Behaviour of Polynuclear Ruthenium Carbonyl Carboxylates in the Presence of Hydrogen and/or Carbon Monoxide *

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The thermal behaviour in the temperature range 293—453 K of [Ru(CO)$_2$(MeCO$_2$)$_2$(PBu$^n{}_3$)$_2$], [Ru$_2$(CO)$_4$(MeCO$_2$)$_2$(PBu$^n{}_3$)$_2$] and [Ru$_4$(CO)$_8$(MeCO$_2$)$_4$(PBu$^n{}_3$)$_2$] in hydrocarbon solution, taken separately or in binary mixtures, with each other or with [{Ru$_2$(CO)$_4$(MeCO$_2$)$_2$}$_m$], under nitrogen or, alternatively, hydrogen, carbon monoxide, or their mixtures, has been monitored by i.r. spectroscopy under reaction conditions. A deficiency of ligands leads to the formation of larger clusters while their abundance in solution shifts the equilibria towards mononuclear complexes. Under carbon monoxide the formation of ruthenium(0) complexes is obtained from the above compounds. The presence of hydrogen together with carbon monoxide seems to facilitate such evolution of the system probably through the formation of intermediate hydridic derivatives which however were not detected.

In the crude reaction product from the homogeneous hydrogenation of free acetic acid carried out in the presence of [Ru$_4$H$_4$(CO)$_8$(PBu$^n{}_3$)$_4$] as catalytic precursor the compounds [Ru(CO)$_2$(MeCO$_2$)$_2$(PBu$^n{}_3$)$_2$] (1), [Ru$_2$(CO)$_4$(MeCO$_2$)$_2$(PBu$^n{}_3$)$_2$] (2), and [Ru$_4$(CO)$_8$(MeCO$_2$)$_4$(PBu$^n{}_3$)$_2$] (3) were detected.[1] In order to get more information on this system and on the eventual role of (1)—(3), the behaviour of these compounds has been investigated, separately, and in binary mixtures, under N$_2$, CO, H$_2$, and CO–H$_2$ in the temperature range 293—453 K.

The thermal behaviour of (1)—(3), or (1) and (3), and the reactivity of (1) or (2) with hydrogen indicate that this system is sensitive to reaction conditions.[1—7] New products of different complexity are formed, in some cases eventually involving changes in the oxidation number of ruthenium, metal cluster formation, and transformation of the ligands.

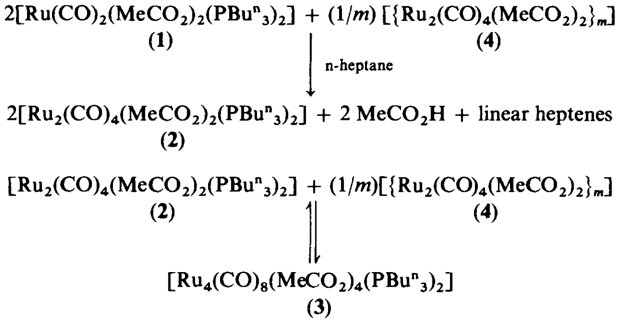
We now report an analogous investigation on (2), (3), and [{Ru$_2$(CO)$_4$(MeCO$_2$)$_2$}$_m$] (4). The evolution of the system has been followed, as previously described[4,5] by i.r. spectroscopy under reaction conditions and, when possible, by isolation and characterization of the new products formed.

Results

Thermal Stability of Cluster Ruthenium Carbonyl Acetates.—The behaviour of polynuclear ruthenium carbonyl acetates (2) or (4), in n-heptane solution, in the presence of (1) at various temperatures was studied.

[Ru$_2$(CO)$_4$(MeCO$_2$)$_2$(PBu$^n{}_3$)$_2$] (2) *and* [Ru(CO)$_2$(MeCO$_2$)$_2$(PBu$^n{}_3$)$_2$] (1) *under nitrogen.* A n-heptane solution of compounds (1) and (2) in equimolecular amounts remains unaltered below 373 K. At 373 K new i.r. bands appear attributable to the presence of [Ru$_2$(CO)$_3$(MeCO$_2$)$_3$(OH)(PBu$^n{}_3$)$_2$] (5)[3] (Table 1). At 393 K the concentration of (5) increases further and the presence of free acetic acid becomes evident. At higher temperatures (413 K), however, (2) becomes the prevailing compound in solution.

[{Ru$_2$(CO)$_4$(MeCO$_2$)$_2$}$_m$] (4) *in a n-heptane solution of* [Ru(CO)$_2$(MeCO$_2$)$_2$(PBu$^n{}_3$)$_2$] (1) *under nitrogen.* Compound (4), suspended in a n-heptane solution of (1) [Ru in (4)/Ru in (1) = 1.6:1], slowly dissolves at 373 K while the solution becomes yellow. The i.r. spectrum of this solution shows absorptions indicative of (1)—(3) and (5) besides the presence of acetic acid. On further heating at 413 K the absorptions related to (1) and (5) fade away while those of (3) and free acetic acid increase considerably; (2), however, still remains the prevailing component.



$$2[\mathrm{Ru(CO)_2(MeCO_2)_2(PBu^n{}_3)_2}]\ (1) + (1/m)\,[\{\mathrm{Ru_2(CO)_4(MeCO_2)_2}\}_m]\ (4) \xrightarrow{\text{n-heptane}} 2[\mathrm{Ru_2(CO)_4(MeCO_2)_2(PBu^n{}_3)_2}]\ (2) + 2\,\mathrm{MeCO_2H} + \text{linear heptenes}$$

$$[\mathrm{Ru_2(CO)_4(MeCO_2)_2(PBu^n{}_3)_2}]\ (2) + (1/m)[\{\mathrm{Ru_2(CO)_4(MeCO_2)_2}\}_m]\ (4) \rightleftharpoons [\mathrm{Ru_4(CO)_8(MeCO_2)_4(PBu^n{}_3)_2}]\ (3)$$

Scheme 1.

The evolution of the system towards the formation of (2) and (3) may be tentatively rationalized according to Scheme 1.

Behaviour of Cluster Ruthenium Carbonyl Acetates under Carbon Monoxide.—[Ru$_2$(CO)$_4$(MeCO$_2$)$_2$(PBu$^n{}_3$)$_2$] (2) *and* CO. Compound (2) in n-heptane solution, under pressure of carbon monoxide (5 MPa), remains unchanged below 373 K. At this temperature [Ru(CO)$_4$(PBu$^n{}_3$)] (6)[4,8,9] is formed in detectable amounts. On prolonged heating at 393 K the concentration of (6) increases while that of (2) decreases. No further changes take place up to 413 K. The i.r. spectrum of the solution after cooling at room temperature under the same pressure of carbon monoxide shows new bands, besides those due to (6), attributable to [Ru(CO)$_5$] (7)[10] and acetic acid (Scheme 2).

[Ru$_4$(CO)$_8$(MeCO$_2$)$_4$(PBu$^n{}_3$)$_2$] (3) *and* CO. A n-heptane solution of compound (3) under carbon monoxide (5 MPa) is readily transformed at room temperature, into [Ru$_2$(CO)$_5$(MeCO$_2$)$_2$(PBu$^n{}_3$)] (8)[6] (Scheme 3). After prolonged heating of the solution at 373 K new absorptions appear due to (6)[4,8,9] and (7).[10] At 413 K (6) and (7) appear to be the only products in

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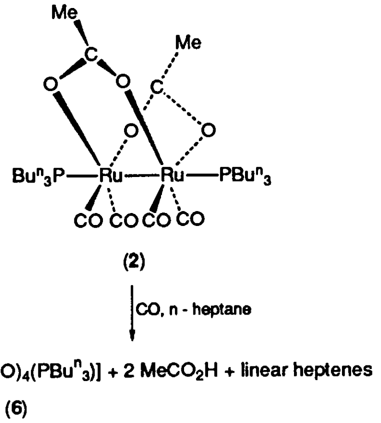
* *Supplementary data available* (No. SUP 56796, 11 pp.): i.r. spectra. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. I.r. data, in the range 2200—1500 cm^{-1}, for the compounds reported in this work[a]

Compound	
(1) $[Ru(CO)_2(MeCO_2)_2(PBu^n{}_3)_2]$	2 041vs, 2 015vw, 1 971vs, 1 952vw, 1 628m, 1 600 (sh)
(2) $[Ru_2(CO)_4(MeCO_2)_2(PBu^n{}_3)_2]$	2 021vs, 2 019 (sh), 1 976m, 1 970 (sh), 1 949vs, 1 940 (sh), 1 921vw, 1 900vw, 1 588m
(3) $[Ru_4(CO)_8(MeCO_2)_4(PBu^n{}_3)_2]$	2 035 (sh), 2 030vs, 1 981s, 1 960vs, 1 938vw, 1 919m, 1 894vw, 1 569s, 1 547 (sh)
(4) $[\{Ru_2(CO)_4(MeCO_2)_2\}_m]$[b]	2 055s, 1 995vs, 1 970vs, 1 910s, 1 555vs
[c]	2 049s, 1 994s, 1 966vs, 1 958s, 1 925 (sh), 1 908 (sh), 1 553vs, 1 439m, 1 416s, 1 402s
(5) $[Ru_2(CO)_3(MeCO_2)_3(OH)(PBu^n{}_3)_2]$	2 060s, 1 991vs, 1 942vs, 1 900w, 1 678m, 1 592m, 1 561m
(6) $[Ru(CO)_4(PBu^n{}_3)]$	2 059s, 1 983mw, 1 946vs
(7) $[Ru(CO)_5]$	2 037m, 2 006s
(8) $[Ru_2(CO)_5(MeCO_2)_2(PBu^n{}_3)]$	2 079vs, 2 022vs, 1 990 (sh), 1 980vs, 1 959 (sh), 1 942m, 1 916w, 1 580m, 1 570 (sh)
(9) $[Ru_2(CO)_6(MeCO_2)_2]$	2 109s, 2 083vs. 2 038s, 2 008vs, 1 954vw, 1 575m
(10) $[Ru_3(CO)_{12}]$	2 060vs, 2 031s, 2 011m
$[Ru_4H_4(CO)_{12}]$	2 081s, 2 068vs, 2 030m, 2 024s, 2 008w
$MeCO_2H$	1 720s

[a] Solvent: n-heptane. [b] In Nujol. [c] As KBr pellet.



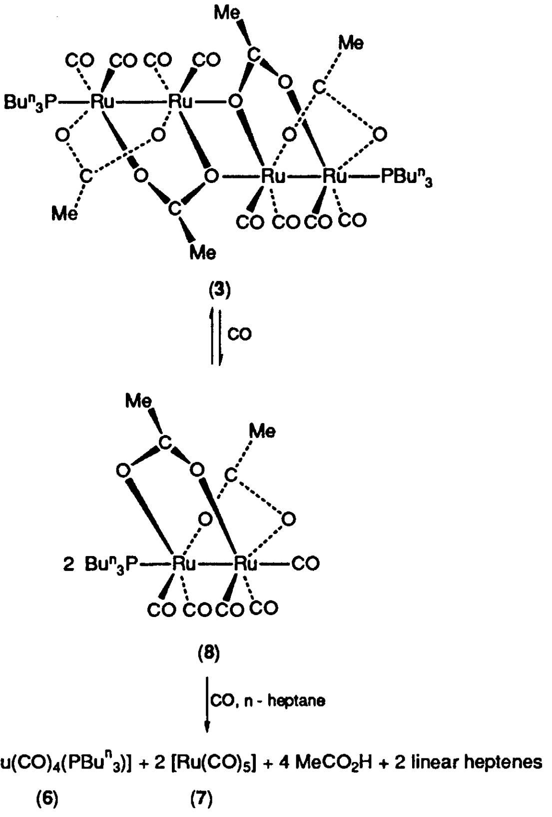
Scheme 2.

solution; after cooling at room temperature the concentration of (7) increases considerably while the presence of acetic acid is now evident. The above reaction is an equilibrium which may be shifted repeatedly by temperature changes.

$[\{Ru_2(CO)_4(MeCO_2)_2\}_m]$ (4) *and* CO. Compound (4) suspended in n-heptane under pressure of carbon monoxide dissolves, at room temperature, giving $[Ru_2(CO)_6(MeCO_2)_2]$ (9).[11] Heating of this solution up to 373 K does not cause detectable changes in its composition. Only at 413 K the i.r. spectrum indicates the presence of $[Ru_3(CO)_{12}]$ (10)[12] and of (7)[10] (Scheme 4). These products are still present in solution after cooling at room temperature. The presence of free acetic acid then becomes evident.

The i.r. spectrum of this solution, kept at room temperature under 0.1 MPa of carbon monoxide, shows, after 8 h, mainly absorptions indicative of (10) which in fact precipitates, after prolonged standing, in the form of orange-yellow crystals. Linear heptenes and acetic acid were identified in the solution at the end of the reaction.

Reactivity of Ruthenium Carbonyl Acetates with Hydrogen.—$[Ru_4(CO)_8(MeCO_2)_4(PBu^n{}_3)_2]$ (3) *and* H_2. The behaviour of a n-heptane solution of compound (3) under 5 MPa of hydrogen was investigated in the temperature range 293—393 K. Only after prolonged heating at 333 K the i.r. spectrum shows absorptions indicative of (2). An increase in temperature leads to a further transformation of (3) into (2). At 373 K the amounts of the two products, after 100 h, are equivalent while at 393 K (2) is predominant (Scheme 5). Compound (4) is recovered as a yellow solid.



Scheme 3.

$$\underset{(4)}{[\{Ru_2(CO)_4(MeCO_2)_2\}_m]} \xrightleftharpoons{\text{CO,n-heptane}} \underset{(9)}{m[Ru_2(CO)_6(MeCO_2)_2]}$$

$$\xrightleftharpoons{\text{CO,n-heptane}} a\underset{(7)}{[Ru(CO)_5]} + b\underset{(10)}{[Ru_3(CO)_{12}]}$$

$$+ 2m\,MeCO_2H + m\ \text{linear heptenes}$$

Scheme 4. $a + 3b = 2m$

Reactivity of Ruthenium Carbonyl Acetates with Carbon monoxide and Hydrogen.—$[Ru_2(CO)_4(MeCO_2)_2(PBu^n{}_3)_2]$ (2). The behaviour of a n-heptane solution of compound (2) under 10 MPa of carbon monoxide and hydrogen (1:1) has been investigated in the range 293—413 K. The first modification in the i.r. spectrum occurs at 333 K after 22 h. New bands appear

$$\begin{array}{c}[Ru_4(CO)_8(MeCO_2)_4(PBu^n_3)_2]\\ (3)\ \rightleftharpoons \\ [Ru_2(CO)_4(MeCO_2)_2(PBu^n_3)_2] + (1/m)\,[\{Ru_2(CO)_4(MeCO_2)_2\}_m]\\ (2) \qquad\qquad\qquad\qquad (4)\end{array}$$

Scheme 5.

indicative of (**6**). The intensity of these bands became predominant after heating at 353 K for 5 d while those of (**2**) had a much lower intensity. New weak bands appear which could not all be attributed. Traces of (**7**) are probably present.

After 24 h at 373 K the bands due to (**7**) increased considerably while those due to (**2**) faded. The latter compound disappears completely after heating at 393 K for 25 h. A further increase of temperature to 413 K does not seem to alter the situation significantly.

The i.r. spectrum of the solution recovered at the end of the experiment, at room temperature and atmospheric pressure, indicates the presence of compounds (**6**), (**7**) and traces of acetic acid.

$[Ru_4(CO)_8(MeCO_2)_4(PBu^n_3)_2]$ (**3**). The behaviour of a n-heptane solution of compound (**3**) under 10 MPa of carbon monoxide and hydrogen (1:1) has been investigated in the temperature range 293—413 K. After 24 h at room temperature the i.r. spectrum changed considerably and new bands appeared due to (**8**). Substantial changes in the i.r. spectrum take place also after heating the solution at 333 K for 8 d. The bands due to (**8**) tend to fade while the predominant absorptions are indicative of (**6**), (**7**), and acetic acid. An unattributed absorption is present at 1775vw cm^{-1}.

By prolonged heating (22 h) at 353 K the absorptions due to compound (**8**) disappear. There is a slight increase in intensity of the band at 1 775 cm^{-1}. By further stepwise increase in temperature, to 373, 393, and 413 K, a steady decrease in intensity of the absorptions due to (**7**) is registered compared with those due to (**6**). Acetic acid and the absorption at 1775 cm^{-1} had nearly disappeared at 373 K.

$[Ru_2(CO)_6(MeCO_2)_2]$ (**9**). The solution of compound (**9**) used in this investigation was prepared *in situ* by keeping a suspension of (**4**) in n-heptane under 5 MPa of carbon monoxide for 8 h at room temperature. Hydrogen was then added in order to have a 1:1 $CO:H_2$ gas mixture. The temperature range explored was 293—393 K.

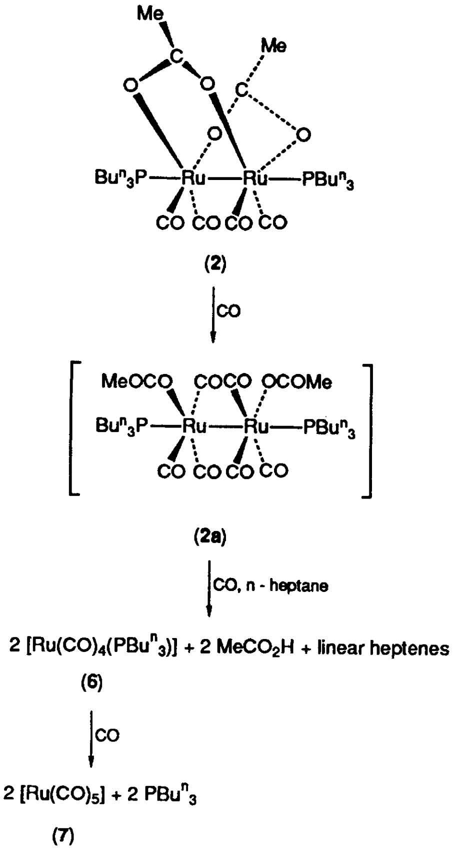
At 333 K, after 24 h, compound (**9**) was still the main product present. Other absorptions, besides those due to the carbon monoxide dissolved and acetic acid, were observed at 2 065 (sh) and 1 775vw cm^{-1}. After 18 h at 353 K the intensity of the absorptions at 1 775w and that due to acetic acid increased; broad absorptions at 2 039 and 2 008 cm^{-1} suggest the presence of (**7**) and (**9**). The presence of (**10**) is also suggested by an absorption at 2060s cm^{-1}: its other absorptions lie in a very crowded area. After another 10 h at 353 K the concentration of (**10**) seems to have slightly increased against a slight decrease of (**9**).

At 373 K, after 16 h, the intensity of the absorptions due to compounds (**7**) and (**10**) increases while there is a distinct decrease in those due to (**9**). The band at 1 775 cm^{-1} and the acetic acid absorptions also increase. The i.r. spectrum of a sample of the solution recovered after filtration from a small amount of solid, which separated on cooling and which could be identified as (**4**), showed absorptions due to (**7**), (**10**), acetic acid, and traces of (**9**). The band at 1 775 cm^{-1} was not present. The i.r. spectrum of the same solution after 48 h at room temperature under 0.1 MPa of CO is indicative of the presence of (**10**) and acetic acid. At 393 K under the initial pressure the absorptions due to (**9**) disappear.

The crude product was recovered after cooling and releasing the pressure as a suspension and was filtered. The i.r. spectrum, of the solid as a KBr pellet, shows absorptions characteristic of compound (**4**). The solution provides an i.r. spectrum with absorptions indicative of (**10**) and acetic acid.

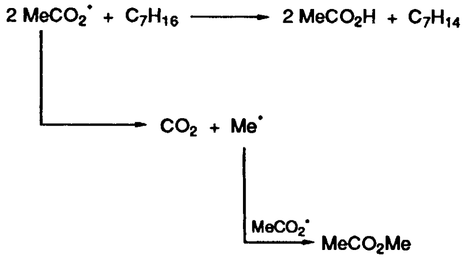
Conclusion

Polynuclear ruthenium(I) complexes (**2**)—(**4**) in n-heptane solution at appropriate temperatures (373 K) under carbon monoxide (5 MPa) evolve towards the formation of ruthenium(0) derivatives. Carbon monoxide causes cleavage of oxygen bridges between Ru atoms as in (**3**) (Scheme 3) and (**4**) (Scheme 4) before monodentation as in (**2**) of the acetato ligands bridging Ru atoms (Scheme 6). The formation of ruthenium(0) complexes could take place through an intermediate such as (**2a**).



Scheme 6.

The detection of acetic acid and linear heptenes in the crude product suggests hydrogen abstraction from the solvent (heptane) by the acetato radicals (Scheme 7).



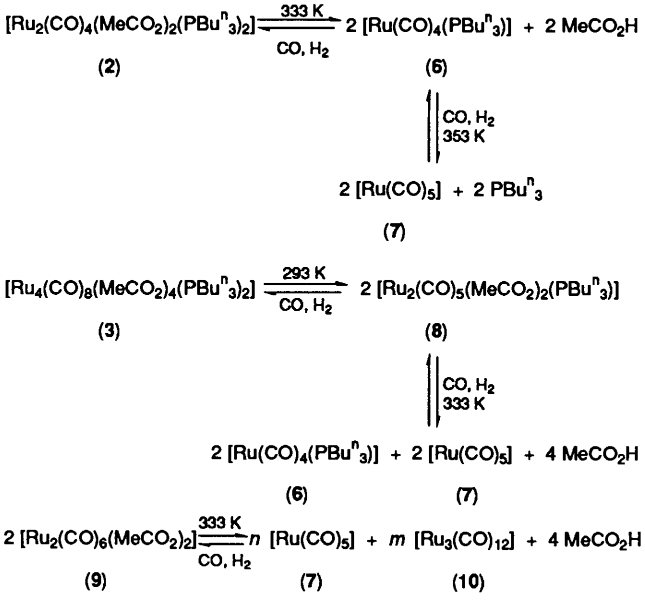
Scheme 7.

The formation of hydrides from compounds (**1**) and (**2**) under hydrogen has been previously shown.[1,5] From (**3**) and hydrogen however such a formation was not directly observed. The formation of (**2**) and (**4**) from (**3**) under hydrogen at 333 K, 90 K below the temperature necessary in its absence, suggests that hydridic species present in undetectable concentration are responsible for the activation of this phosphine redistribution equilibrium at lower temperature.

The behaviour of the ruthenium carbonyl acetato complexes under carbon monoxide and hydrogen (1:1) is analogous to that exhibited in the presence of carbon monoxide alone. Lower temperatures are necessary however in the presence of hydrogen to promote the same reactions. In both cases ruthenium(0) complexes are the final products. The acetato ligand displaced by carbon monoxide and found in the crude product as acetic acid is probably more easily formed in the presence of hydrogen because of intermediate hydridic species which, however, were not detected. Equilibria, involving ruthenium carbonyl hydrides (phosphine substituted or not), hydrogen, and carbon monoxide tend to move towards the decomposition of the hydride even under a few atmospheres of carbon monoxide.[4,13,14]

Carbon monoxide and hydrogen, when present together, generally act on the complexes investigated giving rise to reversible equilibria when the ligands set free remain accessible.

This information is of relevance when considering the mechanism of the hydroformylation of olefins promoted by the carbonyl carboxylates considered above, in view of the importance of the detection, in the crude product, of the catalytic precursors employed (Scheme 8).



Scheme 8. ($n + 3m = 4$)

Experimental

Instruments, materials and test procedures have been reported.[4] We give here a full description of one test. All the others were performed with the same procedure.

$[Ru_2(CO)_4(MeCO_2)_2(PBu^n{}_3)_2]$ (**2**) *and* CO.—A n-heptane solution (60 cm^3) of $[Ru_2(CO)_4(MeCO_2)_2(PBu^n{}_3)_2]$ (120 mg, 1.43×10^{-4} mol) was placed in a stainless-steel autoclave (125 cm^3) equipped with two stopcocks and a high-pressure gauge from which the air was previously evacuated. Then CO up to 5 MPa was added from a high-pressure source. The autoclave was connected by a stainless-steel low-volume (2 cm^3) coil to an i.r. cell, equipped with NaCl windows, capable of withstanding high pressure (20 MPa), which could be heated to 473 K. The coil was kept at the same temperature as that of the system. The solution present in the autoclave could therefore be transferred to the i.r. cell and examined by i.r. spectroscopy under reaction conditions. The solvent (n-heptane) bands were compensated using a variable-path i.r. cell.

The evolution of the systems was monitored by frequent registration of their spectra in order to follow the progressive changes in intensity of the significant bands of the species in solution. These absorptions for each of the starting complexes and for those possibly formed are reported, in the range 2 200—1 500 cm^{-1}, for each experiment.

After heating to 373 K new bands appeared at 2 059s, 1 983m, and 1 946 (sh) cm^{-1} characteristic of compound (**6**). After prolonged heating at 393 K the intensities of the absorptions due to (**6**) increased while those of the bands due to (**2**) decreased. No further changes were noticed after prolonged heating at 413 K. In the i.r. spectrum of the solution after cooling at room temperature under carbon monoxide pressure new bands appeared, besides those due to (**6**), at 2 038 and 2 002 cm^{-1} attributed to (**7**) and a band at 1 719 cm^{-1} due to acetic acid.

At the end of the test the autoclave was cooled at room temperature, the gases were vented, and the residual solution collected and analyzed by g.l.c. using a FFAP column kept at 333 K for 7 min and then heated to 403 K at a rate of 20 K min^{-1}. The solvent, acetic acid, and linear heptenes were identified in the solution. Acetic acid and linear heptenes were confirmed by g.l.c.–mass spectrometry (m.s.)

$[Ru_4(CO)_8(MeCO_2)_4(PBu^n{}_3)_2]$ (**3**) *and* CO.—A n-heptane solution (60 cm^3) of $[Ru_4(CO)_8(MeCO_2)_4(PBu^n{}_3)_2]$ (120 mg, 9.45×10^{-5} mol) was introduced in the autoclave together with CO up to 5 MPa. Compound (**3**) was readily transformed, at room temperature, into $[Ru_2(CO)_5(MeCO_2)_2(PBu^n{}_3)]$ (**8**), as shown by the i.r. absorptions at 2 076vs, 2 020vs, 1 983vs, 1 960w, and 1943m cm^{-1}. After prolonged heating of the solution at 373 K new absorptions appeared at 2 059m and 1 946s cm^{-1} due to (**6**) and at 2 037m and 2 006s cm^{-1} due to (**7**). After heating at 413 K, compounds (**6**) and (**7**) appear to be the only products in solution; at room temperature the intensity of the absorptions due to (**7**) increased considerably while an absorption at 1 719m cm^{-1} appeared, indicative of acetic acid. Repeated heating (413 K) and cooling (293 K) cycles of this solution caused reproducible shifts of the equilibria as shown by the reproduction of the i.r. spectra recorded, after several cycles, at these temperatures. Acetic acid and linear heptenes were identified in the solution at the end of the reaction, by g.l.c. and g.l.c.–m.s.

$[\{Ru_2(CO)_4(MeCO_2)_2\}_m]$ (**4**) *and* CO.—A suspension in n-heptane (60 cm^3) of $[\{Ru_2(CO)_4(MeCO_2)_2\}_m]$ (200 mg, 9.25×10^{-4} mol Ru) was introduced in the autoclave, and then CO up to 6 MPa. Compound (**4**) dissolved, at room temperature, giving $[Ru_2(CO)_6(MeCO_2)_2]$ (**9**) as indicated by the absorptions at 2 110s, 2 083vs, 2 039vs, and 2 010vs cm^{-1} (ref. 11) in the 2 200—1 600 cm^{-1} region. Heating this solution to 373 K does not cause detectable changes in its composition. New bands at 2 060m, 2 030 (sh), and 2 011 (sh) cm^{-1} appeared at 413 K, indicative of the presence of (**10**) and absorptions at 2 037m and 2 006s cm^{-1} characteristic of (**7**). These products are still present in solution after cooling at room temperature. The presence of free acetic acid was also evident (band at 1 719s cm^{-1}). The i.r. spectrum of this solution, kept at room temperature under 0.1 MPa of carbon monoxide, showed, after 8 h, only absorptions at 2 060vs, 2 030s, and 2 010m cm^{-1}, indicative of (**10**) which in fact precipitates, after prolonged standing, in the form of orange-yellow crystals. Acetic acid and linear heptenes were identified in the solution at the end of the reaction, by g.l.c. and g.l.c.-m.s.

$[Ru_4(CO)_8(MeCO_2)_4(PBu^{n}{}_3)_2]$ (**3**) *and* H_2.—Compound (**3**) (120 mg, 9.45×10^{-5} mol) in n-heptane solution (60 cm^3) was introduced in the autoclave, then hydrogen up to 5 MPa. After heating at 333 K for 18 h the i.r. spectrum showed absorptions at 2 021w and 1 949vw cm^{-1} indicative of (**2**). An increase in temperature led to further (**2**). At 373 K the amounts of the two compounds, after 100 h, are equivalent while at 393 K (**2**) is predominant.

$[Ru_2(CO)_4(MeCO_2)_2(PBu^{n}{}_3)_2]$ (**2**), CO, *and* H_2.—A n-heptane solution (60 cm^3) of $[Ru_2(CO)_4(MeCO_2)_2(PBu^{n}{}_3)_2]$ (**2**) (120 mg, 1.43×10^{-4} mol) was introduced in the autoclave, then CO and H_2 (1:1) up to 10 MPa, and finally heat was applied. After 22 h at 333 K new bands appeared at 2 059w, 1 983vw, and 1 946 (sh) cm^{-1} indicative of (**6**). Substantial changes in the spectrum of this solution resulted on heating at 353 K for 5 d. The intensity of the bands due to compound (**6**) became predominant while those of (**2**) were much less intense. New bands appeared at 2 079 (sh), 2 040 (sh), 2 000vw, 1 880w, 1 775w, 1 720w, and 1 640w cm^{-1}. Those at 2 040 and 2 000 cm^{-1} may be due to traces of (**7**). After 24 h at 373 K the bands due to (**7**) increased considerably while those due to (**2**) faded. The latter compound disappeared completely after heating at 393 K for 25 h. A further increase in temperature to 413 K does not seem to alter significantly the i.r. spectrum.

The i.r. spectrum of the solution recovered at the end of the experiment and therefore at room temperature and atmospheric pressure indicated the presence of compounds (**6**), (**7**), and traces of acetic acid. The solution was then examined as described above: acetic acid was identified by g.l.c. and g.l.c.–m.s.

$[Ru_4(CO)_8(MeCO_2)_4(PBu^{n}{}_3)_2]$ (**3**), CO, *and* H_2.—A n-heptane solution (60 cm^3) of $[Ru_4(CO)_8(MeCO_2)_4(PBu^{n}{}_3)_2]$ (120 mg, 9.45×10^{-5} mol) was introduced in the autoclave, then CO and H_2 (in the 1:1 ratio) up to 10 MPa. Heat was then applied gradually. After 24 h at room temperature new bands appeared at 2 079vs, 2 022vs, 1 980vs, 1 955 (sh), 1 945m, 1 910w, and 1 580m cm^{-1} due to (**8**). Substantial changes in the i.r. spectrum took place after heating the solution at 333 K for 8 d. The bands due to compound (**8**) tended to fade while the predominant absorptions are indicative of (**6**) and (**7**). Two absorptions at 1 775vw and 1720mw cm^{-1} were present, the last indicative of the presence of acetic acid.

By prolonged heating (22 h) at 353 K the absorptions due to compound (**8**) disappeared. There was a slight increase in intensity of the band at 1 775 cm^{-1}. Subsequent further stepwise increase in temperature, to 373, 393, and 413 K, resulted in a steady decrease in intensity of the absorptions due to (**7**) compared with those due to (**6**). The absorptions at 1 775 and 1 720 cm^{-1} had nearly disappeared at 373 K.

The crude product was examined by g.l.c. and g.l.c.-m.s. Acetic acid was identified in the solution.

$[Ru_2(CO)_6(MeCO_2)_2]$ (**9**), CO, *and* H_2.—The compound $[Ru_2(CO)_6(MeCO_2)_2]$ was synthesized *in situ* by treating, in a pressure vessel, a suspension of $[\{Ru_2(CO)_4(MeCO_2)_2\}_m]$ (**4**) (250 mg, 1.18 mmol Ru) in n-heptane (60 cm^3) with CO (5 MPa) at room temperature. The autoclave was rocked for 8 h, yielding a complete transformation of (**4**) into $[Ru_2(CO)_6(MeCO_2)_2]$ (**9**). Hydrogen was added to a total pressure of 10 MPa and the system was analyzed, in the temperature range 293—393 K, using the i.r. technique reported above.

After heating at 333 K for 24 h the i.r. spectrum of the solution showed, besides absorptions at 2 109s, 2 083vs, 2 038vs, 2 008vs, 1 954w, and 1 575 cm^{-1} due to (**9**), others at 2 065 (sh), 1 775vw, and 1 720 cm^{-1}. On increasing the temperature to 353 K, after 18 h, the intensity of the absorptions at 1 775 and 1 720 cm^{-1} increased. The large absorptions at 2 039vs and 2 008vs cm^{-1} seem to support the presence of compounds (**7**) and (**9**). The absorption at 2 060vs cm^{-1} suggests the formation of (**10**).

At 373 K, after 16 h, the intensity of the absorptions due to (**7**) and (**10**) increased while that of (**9**) decreased. A sample of this solution, collected from the autoclave and cooled at room temperature, yielded an orange-yellow solid; its i.r. spectrum, as a KBr pellet, showed absorptions at 2 049s, 1 994s, 1 966vs, 1 958s 1 925 (sh), 1 908 (sh), 1 553vs, 1 439m, 1 416s, and 1 402s cm^{-1} characteristic of compound (**4**). Acetic acid was identified in the filtrate analyzed by g.l.c. and g.l.c.-m.s.

At 393 K there is a lack of i.r. absorptions due to compound (**9**). The vessel was cooled at room temperature and the gases vented. The same products identified in the sample collected at 373 K were still present. Yellow-orange crystals of (**10**) separated from the solution cooled at 273 K.

$[Ru_2(CO)_4(MeCO_2)_2(PBu^{n}{}_3)_2]$ (**2**) *and* $[Ru(CO)_2(MeCO_2)_2(PBu^{n}{}_3)_2]$ (**1**) *under Nitrogen*.—A n-heptane solution (6 cm^3) of $[Ru_2(CO)_4(MeCO_2)_2(PBu^{n}{}_3)_2]$ (49.96 mg, 5.97×10^{-5} mol) and $[Ru(CO)_2(MeCO_2)_2(PBu^{n}{}_3)_2]$ (40.58 mg, 5.97×10^{-5} mol) was introduced under nitrogen in the pressure vessel, which was then heated gradually. Samples of the solution at various times were collected and examined by i.r. spectroscopy. At 373 K new bands appeared at 2 056, 1 991, 1 943, 1 678, 1 590, and 1 561 cm^{-1} attributed to (**5**)[3] and a band at 1 719 cm^{-1} attributed to acetic acid. At 393 K the bands due to compound (**5**) increased with respect to those of (**2**), but at 413 K (**2**) is the prevailing product in solution.

$[\{Ru_2(CO)_4(MeCO_2)_2\}_m]$ (**4**) and $[Ru(CO)_2(MeCO_2)_2(PBu^{n}{}_3)_2]$ (**1**) *under Nitrogen*.—A n-heptane solution (6 cm^3) of $[Ru(CO)_2(MeCO_2)_2(PBu^{n}{}_3)_2]$ (40.58 mg, 5.97×10^{-5} mol) was introduced in the pressure vessel together with $[\{Ru_2(CO)_4(MeCO_2)_2\}_m]$ (15.88 mg, 7.35×10^{-5} mol Ru). Then, after heating, samples of the solution were analyzed. At 373 K absorptions due to compounds (**1**)—(**3**) and (**5**) were observed besides a band at 1 719 cm^{-1} suggesting the presence of acetic acid. At 413 K (**2**) is the main component in the solution, (**3**) and acetic acid are also present, while (**1**) and (**5**) have disappeared.

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