

Trends in Hydride Positions, ^1H Chemical Shifts and Reactivity with Phosphines in $\text{HRuCo}_x\text{Rh}_{3-x}(\text{CO})_{12}$ ($x = 0-3$) and $\text{H}_2\text{Ru}_2\text{Co}_x\text{Rh}_{2-x}(\text{CO})_{12}$ ($x = 0-2$) Clusters

Jouni Pursiainen and Tapani A. Pakkanen

Department of Chemistry, University of Joensuu, P.O. Box 111, SF-80101 Joensuu, Finland

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Hydride positions, reactivity with phosphines and ^1H chemical shifts of $\text{HRuCo}_x\text{Rh}_{3-x}(\text{CO})_{12}$ ($x = 0-3$) and $\text{H}_2\text{Ru}_2\text{Co}_x\text{Rh}_{2-x}(\text{CO})_{12}$ ($x = 0-2$) are shown to have systematic trends with respect to the metal combination of the clusters.

Tetranuclear dodecacarbonyl mixed metal clusters of cobalt, rhodium and ruthenium form an exceptionally large and well defined group of isoelectronic cluster compounds. Parent carbonyl clusters of this group have been synthesized and characterized with few exceptions. These compounds can be expected to be of importance in studying the influence of different metal combinations on the cluster properties.

In this work the hydride positions, reactivity with phosphines and ^1H chemical shifts of $\text{H}_2\text{Ru}_2\text{Co}_x\text{Rh}_{2-x}(\text{CO})_{12}$ ($x = 0-2$) and $\text{HRuCo}_x\text{Rh}_{3-x}(\text{CO})_{12}$ ($x = 0-3$) clusters (Figs. 1 and 2) and some of their phosphine derivatives have been studied. Their properties are shown to have systematic trends with respect to the metal combination of the clusters.

Experimental

Reactions and manipulations, except chromatographic separations, were carried out under N_2 using standard Schlenk tube techniques. The products, however, are not especially sensitive to air. ^1H NMR spectra were recorded on a Bruker AM-250 spectrometer using CDCl_3 as the solvent. All the data in Tables 1–3 were recorded at 0°C . Chemical shifts are relative to TMS. Infrared spectra were recorded on a Nicolet 20SXC FT-IR spectrometer.

Syntheses. The preparation of the parent $\text{HRuCo}_x\text{Rh}_{3-x}(\text{CO})_{12}$ ($x = 0-3$) clusters^{1,2,3} as well as $\text{HRuCo}_3(\text{CO})_{11}(\text{PPh}_3)$,⁴ $\text{HRuCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$,^{2,4} and $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$ ² has been published previously. When cluster mixtures are discussed, the molecular formulas are replaced by metal cores.

General procedure. Parent clusters and phosphines were dissolved in ca. 20 ml of CH_2Cl_2 and the solutions stirred at room temperature for 1 h. A clear change in the IR spectrum was observed. The solvent was then evaporated and

the products were separated by chromatography on silica. Hexane eluted first a yellow band (usually not characterised; in those cases where the IR spectrum was measured, the peaks for $\text{Ru}_3(\text{CO})_{12}$ were present, sometimes together with a few other peaks). Hexane usually also eluted a reddish band containing unreacted parent clusters. Mono-substituted products were eluted by a hexane/ CH_2Cl_2 (5:1) mixture, and disubstituted derivatives by a 1:1 mixture. The yields were determined by weighing after evaporation of the eluent. No general method has been found to isolate the clusters that are not separable by this chromatographic procedure. Amounts of some of the clusters adequate for spectroscopic measurements could be isolated by careful thin-layer chromatography, but TLC experiments were usually unsuccessful. The relative amounts of cluster mixtures are based on ^1H NMR measurement unless otherwise stated. This means that the amounts of, e.g., $\text{Co}_x\text{Rh}_{4-x}(\text{CO})_{12}$ ($x = 0-4$) clusters and their derivatives were not determined. The data in Table 1 were collected with an acquisition time of 1.638 s with no relaxation delay. No change of relative intensities was observed in experiments with relaxation delays of up to 8 s.

$\text{HRuCo}_3(\text{CO})_{11}(\text{PMe}_3)$. 200 mg (0.33 mmol) of $\text{HRuCo}_3(\text{CO})_{12}$ and 34 μl (0.33 mmol) of PMe_3 were used. Yield of the reddish title compound was 168 mg (0.25 mmol, 76%). Small fractions eluted by hexane/ CH_2Cl_2 2:1 mixture were not characterised. ν_{CO} (cm^{-1}): 2076m, 2041s, 2030vs, 2020w, 1980m, 1879m, 1872m.

$\text{HRuCo}_3(\text{CO})_{11}(\text{PMe}_2\text{Ph})$. 200 mg (0.33 mmol) of $\text{HRuCo}_3(\text{CO})_{12}$ and 46.5 μl (0.33 mmol) of PMe_2Ph were used. Yield of the reddish title compound was 170 mg (0.23 mmol, 77%). ν_{CO} (cm^{-1}): 2081m, 2043vs, 2031vs, 2010s, 1857m, 1849m.

$\text{HRuCo}_3(\text{CO})_{11}(\text{PMePh}_2)$. 200 mg (0.33 mmol) of $\text{HRuCo}_3(\text{CO})_{12}$ and 65 μl (0.33 mmol) of PMePh_2 were used. Yield

of the reddish title compound was 235 mg (0.30 mmol, 90 %). ν_{CO} (cm^{-1}): 2082s, 2045vs, 2032vs, 2011s, 1869m, 1848m.

HRuRh₃(CO)₁₁(PMe₃). 133 mg (0.18 mmol) of impure HRuRh₃(CO)₁₂ and 13 μl (0.13 mmol) of PMe₃ were used. In this and in the following reactions, formally less than an equimolar amount of the phosphine was used because of the impurities and also because of the ease of formation of disubstituted products. Yield of the reddish monosubstituted product was 40 mg (0.05 mmol). ν_{CO} (cm^{-1}): 2086m, 2064m, 2057vs, 2052vs, 2033m, 2021m, 2003m, 1988m, 1869s.

HRuRh₃(CO)₁₁(PMe₂Ph). 150 mg (0.20 mmol) of impure HRuRh₃(CO)₁₂ and 23 μl (0.16 mmol) of PMe₂Ph were used. Yield of the title compound was 50 mg (0.06 mmol). 14 mg of HRuRh₃(CO)₁₀(PMe₂Ph)₂ was eluted by a 1:1 hexane/CH₂Cl₂ mixture. ν_{CO} (cm^{-1}): 2085m, 2057vs, 2052s, 2031m, 2021m, 2003m, 1988w, 1868m.

HRuRh₃(CO)₁₁(PMePh₂). 150 mg (0.20 mmol) of impure HRuRh₃(CO)₁₂ and 33 μl (0.16 mmol) of PMePh₂ were used. Yield of the title compound was 84 mg (0.09 mmol). 34 mg of HRuRh₃(CO)₁₀(PMePh₂)₂ was eluted by a 1:1 hexane/CH₂Cl₂ mixture. ν_{CO} (cm^{-1}): 2086m, 2065w, 2058vs, 2052vs, 2031m, 2021m, 2004m, 1988w, 1871m.

HRuCo₃(CO)₁₁(PPh₃). 150 mg (0.20 mmol) of impure HRuRh₃(CO)₁₂ and 40 mg (0.15 mmol) of PPh₃ were used. Yield of the reddish title compound was 73 mg (0.07 mmol). 13 mg of HRuRh₃(CO)₁₀(PPh₃)₂ was eluted by a 1:1 hexane/CH₂Cl₂ mixture. ν_{CO} (cm^{-1}): 2085m, 2058vs, 2052vs, 2030s, 2004m, 1988m, 1886m, 1878m, 1869m.

Mixture containing HRuCo₂Rh(CO)₁₁(PMe₃) and HRuCoRh₂(CO)₁₁(PMe₃). 450 mg of parent cluster mixture, in which the relative amounts were 45 % RuCo₃, 12 % RuCo₂Rh, 16 % RuCoRh₂, 21 % RuRh₃ and 6 % Ru₂Rh₂ (totally ca. 0.7 mmol), and 50 μl (0.50 mmol) of PMe₃ were used. In addition to the effects mentioned above, the use of less than an equimolar amount of phosphine decreased the relative amount of RuCo₃ derivatives, as a result of the higher reactivity of the rhodium-containing compounds. 110 mg of unreacted tetranuclear clusters were recovered. Yield of the monosubstituted mixture, which contained 13 % RuCo₃, 16 % RuCo₂Rh, 32 % RuCoRh₂, 35 % RuRh₃ and 4 % Ru₂Rh₂, was 154 mg (ca. 0.21 mmol). 41 mg of disubstituted clusters were obtained.

Mixture containing HRuCo₂Rh(CO)₁₁(PMe₂Ph) and HRuCoRh₂(CO)₁₁(PMe₂Ph). 438 mg of parent cluster mixture (ca. 0.6 mmol), which was prepared in a manner similar to that in the previous reaction, and 88 μl (0.62 mmol) of PMe₂Ph were used. The yield of the monosubstituted products was 106 mg (ca. 0.11 mmol). RuCoRh₂ and

RuRh₃ were dominant, and smaller amounts of RuCo₂Rh, RuCo₃ and obvious Ru₂Rh₂ derivatives were obtained.

Mixture containing HRuCo₂Rh(CO)₁₁(PMePh₂) and HRuCoRh₂(CO)₁₁(PMePh₂). 432 mg of parent cluster mixture (ca. 0.65 mmol), which was prepared in a manner similar to that in the previous reaction, and 110 μl (0.55 mmol) of PMePh₂ were used. The yield of the monosubstituted products was 164 mg (ca. 0.19 mmol), the relative amounts being RuCo₃ 20 %, RuCo₂Rh 29 %, RuCoRh₂ 39 %, RuRh₃ 10 %. A small amount of uncharacterised derivatives was also obtained.

Mixture containing HRuCo₂Rh(CO)₁₁(PPh₃) and HRuCoRh₂(CO)₁₁(PPh₃). 612 mg (ca. 0.85 mmol) of parent cluster mixture (relative amounts RuCo₃ 15 %, RuCo₂Rh 47 %, RuCoRh₂ 23 %, RuRh₃ 9 %, Ru₂CoRh 3 % and Ru₂Rh₂ 3 %) and 200 mg of PPh₃ (0.76 mmol) were used. In this case the reaction was carried out at -60°C . At room temperature, the main difference would have been the higher relative amount of HRuCo₃(CO)₁₁(PPh₃) (see the reaction at -90°C). The yield of the monosubstituted compounds was 176 mg (ca. 0.18 mmol), the relative amounts being RuCo₃ 6 %, RuCo₂Rh 63 %, RuCoRh₂ 19 %, RuRh₃ 12 % and Ru₂Rh₂ 0.6 %. A small ¹H NMR signal possibly due to Ru₂CoRh was also observed. 54 mg of disubstituted derivatives were obtained.

HRuCo₂Rh(CO)₁₀(PPh₃)₂. 220 mg of HRuCo_xRh_{3-x}(CO)₁₁(PPh₃) ($x = 2, 3$) mixture, containing 26 % RuCo₃ and 74 % RuCo₂Rh (ca. 0.25 mmol), and 60 mg (0.22 mmol) of PPh₃ were heated under reflux in THF for 1 h (no significant reaction was observed on stirring the starting clusters for 1 h at room temperature in CH₂Cl₂). Hexane/CH₂Cl₂ 4:1 mixture was used as eluent in the chromatographic separation. The first brown fraction of monosubstituted compounds contained 71 % RuCo₃ and 29 % RuCo₂Rh (31 mg, 0.03 mmol). In the second fraction of dark reddish-brown disubstituted clusters, only the title compound was present in significant amount according to ¹H NMR spectrum. Yield 128 mg (0.11 mmol). ν_{CO} (cm^{-1}): 2065vs, 2034w, 2019vs, 2013vs, 1995s, 1854m, 1834m.

HRuCoRh₂(CO)₁₀(PPh₃)₂. The synthesis is described in the next section ν_{CO} (cm^{-1}): 2064vs, 2018s, 2012s, 1966m, 1854m.

Site selective reactions. HRuCo_xRh_{3-x}(CO)₁₂ ($x = 0-3$) + PPh₃, -90°C , CH₂Cl₂. 677 mg (ca. 1.0 mmol) of the parent cluster mixture (relative amounts according to ¹H NMR spectrum: RuCo₃ 24 %, RuCo₂Rh 29 %, RuCoRh₂ 23 %, RuRh₃ 14 %, Ru₂CoRh 5 % and Ru₂Rh₂ 5 %; the amounts of Co_xRh_{4-x}(CO)₁₂ ($x = 0-4$) clusters were not estimated) was dissolved in 60 ml of CH₂Cl₂ and cooled to ca. -90°C in an ethanol bath which was cooled by liquid nitrogen. The solution was stirred with 270 mg (1.0 mmol) of PPh₃ for

2 h. Solvent was then evaporated *in vacuo* and the products were separated by chromatography on silica. Hexane eluted first a yellow uncharacterised fraction, followed by a red fraction of tetranuclear parent clusters (30 mg, relative amounts RuCo₃ 63 %, RuCo₂Rh 25 %, Ru₂CoRh 2.5 % and Ru₂Rh₂ 8 %). Hexane/CH₂Cl₂ 5:1 mixture then eluted a red band of monosubstituted derivatives (143 mg (ca. 0.16 mmol), the relative amounts of hydride clusters being: RuCo₃ 2.4 %, RuCo₂Rh 47 %, RuCoRh₂ 19 %, RuRh₃ 30 % and Ru₂Rh₂ 1.9 %), and 1:1 mixture eluted a brownish-red band of disubstituted compounds (63 mg; relative amounts RuCoRh₂ 15 %, RuRh₃ 72 % and uncharacterised products 13 %).

$\text{HRuCo}_x\text{Rh}_{3-x}(\text{CO})_{11}(\text{PPh}_3)$ ($x=0-2$) + PPh_3 , CH_2Cl_2 , +25°C. 143 mg (ca. 0.16 mmol) of monosubstituted derivatives from the previous reaction was dissolved in CH₂Cl₂ and stirred with 25 mg (0.1 mmol) of PPh₃ at room temperature for 1 h. Solvent was then evaporated *in vacuo* and the products were separated by chromatography on silica. Hexane/CH₂Cl₂ 5:1 mixture eluted a brownish-red band of unreacted compounds (62 mg; relative amounts according to ¹H and ³¹P NMR spectra: RuCo₃ 4 %, RuCo₂Rh 64 % and Co₃Rh 32 %). 1:1 mixture eluted a red band of disubstituted clusters (70 mg, relative amounts RuRh₃ 68 %, RuCoRh₂ 26 %, uncharacterised 6 %).

$\text{HRuCo}_x\text{Rh}_{3-x}(\text{CO})_{10}(\text{PPh}_3)$ ($x=0,1$) + PPh_3 , THF, under reflux. 180 mg (ca. 0.15 mmol) of disubstituted compounds (relative amounts of hydride clusters: RuCoRh₂ 60 % and RuRh₃ 40 %) was dissolved in THF and heated under reflux for 1 h with 20 mg (0.08 mmol) of PPh₃. After evaporation of the solvent the products were separated by chromatography on silica. Hexane/CH₂Cl₂ 1:1 mixture eluted first a yellow fraction followed by a brownish-red band (113 mg, 0.1 mmol, 97 % pure RuCoRh₂ with respect to RuRh₃; ³¹p NMR revealed some uncharacterised impurities, so that the real purity is ca. 80 %). Finally, a smaller (23 mg) red band was eluted.

Discussion

Site selective reactions. There are several examples of phosphines coordinating to rhodium in Co–Rh⁵ and Ru–Rh^{2,6} mixed metal clusters. It has been shown recently that in trinuclear (μ_3 -butyne)FeCo₂(CO)₉ and (μ_3 -X)RuCo₂(CO)₉ (X = alkyne, vinylidene, sulphur, phosphinidene) mixed-metal clusters, the metals show a tendency for substitution in the order Fe < Co < Ru.⁷

In the phosphine substitution reactions of this work the reactivity of basal rhodium relative to basal cobalt is so high that it could be used as a means of separation of clusters with different metal combinations (Fig. 3). No reactions were observed with the apical ruthenium atom. In each reaction the essential feature is that rhodium sites react with PPh₃ but corresponding cobalt sites do not. Although quantitative site selectivity was not achieved, this kind of separation procedure is important since the clusters with the same number of phosphine groups were difficult to separate even by thin layer chromatography. The structural similarity of the compounds is emphasized by the observation that they easily co-crystallise.⁸ Reactivity towards other ligands is likely to produce different trends which also could be used for separation purposes.

In the first reaction at –90°C there is practically no reaction between HRuCo₃(CO)₁₂ and PPh₃, whereas all the clusters containing Rh form derivatives in which the phosphines are coordinated to rhodium. The unreacted parent cluster can be easily separated from the phosphine derivatives chromatographically. Disubstituted compounds are easily formed from compounds containing more than one rhodium atom, although unreacted HRuCo₂Rh(CO)₁₂ is present.

In the second reaction at room temperature the monosubstituted HRuCo₂Rh(CO)₁₁(PPh₃) does not react, but the corresponding clusters with unoccupied rhodium sites react forming disubstituted derivatives. HRuCo₂Rh(CO)₁₁(PPh₃), which remained unreacted above, reacts easily with

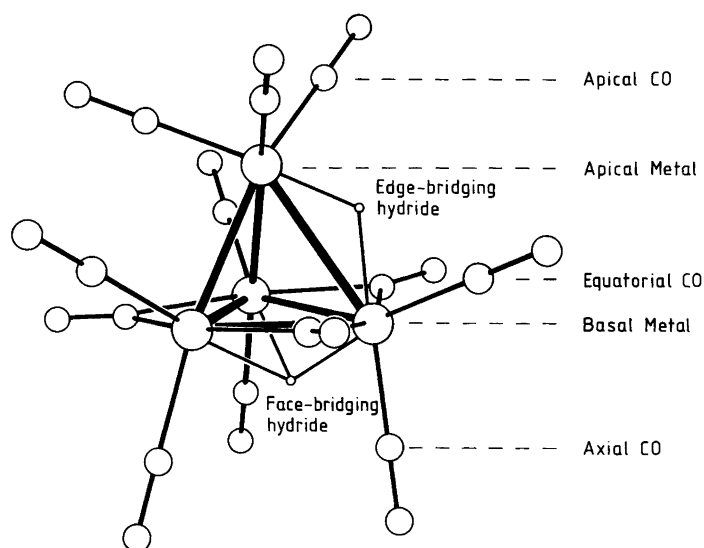


Fig. 1. Classification of metals and ligands in the clusters studied.

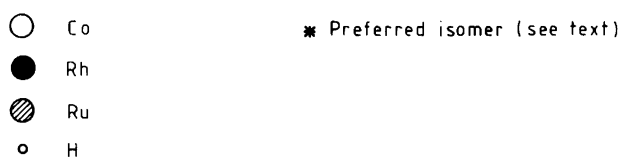
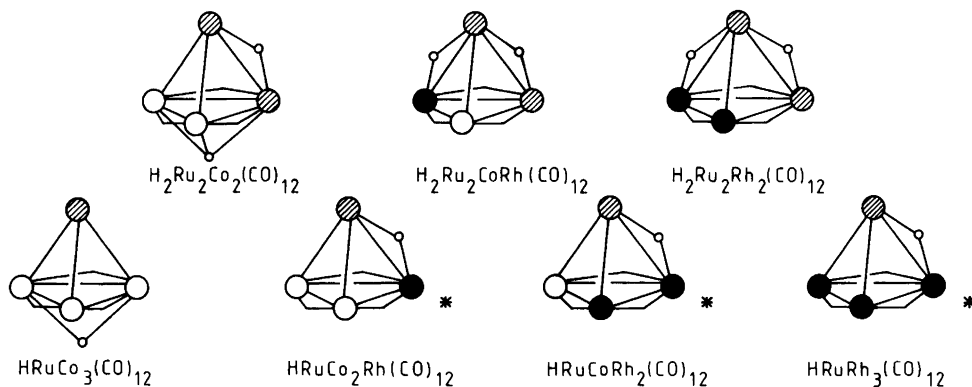


Fig. 2. $\text{H}_2\text{Ru}_2\text{Co}_x\text{Rh}_{2-x}(\text{CO})_{12}$ ($x=0-2$) and $\text{HRuCo}_x\text{Rh}_{3-x}(\text{CO})_{12}$ ($x=0-3$) clusters.



PPh_3 in THF under reflux. It should be noted that $\text{Co}_3\text{Rh}(\text{CO})_{11}(\text{PPh}_3)$, which was identified from the ^{31}P NMR spectrum,⁵ could not be separated from $\text{HRuCo}_2\text{Rh}(\text{CO})_{11}(\text{PPh}_3)$ on the grounds of its reactivity towards PPh_3 .

When the mixture of $\text{HRuCoRh}_2(\text{CO})_{10}(\text{PPh}_3)_2$ and $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$ was heated under reflux in THF with PPh_3 , only $\text{HRuCoRh}_2(\text{CO})_{10}(\text{PPh}_3)_2$ remained unreacted after 1 h of reaction.

Hydride positions and ^1H chemical shifts. The compounds have similar $\text{Rh}_4(\text{CO})_{12}$ -like arrangement of carbonyl ligands with three carbonyls bridging the basal metal atoms, as evidenced by several crystal structures^{2,4,6,8-10} (Figs. 1 and 2). The conclusion that ruthenium occupies the apical position is based both on crystal structures (especially RuCo_3 clusters) and, indirectly, on the ^1H NMR data [line-widths and $1J(\text{Rh}-\text{H})$ coupling patterns]. Hydrides are in either edge- or facebridging positions, which can be identified by their ^1H NMR spectra, where the different metals affect the signals in different ways. Peaks for $\text{Ru}(\mu_2-\text{H})\text{Ru}$ hydrides are relatively sharp singlets, whereas $\text{Ru}(\mu_2-\text{H})\text{Rh}$ give rise doublets [$^1J(\text{Rh}-\text{H})$ coupling] possibly further split by equatorial phosphorus atoms (Table 4). The signals for $\text{Co}_3(\mu_3-\text{H})$, $\text{Co}^2\text{Rh}(\mu_3-\text{H})$ or $\text{Co}_2\text{Ru}(\mu_3-\text{H})$ ¹⁰ hydrides are always broad, due to the quadrupolar cobalt atoms. Significant line-broadening can be seen also for the $\text{CoRh}_2(\mu_3-\text{H})$ signals, but usually the triplet pattern due to $^1J(\text{Rh}-\text{H})$ couplings is observable. $\text{Rh}_3(\mu_3-\text{H})$ signals are always quartets, which are further split by axial phosphorus atoms. No evidence of $\text{Ru}(\mu_2-\text{H})\text{Co}$, $\text{Co}(\mu_2-\text{H})\text{Co}$ or $\text{Rh}(\mu_2-\text{H})\text{Rh}$ edgebridging hydrides is found for any of the compounds studied.

The preference of the hydrogen sites can be qualitatively stated. In $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$ ⁶ and $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{11}(\text{PPh}_3)$,⁹ $\text{Ru}-\text{Ru}$ and $\text{Ru}-\text{Rh}$ edges are occupied by the hydrides.

Thus, $\text{Ru}(\mu_2-\text{H})\text{Ru}$ hydride is preferred with respect to $\text{Ru}(\mu_2-\text{H})\text{Rh}$ hydrides, since the other of the $\text{Ru}-\text{Rh}$ edges is not occupied. Hydrogens are also in $\text{Ru}-\text{Ru}$ and $\text{Ru}-\text{Rh}$ edges in $\text{H}_2\text{Ru}_2\text{CoRh}(\text{CO})_{12}$,¹ but in $\text{H}_2\text{Ru}_2\text{Co}_2(\text{CO})_{12}$, where no $\text{Ru}-\text{Rh}$ edge is available, the basal RuCo_2 face is occupied in addition to the $\text{Ru}-\text{Ru}$ edge.¹⁰

These preferences were observed also for the $\text{HRuCo}_x-\text{Rh}_{3-x}(\text{CO})_{12}$ ($x=0-2$) parent clusters, which according to ^1H NMR spectra occur in solution as two isomers with the hydride bridging either one of the $\text{Ru}-\text{Rh}$ edges or the basal trimetallic face. At 0°C , slow H-exchange was observed by selective irradiation, which caused significant intensity decrease of the peak which was not irradiated. The H-exchange was slow enough not to cause observable effects on chemical shifts or coupling constants, which were not affected by lowering the temperature below 0°C .

The hydrogen bridging of an $\text{Ru}-\text{Rh}$ edge is dominant (Table 1) in all the parent clusters. In $\text{HRuCo}_3(\text{CO})_{12}$, where no $\text{Ru}-\text{Rh}$ edge is available, the hydride bridges the Co_3 face. There is obviously no great difference in energy between these two sites since both forms coexist, and also because the preference between the sites can be affected by phosphine groups. Table 1 shows the relative amount of the face-bridged form for the parent clusters and some of their phosphine derivatives. In the parent clusters the edgebridging form is dominant, but in the PPh_3 derivatives this preference is inverted. The relative occupancies of the facebridged forms decrease with different ligands in the order $\text{PPh}_3 > \text{PMePh}_2 > \text{PMe}_2\text{Ph} > \text{PMe}_3$. Also, the relative amounts of the facebridged forms decrease with the metal combination, independent of the phosphine ligand, in the order $\text{RuCo}_2\text{Rh} > \text{RuCoRh}_2 > \text{RuRh}_3$. This effect may be related to the number of $\text{Ru}-\text{Rh}$ edges in the compounds. If the relative stabilities of the edge- and facebridged sites are not significantly different, statistical distribution will favour more numerous edge sites.

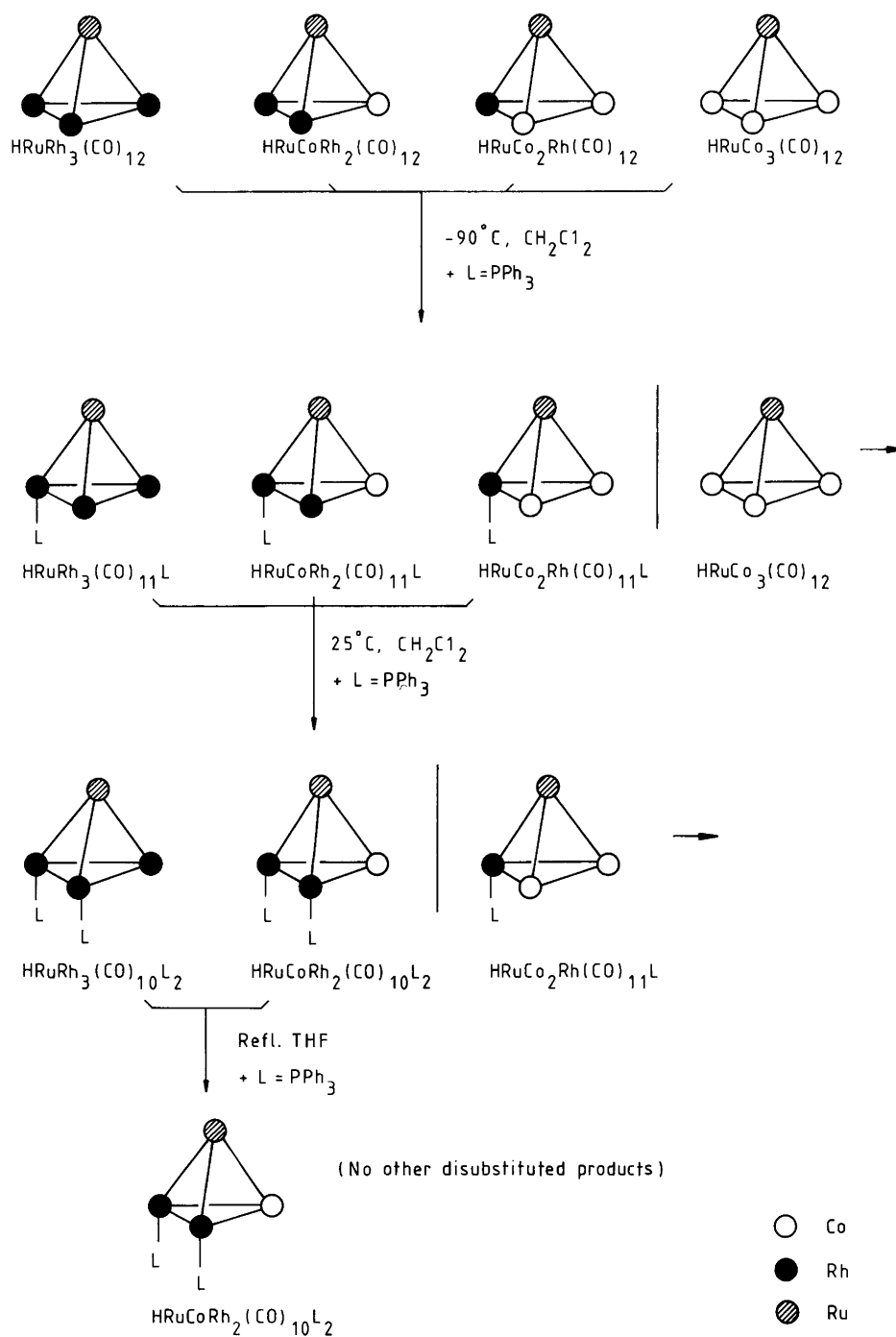


Fig. 3. A separation scheme for $\text{HRuCo}_x\text{Rh}_{3-x}(\text{CO})_{12}$ ($x = 0-3$) clusters.

In these clusters edge-bridging hydrides are associated with the presence of equatorial phosphines, which are coordinated to the rhodium with the hydride and further face-bridging hydrides with axial phosphines. The forms that are preferred in solution can also be crystallized.⁸

There is rapid H-exchange between the Ru–Rh edges of the clusters. At low temperatures ($\leq -10^\circ\text{C}$) the $\text{Ru}(\mu_2\text{-H})\text{Rh}$ signals are well-resolved doublets due to $^1J(\text{Rh-H})$ coupling. As a result of the H-exchange, the

$\text{Ru}(\mu_2\text{-H})\text{Rh}$ signal is a quartet for $\text{HRuRh}_3(\text{CO})_{12}$, and a triplet for $\text{HRuCoRh}_2(\text{CO})_{12}$ and for $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$ at certain temperatures near $+10^\circ\text{C}$, whereas the signals for $\text{HRuCo}_2\text{Rh}(\text{CO})_{12}$ and $\text{H}_2\text{Ru}_2\text{CoRh}(\text{CO})_{12}$ remain as doublets when the temperature is increased. For the phosphine derivatives such H-exchange processes were not confirmed. On raising the temperature broad signals were observed, with couplings no longer being visible. This might be caused by averaging of several different Rh–H and P–H

Table 1. Relative amounts of the face-bridging hydride (%) in $\text{HRuM}_3(\text{CO})_{12-x}(\text{PR}_3)_x$ according to ^1H NMR spectra.

	RuM_3			
	RuCo_3	RuCo_2Rh	RuCoRh_2	RuRh_3
$x=0$	100	30	29	25
$x=1, \text{PMe}_3$	100	22	14	3
$x=1, \text{PMe}_2\text{Ph}$	100	49	29	8
$x=1, \text{PMePh}_2$	100	66	49	38
$x=1, \text{PPh}_3$	100	81	72	60
$x=2, \text{PPh}_3$	100	78	77	72

Table 2. Chemical shifts (ppm) of the face-bridging hydrides in $\text{HRuM}_3(\text{CO})_{12-x}(\text{PR}_3)_x$ ($\text{CDCl}_3, 0^\circ\text{C}$).

	RuM_3			
	RuCo_3	RuCo_2Rh	RuCoRh_2	RuRh_3
$x=0$	-19.7	-18.4	-16.8	-15.5
$x=1, \text{PMe}_3$	-20.3	-18.8	-17.3	-16.0
$x=1, \text{PMe}_2\text{Ph}$	-20.2	-18.7	-17.3	-16.0
$x=1, \text{PMePh}_2$	-20.1	-18.7	-17.2	-15.9
$x=1, \text{PPh}_3$	-19.8	-18.4	-17.0	-15.7
$x=2, \text{PPh}_3$	-19.4	-18.0	-16.5	-15.3

couplings. All the data in Tables 1–4 concern cases where phosphines and hydrides are coordinated to the same rhodium atom.

NMR studies also revealed trends in the chemical shifts when these compounds are compared with each other (Tables 2 and 3, Figs. 4 and 5). The resonance of the face-bridging hydride moves 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 ^1H NMR resonances of $\text{HCoRu}_x\text{Os}_{3-x}(\text{CO})_{13}$ ($x=1-3$) and $\text{H}_2\text{FeRu}_x\text{Os}_{3-x}(\text{CO})_{13}$ ($x=1-3$) clusters.¹¹

Table 3. Chemical shifts (ppm) of the edge-bridging hydrides in $\text{HRuM}_3(\text{CO})_{12-x}(\text{PR}_3)_x$ ($\text{CDCl}_3, 0^\circ\text{C}$).

	RuM_3		
	RuCo_2Rh	RuCoRh_2	RuRh_3
$x=0$	-17.5	-17.9	-18.4
$x=1, \text{PMe}_3$	-17.9	-18.5	-19.2
$x=1, \text{PMe}_2\text{Ph}$	-17.8	-18.4	-19.1
$x=1, \text{PMePh}_2$	-17.7	-18.3	-18.9
$x=1, \text{PPh}_3$	-17.5	-18.0	-18.6
$x=2, \text{PPh}_3$	-17.0	-17.8	-18.0

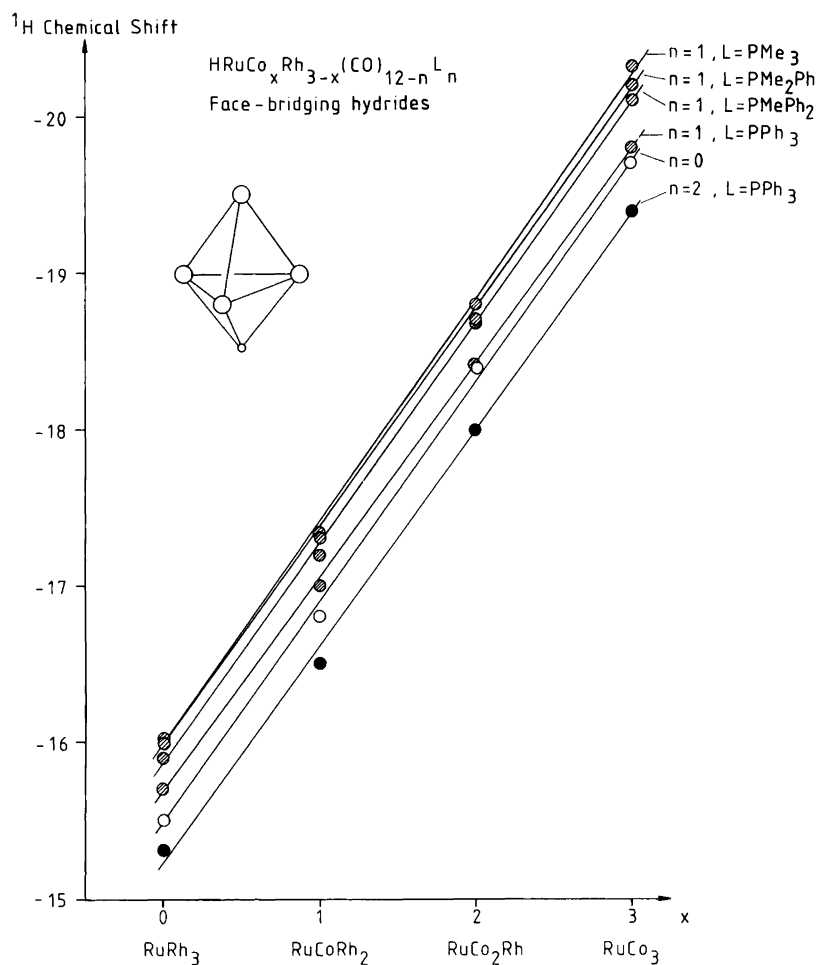
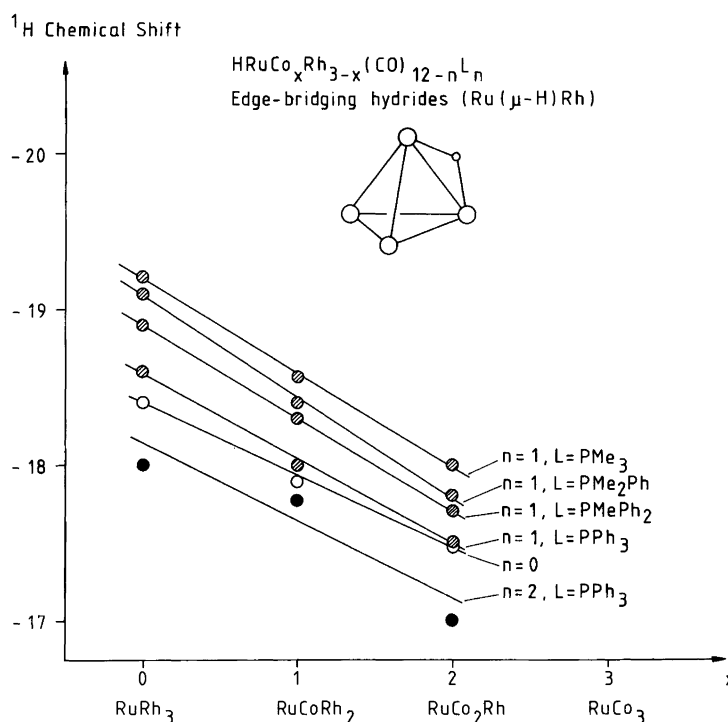


Fig. 4. 250 MHz ^1H chemical shift trends for face-bridging hydrogens in $\text{HRuCo}_x\text{Rh}_{3-x}(\text{CO})_{12-n}(\text{PR}_3)_n$ ($x=0-3$, $n=0-2$, $\text{PR}_3 = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2$ or PPh_3).

Fig. 5. 250 MHz ^1H chemical shift trends for edge-bridging hydrogens in $\text{HRuCo}_x\text{Rh}_{3-x}(\text{CO})_{12-n}(\text{PR}_3)_n$ ($x = 0-3$, $n = 0-2$, $\text{PR}_3 = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2$ or PPh_3).



The ^{31}P resonances of the gold phosphine derivatives $\text{Ph}_3\text{PAuRuCo}_x\text{Rh}_{3-x}(\text{CO})_{12}$ ($x = 0-3$), in which the gold phosphine bridges the basal metal face, also showed linear dependence on the metal combination.¹² The proton resonance change is not unexpected since the hydrides are directly bonded to the metal which is replaced. On the other hand, there is a ca. 0.5 ppm shift to lower frequency of the $\text{Ru}(\mu_2\text{-H})\text{Rh}$ hydride resonances during the same replacement of cobalt by rhodium. Similarly, both the $\text{Ru}(\mu_2\text{-H})\text{Ru}$ and $\text{Ru}(\mu_2\text{-H})\text{Rh}$ resonances of $\text{H}_2\text{Ru}_2\text{CoRh}(\text{CO})_{12}$ are ca. 0.7 ppm in higher frequency than for $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$.¹ In $\text{H}_2\text{Ru}_2\text{Co}_2(\text{CO})_{12}$ the $\text{Ru}(\mu_2\text{-H})\text{Ru}$ resonance is at -20.36 ppm, which does not fit with the trends observed above. This, however, is not unexpected, since $\text{H}_2\text{Ru}_2\text{Co}_2(\text{CO})_{12}$ differs structurally from the Rh-containing analogues by having a face-bridging $\text{RuCo}_2(\mu_3\text{-H})$ hydride.¹⁰ In the edge-bridging case the trends are caused by changing metal atoms that are not directly bonded to the hydride ligand. The only significant deviation from the trends is for the disubstituted clusters in Fig. 5.

In Table 4, the $^1J(\text{Rh-H})$ and $^2J(\text{P-H})$ coupling constants for $\text{Ru}(\mu_2\text{-H})\text{Rh}$ hydrides are collected. There is a slight dependence of both values on the nature of the phosphines in the order $\text{PPh}_3 < \text{PMePh}_2 < \text{PMe}_2\text{Ph} < \text{PMe}_3$. As mentioned above, the relative amount of the edge-bridging isomers follows the same order. The corresponding $^1J(\text{Rh-H})$ values for the face-bridging isomer were observed only for $\text{HRuRh}_3(\text{CO})_{11}(\text{PMePh}_2)$ (ca. 12 Hz), $\text{HRuRh}_3(\text{CO})_{11}(\text{PPh}_3)$ (12.5 and 10.6 Hz, simulated), $\text{HRuCoRh}_2(\text{CO})_{10}(\text{PPh}_3)_2$ (10.6 Hz) and $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$ (13.6 and 11.3 Hz).² The corresponding $^2J(\text{P-H})$

values were ca. 5 Hz for $\text{HRuRh}_3(\text{CO})_{11}(\text{PMePh}_2)$, 3.7 Hz for $\text{HRuRh}_3(\text{CO})_{11}(\text{PPh}_3)$ and 2.4 Hz for $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$. The $\text{Ru}(\mu_2\text{-H})\text{Rh}$ signal of $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$ showed couplings to one rhodium (ca. 16 Hz) and to two phosphorus atoms (8.4 and 5.3 Hz) at -20°C . The probable structure of $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$ is that of $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$ ¹³ with one equatorial and one axial phosphine, the hydride being coordinated to the rhodium with the equatorial phosphine. At 0°C the $\text{Ru}(\mu_2\text{-H})\text{Rh}$ signals for both $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$ and $\text{HRuCoRh}_2(\text{CO})_{10}(\text{PPh}_3)_2$ have similar splittings (nearly quintets due to coincidence of coupling constants), suggesting structural similarity of the edge-bridged isomers of both.

The importance of heteronuclear cluster compounds lies in combining the different properties of different metals in one compound. In this work, the different metal combinations are shown to affect the coordination sites of hydride and phosphine ligands and the reactivity of clusters with

Table 4. $^1J(\text{Rh-H})$ (A) and $^2J(\text{P-H})$ (B) coupling constants of edge-bridging hydrides in $\text{HRuM}_3(\text{CO})_{11}(\text{PR}_3)$ (CDCl_3 , 0°C).

	RuM_3					
	RuCo_2Rh		RuCoRh_2		RuRh_3	
	A	B	A	B	A	B
PMe_3	17.9	8.6	17.8	10.3	18.0	10.8
PMe_2Ph	17.6	8.9	17.5	10.0	18.0	10.3
PMePh_2	17.1	7.9	17.7	9.2	17.3	9.3
PPh_3	16.8	6.3	16.8	8.3	17.0	7.3

phosphines. The NMR results indicate that in isostructural clusters it is possible to find trends in the NMR parameter changes caused by changes of metal atoms. These in turn reflect the electronic changes of similar nature.

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