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Characterisation of mixed metal clusters $HRuCo_2Rh(CO)_{12}$, $HRuCoRh_2(CO)_{12}$ and $H_2Ru_2CoRh(CO)_{12}$ by ^1H NMR spectroscopy

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Abstract

A mixture containing $HRuCo_3(CO)_{12}$, $HRuCo_2Rh(CO)_{12}$, $HRuCoRh_2(CO)_{12}$, $HRuRh_3(CO)_{12}$, $H_2Ru_2CoRh(CO)_{12}$ and $H_2Ru_2Rh_2(CO)_{12}$ has been prepared by the reaction of $[Rh(CO)_4]^-$ with $RuCo_2(CO)_{11}$. The new tetranuclear clusters have been characterised by ^1H NMR spectroscopy.

Introduction

Tetranuclear mixed metal carbonyls of cobalt, rhodium and iridium form a well defined group of cluster compounds, for which the influence of various metals on the cluster properties can be analyzed. Mixed metal carbonyl clusters of this type containing two different metals, mainly Co and Rh, Ru and Co and Ru and Rh, have been synthesized and characterized. Clusters of this type containing three different metals have received little attention. In this study the synthesis of such clusters by the reaction of $[Rh(CO)_4]^-$ [1] with $RuCo_2(CO)_{11}$ [2] and their NMR characterisation are described. These complexes can be expected to be of value in studies of heterosite reactivity, since they have similar carbonyl geometries but different metal combinations.

Results and discussion

Synthesis

Several metal combinations are formed in a reaction that at first sight could be expected to involve simple capping of the $RuCo_2$ triangle by the Rh unit; the products are the new clusters $HRuCo_2Rh(CO)_{12}$, $HRuCoRh_2(CO)_{12}$ and $H_2Ru_2CoRh(CO)_{12}$, along with $HRuCo_3(CO)_{12}$, $HRuRh_3(CO)_{12}$, and $H_2Ru_2Rh_2(CO)_{12}$. The various metal combinations are obviously formed through fragmentation and recombination reactions following the first capping step. This type of reconstruction of the metal core has been observed previously in metal exchange reactions [3].

The proportions of the various clusters depend on the relative amounts of the starting materials. An increase in the mole ratio $[Rh(CO)_4]^-/RuCo_2(CO)_{11}$ resulted in an increase in the proportion of $HRuRh_3(CO)_{12}$ (in particular), $HRuCoRh_2(CO)_{12}$, and $H_2Ru_2Rh_2(CO)_{12}$. The relative amounts of the clusters are also temperature dependent. When the synthesis was carried out with equimolar starting materials at ca. −60°C up to stage of the H_3PO_4 treatment (see Experimental section) the proportions of $HRuCo_2Rh(CO)_{12}$ and $HRuCoRh_2(CO)_{12}$ in the products were 50–70% and 20–30%, respectively. This implies that the reaction sequence is initiated by capping of $RuCo_2(CO)_{11}$ by $[Rh(CO)_4]^-$. Subsequent metal exchange-type reactions could then lead to the other clusters.

The assumption that the metal combinations are formed before the acid treatment is supported by an experiment in which a mixture of $HRuCo_3(CO)_{12}$ and $HRuRh_3(CO)_{12}$ in CH_2Cl_2 was not found to undergo metal exchange reactions at room temperature.

Variable temperature ^1H NMR studies

The ^1H NMR spectra for the new clusters $HRuCo_2Rh(CO)_{12}$, $HRuCoRh_2(CO)_{12}$ and $H_2Ru_2CoRh(CO)_{12}$ were obtained from the spectrum of a mixture of the six clusters mentioned above. Of these six, the spectra of $HRuCo_3(CO)_{12}$ [4] and $H_2Ru_2Rh_2(CO)_{12}$ [5] have been described previously. The ^1H NMR data for $HRuRh_3(CO)_{12}$ were determined separately [6]. Thus the signals due to the three new clusters can be assigned. Chemical shifts, couplings, line widths, and H-exchange behaviour for $HRuCo_2Rh(CO)_{12}$, $HRuCoRh_2(CO)_{12}$ and $H_2Ru_2CoRh(CO)_{12}$ show trends that are consistent with those for the previously known compounds.

The ^1H chemical shifts and $^1J(Rh-H)$ coupling constants for the compounds are listed in Tables 1 and 2. The structures of the compounds are shown diagrammatically in Fig. 1.

$HRuRh_3(CO)_{12}$. The variable temperature ^1H NMR spectra of $HRuRh_3(CO)_{12}$ were measured separately from pure samples (Fig. 2). Below −10°C the spectrum consists of a doublet at −18.4 ppm ($^1J(Rh-H)$ 16.8 Hz) and of a quartet at −15.4 ppm ($^1J(Rh-H)$ 11.1 Hz), which correspond to edge-bridging $Ru_{ap}(\mu\text{-}H)Rh$ and face-bridging $Rh_3(\mu\text{-}H)$ hydrides (Fig. 1), respectively. These indicate the presence

Table 1

^1H Chemical shifts (TMS reference, −10°C, $CDCl_3$ solution)

	Face-bridging (basal)	Edge-bridging	
		(Ru–Rh edge)	(Ru–Ru edge)
$HRuCo_3(CO)_{12}$	−19.7		
$HRuCo_2Rh(CO)_{12}$	−18.4	−17.5 [a]	
$HRuCoRh_2(CO)_{12}$	−16.8	−17.9 [a]	
$HRuRh_3(CO)_{12}$	−15.5	−18.4 [a]	
$H_2Ru_2CoRh(CO)_{12}$		−18.5	−20.5
$H_2Ru_2Rh_2(CO)_{12}$		−19.2	−21.3

[a] Represents 70–75% of the total intensity of the two signals.

Table 2

${}^{1}J$(Rh–H) coupling constants (Hz, −60 °C, $CDCl_3$ solution)

	Face-bridging (basal)	Edge-bridging (Ru–Rh)
$HRuCo_2Rh(CO)_{12}$		16.8
$HRuCoRh_2(CO)_{12}$	11.1	16.8 (8.0 Hz, 10 °C)
$HRuRh_3(CO)_{12}$	11.1 (−40 °C)	16.8 (5.3 Hz, 0 °C)
$H_2Ru_2CoRh(CO)_{12}$		16.8
$H_2Ru_2Rh_2(CO)_{12}$		17.3

of two isomeric forms of the compound in solution. The integral of the Ru(μ-H)Rh signal corresponds to ca. 75% of the total intensity. At +2 °C irradiation of the Ru(μ-H)Rh signal causes total disappearance of the $Rh_3(\mu\text{-}H)$ signal, and irradiation of the $Rh_3(\mu\text{-}H)$ peak significantly decreases the height of the Ru(μ-H)Rh signal. This indicates that there is H-exchange between these two positions, and that it is fast enough for the transfer of the saturation on the NMR time scale. At +2 °C the Ru(μ-H)Rh signal becomes a well-resolved quartet owing to rapid H-exchange between the three equivalent Ru_{ap}–Rh edges (time averaged ${}^{1}J$(Rh–H) 5.3 Hz). Such exchange has been previously observed between the two equivalent Ru_{ap}–Rh edges of $H_2Ru_2Rh_2(CO)_{12}$. It is noteworthy that while the hydride in $HRuCo_3(CO)_{12}$ occupies the basal Co_3 face, only 25% of $HRuRh_3(CO)_{12}$ is in the corresponding $Rh_3(\mu\text{-}H)$ form. This can be accounted for in terms of the fact that the Ru–Rh edge is a much more favourable position for a edge-bridging hydride than a Ru–Co edge, and edge-bridging Ru(μ-H)Co hydrides are rare. The crystal structure of $HRuRh_3(CO)_{12}$ was disordered, and gave no clear indication of the hydride position [7].

$HRuCoRh_2(CO)_{12}$. Below −10 °C there is a doublet at −17.9 ppm (${}^{1}J$(Rh–H) 16.8 Hz) due to the $Ru_{ap}(\mu\text{-}H)Rh$ hydride and a smaller signal at −16.8 ppm due to the face bridging $CoRh_2(\mu\text{-}H)$ hydride (Fig. 3). As in the case of $HRuRh_3(CO)_{12}$, the H-exchange between the isomeric forms was evidenced by irradiation experiments. At −60 °C the latter is a well resolved triplet owing to coupling with the two equivalent basal Rh atoms (${}^{1}J$(Rh–H) 11.1 Hz). However, there is still some line broadening caused by the quadrupolar Co. At +10 °C the Ru(μ-H)Rh signal also becomes a triplet because of a rapid H-exchange between the two equivalent Ru–Rh edges (time-averaged ${}^{1}J$(Rh–H) 8.0 Hz). There is no indication of $Ru_{ap}(\mu\text{-}H)Co$ bonding.

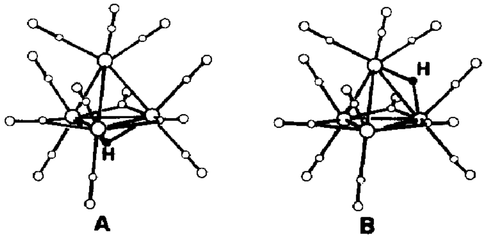

Fig. 1. The carbonyl geometry and the face-bridging (A) and edge-bridging (B) hydride positions. The ruthenium atom occupies the apical metal site in all the compounds.

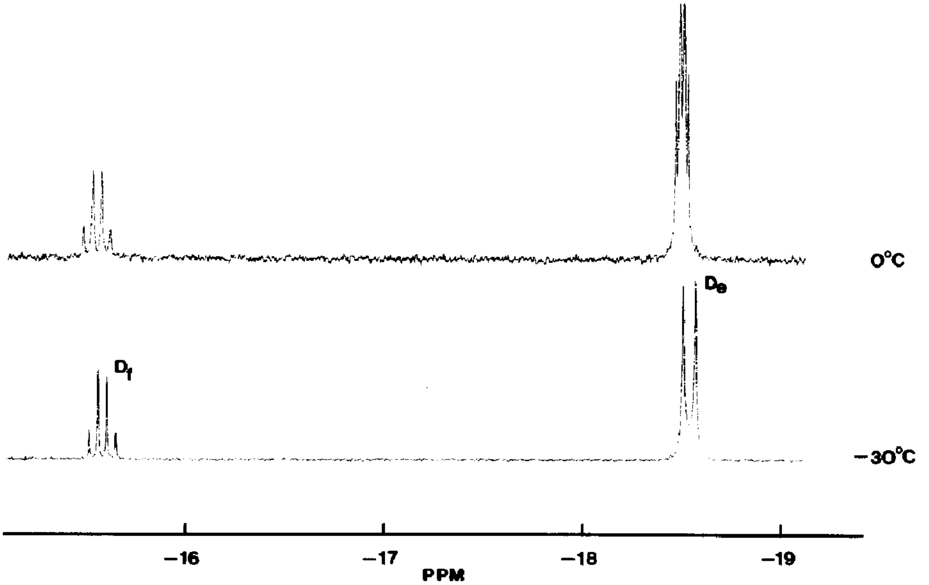

Fig. 2. ^{1}H NMR spectra of $HRuRh_3(CO)_{12}$ at −30 °C and 0 °C (see Fig. 3 for the meaning of D_e and D_f).

$HRuCo_2Rh(CO)_{12}$. Below +10 °C there is a doublet at −17.5 ppm (^1J(Rh–H) 16.8 Hz) due to the $Ru_{ap}(\mu$-H)Rh hydride and a broad peak at −18.4 ppm due to the $Co_2Rh(\mu$-H) face-bridging hydride. H-exchange between the two positions was

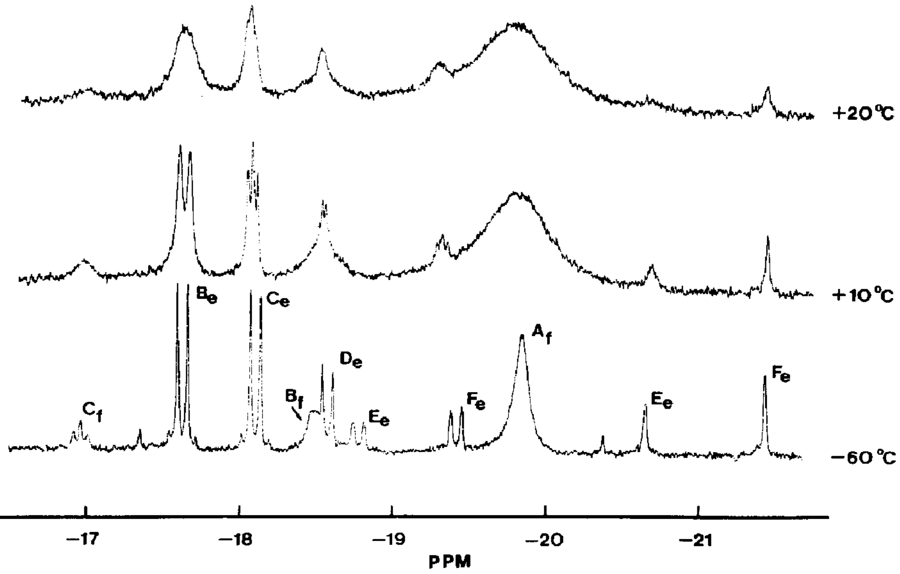

Fig. 3. Variable temperature ^{1}H NMR spectra of the mixture containing $HRuCo_3(CO)_{12}$ (**A**), $HRuCo_2Rh(CO)_{12}$ (**B**), $HRuCoRh_2(CO)_{12}$ (**C**), $HRuRh_3(CO)_{12}$ (**D**), $H_2Ru_2CoRh(CO)_{12}$ (**E**), and $H_2Ru_2Rh_2(CO)_{12}$ (**F**). Indexes e and f refer to edge-bridging and face-bridging hydride ligands. The signal D_f is omitted to avoid extending the scale (see Fig. 2). The signals of **B** and **C** coalesce at +40 °C into a broad peak (−17.7 ppm), which sharpens slightly at +50 °C, but is still broad +70 °C.

again observed (Fig. 3). The former signal corresponds to ca. 75% of the total intensity. At $-60\,^{\circ}C$ the $Co_2Rh(\mu\text{-}H)$ signal becomes narrower, but the $^1J(Rh\text{-}H)$ coupling is still not observable, though the flat top of the peak suggests that such coupling is present. Again there is no evidence for a $Ru(\mu\text{-}H)Co$ edge-bridging hydride.

$H_2Ru_2CoRh(CO)_{12}$. As in $H_2Ru_2Rh_2(CO)_{12}$ the hydrides occupy the Ru–Ru edge (-20.5 ppm) and the Ru–Ru edge (-18.5 ppm, $^1J(Rh\text{-}H)$ 16.8 Hz at $-60\,^{\circ}C$). Below $-10\,^{\circ}C$ the spectra of $H_2Ru_2Rh_2(CO)_{12}$ and $H_2Ru_2CoRh(CO)_{12}$ (Fig. 3) are similar except for the 0.7–0.8 ppm highfield shift for the signals of the latter compound. A weak coupling between the hydrides ($^3J(H(1)\text{-}H(2))$ 2 Hz) could be seen in the signals of both compounds. At $+2\,^{\circ}C$ irradiation of either of the signals caused more or less total disappearance of the other signal, indicating that there is mutual exchange of the two hydrides. Similar behaviour was observed for $H_2Ru_2Rh_2(CO)_{12}$. No such effects could be seen upon irradiation at $-20\,^{\circ}C$. It is noteworthy that although there was H-exchange between the two Ru–Rh edges in $H_2Ru_2Rh_2(CO)_{12}$, giving rise to a triplet signal at $0\,^{\circ}C$, the $Ru(\mu\text{-}H)Rh$ signal of $H_2Ru_2CoRh(CO)_{12}$ remained a well-resolved doublet at these temperatures. No evidence of $Ru(\mu\text{-}H)Co$ or face bridging $RuCoRh(\mu\text{-}H)$ hydrides was found at these low temperatures. This contrasts with observations on $H_2Ru_2Co_2(CO)_{12}$, for which the other hydride was found to bridge the basal $RuCo_2$ face [8]. The hydride again prefers to bridge a Ru–Rh edge rather than a Ru–Co edge or a basal face. At room temperature the signals are no larger visible because of line broadening.

Comparison of the compounds. In respect of the valence electrons all the six compounds are isoelectronic, with similar arrangement of carbonyl ligands, and show many similarities in the behaviour of the hydride ligands. They are therefore of interest for studies of effects caused by a change of one metal atom in a cluster. In the present case the differences between the compounds are caused by replacement of basal cobalt atoms by rhodium atoms. First there are gradual changes in the proton chemical shifts. The resonance of the face-bridging hydride in $HRuCo_xRh_{3-x}(CO)_{12}$ ($x = 0\text{–}3$) changes by ca. 1.3 ppm to higher frequency, when a basal cobalt atom is replaced by a rhodium atom. Similar additive changes have been observed previously for the ^{31}P resonances of the gold phosphine derivatives of these compounds, $Ph_3PAuRuCo_xRh_{3-x}(CO)_{12}$ ($x = 0\text{–}3$), where the gold phosphine bridges the basal metal face [9]. The change in the proton chemical shift is not unexpected since the hydrides are directly bonded to the metal which is replaced.

In contrast there is a ca. 0.5 ppm shift to lower frequency of the $Ru(\mu\text{-}H)Rh$ hydride resonances upon this replacement of cobalt by rhodium. Similarly, both the $Ru(\mu\text{-}H)Ru$ and $Ru(\mu\text{-}H)Rh$ resonances of $H_2Ru_2CoRh(CO)_{12}$ are at ca. 0.7 ppm higher frequencies than those for $H_2Ru_2Rh_2(CO)_{12}$. In $H_2Ru_2Co_2(CO)_{12}$ the $Ru(\mu\text{-}H)Ru$ resonance is at -20.36 ppm, which does not fit with the trends observed above. This is not unexpected, however, since $H_2Ru_2Co_2(CO)_{12}$ differs structurally from the Rh-containing analogue in containing a face-bridging $RuCo_2(\mu\text{-}H)$ hydride. In these three compounds the effects are caused by changing a metal atom that is not directly bonded to the hydride ligand. The NMR results indicate that in isostructural clusters it is possible to observe some order in the changes in NMR parameters caused by changes of metal atoms, and these reflect the electronic changes. However, when the change of a metal atom offers possibilities of new types of bonding, structural changes may occur.

Experimental

Literature methods were used to prepare $[Rh(CO)_4]^-$ [10,11], $[Co(CO)_4]^-$ [12] and $RuCo_2(CO)_{11}$ [13]. Other reagents were obtained from commercial sources. Except for chromatographic separations reactions and manipulations were carried out under N_2 by Schlenk tube techniques. ^1H NMR spectra were recorded on a Bruker AM-250 spectrometer with $CDCl_3$ as the solvent, except for the highest temperature spectra which were recorded for solutions in C_6D_6. Chemical shifts are relative to TMS. Infrared spectra were recorded on a Nicolet 20SXC FT-IR-spectrometer.

Syntheses. $[Rh(CO)_4]^-$ was prepared from $Rh_2(CO)_4Cl_2$ (300 mg, 0.77 mmol) in tetrahydrofuran (thf) under a CO atmosphere with sodium as the reducing agent. When the mixture was stirred overnight the solution became colourless. (This is not easy to see since finely divided black solid was also formed.) The solution was filtered under nitrogen and added to a thf solution of $RuCo_2(CO)_{11}$ (408 mg, 0.77 mmol). It was assumed that ca. 50% of the rhodium was incorporated in the $[Rh(CO)_4]^-$. The solution was stirred for 1 h, during which a slight change of colour to brownish red was observed. The solvent was evaporated off in vacuo and the solid residue was treated with 3 ml of 85% H_3PO_4. The product was extracted with a CH_2Cl_2/hexane 1/3 mixture (180 ml). After evaporation of the solvent 460 mg of solid was left. According to ^1H NMR spectra the percentages of the various hydride clusters were: $HRuCo_3(CO)_{12}$ 53; $HRuCo_2Rh(CO)_{12}$ 23; $HRuCoRh_2(CO)_{12}$ 16; $HRuRh_3(CO)_{12}$ 4; $H_2Ru_2CoRh(CO)_{12}$ 2; and $H_2Ru_2Rh_2(CO)_{12}$ 2%.

Increasing the amount of $[Rh(CO)_4]^-$ with respect to $RuCo_2(CO)_{11}$ increased the proportion of $HRuRh_3(CO)_{12}$ in particular, along with those of $HRuCoRh_2(CO)_{12}$ and $H_2Ru_2Rh_2(CO)_{12}$. For example with Rh/$RuCo_2$ ratio 3/1 the percentages of the six clusters were $HRuCo_3(CO)_{12}$ 8; $HRuCo_2Rh(CO)_{12}$ 12; $HRuCoRh_2(CO)_{12}$ 32; $HRuRh_3(CO)_{12}$ 32; $H_2Ru_2CoRh(CO)_{12}$ 1; and $H_2Ru_2Rh_2(CO)_{12}$ 7%.

Attempts were made to separate the components by chromatography on silica. Hexane eluted a small amount of $Ru_3(CO)_{12}$ followed by a dark band of the tetranuclear clusters. The latter could not, however, be separated from one another, and the rhodium-containing compounds decomposed during the separation so that with a long column (40 cm) only $HRuCo_3(CO)_{12}$ was collected. Attempts to separate the components on Florisil or aluminum oxide were unsuccessful. The possible presence of $Co_4(CO)_{12}$ or $Rh_4(CO)_{12}$ could not be confirmed by IR spectroscopy because of many peaks in the 2050–2070 and 1850–1890 cm^{-1} ranges.

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