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SYNTHESIS OF HETEROPENTAMETALLIC CLUSTERS CONTAINING THREE DIFFERENT METALS: $MCo_3(CO)_{12}M'L$ (M = Fe, Ru; M′ = Cu, Ag)

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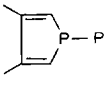
Summary

The new heteropentametallic clusters $MCo_3(CO)_{12}M'L$ (**1**–**7**), of trigonal bipyramidal structure, have been prepared from the tetrametallic anions $[MCo_3(CO)_{12}]^-$ (M = Fe, Ru) and $L \rightarrow M'Cl$ (M′ = Cu, Ag; L = PPh_3, ) or $[Cu(CH_3CN)_4]^+$. Metal exchange is observed when $Na[RuCo_3(CO)_{12}]$ reacts with $[Rh(\mu\text{-}Cl)(CO)]_2$ and with $CpMo(CO)_3Cl$, affording $RhCo_3(CO)_{12}$ and $CpMoCo_3(CO)_{14}$, respectively.

Introduction

The reactions of $[FeCo_3(CO)_{12}]^-$ and $[RuCo_3(CO)_{12}]^-$ with $Ph_3P \rightarrow AuCl$ have recently been described and afford the pentametallic clusters $Fe(Ru)Co_3(CO)_{12}AuPPh_3$ [1,2]. These have a trigonal bipyramidal structure (X-ray diffraction), the basis of which is constituted by the Co_3 triangle.

In view of the growing synthetic, structural and theoretical interest for this class of compounds [3–5] and of the possible relevance of Group IB–Group VIII mixed-metal clusters for catalysis in CO chemistry [6], we have extended these studies to related pentametallic clusters containing copper and silver. Surprisingly indeed, only few mixed-metal carbonyl clusters containing Cu or Ag have been reported until recently [7].

Results and discussion

We have now found that immediate reaction of the anionic clusters $K[MCo_3(CO)_{12}]$ (M = Fe, Ru) with $L \rightarrow M'Cl$ (M′ = Cu, Ag) occurs in toluene at room temperature. It affords the new clusters **1**, **2**, **4**, **5** and **7** in 30–60% yield. The

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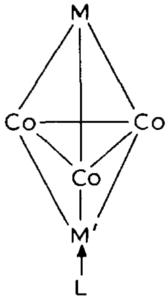
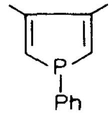
analogy between their spectroscopic properties and those of $RuCo_3(CO)_{12}(\mu_3\text{-}AuPPh_3)$ [2] suggest a similar structure for these molecules, although **4** and **7** show slightly different IR spectra (see Experimental).



1, M = Fe ; M' = Cu ; L = PPh_3

2, M = Fe ; M' = Cu ; L =  (phosphole)

3, M = Fe ; M' = Cu ; L = CH_3CN

4, M = Fe ; M' = Ag ; L = phosphole

5, M = Ru ; M' = Cu ; L = phosphole

6, M = Ru ; M' = Cu ; L = CH_3CN

7, M = Ru ; M' = Ag ; L = phosphole

Suggested core structure of $MCo_3(CO)_{12}M'L$ **1**–**7**

Clusters **3** and **6** were prepared by reaction of $NEt_4[MCo_3(CO)_{12}]$ with $[Cu(CH_3CN)_4]BF_4$ in acetone.

In contrast to the above reactions leading to pentanuclear clusters, metal exchange was observed in reaction 1:

$$Na[RuCo_3(CO)_{12}] + 0.5[Rh(\mu\text{-}Cl)(CO)]_2 \xrightarrow[\substack{0\text{–}25\,°C \\ 3\,h}]{\text{toluene}} RhCo_3(CO)_{12} + Ru_3(CO)_{12} + NaCl + \ldots \quad (1)$$

since $RhCo_3(CO)_{12}$ was formed (35–45% yield), perhaps via an unstable pentametallic intermediate. Similarly, Mo could be introduced into the metallic core in place of Ru, as shown in eq. 2:

$$Na[RuCo_3(CO)_{12}] + CpMo(CO)_3Cl \rightarrow [CpMo(CO)_3]_2 + CpMoCo_3(CO)_{14} + HRuCo_3(CO)_{12} + NaCl + \ldots \quad (2)$$

This reaction afforded the tetrahedral $MoCo_3$ cluster, identified by elemental analysis, IR and mass spectrometry [8].

Using $CpFe(CO)_2Cl$ in place of $CpMo(CO)_3Cl$ in the above reaction, produced $[CpFe(CO)_2]_2$, the ionic $[CpFe(CO)_3][RuCo_3(CO)_{12}]$ and $HRuCo_3(CO)_{12}$. Some $Ru_3(CO)_{12}$ was detected in this reaction, together with a new complex, not yet fully identified (see Experimental).

The stepwise cluster construction illustrated in the synthesis of **1**–**7** has therefore certain limitations but may be a valuable route to heteropolymetallic clusters containing three different metals. Further work is in progress to evaluate this synthetic approach and the reactivity of the resulting clusters.

Experimental

Preparation of $FeCo_3(CO)_{12}[Cu(PPh_3)]$ (1)

To a suspension of $K[FeCo_3(CO)_{12}]$ (0.625 g, 1.0 mmol) in toluene (20 ml) was added a solution of $[Cu(PPh_3)Cl]_4$ (0.361 g, 0.25 mmol) in toluene (20 ml). After 2 h stirring at room temperature, the red solution was filtered and evaporated under reduced pressure. Extraction of the solid residue with hexane gave **1** (0.480 g, 53.7%), dec. 170–175°C. IR (KBr) ν(CO): 2074m, 2012vs, 1981s, 1972s, 1856s cm^{-1}. UV (CH_2Cl_2) λmax: 344, 416sh, 552 nm. Found: C, 40.5; H, 1.8. $C_{30}H_{15}Co_3CuFeO_{12}P$ (894.5) calcd.: C, 40.27; H, 1.69%.

Compounds **2**, **4**, **5** and **7** were prepared by the same procedure as that described for **1**.

2: (0.460 g, 56.0%), m.p. 145–147°C. IR (KBr) ν(CO): 2072m, 2000vs, 1978sh, 1957sh, 1920sh, 1846s cm^{-1}. UV (CH_2Cl_2) λmax: 343, 416sh, 552 nm. Found: C, 35.1; H, 1.7. $C_{24}H_{13}Co_3CuFeO_{12}P$ (820.5) calcd.: C, 35.13; H, 1.60%.

4: (0.320 g, 37.0%), m.p. 134–136°C. IR (KBr) ν(CO): 2071m, 2006vs, 1975sh, 1961s, 1867w, 1825s, 1816s cm^{-1}. UV (CH_2Cl_2) λmax: 335, 390sh, 550 nm. Found: C, 33.2; H, 1.5. $C_{24}H_{13}AgCo_3FeO_{12}P$ (864.8) calcd.: C, 33.33; H, 1.51%.

5: (0.370 g, 42.7%), m.p. 148–150°C. IR (KBr) ν(CO): 2080m, 2020sh, 2000vs, 1968m, 1886w, 1848s cm^{-1}. UV (CH_2Cl_2) λmax: 320, 395, 495 nm. m/e 866 (M^+). Found: C, 33.8; H, 1.7. $C_{24}H_{13}Co_3CuO_{12}PRu$ (865.7) calcd.: C, 33.30; H, 1.51%.

7: (0.280 g, 30.8%), m.p. 138–140°C. IR (KBr) ν(CO): 2079m, 2014vs, 1974sh, 1958sh, 1860w, 1824s, 1816s cm^{-1} UV (CH_2Cl_2) λ max : 320, 400, 488 nm. Found: C, 32.3; H, 1.5. $C_{24}H_{13}AgCo_3O_{12}PRu$ (910.1) calcd.: C, 31.67; H, 1.44%.

Preparation of $FeCo_3(CO)_{12}[Cu(CH_3CN)]$ (3)

To a solution of $(NEt_4)[FeCo_3(CO)_{12}]$ (0.350 g, 0.5 mmol) in acetone (20 ml), was added a solution of $[Cu(CH_3CN)_4]BF_4$ (0.150 g, 0.5 mmol) in acetone (10 ml). After 2 h stirring at room temperature, the purple solution was evaporated under reduced pressure. The solid residue was extracted with toluene and the solution was evaporated in vacuo. Crystallisation of the solid residue in dichloromethane/hexane (1/1) afforded **3** as black crystals (0.160 g, 47.5%) (dec. 135–140°C). IR (KBr) ν(CO): 2071m, 2010vs, 1987sh, 1967s, 1958s, 1928sh, 1885w, 1854s, 1835s cm^{-1} UV (CH_2Cl_2) λmax: 341, 395sh, 550 nm. Found: C, 25.1; H, 0.6; N, 1.9. $C_{14}H_3Co_3CuFeNO_{12}$ (673.4) calcd.: C, 24.97; H, 0.45; N, 2.08%.

Compound **6** was prepared by the same procedure.

6: (0.138 g, 38.4%) (decomp. 170–175°C) IR (KBr) ν(CO): 2079m, 2000vs, br, 1947sh, 1882w, 1846sh, 1837s cm^{-1}. UV (CH_2Cl_2) λmax: 320, 398, 485 nm. Found: C, 23.5; H, 0.8; N, 1.7. $C_{14}H_3Co_3CuNO_{12}Ru$ (718.6) calcd.: C, 23.4; H, 0.42; N, 1.95%.

Reaction of $Na[RuCo_3(CO)_{12}]$ with $CpMo(CO)_3Cl$

To a suspension of $Na[RuCo_3(CO)_{12}]$ (0.300 g, 0.47 mmol) in toluene (20 ml) was added a solution of $CpMo(CO)_3Cl$ (0.140 g, 0.5 mmol) in toluene (10 ml). After 3 h stirring at 80°C, the red solution was evaporated under reduced pressure. Extraction of the solid residue with hexane afforded $[CpMo(CO)_3]_2$, $HRuCo_3(CO)_{12}$ and $CpMoCo_3(CO)_{14}$ which were separated by fractional crystallization from hexane. The insoluble fraction contained some $Na[RuCo_3(CO)_{12}]$.

Reaction of $Na[RuCo_3(CO)_{12}]$ with $CpFe(CO)_2Cl$

The procedure was the same as described above. Extraction of the solid residue with hexane afforded $[CpFe(CO)_2]_2$, $HRuCo_3(CO)_{12}$, $Ru_3(CO)_{12}$ which were separated by fractional crystallization from hexane. A new complex, IR (hexane)

ν(CO): 2072s, 2020vs, 2007s, 1982sh, 1961s cm^{-1}, was also detected and is under investigation. The remaining solid contained some Na[$RuCo_3(CO)_{12}$] and [$CpFe(CO)_3$][$RuCo_3(CO)_{12}$], which were separated by fractional crystallization from THF/toluene. The latter showed ν(CO) stretching absorption characteristic of $[CpFe(CO)_3]^+$ [9] (2136m and 2086m cm^{-1}) and of $[RuCo_3(CO)_{12}]^-$ [2,10] (1988vs, 1960s and 1806m cm^{-1}).

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