluxing di-n-butyl ether;[2] (*ii*) $[Fe(CO)_5]$ or $[Fe_3(CO)_{12}]$ in refluxing light petroleum (b.p. 80—100 °C);[5] (*iii*) zinc–CO (1 atm)–EtOH and $Li[O_2CMe]$;[6] (*iv*) zinc–CO (10 atm)–MeOH (or EtOH) at 65 °C;[7] (*v*) sodium amalgam–tetrahydrofuran (thf) followed by acidification with H_3PO_4;[3] (*vi*) EtOH–CO–H_2 (80 atm) at 75 °C;[3] (*vii*) K[OH]–MeOH followed by acidification with H_2SO_4;[3] (*viii*) $Na[BH_4]$–thf;[3] (*ix*) refluxing n-octane or n-nonane.[1,4]

TABLE 1

Hydrogen-1 n.m.r. spectra of some ruthenium carbonyl hydrides

Compound	Hydride resonance (τ) [a]
α$[Ru_4(CO)_{12}H_4]$	27.6 [b]
β-$[Ru_4(CO)_{12}H_4]$	18.6 [b]
α-$[Ru_4(CO)_{13}H_2]$	28.6 [b]
β-$[Ru_4(CO)_{13}H_2]$	19.1 [b]
$[Ru(CO)_4H_2]$ [10]	17.6 [c]

[a] All sharp singlets. [b] In $CDCl_3$. [c] In n-pentane.

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[1] Part 27, C. R. Eady, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1976, 1706.

[2] B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc.* (*A*), 1970, 901.

[3] B. F. G. Johnson, R. D. Johnston, J. Lewis, B. H. Robinson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2856.

[4] B. F. G. Johnson, R. D. Johnston, and J. Lewis, *J. Chem. Soc.* (*A*), 1968, 2865.

[5] D. B. Yawney and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 502.

[6] R. B. King and P. N. Kapoor, *Inorg. Chem.*, 1972, **11**, 336.

[7] M. I. Bruce and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1967, 1238.

[8] (*a*) H. D. Kaesz, S. A. R. Knox, J. W. Koepke, and R. B. Saillant, *Chem. Comm.*, 1971, 477; (*b*) S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1975, **97**, 3942.

[9] F. Piacenti, M. Bianchi, P. Fediani, and E. Benedetti, *Inorg. Chem.*, 1971, **10**, 2759.

[10] J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2162.

to hydride clusters the origin of which is probably the result of reduction of the carbonyl groups in [$Ru_3(CO)_{12}$]. In comparison, the carbonylation of methanolic or ethanolic ruthenium trichloride in the presence of zinc [route *(iv)*], which is the established preparative route to [$Ru_3(CO)_{12}$], also leads to the formation of a range of tetranuclear clusters, of general formula [$Ru_4(CO)_{10}X_4$]. These clusters which contain co-ordinated alkoxy-groups indicate that the previously observed activation of water by ruthenium carbonyl species[1] can be generally extended to include at least the lower alcohols.

RESULTS AND DISCUSSION

The Isomeric Nature of [$Ru_4(CO)_{13}H_2$] *and* [$Ru_4(CO)_{12}H_4$].—A complete repetition of all the synthetic routes shown in Scheme 1 has clearly revealed that the tetranuclear hydrides [$Ru_4(CO)_{12}H_4$] and [$Ru_4(CO)_{13}H_2$] only exist in the so-called α form. The resulting reaction mixtures, as well as the pure hydrides which were isolated by t.l.c., were all examined by ^1H Fourier-transform n.m.r. spectroscopy over the range τ 0—50 for at least 5 000 transients. In no case, even under high amplification, were signals observed in the τ 18—20 region apart from the one case described in the next section. The observation of sharp singlets in the τ 18—20 region cannot be doubted, but under the conditions used all our present data are consistent with the resonances not being associated with the tetranuclear hydrides [$Ru_4(CO)_{13}H_2$] and [$Ru_4(CO)_{12}H_4$]. The structures of these two clusters have been reported[11,12] and their i.r. spectra in the carbonyl-stretching region, their molecular-ion values, and hydride chemical-shift positions are shown in Figure 1. Significantly, these spectroscopic data compare very favourably with those of [$Os_4(CO)_{13}H_2$] and [$Os_4(CO)_{12}H_4$] for which no α and β isomers have yet been reported.[1]

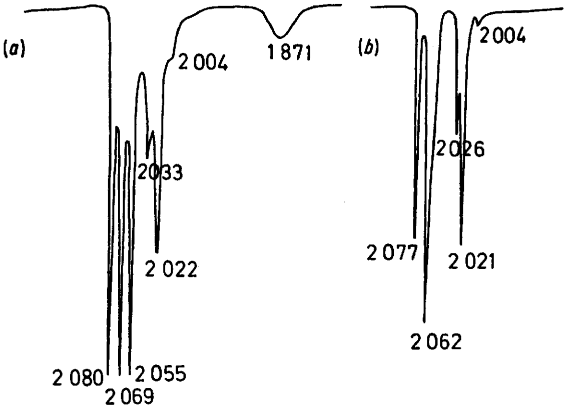

FIGURE 1 I.r. spectra (1 600—2200 cm^{-1}), molecular-ion values (M^+), and ^1H n.m.r. data for (*a*) [$Ru_4(CO)_{13}H_2$] and (*b*) [$Ru_4(CO)_{12}H_4$]

Compound	$\bar{\nu}$(CO) [a]/cm^{-1}	M^+	Hydride chemical shift [b] (τ)
[$Ru_4(CO)_{13}H_2$]	2 080vs, 2 022s, 2 069vs, 2 004w, 2 055vs, 1 871w (br), 2 033m	772	28.60
[$Ru_4(CO)_{12}H_4$] [c]	2 077s, 2 021s, 2 062vs, 2 004w, 2 026m (sh)	746 [d]	27.75

[a] In n-heptane. [b] In $CDCl_3$. [c] Apart from a calibration and/or solvent shift the spectrum given by Kaesz [8] is identical to that presented here. [d] See Experimental section.

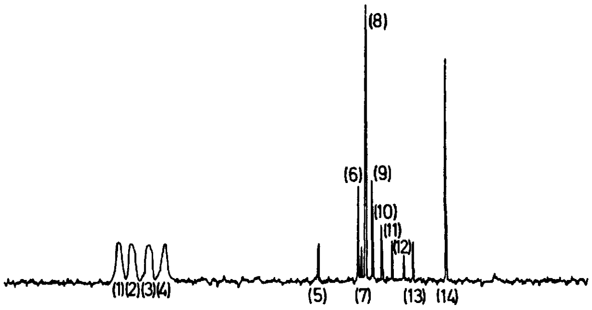

FIGURE 2 Hydrogen-1 Fourier-transform n.m.r. spectra of the total products of the reaction of [$Ru_3(CO)_{12}$] with Na[BH_4] in thf ($CDCl_3$ as solvent). Resonances: (1) τ 17.4, (2) 18.1, (3) 18.8, (4) 19.4, (5) 25.62, (6) 27.45, (7) 27.52, (8) 27.75, (9) 28.00, (10) 28.42, (11) 28.87, (12) 19.18, (13) 29.67, and (14) 31.12. The concentration of [$Ru_4(CO)_{13}H_2$] was so low that a resonance at τ 28.60 could not be observed

The Reaction of Sodium Tetrahydridoborate with [$Ru_3(CO)_{12}$].—On repeating the reaction of Na[BH_4] with [$Ru_3(CO)_{12}$] in refluxing thf [3] the tetranuclear hydrides [$Ru_4(CO)_{13}H_2$] and [$Ru_4(CO)_{12}H_4$] were produced, but as the ^1H Fourier-transform n.m.r. spectrum (Figure 2) indicated they were by no means the only products of the reaction. In particular, this spectrum showed four broad signals at τ 17.4, 18.1, 18.8, and 19.4. When the yellow cyclohexane extracts were separated by t.l.c. (cyclohexane as eluant), five major yellow bands were observed together with a number of minor ones. By using extra long t.l.c. plates each of these major bands could be shown to consist of a number of ruthenium cluster components, some of which could not be satisfactorily separated into single pure compounds. In the case of band one, ^1H Fourier-transform n.m.r. spectroscopy showed three hydride resonances at τ 27.45, 27.52, and 28.00, together with a strong low-field singlet at τ 5.88. The relative intensities of the three high-field peaks varied from one reaction to another, clearly illustrating that three individual compounds were involved. The carbonyl-stretching region in the i.r. spectrum of this fraction also showed a corresponding fluctuation in intensity, and by a process of comparison and elimination it was possible to associate sets of bands with a particular compound. In a similar manner it was possible to identify the components of this mixture from mass-spectroscopic studies as [$Ru_3(CMe)(CO)_9H_3$] (1), [$Ru_3(CH)(CO)_9H_3$] (2), and [$Ru_3(CH_2)(CO)_{10}H_2$] (3) together with trace amounts of [$Ru_3(CHMe)(CO)_{10}H_2$] (4). All these clusters gave molecular ions in their mass spectra and showed the stepwise loss of the required number of carbonyl groups together with the hydride ligands. The most abundant

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[11] D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, 1972, **11**, 838.

[12] S. A. R. Knox and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1971, **93**, 4594.

ion was $[Ru_3X]^+$ [X = CMe (1), CH (2), CH_2 (3), and CHMe for (4)]. These mass spectra gave rise to a number of general features which were of some structural significance: (*a*) the molecular-ion isotope patterns completely agreed with computed isotopic patterns; (*b*) the number of hydride ligands corresponded to the number of hydrogen atoms lost during the stepwise fragmentation of the carbonyl groups; (*c*) the number of hydrocarbon hydrogens could be deduced since they remained after the stepwise loss of carbonyl and hydride groups; (*d*) the hydrocarbon unit, X, was not fragmented apart from the loss in some cases of one or two hydrogen atoms; and (*e*) the retention of the Ru_3X unit under mass-spectroscopic conditions pointed to a strongly stabilised substituted cluster.[13,14]

The major compound present in this first chromatography band was (1) and the spectroscopic data (Table 2) were similar to that of a sample prepared by an alternative route.[15] The structure of cluster (1) has been determined by a single-crystal *X*-ray diffraction study,[16] and since the i.r. spectra in the carbonyl-stretching region of clusters (1) and (2) are identical the compounds are expected to be isostructural [Figure 3(*a*)]. The proposed structure of (3) is shown in Figure 3(*b*) and, like all the clusters produced from this reaction of $[Ru_3(CO)_{12}]$ with $Na[BH_4]$ it is derived from an expected compliance with the effective-atomic-number rule without invoking unobserved bridging carbonyl groups.

TABLE 2

Infrared spectra (1 600—2 200 cm^{-1}), molecular-ion values (M^+), and ^1H n.m.r. data for some products isolated from the reaction of $[Ru_3(CO)_{12}]$ with $Na[BH_4]$ in tetrahydrofuran

Compound	ν(CO)[a]		M^+	N.m.r. (τ)[b]
$[Ru_3(CMe)(CO)_9H_3]$	2 078s 2 071w		587	27.45 (s) (3 H) 5.88 (s) (3 H)
$[Ru_3(CH)(CO)_9H_3]$	2 033s 2 029m (sh) 2 014m		573	27.52 (s)[c]
$[Ru(CH_2)(CO)_{10}H_2]$	*d*		601	28.00 (s)[c] (2 H) 8.38 (s)[c] (2 H)
$[Ru_3(C_2H_2)(CO)_9H_2]$	2 106w 2 080s 2 058vs 2 043s	2 028w 2 022s 2 002vw 1 991w	585	25.62 (s) (1 H) 29.67 (s) (1 H) 4.97 (s) (2 H)
$[Ru_3(C_2HMe)(CO)_9H_2]$	*d*		599	25.88 (s)[c] (1 H) 29.40 (s)[c] (1 H) 7.98 (d) (*J* 6 Hz) (3 H) 3.87 (q) (1 H)
$[Ru_3(C_2H_2)(CO)_{10}H_2]$	*d*		613	29.18[c] (s)
$[Ru_3(B_2H_6)(CO)_9]$	2 111w 2 086s 2 062w	2 057s 2 045m 2 032w	584	*e*
$[Ru_4(BH_2)(CO)_{12}H]$	2 074vs 2 062vs 2 050m	2 030s 2 015w 2 000w	756	17.4 (br) 18.1 (br) } (2 H) 18.8 (br) 19.4 (br) 31.12 (s) (1 H)
$[Ru_5(C_2H_2)(CO)_{15}H_2]$	2 071s 2 065m 2 016w		954	*e*
$[Ru_6(C_2H_2)(CO)_{16}H_2]$	*e*		1 083	*e*
$[Ru_4(C_2H_2)(CO)_{12}]$	2 085vw 3 069s 2 043s 2 036s 2 017w 2 009w		768	*e*

[a] In n-heptane. [b] In $CDCl_3$. [c] Tentative assignment. [d] Not yet isolated spectroscopically pure. [e] Insufficient material available.

Whilst the hydride resonance at τ 27.52 was tentatively assigned to (2), that at τ 28.00 was assigned to (3).

The major component of the second chromatography band was $[Ru_3(C_2H_2)(CO)_9H_2]$ (5). The ^1H Fourier-transform spectrum showed sharp hydride singlets of equal intensity at τ 25.62 and 29.67 together with a singlet at τ 4.97. The osmium analogue has been prepared[17] and single-crystal *X*-ray diffraction studies have revealed a structure[18] similar to that proposed for (5) [Figure 3(*c*)]. The compound $[Ru_3(C_2HMe)(CO)_9H_2]$ (6) was also characterised by mass and n.m.r. spectroscopy (Table 2) and a structure similar to that of (5) is proposed [Figure 3(*c*)]. The coupling constants of

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[13] O. Gambino, E. Sappa, and G. Cetini, *J. Organometallic Chem.*, 1972, **44**, 185.

[14] O. Gambino, G. A. Vaglio, R. P. Ferrari, and G. Cetini, *J. Organometallic Chem.*, 1971, **30**, 381.

[15] A. J. Canty, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J.C.S. Chem. Comm.*, 1972, 1331.

[16] G. M. Sheldrick and J. P. Yesinowski, *J.C.S. Dalton*, 1975, 873.

[17] A. J. Deeming and M. Underhill, *J. Organometallic Chem.*, 1972, **42**, C60.

[18] A. J. Deeming and M. Underhill, *J.C.S. Chem. Comm.*, 1973, 277.

the methyl group are best explained by the structure proposed in Figure 3(*c*) rather than 3(*d*).[19]

In addition to these two major components, smaller amounts of other species based on Ru_3 units were formed. Complete characterisation of these clusters was difficult because of the small amounts of material available. However, on the basis of mass-spectroscopic data these compounds can be tentatively assigned the molecular formulae $[Ru_3(C_2H_2)(CO)_{10}H_2]$ (7) and $[Ru_3(B_2H_6)(CO)_9]$, the latter being unstable in air. A possible structure for (7) is shown in Figure 3(*e*). The third band was identified on the basis of spectroscopic data as $[Ru_4(CO)_{12}H_4]$ (8) {together with a trace amount of unchanged $[Ru_3(CO)_{12}]$}. This was one of the major products of the reaction and accounted for the hydride resonance at τ 27.75.

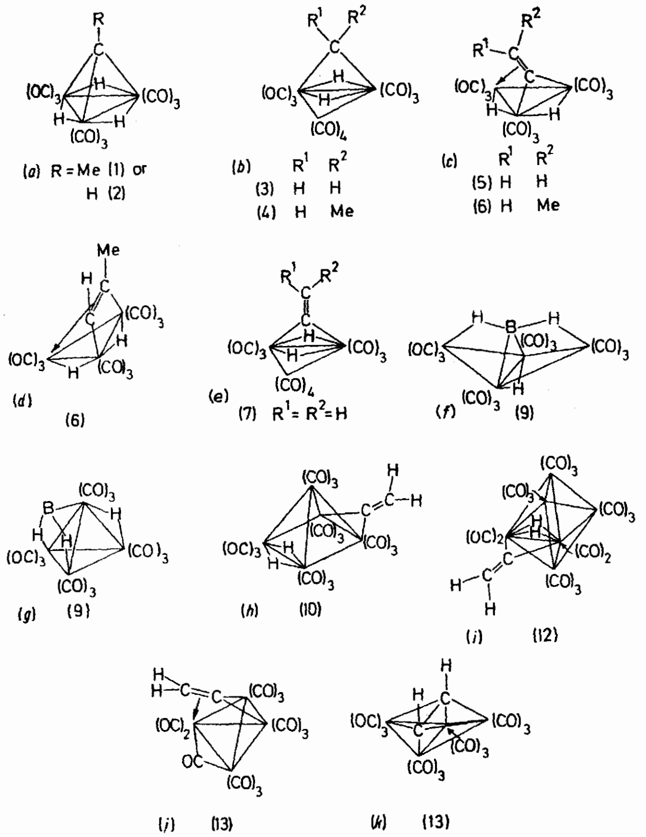

FIGURE 3 Proposed structures of the compounds produced during the reduction of $[Ru_3(CO)_{12}]$ with $Na[BH_4]$ in thf

The fourth chromatography band, which was also a major product of the reaction of $Na[BH_4]$ with $[Ru_3(CO)_{12}]$, was shown by mass spectroscopy to have the molecular formula $[Ru_4(BH_2)(CO)_{12}H]$ (9). Such metal clusters containing small borohydride units would be expected to give molecular ions in their mass spectra.[20-22] The presence of a boron atom was supported by complete agreement of the molecular-ion isotope pattern with computed patterns and more particularly by the formation of a characteristic $[Ru_4B]^+$ ion. Furthermore, ^1H Fourier-transform n.m.r. studies showed a series of broad resonances at τ 17.4, 18.1, 18.8, and 19.4 together with a sharp singlet at τ 31.12. The chemical-shift values and coupling constants of these four broad resonances are typical of bridging Ru–H–B bonds.[23] Previous examples [24,25] have indicated that the borohydride unit would be co-ordinated in such a manner that the metal atoms would obey the effective-atomic-number rule. For this reason the butterfly structure [26] proposed in Figure 3(*f*) would be preferred to the tetrahedral structure shown in 3(*g*). In particular, a four-co-ordinate boron atom, in which all the available orbitals are used, would be more acceptable. As in earlier cases,[23,24] the bridging B–H bond would act as a two-electron donor whilst the boron and hydride ligand would each donate half an electron to the 'hinge' ruthenium atoms. Somewhat similar types of borohydride clusters bonded to other metal carbonyl systems have been reported.[21,26-29]

The amounts of material collected by t.l.c. in band five were very small but when rechromatographed sufficient quantities of pure compound were available for mass-spectroscopic characterisation. Four ruthenium clusters were identified and formulated as $[Ru_5(C_2H_2)(CO)_{15}H_2]$ (10), $[Ru_4(CO)_{13}H_2]$ (11), $[Ru_6(C_2H_2)(CO)_{16}H_2]$ (12), and $[Ru_4(C_2H_2)(CO)_{12}]$ (13). Possible structures for clusters (10) and (12) in which the C_2H_2 group acts as a two-electron donor as in (7) are shown in Figures 3(*h*) and 3(*i*). However, other regular octahedral ruthenium clusters such as $[Ru_6(CO)_{18}H_2]$ and $[Ru_6C(CO)_{17}]$ have 86 rather than 84 valence electrons; this feature could be accommodated in (12) by allowing the C_2H_2 group to become a four-electron donor as in (5).

The t.l.c. R_F value of compound (13) together with its mass-spectroscopic breakdown pattern strongly suggest that this is not a hydride cluster. Under mass-spectroscopic conditions, (13) was the only species isolated from this $Na[BH_4]$–$[Ru_3(CO)_{12}]$ reaction in which the $[Ru_4(C_2H_2)]^+$ ion was broken down further to give a strong $[Ru_3(C_2H_2)]^+$ ion. This suggests that the tetrahedral structure shown in Figure 3(*j*), which would require a bridging carbonyl group in order for the cluster to obey the effective-atomic-number rule, is incorrect. A similar type of mass-spectroscopic behaviour has been observed

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[19] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, 1966, p. 725.

[20] A. Davison, D. D. Traficante, and S. S. Wreford, *J.C.S. Chem. Comm.*, 1972, 1155.

[21] C. R. Lucas and M. L. H. Green, *J.C.S. Chem. Comm.*, 1972, 1005.

[22] O. Hollander, W. R. Clayton, and S. G. Shore, *J.C.S. Chem. Comm.*, 1974, 604.

[23] F. Klanberg and L. J. Guggenberger, *Chem. Comm.*, 1967, 1293.

[24] H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1965, **87**, 2753.

[25] T. J. Marks, W. J. Kennelly, J. R. Kolb, and L. A. Shimp, *Inorg. Chem.*, 1972, **11**, 2540.

[26] G. W. Parshall, *J. Amer. Chem. Soc.*, 1964, **86**, 361.

[27] A. T. T. Hsieh, J. D. Ruddick, and G. Wilkinson, *J.C.S. Dalton*, 1972, 1966.

[28] T. J. Marks and J. R. Kolb, *J.C.S. Chem. Comm.*, 1972, 1019.

[29] D. F. Gaines and T. V. Iorns, *Inorg. Chem.*, 1968, **7**, 1041.

for the butterfly-type molecule $[Ru_4(C_8H_{10})(CO)_{11}]$ [30-32] and indeed this cluster can be closely related to (13) by the structure presented in Figure 3(*k*). The C_2H_2 group is essentially a co-ordinated acetylene whilst the olefinic group of the C_8H_{10} fragment is replaced by another carbonyl group.

With such an array of complex products an understanding of the nature and course of this reaction of $Na[BH_4]$ with $[Ru_3(CO)_{12}]$ was essential. Whilst it is reasonable to assume, for example, that (7) would be the precursor to (5), it has been found that the action of hydrogen on (5) leads to (1).[18,33] Thus this interconversion process can be used to explain the formation of a number of the clusters but it does not account for the original production of, for example, (7). However, when $Na[BD_4]$ rather than $Na[BH_4]$ was treated with $[Ru_3(CO)_{12}]$ in refluxing thf, the ^1H Fourier-transfer n.m.r. spectrum of the total reaction product only showed very weak hydride resonances and in particular the absence of bands in the τ 0—10 region. This suggests that the various clusters presented in Table 2 and Figure 3 are produced by the reduction of a coordinated carbonyl group. As far as we know, the only other example of such a mechanism has been reported by Treichel and Shubkin [34] in which the reaction of $[M(C_5H_5)(CO)_3(PPh_3)]^+$ (M = Mo or W) with $Na[BH_4]$ leads to $[MMe(C_5H_5)(CO)_2(PPh_3)]$ in high yield. Furthermore, it has been established [35,36] by *X*-ray diffraction techniques that a $[BH_4]^-$ group can add across two coordinated isocyanide groups to give a six-membered ring containing H_2B-N bonds and in which hydrogen transfer to the carbon atom of the isocyanide group has occurred. The isolation of ruthenium clusters to which borohydride units are co-ordinated could be taken as a further indication of such a mechanism.[37] The nonisolation of the corresponding boron–oxygen heterocyclic compounds is perhaps a reflection of their lower stability relative to the boron–nitrogen complex.

In conclusion, therefore, the reaction of $Na[BH_4]$ with $[Ru_3(CO)_{12}]$ in refluxing thf has been shown to be complex and does not lead simply to the formation of $[Ru_4(CO)_{13}H_2]$ and $[Ru_4(CO)_{12}H_4]$. The difficulties of completely characterising some of the products have been emphasised, yet it is our contention that sufficient data are available to establish, beyond reasonable doubt, that the products are the result of the reduction of coordinated carbonyl groups. It was not possible to assign the hydride resonances at τ 28.42 and 28.87 to particular compounds; significantly the synthesis of many of the products shown in Table 2 and their osmium analogues can now be more conveniently achieved by alternative routes.[15,33,38] As a series of clusters, they demonstrate the remarkable number of ways in which ruthenium carbonyl units can stabilise hydrocarbon fragments. Variable-temperature ^1H Fourier-transform studies have shown that most of these clusters are highly fluxional at room temperature; [33] this suggests that, in physical terms, they could be regarded as metal surfaces across which carbon monoxide, hydrogen, and hydrocarbon units are rapidly moving. The relevance of these clusters to an understanding of the mechanism of hydrogen transfer to unsaturated species on metal surfaces provides a stimulus for our continued studies.

The Carbonylation of Methanolic and Ethanolic Ruthenium Trichloride.—The carbonylation of hydrated ruthenium trichloride in methanol using zinc shavings as a halogen acceptor is a common method for preparing trinuclear $[Ru_3(CO)_{12}]$ in yields of up to 75%.[7] An i.r. spectrum [ν(CO)] of the benzene mother liquors resulting from the recrystallisation of $[Ru_3(CO)_{12}]$ indicated the presence of a number of carbonyl-containing compounds. Significantly, the preparation of $[Os_3(CO)_{12}]$ by carbonylating OsO_4 in methanol has led to the characterisation of the trinuclear derivatives $[Os_3(CO)_{10}XY]$ [X = Y = H or OMe; X = H, Y = OH or OMe].[39] It is possible therefore that similar compounds are produced in this analogous ruthenium reaction. However, it has been shown by previous workers in this group that the reaction of $[Ru_3(CO)_{12}]$ with alcohols is complex.[40] Moreover we have found that, although $[Ru_3(CO)_{12}]$ is capable of interacting with H–OH to give $[Ru_4(CO)_{13}H_2]$ and $[Ru_4(CO)_{12}H_4]$, no organoruthenium intermediates containing co-ordinated hydroxyl groups could be characterised.

When the ^1H Fourier-transform n.m.r. spectrum of the solids obtained from the $[Ru_3(CO)_{12}]$-recrystallisation mother liquors was recorded, five sharp hydride singlets were observed [Figure 4(*a*)]. T.l.c. (cyclohexane as eluant) on the solid mixture followed by i.r. [ν(CO)] and mass spectroscopy revealed the presence of the tetranuclear hydrides $[Ru_4(CO)_{12}H_4]$ (τ 27.75) and $[Ru_4(CO)_{13}H_2]$ (τ 28.60); as Figure 4(*a*) indicates, these compounds were one of the major products of the reaction. These two tetranuclear clusters are probably the result of the interaction of $[Ru_3(CO)_{12}]$ with water present in the methanol and $RuCl_3$. Further t.l.c. [ethyl acetate–cyclohexane (1 : 49)] revealed at least 10 more bands, alternating in colour between yellow and purple with the latter quickly decomposing on the silica plates. The various properties of these yellow air-stable

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[30] R. Mason and K. M. Thomas, *J. Organometallic Chem.*, 1972, **43**, C39.

[31] A. J. Canty, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1972, **43**, C35.

[32] A. J. Canty, A. J. P. Domingos, B. G. F. Johnson, and J. Lewis, *J.C.S. Dalton*, 1973, 2056.

[33] A. J. Canty, personal communication.

[34] P. M. Treichel and R. L. Shubkin, *Inorg. Chem.*, 1967, **6**, 1328.

[35] W. M. Butler and J. H. Enemark, *J. Organometallic Chem.*, 1973, **49**, 233.

[36] P. M. Treichel, J. P. Stenson, and J. J. Benedict, *Inorg. Chem.*, 1971, **10**, 1183.

[37] D. G. Holah, A. N. Hughes, and B. C. Hui, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 427.

[38] A. J. Deeming, S. Hasso, M. Underhill, A. J. Canty, B. F. G. Johnson, W. G. Jackson, J. Lewis, and T. W. Matheson, *J.C.S. Chem. Comm.*, 1974, 807.

[39] B. F. G. Johnson, J. Lewis, and P. A. Kilty, *J. Chem. Soc.* (*A*), 1968, 2859.

[40] G. R. Crooks, B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc.* (*A*), 1969, 797.

TABLE 3

Molecular-ion values (M^+), i.r. spectra (1 600—2 200 cm^{-1}), and ^{1}H n.m.r. data for the yellow products isolated from the benzene-extraction filtrate of the preparation of $[Ru_3(CO)_{12}]$

Compound	M^+	ν(CO) [a]		^{1}H N.m.r. spectra (τ)
$[Ru_4(CO)_{10}Cl_2(OMe)_2]$	818	2 103m 2 078s 2 036m (sh) 2 032vs	2 022vs 2 002w 1 958s	5.95 (s) (C_6D_6) 5.27 (s) ($CDCl_3$)
$[Ru_4(CO)_{10}Cl(OMe)_3]$	814	2 094m 2 058s 2 029m (sh) 2 024vs 2 012vs	2 006w (sh) 1 994m 1 951w (sh) 1 946m	[b]
$[Ru_4(CO)_{10}Cl_2(OMe)(OH)]$	804	2 094w 2 069s 2 023vs 2 016vs 1 950m		
$[Ru_4(CO)_{10}Cl_2(OH)_2]$	790	2 093w 2 073s 2 070s 2 072s (sh) 2 023vs	2 015s (sh) 2 011vs 1 956m 1 951m	
$[Ru_4(CO)_{10}Cl(OMe)_2(OH)]$	800	2 090m 2 058m (sh) 2 055s 2 024s (sh) 2 019vs	2 010s 1 990m 1 943m	

[a] In n-heptane. [b] Singlets exist at τ 5.21, 5.69, 5.74, 6.11, 6.17, and 6.53 ($CDCl_3$), but cannot be conclusively assigned.

compounds are given in Table 3 in order of decreasing R_F value. As in the previous section, separation of these somewhat similar compounds was difficult and only small amounts (5 mg) of pure material could be obtained.

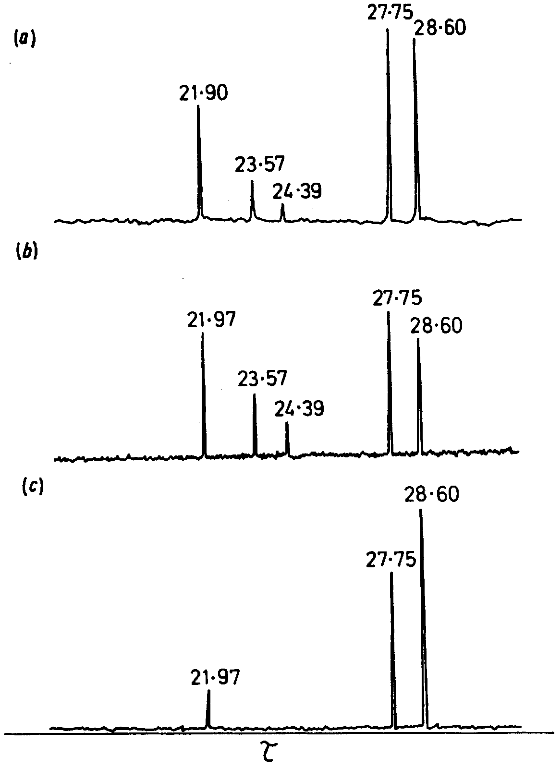


FIGURE 4 Hydrogen-1 Fourier-transform n.m.r. spectra (hydride region) of the products arising from the carbonylation of ruthenium trichloride: (*a*) in methanol; (*b*) in ethanol; (*c*) the King and Kapoor reaction

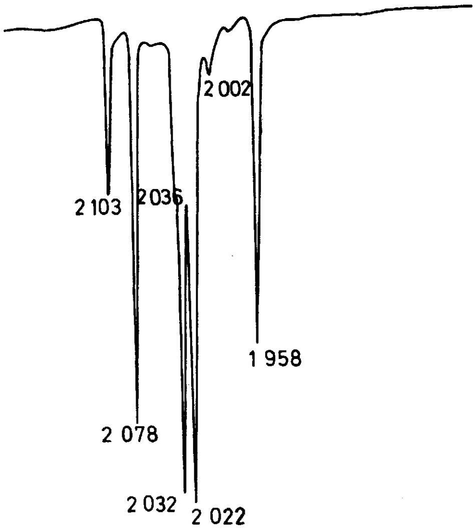


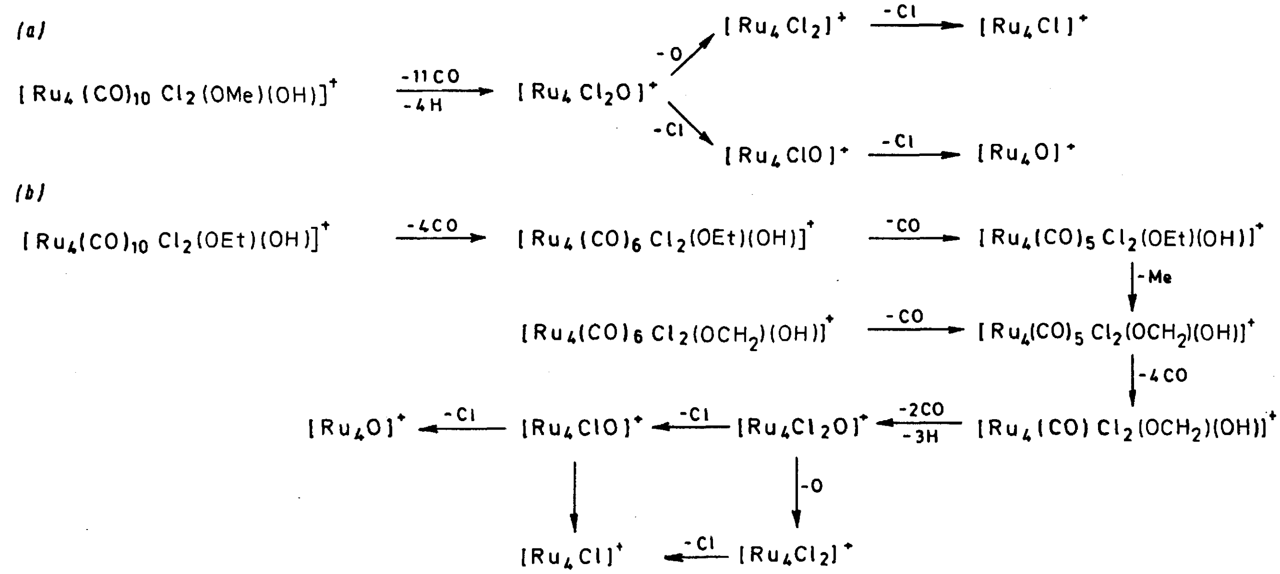
FIGURE 5 Infrared spectrum (1 600—2 200 cm^{-1}) of $[Ru_4(CO)_{10}Cl_2(OMe)_2]$ in n-heptane

A similar i.r. spectrum [ν(CO)] {as typified by that of $[Ru_4(CO)_{10}Cl_2(OMe)_2]$, Figure 5} was obtained for each of the five compounds presented in Table 3 apart from a small downward shift in the general pattern with decreasing R_F value. All the compounds gave intense molecular ions in their mass spectra; the fragmentation patterns, which are well illustrated by $[Ru_4(CO)_{10}Cl_2(OMe)(OH)]$ [Scheme 2(*a*)], showed a number of general features: (*a*) observed and computed isotopic patterns agreed completely; (*b*) weak doubly-charged ions were observed; (*c*) intense peaks due to $[Ru_4Cl_x]^+$ ($x = 1$ or 2) were always observed whilst the $[Ru_4]^+$ fragment gave only a very weak pattern; (*d*) where methoxo- rather than hydroxo-groups were present, the breakdown pattern did not distinguish these from the stepwise loss of the 10 carbonyl groups, *e.g.* [$Ru_4(CO)_{10}Cl_2(OMe)_2$] apparently showed ejection of 12 CO groups together with six hydrogen atoms.

The ^1H Fourier-transform n.m.r. spectra were recorded on the five clusters shown in Table 3 and whilst [$Ru_4(CO)_{10}Cl_2(OMe)_2$] clearly showed a sharp singlet at τ 5.27 ($CDCl_3$) the remaining compounds gave similar resonances but they could not be conclusively assigned. Whereas the hydride region under Fourier-transform conditions was clear, the τ 0—10 region was complicated by solvent impurities. The complete absence of hydride resonances in these molecules, particularly those bands at τ 21.9, 23.57, and 24.39 [Figure 4(*a*)] together with the observation of resonances in the τ 0—10 region, strongly suggested organoruthenium clusters in which co-ordinated hydroxo- and methoxo-groups were involved. In confirming the presence of co-ordinated alkoxo-groups, the carbonylation of $RuCl_3$ was repeated in ethanol rather than methanol. Figure 4(*b*) shows the ^1H Fourier-transform n.m.r. spectrum in the hydride region of the [$Ru_3(CO)_{12}$] recrystallisation residue. Five sharp hydride singlets, four of which corresponded to those of the methanol reaction, were observed and once again [$Ru_4(CO)_{12}H_4$] and [$Ru_4(CO)_{13}H_2$] were established as major components of the mixture. T.l.c. also revealed a number of minor compounds which had similar i.r. [ν(CO)] spectra to the compounds presented in Table 3; the compounds were formulated by mass spectroscopy as [$Ru_4(CO)_{10}Cl_2(OEt)(OH)$], [$Ru_4(CO)_{10}Cl_2(OH)_2$], and [$Ru_4(CO)_{10}Cl(OEt)_2(OH)$]. The fragmentation scheme for the first of these three tetranuclear clusters is presented in Scheme 2(*b*) and represents an excellent example of how a breakdown pattern of a complex cluster can be used to assign a molecular formula. The yield and number of these tetranuclear [$Ru_4(CO)_{10}X_4$] clusters was very much less than those from the equivalent methanol reaction and in only one case, [$Ru_4(CO)_{10}Cl_2(OEt)(OH)$], was it possible to record a ^1H Fourier-transform n.m.r. spectrum. A quartet centred at τ 6.22 ($CDCl_3$) was assigned to the CH_2–O protons of the ethoxo-group.

No organometallic species could be isolated which gave rise to the hydride resonances at τ 21.9, 21.97, 23.57, and 24.39 [Figures 4(*a*) and 4(*b*)]. However, these resonances, together with a sharp intense singlet at τ 6.63 (methanolic carbonylation) and a strong quartet centred at τ 6.63 (ethanolic carbonylation), disappeared after t.l.c. This suggests that these compounds decompose in silica and the observation of intense baselines and quickly decomposing purple bands supports this conclusion. It can be assumed that the resonances at τ 23.57 and 24.39 are associated with carbonylhydrido-clusters which do not contain co-ordinated methoxo- or ethoxo-groups. The converse is true for the two hydride resonances differing by τ 0.07 (21.90 and 21.97) which are likely to be associated with the unassigned alkoxy-resonances described above and arise from ruthenium carbonylhydrido-clusters containing either methoxo- or ethoxo-groups. This proposal was further strengthened by repeating reaction (1) of King and Kapoor.[6] Although the tetranuclear hydrides Li-[O_2CMe]–[$Ru_4(CO)_{13}H_2$] and [$Ru_4(CO)_{12}H_4$] were produced, the ^1H Fourier-transform spectrum of the complete product [Figure 4(*c*)] also showed resonances at τ 21.97 (s) and 6.63 (q) and these were identical to those just described. These various unisolated hydrido-clusters could be members of the [$Ru_4(CO)_{10}X_4$] class. Alternatively they could be the ruthenium analogues of the trinuclear osmium clusters, [$Os_3(CO)_{10}XY$],[39] briefly mentioned at the beginning of this section.

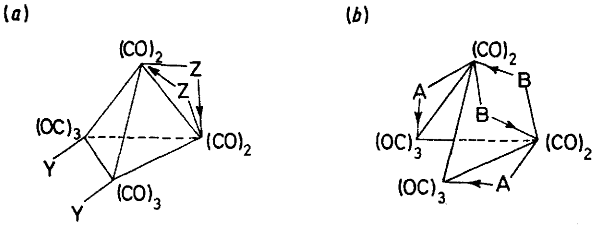
$$[\{Ru(C_6H_6)Cl_2\}_n] \xrightarrow[\text{boiling ethanol, Li[O}_2\text{CMe]-zinc shot}]{\text{CO, 1 atm}} [Ru_4(CO)_{13}H_2] \quad (1)$$



SCHEME 2 The mass-spectral breakdown pattern of (*a*) [$Ru_4(CO)_{10}Cl_2(OMe)(OH)$] and (*b*) [$Ru_4(CO)_{10}Cl_2(OEt)(OH)$]

The structure of the $[Ru_4(CO)_{10}X_4]$ clusters is likely to be dominated by adherence to the effective-atomic-number rule. Our i.r. data [ν(CO)] are consistent with only terminally bonded carbonyl groups. The three ligands Cl, OH, and OMe (or OEt) can all act as one- (terminal) or three-electron (bridging) ligands. These facts give rise to two distinct types of possible structures (Figure 6). If clusters responsible for the unassigned hydride resonances, which are at chemical-shift positions more consistent with bridging than terminal hydrides, belong to the general $[Ru_4(CO)_{10}X_4]$ series, structural features observed in the trinuclear clusters $[Os_3(CO)_{10}(OMe)_2]$, $[Os_3(CO)_{10}H(OMe)]$, $[Os_3(CO)_{10}H(OH)]$, and $[Os_3(CO)_{10}H_2]$ [39,41] are possible. As was discussed in the previous section, a 'butterfly' conformation of metal atoms similar to that proposed in Figure 6(*b*) has been observed in $[Ru_4(C_8H_{10})(CO)_{11}]$.[30,31]

Thus in the same way that $[Ru_3(CO)_{12}]$ can activate water to give $[Ru_4(CO)_{13}H_2]$ and $[Ru_4(CO)_{12}H_4]$,[1] it has been shown that ruthenium carbonyl chloride species also activate alcohols leading to the fission of the O–H bond. Such an interaction is not unknown as it is well established that ruthenium chloride–tertiary phosphine compounds react with alcohols to give stable carbonyl-hydrido-compounds.[42] Significantly $[\{Ru(CO)_3Cl_2\}_2]$ interacts with ethanol, but although the formation of mononuclear ethoxohydrido-species was proposed they were not isolated.[43] Similar types of intermediates have been proposed by Eberhardt *et al.*[44] in the catalytic exchange of the hydroxyl hydrogen [45] in methanol or ethanol with deuterium gas, using $[RuCl_2(PPh_3)_3]$.



Z = three-electron donor
Y = one-electron donor
A,B= three-electron donor

FIGURE 6 Proposed structures for the tetranuclear $[Ru_4(CO)_{10}X_4]$ clusters

EXPERIMENTAL

All the manipulations were made under dry oxygen-free nitrogen although most of the compounds were air-stable solids. Whereas AnalaR grade methanol and ethanol were used without further purification, all the other solvents were dried, deoxygenated, and distilled before use. Tetrahydrofuran was purified by initially removing any sulphur using an alumina column and then distilling over sodium immediately prior to use. Di-n-butyl ether was fractionated over potassium hydroxide pellets, whilst alkanes were purified by stirring over concentrated sulphuric acid for 24 h, washing with sodium hydrogencarbohate solution and water, and then distilling over calcium hydride in a stream of nitrogen through a Vigreux column. The compound $[Ru_3(CO)_{12}]$ was prepared by the route of Bruce and Stone.[7]

Infrared spectra were recorded as solutions in 0.5-mm NaCl cells using a Perkin-Elmer 257 spectrometer with polystyrene film as calibrant. T.l.c. plates were prepared in these laboratories using 20-cm square glass plates coated with a 0.3 mm layer of Reeve Angel Scientific silica gel (type S13FTLC). Mass spectra were obtained using an A.E.I. MS12 instrument at 70 eV ionising potential with either tris(perfluoroheptyl)-s-triazine or perfluorotributylamine as internal standard.* Hydrogen-1 n.m.r. spectra were recorded at 100 MHz on Varian Associates HA100 or XL100 spectrometers.

Preparation of $[Ru_4(CO)_{12}H_4]$ *and* $[Ru_4(CO)_{13}H_2]$.—The various routes to these two tetranuclear clusters were, in general, repeated at least twice as described in the literature (Scheme 1). It was, however, more convenient to repeat the reaction of $[Ru_3(CO)_{12}]$ with potassium hydroxide and methanol in a sealed evacuated Carius tube. Hydrogen-1 Fourier-transform n.m.r. spectra were recorded on the total reaction products of these various $[Ru_4(CO)_{12}H_4]$ and $[Ru_4(CO)_{13}H_2]$ syntheses. Tetramethylsilane was not used as an internal standard because it produced fold-in peaks in the hydride region. Instead the solvent $CDCl_3$ was used as internal calibrant ($CHCl_3$, τ 2.75); the spectra were recorded over a τ 0—50 range for 5 000 transients. Even after leaving a mixture of the two clusters in $CDCl_3$ for 2 weeks, the two hydride resonances neither decreased in intensity nor gave rise to bands in the τ 18—20 region. The individual hydrides could be readily separated by t.l.c. using cyclohexane as eluant. Whereas the mass spectrum of $[Ru_4(CO)_{13}H_2]$ gave an intense molecular ion, the isotopic pattern of which was identical to that of a computed pattern, $[Ru_4(CO)_{12}H_4]$ did not (maximum source temperature 90 °C). This agrees with previous observations,[2,3,8b] but under the operating conditions prevailing the mass number 746 was marginally the most intense peak; however, overall, the observed isotope pattern did not agree with the computed molecular-ion pattern thus suggesting some decomposition of the cluster under ionisation. It should be realised that the degree of this decomposition will vary from one machine to another and depend critically on the particular geometry and operating conditions associated with it.[8b]

Reaction of $[Ru_3(CO)_{12}]$ *with* $Na[BH_4]$ *in Tetrahydrofuran.*—The compound $[Ru_3(CO)_{12}]$ (0.5 g) was heated under reflux with $Na[BH_4]$ (0.1 g) in thf (50 cm³) for 45 min. The resulting mixture was filtered through silica and the solvent removed to give a red oil which was dried *in vacuo* and then extracted with boiling cyclohexane (5 × 40 cm³). After removal of the solvent from these extracts, the yellow solid (*ca.* 100 mg, 10%) was separated into five bands using t.l.c. (cyclohexane as eluant). It was essential to quickly extract these compounds from the silica using ethyl acetate because of decomposition; apart from $[Ru_4(BH_2)(CO)_{12}H]$ and

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* 1 eV ≈ 1.6 × 10^{-19} J; 1 atm = 101 325 Pa.

[41] R. Mason and D. M. P. Mingos, *J. Organometallic Chem.*, 1973, **50**, 53.

[42] J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 1964, 3466.

[43] E. Benedetti, G. Braca, G. Sbrana, F. Salvetti, and B. Grassi, *J. Organometallic Chem.*, 1972, **37**, 361.

[44] G. C. Eberhardt, M. E. Tadros, and L. Vaska, *J.C.S. Chem. Comm.*, 1972, 290.

[45] L. Kh. Freidlin, V. Z. Sharf, V. N. Krutii, and S. J. Shcherbakova, *Zhur. org. Khim.*, 1972, **8**, 979.

$[Ru_3(B_2H_6)(CO)_9]$, the resulting solids were air stable. Using long chromatography plates (20 × 40 cm) and cyclohexane as eluant it was possible to further partially separate these five major bands. The various components of the first two bands were analysed by mass spectrometry using a water-cooled source whilst the remaining three were identified using a conventionally heated source (90 °C). Hydrogen-1 Fourier-transform n.m.r. spectra were recorded on the total reaction products and the various t.l.c. components over the ranges τ 0—10 (200 transients) and τ 0—50 (5 000 transients) using $CDCl_3$ as solvent and internal standard. Yields of individual compounds were difficult to determine because of the techniques used for their separation. Figure 2 provides some indication of relative yields but even this spectrum showed considerable variation in peak heights from one reaction to another.

Carbonylation of $RuCl_3$.[7]—Ruthenium trichloride (6.0 g), zinc shot (6.0 g) washed in dilute hydrochloric acid, and AnalaR methanol (150 cm³) were allowed to react in a 1-l stirring autoclave with CO (10 atm) at 65 °C for 30 h. The autoclave with CO (10 atm) at 65 °C for 30 h. The autoclave mixture was filtered through Kieselguhr under nitrogen and the solid was extracted into boiling benzene (5 × 200 cm³). No attempt was made to analyse the weakly coloured methanol filtrate. The volume of benzene was reduced (20 cm³), the $[Ru_3(CO)_{12}]$ filtered off, and the resulting filtrate evaporated to dryness to give a reddish brown solid. This solid was separated into its various components by t.l.c. with the bands being extracted from the silica using ethyl acetate. When cyclohexane was used as eluant, three bands were observed (in order of decreasing R_F value): $[Ru_4(CO)_{12}H_4]$, yellow; $[Ru_4(CO)_{13}H_2]$, red; and $[Ru_4(CO)_{10}Cl_2(OMe)_2]$, yellow. Using a mixture of 2% ethyl acetate in cyclohexane as eluant, the above three compounds were not separated but below them came a series of yellow and purple bands, the latter quickly decomposing. These bands in order of decreasing R_F value were: $[Ru_4(CO)_{10}Cl(OMe)_3]$, yellow; $[Ru_4(CO)_{10}Cl_2(OMe)(OH)]$, yellow; $[Ru_4(CO)_{10}Cl_2(OH)_2]$, yellow; and $[Ru_4(CO)_{10}Cl(OMe)_2(OH)]$, yellow. These clusters were characterised by i.r., mass (source temperature 100 °C), and ^1H Fourier-transform n.m.r. spectroscopy ($CDCl_3$ as solvent and internal standard).

When ethanol rather than methanol was used as solvent in the carbonylation of $RuCl_3$, the experimental procedure was similar to that described above. T.l.c. revealed the following bands in order of decreasing R_F value: $[Ru_4(CO)_{12}H_4]$, yellow; $[Ru_4(CO)_{13}H_2]$, red; $[Ru_4(CO)_{10}Cl_2(OEt)(OH)]$, yellow; $[Ru_4(CO)_{10}Cl_2(OH)_2]$, yellow, and $[Ru_4(CO)_{10}Cl(OEt)_2(OH)]$, yellow.

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