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Preliminary Communication

Solution structures of cobalt–rhodium clusters: the identification of a new hexanuclear cobalt–rhodium species ☆

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Abstract

The thermolysis of $Co_2Rh_2(CO)_{12}$ leads to the quantitative formation of $Co_3Rh_3(CO)_{16}$. The solution structures of these clusters have been established by IR and low temperature ^{13}C NMR spectroscopy. $Co_3Rh_3(CO)_{16}$ reacts with carbon monoxide at moderate pressure to give the equilibrium mixture of $Co_2Rh_2(CO)_{12}$ and $CoRh(CO)_7$.

Keywords: Cobalt; Rhodium; Mixed-metal carbonyl clusters

The chemistry of mixed-metal compounds [1] is important for the molecular level understanding of synergetic effects in multimetallic catalysis [2]. Cobalt–rhodium synergism in the catalytic hydrocarbonylation of diketene was first recognized by Pino and von Bézard [3] and was attributed to the presence of a mixed-metal species. The existence and solution structure of $CoRh(CO)_7$, one of the simplest mixed-metal compounds, was first *envisioned* by György Bor from seven IR bands obtained by subtracting the bands of $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ from the in situ IR spectrum of a reaction mixture (Eq. (1)) under carbon monoxide pressure [4]. One of us (I.T.H.) has had the pleasure

$$2Co_2(CO)_8 + Rh_4(CO)_{12} \rightleftharpoons 4CoRh(CO)_7 \qquad (1)$$

of proving him right in his proposal. A solution of pure $CoRh(CO)_7$ was first obtained by reaction (2) [5]. Upon seeing the IR spectrum of this sample, Bor immediately

$$2Na[Co(CO)_4] + [Rh(CO)_2Cl]_2 \xrightarrow[\text{n-hexane, 1 day}]{-65\ ^\circ\text{C, CO-purge}} 2CoRh(CO)_7 \qquad (2)$$

performed a vibrational analysis (see Fig. 4 in Ref. [5]), smiled and said ‘Ugye megmondtam’ (English translation: I told you so). Another leader in the cobalt–rhodium cluster chemistry, Chini, reported the synthesis and solution structure of $Co_2Rh_2(CO)_{12}$ [6]. Subsequently it has been shown that $Co_2Rh_2(CO)_{12}$ undergoes a reversible fragmentation under low pressure of CO to give $CoRh(CO)_7$ according to reaction (3) [5,7]. Chini and co-workers also reported that $Co_2Rh_2(CO)_{12}$ undergoes a redistribution reaction at

$$Co_2Rh_2(CO)_{12} + 2CO \rightleftharpoons 4CoRh(CO)_7 \qquad (3)$$

60 °C to give a hexanuclear species, formulated as ‘$Co_2Rh_4(CO)_{16}$’ [6], and $Co_3Rh(CO)_{12}$ (Eq. (4)) [6,8]. The X-ray crystallographic analysis of the hexanuclear

$$Co_2Rh_2(CO)_{12} \xrightarrow[\text{n-hexane}]{65\ ^\circ\text{C}} \text{‘}Co_2Rh_4(CO)_{16}\text{’} + Co_3Rh(CO)_{12} \qquad (4)$$

species indicated a disordered structure, isomorphous with $Co_6(CO)_{16}$ [9] and $Rh_6(CO)_{16}$ [10] and with comparable cell constants consistent with a hexanuclear cluster containing both Co and Rh atoms. Similarly, the X-ray crystallographic analysis of $Co_2Rh_2(CO)_{12}$ also shows disorder. In order to determine the isomers present in solution for both these species, we have studied their solution structure using IR and ^{13}C NMR spectroscopy, and have established that the hexanuclear species formulated as ‘$Co_2Rh_4(CO)_{16}$’ is actually $Co_3Rh_3(CO)_{16}$.

☆ This paper is dedicated to Professor György Bor on the occasion of his 70th birthday.

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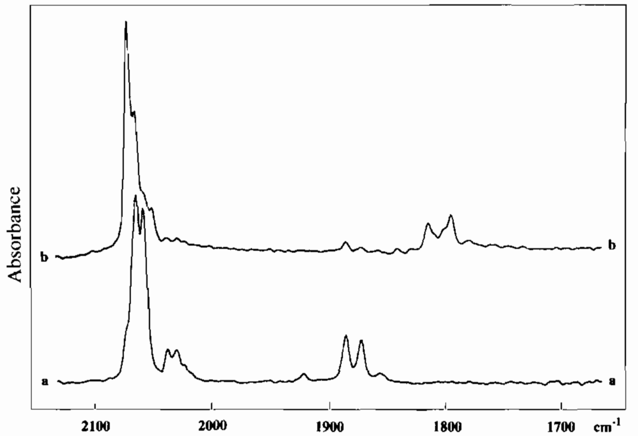
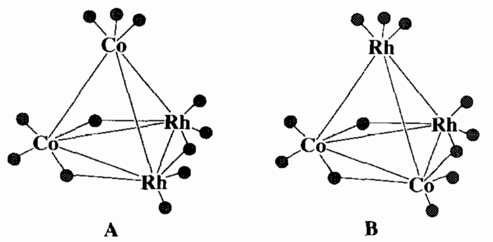


Fig. 1. (a) IR spectrum of $Co_2Rh_2(CO)_{12}$ in n-hexane. (b) IR spectrum of a reaction mixture obtained by heating a solution of $Co_2Rh_2(CO)_{12}$ in n-hexane for 1 h.



Scheme 1.

The solution structure of $Co_2Rh_2(CO)_{12}$ has been previously investigated by IR spectroscopy [6]. In n-hexane (Fig. 1(a)) four bands are observed in the bridging carbonyl region which were attributed to the possible presence of two isomers A and B (Scheme 1), in which two rhodium or two cobalt atoms lie in the basal plane of the *closo*-Co_2Rh_2 tetrahedral framework, respectively. The predominant isomer was proposed to be A [6], which we have now confirmed by ^{13}C NMR. A 99% ^{13}C-enriched sample of $Co_2Rh_2(CO)_{12}$ was prepared by stirring an n-hexane solution of $Co_2Rh_2(CO)_{12}$ under 99% ^{13}C-enriched CO. The ^{13}C NMR spectrum of $Co_2Rh_2(CO)_{12}$ at −70 °C in CD_2Cl_2 shows seven intense resonances of relative intensity 2:1:3:1:1:2:2 (Fig. 2). These resonances unequivocally assign the structure as A.

When a solution of $Co_2Rh_2(CO)_{12}$ in n-hexane is heated at 60 °C it reacts over one hour to give the hexanuclear species $Co_3Rh_3(CO)_{16}$ as the only product. The reaction may be monitored by IR which shows the disappearance of the peaks of $Co_2Rh_2(CO)_{12}$ and the appearance of new peaks around 2070 and 1800 cm⁻¹ (Fig. 1(b))[1]. Compound $Co_3Rh_3(CO)_{16}$ precip-

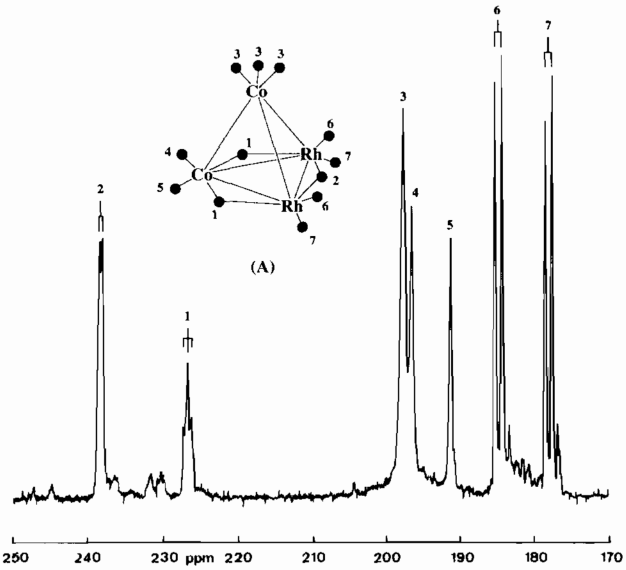


Fig. 2. ^{13}C NMR spectrum of $Co_2Rh_2(CO)_{12}$ at −70 °C in CD_2Cl_2.

itates from the solution at room temperature and may be isolated in high yield. Its molecular formula was established by elemental and MS analysis[2] and ^{13}C NMR spectroscopy. The X-ray data reported by Chini and co-workers [6] indicates that $Co_3Rh_3(CO)_{16}$ is isostructural with $Co_6(CO)_{16}$ [9] and $Rh_6(CO)_{16}$ [10]. This is further supported by the observation of carbonyl stretching vibrations between 1815 and 1796 cm⁻¹ which are consistent with the presence of triply bridging carbonyl ligands. Three isomers are possible for $Co_3Rh_3(CO)_{16}$ (Scheme 2). One meridial isomer, *mer*, with three rhodium atoms in the same equatorial plane and two facial isomers, *fac*-A and *fac*-B, with three rhodium atoms on the same triangular face. These two isomers differ by the bridging carbonyls; one contains a $Co_3(\mu_3\text{-}CO)$ (*fac*-A) and the other an $Rh_3(\mu_3\text{-}CO)$ (*fac*-B). A ^{13}C-enriched sample of $Co_3Rh_3(CO)_{16}$ was prepared from ^{13}C-enriched $Co_2Rh_2(CO)_{12}$. The ^{13}C NMR spectrum of $Co_3Rh_3(CO)_{16}$ at −70 °C in CD_2Cl_2 is very complex (Fig. 3) consisting of several signals between 230 and 260 ppm for triply bridging carbonyls[3], five singlets between 200 and 190 ppm for terminal carbonyls bound to cobalt atoms, and five doublets[4] between 185 and 175 ppm for terminal carbonyls bound to rhodium atoms. The ratio of these three sets of

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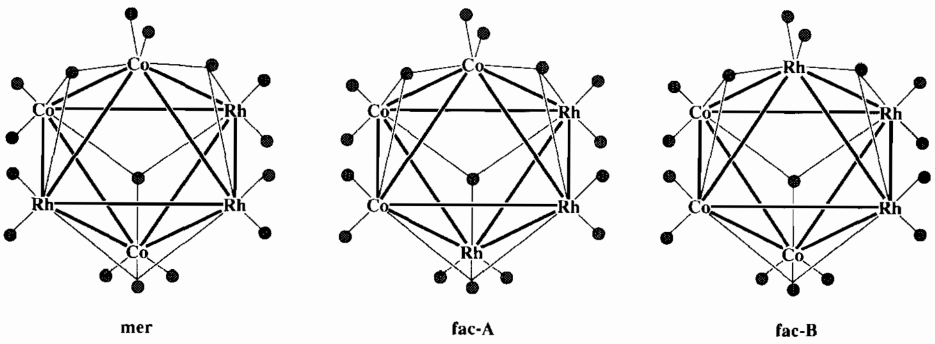
[1] The small peak at 1870 cm⁻¹ is attributed to the presence of $Co_3Rh(CO)_{12}$, carried through as a frequently forming byproduct in the preparation of $Co_2Rh_2(CO)_{12}$. This is probabl the source of the incorrect formulation by Chini and co-workers [6] since the presence of $Co_3Rh(CO)_{12}$ in the starting material is initially masked and could be mistaken for a product.

[2] *Anal.*: Co, 17.04; Rh, 31.79. Calc. for $Co_3Rh_3(CO)_{16}$: Co, 18.93; Rh, 33.07%. MS: molecular ion corresponding to $Co_3Rh_3(CO)_{16}$ (933.4) and the successive loss of 16 CO. A weaker peak is observed at 977 *m/e* which could indicate the presence of $Co_2Rh_4(CO)_{16}$ as a trace impurity.

[3] The $Rh_3(\mu_3\text{-}CO)$ signal cannot be unambiguously assigned. It is predicted to be a quartet with intensity comparable to the signal assigned to $Co_3(\mu_3\text{-}CO)$. It would therefore be a broad weak signal which would be obscured by the noise.

[4] The doublets were assigned by the comparison of spectra obtained at different magnetic fields.



Scheme 2.

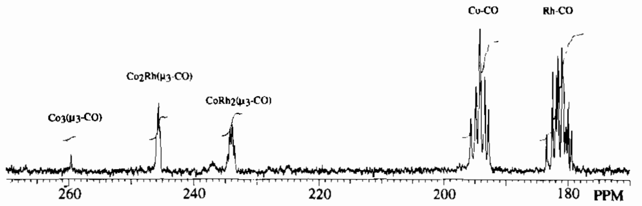
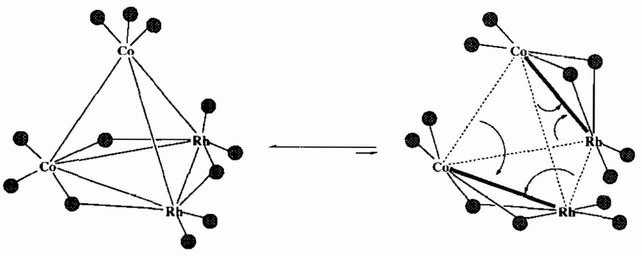


Fig. 3. ^{13}C NMR spectrum of $Co_3Rh_3(CO)_{16}$ at −70 °C in CD_2Cl_2.

signals is 2:3:3 confirming the $(\mu_3\text{-}CO)_4\{Co_3(CO)_6\}\{Rh_3(CO)_6\}$ molecular formula. Analysis of the signals due to the terminal carbonyl ligands indicate that three isomers must be present in solution with one signal obscured in each case. In addition, the triply bridging carbonyl region is consistent with this interpretation and indicates that the isomer ratio of *mer*:*fac*-A:*fac*-B is approximately 3:1:1.

Finally, $Co_3Rh_3(CO)_{16}$ reacts with carbon monoxide under moderate CO pressure (30 bar) to give the equilibrium mixture of $Co_2Rh_2(CO)_{12}$ and $CoRh(CO)_7$. This reaction is another example of reversible cluster fragmentation involving dinuclear CoRh units reported for $Co_2Rh_2(CO)_{11}(PEt_3)$ [11], $Co_2Rh_2(CO)_{10}(PEt_3)_2$ [11] and $Co_2Rh_2(CO)_{10}(PhC_2Ph)$ [12]. The simplest formula for the common dinuclear CoRh intermediate could be $\{CoRh(CO)_6\}$ containing two bridging carbonyl ligands which would require the presence of a Co–Rh triple bond:



The chemistry of the new hexanuclear species is currently under investigation.

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