

which organic molecules can be "decomposed" by a metal center into smaller molecules. The proton affinity rule works well in providing insights into mechanisms and ion structures. Metal ions such as Co^+ react with 1-halobutanes by mechanisms similar to smaller haloalkanes. Such reactants containing a four-carbon chain readily form metal-butadiene complexes. Bifunctional butanes exhibit an unexpected chemistry with metal ions. Co^+ attacks the central C-C bond of halobutanols while CoCO^+ prefers to attack the C-C(OH) bond. CID analysis can be very useful but can be difficult to interpret because of the ease with which collision-induced decomposition of ligands occurs.

When Co^+ is forced to "choose" over the OH and X groups of a 1,4-bisubstituted butane, some preference for the halogen is suggested.

Work is now under way investigating the reactions of Co^+ with molecules containing three- to six-carbon chains in an effort to shed more light on the mechanisms suggested here.

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Registry No. Co^+ , 16610-75-6; CoCO^+ , 28963-35-1; $\text{Co}(\text{CO})_2^+$, 28963-34-0; CoNO^+ , 87616-10-2; CoCONO^+ , 61816-95-3; $\text{Co}(\text{CO})_2\text{NO}^+$, 61816-96-4; $\text{Co}(\text{CO})_3\text{NO}^+$, 52309-13-4; $\text{Co}(\text{CO})_3\text{NO}$, 14096-82-3; $n\text{-C}_4\text{H}_9\text{F}$, 2366-52-1; $n\text{-C}_4\text{H}_9\text{Cl}$, 109-69-3; $n\text{-C}_4\text{H}_9\text{Br}$, 109-65-9; $n\text{-C}_4\text{H}_9\text{OH}$, 71-36-3; $\text{HO}(\text{CH}_2)_4\text{F}$, 372-93-0; $\text{HO}(\text{CH}_2)_4\text{Cl}$, 928-51-8; $\text{HO}(\text{CH}_2)_4\text{Br}$, 33036-62-3; $\text{Cl}(\text{CH}_2)_4\text{Br}$, 6940-78-9.

Syn-Gas Reactions with Co Subgroup Cluster Catalysts. 1. Interaction of $\text{M}_x\text{Co}_{4-x}(\text{CO})_{12}$ ($\text{M} = \text{Rh}$, $x = 4, 2-0$; $\text{M} = \text{Ir}$, $x = 4, 2, 0$) with Tertiary Amine Functionalized Supports

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The interaction of the series of Co subgroup clusters $\text{Rh}_x\text{Co}_{4-x}(\text{CO})_{12}$ ($x = 4, 2-0$) and $\text{Ir}_x\text{Co}_{4-x}(\text{CO})_{12}$ ($x = 4, 2, 0$) with amine-functionalized polystyrene, polyacrylate, or silica has been examined. Infrared studies, extractive separations with quaternary ammonium perchlorate, and plasma emission metal analyses reveal the clusters undergo fragmentation and redistribution to give mononuclear and polynuclear anionic and/or cationic products. The influence of residual Cl^- on the functionalized resins has been examined. All evidence points to segregation of the two metals in the products. Although such studies do not allow unequivocal structural assignment for all the products observed, it is clear that different reactivity patterns exist for the different clusters with the different supports.

Introduction

Homogeneous catalysis by cluster complexes has recently attracted much attention¹⁻³ as systems have been reported that catalyze commercially important reactions such as hydroformylation,⁴ water gas shift,⁵ oxidation⁶ and CO/H_2 to ethylene glycol.⁷ Although these catalyst sys-

tems initially contain metal clusters, proving the clusters remain intact and/or are the catalytically active species is always more difficult. Indeed, reports on catalysis of the Fischer-Tropsch reaction by $\text{Ru}_3(\text{CO})_{12}$ ⁸ and catalysis of hydroformylation by $\text{Co}_3(\text{CO})_9(\mu_3\text{-CPh})$ ⁹ have recently been reinterpreted as catalysis due to mononuclear species.^{10,11} The potential of bimetallic clusters in syn-gas catalysis has, in general, been cast into doubt since the reports of Geoffroy et al.¹² indicated that a variety of such

(1) Robinson, A. L. *Science (Washington, D.C.)* **1976**, *194*, 1150.
 (2) Smith, A. K.; Basset, J. M. *J. Mol. Catal.* **1977**, *2*, 229.
 (3) Ciardelli, F.; Braca, G.; Carlini, C.; Sbrama, G.; Valentini, G. *J. Mol. Catal.* **1982**, *14*, 1.
 (4) Chini, P.; Martinengo, S.; Garlaschelli, G. *J. chem. Soc., Chem. Commun.* **1972**, 709.
 (5) Ford, P. C.; Rinker, R. G.; Ungerman, C.; Laine, R. M.; Landis, V.; Maya, S. A. *J. Am. Chem. Soc.* **1978**, *100*, 4595.
 (6) Mercer, G. D.; Shu, J. S.; Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1975**, *97*, 1067.
 (7) Vidal, J. L.; Walker, W. E. *Inorg. Chem.* **1980**, *19*, 896.

(8) Masters, C.; van Dorn, J. A. U.K. Patent. Appl., 75/40322, 1975.
 (9) Ryan, R. C.; Pittmann, C. U.; O'Connor, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 1986.
 (10) Doyle, M. J.; Kouwenhoven, A. P.; Schaap, C. A.; VanOort, B. J. *Organomet. Chem.* **1979**, *174*, C55.
 (11) King, R. B.; King, A. D.; Tanaka, K. *J. Mol. Catal.* **1981**, *10*, 75.
 (12) Fox, J. R.; Gladfelter, W. L.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 2574. Geoffroy, G. L. *Acc. Chem. Res.* **1980**, *13*, 469.

bimetallic carbonyl clusters have a tendency to fragment under moderate CO pressures.

Several years ago we began a study of bimetallic clusters of the cobalt subgroup attempting to understand their stability under syn-gas reaction conditions and attempting to observe any unique selectivities imparted to catalytic reactions due to the "alloy" nature of such mixed-metal clusters.

The homogeneous reaction of clusters with amines have been shown to lead to cluster degradation via attack of the amine base on the carbonyl ligands.¹³ Indeed rhodium carbonyl clusters are known to be readily degraded to simpler species, e.g., $\text{Rh}(\text{CO})_4^-$, in strongly basic media under CO or in the presence of water.¹⁴ The Union Carbide group, who have been heavily involved with the examination of Rh clusters as precatalysts,¹⁵ have observed that rhodium carbonyl clusters such as $\text{Rh}_6(\text{CO})_{15}^{2-}$, $\text{Rh}_7(\text{CO})_{16}^{3-}$, $\text{Rh}^6(\text{CO})_{16}$, and $\text{Rh}_4(\text{CO})_{12}$ react with synthesis gas, in the presence of amines or salts, to give species whose infrared spectra indicate the presence of $\text{Rh}_5(\text{CO})_{15}^-$ and $\text{Rh}(\text{CO})_4^-$. Changes in the IR spectra of such samples, caused by cooling and venting such systems to ambient conditions, have been interpreted as indicative of the conversion of the above complexes into $\text{Rh}_6(\text{CO})_{15}^{2-}$ and $\text{Rh}_7(\text{CO})_{16}^{3-}$. It was our hope that if similar degradation reaction occurred when our mixed-metal clusters interacted with heterogenized amines, new mixed-metal clusters would result.

From the outset it was clear that several analytical problems would exist. IR spectroscopy would, of necessity, be the major tool for structural characterization of the resultant polymer-supported clusters. It is known that IR does not usually provide enough information for complete structural characterization of high nuclearity cluster.¹⁴ It was, however, felt that it would allow us to eliminate the presence of numerous species and thus allow us to draw some general, although admittedly tenuous, structural conclusions. Since IR spectroscopy would obviously not be of help in identifying the composition of the higher nuclearity clusters, i.e., whether they were mixed-metal in nature, it was hoped that the metallic species could be selectively extracted from the polymer and analyzed. The identity of the extracted species could be investigated by plasma emission analysis, which would reveal relative metal ratios, and field desorption mass spectrometry (FDMS), which would reveal molecularity since both neutral and ionic species are detectable as their molecular ions without any fragmentation. To our knowledge this report documents the first attempt of analysis of the products of the reaction of mixed-metal clusters with polymeric supports.

Results and Discussion

Interaction of $\text{Rh}_x\text{Co}_{4-x}(\text{CO})_{12}$ ($x = 4, 2-0$) with Dowex MWA-1. Figure 1 shows the carbonyl region of the infrared spectra of the products obtained by interacting $\text{Rh}_x\text{Co}_{4-x}(\text{CO})_{12}$, ($x = 4, 2-0$) with Dowex MWA-1 resin.¹⁶ An attempt was made to keep the total metal loadings as equal as possible since it is known that the reaction of polymeric ligands with metal complexes will give different

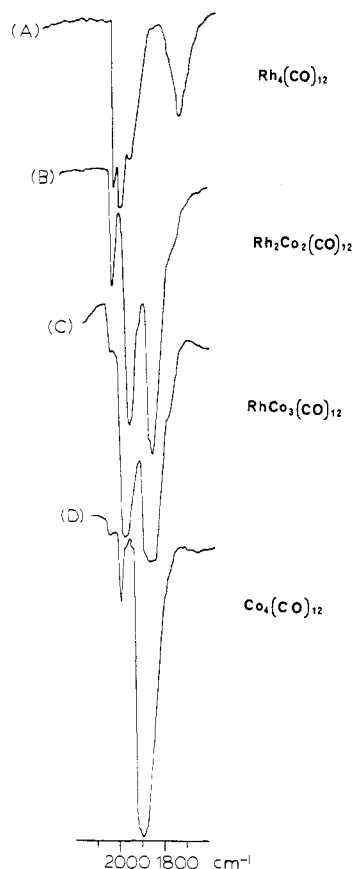


Figure 1. Rhodium/cobalt clusters loaded onto Dowex MWA-1 resin: (A) $\text{Rh}_4(\text{CO})_{12}$, 1.08% Rh; (B) $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$, 1.19% Rh, 0.67% Co; (C) $\text{RhCo}_3(\text{CO})_{12}$, 0.64% Rh, 1.09% Co; (D) $\text{Co}_4(\text{CO})_{12}$, 0.80% Co.

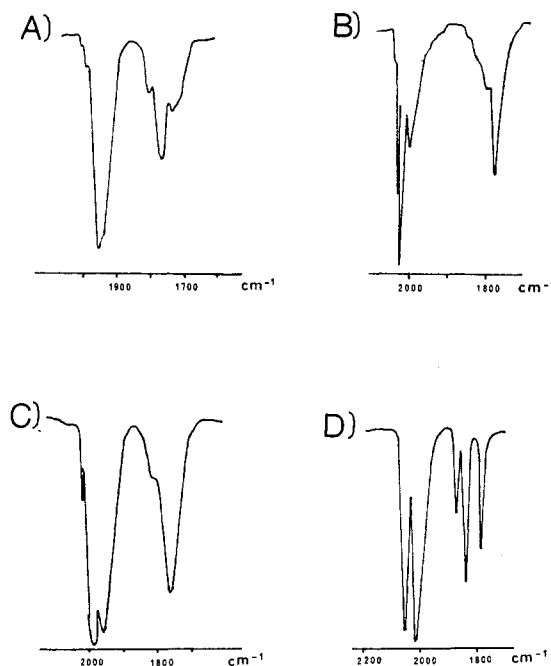


Figure 2. Infrared spectra of the $\nu(\text{CO})$ region of some common $[\text{Rh}_x(\text{CO})_y]^-$ fragments: (A) $\text{Rh}_7(\text{CO})_{16}^{3-}$; (B) $\text{Rh}_{12}(\text{CO})_{30}^{2-}$; (C) $\text{Rh}_6(\text{CO})_{15}^{2-}$; (D) $\text{Rh}_5(\text{CO})_{15}^-$.

metal species depending on the polymer to metal ratio.³ Reaction of MWA-1 with $\text{Co}_4(\text{CO})_{12}$ results in a resin that exhibits a single absorption at 1895 cm^{-1} that can be assigned to $\text{Co}(\text{CO})_4^-$. This is consistent with the disproportionation of $\text{Co}_4(\text{CO})_{12}$ upon interaction with amines to give $[\text{Co}(\text{L})_6^{2+}][\text{Co}(\text{CO})_4]_2^-$.¹⁷ The products of the re-

(13) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207.

(14) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285.

(15) Pruett, R. L.; Walker, W. E. U.S. Patent 3833 634, 1974, to Union Carbide Corp. Walker, W. E.; Brown, E. S.; Pruett, R. L. U.S. Patent 3878 214, 1975, to Union Carbide Corp. Walker, W. E.; Brown, E. S.; Pruett, R. L. U.S. 3878 290, 1975, to Union Carbide Corp.

(16) Dowex MWA-1 is a trademark of the Dow Chemical Co. It is a macroreticular, weak base anion exchange resin having $-\text{CH}_2\text{NMe}_2$ functionality. For drying procedure, see Experimental Section.

action of MWA-1 with the mixed clusters $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ or $\text{RhCo}_3(\text{CO})_{12}$ exhibits an absorption band in the same 1895 cm^{-1} region, assignable to $\text{Co}(\text{CO})_4^-$ and/or $\text{Rh}(\text{CO})_4^-$. Peaks also appear at 2075, 1995, and $1830\text{ (sh, br)}\text{ cm}^{-1}$ (which vary in intensity dependent on the concentration of metal on the support). The lack of any absorption in the 1790 cm^{-1} region indicates the absence of $\text{Rh}_{12}(\text{CO})_{30}^{2-}$ or $\text{Rh}_5(\text{CO})_{15}^-$ as shown by comparison with the spectra shown in Figure 2. The infrared absorptions at 2075 and 1995 cm^{-1} can be assigned to either $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ or $\text{Rh}(\text{CO})_2(\text{A})_2^+$ (A = amine), and we shall see later either or both can be present depending on the degree of Cl^- contamination.¹⁸ To account for the nonequivalent intensities of the two $\nu(\text{CO})$ absorptions (they are of equal intensity for a *cis*- $\text{Rh}(\text{CO})_2$ fragment), one must propose the presence of another species with $\nu(\text{CO})$ absorptions at ~ 2000 and 1830 cm^{-1} . Positive identification of such a species cannot be made at this time since there are several known anions whose $\nu(\text{CO})$ absorptions fit such a spectral pattern, i.e.; $\text{Rh}_{15}(\text{CO})_{27}^{3-}$, $\nu(\text{CO})$ 1998 (s), 1850–1805 (m, br) cm^{-1} ; $\text{Rh}_{13}(\text{CO})_{24}\text{H}_2^{3-}$, $\nu(\text{CO})$ 1990 (s), 1825 (m-br) cm^{-1} ; or $\text{Rh}_6(\text{CO})_{15}\text{C}^{2-}$, $\nu(\text{CO})$ 1993 (s), 1843–1831 (m) cm^{-1} . We favor, on the basis of these analogies, the assignment of these absorptions to a large anionic Rh cluster.

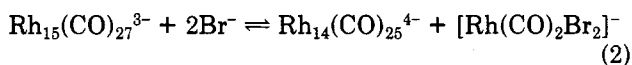
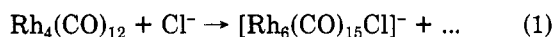
Interaction of $\text{Rh}_4(\text{CO})_{12}$ with MWA-1 results in an obviously different product with bridging CO absorptions in the 1770 cm^{-1} region. Comparison to Figure 2B reveals a very good fit with $\text{Rh}_{12}(\text{CO})_{30}^{2-}$ with possible minor impurities in the high wavenumber region. In this case the presence of $\text{Rh}(\text{CO})_4^-$, $\text{Rh}_7(\text{CO})_{16}^{3-}$, and $\text{Rh}_6(\text{CO})_{15}^{2-}$ can be discounted based on the lack of absorption in the 1900, 1950, and 1883 cm^{-1} regions, respectively.¹⁹ Although complete assignments cannot be made, it is clear from Figure 1 that fragmentation or disproportionation is occurring and that different patterns are followed for the different clusters.

One cannot a priori determine the composition of a bimetallic carbonyl cluster fragment by simply comparing infrared $\nu(\text{CO})$ absorptions to known species. It is known that the Co subgroup carbonyl anions are isostructural and therefore exhibit nearly identical infrared spectra in the $\nu(\text{CO})$ region. For example the $\text{M}(\text{CO})_4^-$ series exhibit $\nu(\text{CO})$ absorptions at 1890 (Co), 1895 (Ir), and 1900 (Rh) cm^{-1} , respectively.¹⁴ Thus the problems inherent to taking infrared spectra of polymer-supported organometallics, such as minor peak shifting and/or broadening, make it extremely difficult to make compositional assignments based on exact wavenumber comparisons. We therefore resorted to attempting extractive separation techniques in order to identify the metal composition of the component reaction products.

We first had to ensure that the extractive techniques themselves did not cause further fragmentation or dis-

proportionation of the complexes. Reaction of Aliquat 336²³ with $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ or $\text{Rh}_4(\text{CO})_{12}$ in methylene chloride reveals cluster breakdown to fragments with CO absorptions that can be assigned to $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ ($\nu(\text{CO})$ 2068, 2003 cm^{-1}) and $\text{M}(\text{CO})_4^-$ (Rh or Co). We feel the anion and not the cation is attacking the cluster since examination of solutions of $\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$, or $\text{Co}_4(\text{CO})_{12}$ after interaction with Bu_4NClO_4 for 6 h revealed no reaction had occurred. The perchlorate anion, a weaker nucleophile obviously, does not cause breakdown or disproportionation of these neutral clusters.²⁴ These results lead one to conclude that adventitious chloride ion present in the amine-functionalized supports can indeed cause cluster fragmentation.

Similar cleavage of rhodium neutral and anionic clusters by halide ions has been observed by Chini et al. in solution²⁵ (eq 1 and 2).



Quaternary ammonium perchlorate extraction of Amberlite IRA-68^{26,27} loaded with $\text{RhCo}_3(\text{CO})_{12}$ first removes $\text{M}(\text{CO})_4^-$. Subsequent plasma emission analysis of the extract reveals 83% Co and 17% Rh. In addition, chloride analysis reveals a Rh/Cl ratio of 0.5, indicating the Rh present is in the form of $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ (see Experimental Section for complete analytical details). One can thus safely say that the $\text{M}(\text{CO})_4^-$ absorption is due to $\text{Co}(\text{CO})_4^-$ not $\text{Rh}(\text{CO})_4^-$. Vidal et al.⁷ note that upon cooling and lowering the presence of solutions containing $\text{Rh}(\text{CO})_4^-$ and the other anions such as $\text{Rh}_5(\text{CO})_{15}^-$ one observes disproportionation to species such as $\text{Rh}_6(\text{CO})_{15}^{2-}$ and $\text{Rh}_7(\text{CO})_{16}^{3-}$. Thus while no $\text{Rh}(\text{CO})_4^-$ can be identified on the resin at ambient conditions, it may be present when the resin is exposed to high temperatures and pressures of synthesis gas.

The anions with $\nu(\text{CO})$ at 2075 (s), 1995 (s) cm^{-1} and ~ 2000 (s), 1830 (m, br) cm^{-1} are extracted next and reveal very high concentrations of Rh (>83%) and lead us to the conclusion that there are very few, if any, Rh/Co or Co anions present having $\nu(\text{CO})$ absorptions in this region. After such extractions the infrared spectrum of the remaining blue resin reveals no $\nu(\text{CO})$ absorptions, thus precluding the presence of any neutral carbonyl species. Plasma emission analysis of this remaining polymer reveals 19% of the initial Co loading and only a trace of Rh. This material does not react with CO. We offer these observations as being consistent with presence of " $\text{Co}(\text{A})_x^{2+}$ " cationic species (A = amine).

We sought to confirm these assignments by FDMS (Field Desorption Mass Spectrometry).²⁸ We are able to

(17) Chini, P. *Inorg. Chem.* 1969, 8, 1207.

(18) Typical analyses of MWA-1 reveal 6.2% N and 0.82% Cl. The chloride is 90–95% present in quaternary amine complexes, the remainder being inaccessible CH_2Cl groups.

(19) Rollman²⁰ has reported that the reaction of $\text{Rh}_2(\text{CO})_2\text{Cl}_2$ with *N,N*-dimethylbenzylamine or its polymeric analogue Amberlist A-21²¹ produces *cis*- $\text{Rh}(\text{CO})_2\text{Cl}$ (L) ($\nu(\text{CO})$ 2088 (s), 2004 (s) cm^{-1}). Examination of the resin after exposure to 1000 psig CO, Co/H₂, and/or 100 °C resulted in $\nu(\text{CO})$ absorptions characteristic of $\text{Rh}_6(\text{CO})_{15}\text{C}^{2-}$, $\text{Rh}_{12}(\text{CO})_{30}^{2-}$, and $\text{Rh}_7(\text{CO})_{16}^{3-}$.²²

(20) Rollmann, L. D. *Inorg. Chim. Acta* 1971, 6, 137. Jurewicz, A. T.; Rollman, L. D.; Whitehurst, D. D. *ACS Monogr.* 1974, No. 132, p 240.

(21) Amberlyst A-21 is a trademark of the Rohm and Haas Co. It is a weakly basic macroreticular anion exchange resin containing $-\text{CH}_2\text{NMe}_2$ functionality.

(22) We noted that $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ was observed if care was not taken to exclude ammonium ion "impurity" in the resin. Rollman originally reported $\text{Rh}_3(\text{CO})_{10}^-$, but we now know that what Chini originally formulated as $\text{Rh}_3(\text{CO})_{10}^-$ is actually $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$. See ref 14, p 31.

(23) Aliquat 336 is a trademark of the General Mills Corp. It is methyldiacrylammonium chloride.

(24) A reviewer has correctly pointed out that this does not completely preclude attack of the perchlorate salt on the more reduced anionic clusters. We agree, however, we can state that the $\nu(\text{CO})$ values of the species that are extracted match $\nu(\text{CO})$ values observed on the resin. No new $\nu(\text{CO})$ stretches are observed upon extraction.

(25) Martinengo, S.; Ciani, G.; Sironi, A.; Chini, P. *J. Am. Chem. Soc.* 1978, 100, 7096. Chini, P.; Cavaliere, A.; Martinengo, S. *Gazz. Chim. Ital.* 1972, 102, 330.

(26) Amberlite IRA-68 is a trademark of the Rohm and Haas Co. It is a gel-type, weakly basic anion exchange resin possessing tertiary amine functionality in a cross-linked acrylic matrix. For drying procedure, see Experimental Section.

(27) Even though Amberlite Resin should contain no Cl^- contamination, we typically found 2% Cl upon analysis.

(28) We thank C. Costello of the K. Bieman MIT Mass Spectrometry Facility for her help in obtaining the FSMS data.

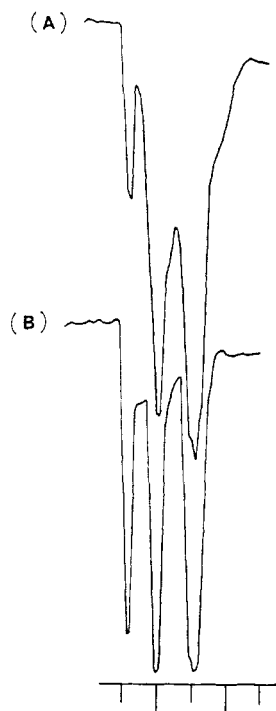


Figure 3. Comparison of $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ reacted with (A) Dowex MWA-1 vs. (B) Amberlite IRA-68.

clearly identify $[(\text{Bu}_4\text{N}^+)_2(\text{Co}(\text{CO})_4^-)]^+$ and $[(\text{Bu}_4\text{N}^+)_2(\text{Rh}(\text{CO})_2(\text{Cl})_2^-)]^+$ but could not obtain intelligible FDMS for the species with $\nu(\text{CO})$ at 2000 (s) and 1830 (m, br) cm^{-1} .

Attempts to selectively extract the species having $\nu(\text{CO})$ absorptions at 2000 (s) and 1840 (m, br) cm^{-1} have met with failure as it is either contaminated with $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ or $\text{Co}(\text{CO})_4^-$, and the small quantity that we obtain from our extraction studies (i.e., 5 g of a 1% loaded resin gives only 50 mg of total rhodium species of which this species is only a part) has precluded ^{13}C NMR identification.

Interaction of $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ with Amberlite IRA-68.

Figure 3 shows a comparison of the CO region of the infrared spectra of the products of $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ reaction with Dowex MWA-1 vs. Amberlite IRA-68^{16,26} both at $1.30 \pm 0.1\%$ Rh loadings. One notices that although the same absorptions are present, their intensities vary tremendously. $\text{Co}(\text{CO})_4^-$ is observable²⁷ at $\sim 1900 \text{ cm}^{-1}$, and the 2075 and 1995 cm^{-1} absorptions are present although not in equal intensities. On amberlite the two absorptions are of equal intensity and thus can, when combined with extraction studies,²⁹ be clearly assigned to $\text{Rh}(\text{CO})_2\text{Cl}_2^-$.

Interaction of $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ with Chloride-Free Amberlite IRA-68. Treatment of Amberlite IRA-68 with 1 N NH_4OH (see Experimental Section) results in a resin with $<0.03\%$ chloride contamination. Chloride level for this resin and MWA-1 could not be reduced below this level. When such a "cleaned up" resin is reacted with $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$, one obtains an infrared spectrum identical with that shown in Figure 3b. One thus observes the same cluster fragmentation that one sees using the "normal" chloride-contaminated resins or the homogeneous methyltricaprylammonium chloride. It can be argued that even this much chloride ion nucleophile can act catalytically in the sense that it fragments a portion of the neutral cluster to anions which then further attack the remaining neutral clusters. In any case future workers should be aware that these chloride levels are present and must be

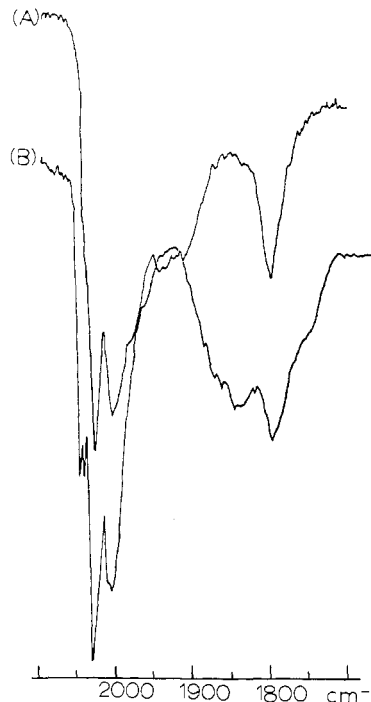
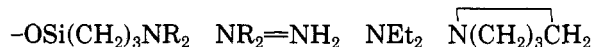


Figure 4. Reaction of $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ (A) or $\text{Rh}_4(\text{CO})_{12}$ (B) on amine-functionalized silica.

lived with. Although the infrared spectra of this material is identical with the chloride-contaminated material, its extraction properties are not. After quaternary ammonium perchlorate extraction of a very minor amount of $\text{Rh}(\text{C}-\text{O})_2\text{Cl}_2^-$ the remainder of the species responsible for the 2075 and 1995 cm^{-1} absorptions cannot be extracted. This we feel is indicative of the presence of $\text{Rh}(\text{CO})_2(\text{A})_2^+$ which should not be extractable. Interaction of the various Rh/Co clusters with "cleaned up" Dowex MWA-1 also reveals spectra that are identical with those of resins contaminated by higher levels of chloride.¹⁸ The bulk of our work was done by using the "normal" chloride contaminated materials.

Interaction of $\text{Rh}_x\text{Co}_{4-x}(\text{CO})_{12}$ with Amine-Functionalized Silica. Hancock et al.³⁰ have examined the interaction of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ with the ligands



and observed $\nu(\text{CO})$ absorptions at ~ 2080 and 2000 cm^{-1} indicative of the aforementioned mononuclear Rh species with cis carbonyls. Knozinger et al.³¹ reported that $\text{Rh}_6(\text{CO})_{16}$ reacts with $\text{sil}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NHC}_6\text{H}_{11}$ to give what they believe is $(\text{A})_2\text{Rh}(\text{CO})_2^+$ with $\nu(\text{CO})$ absorptions at 2085 and 2003 cm^{-1} .

Figure 4 reveals the CO absorption region of the infrared spectra of the products of the reaction of $\text{Rh}_x\text{Co}_{4-x}(\text{CO})_{12}$ ($x = 2, 4$) with an amine-functionalized silica.³² One observes that $\text{Co}_4(\text{CO})_{12}$ reacts in typical fashion revealing only $[\text{Co}(\text{CO})_4^-]$ and $[\text{Co}(\text{A})_x^{2+}]$ type species.²⁹ $\text{Rh}_4(\text{CO})_{12}$ once again reacts to produce a material whose spectrum reveals absorptions previously assigned to $\text{Rh}_{12}(\text{CO})_{30}^{2-}$. Again the lack of absorptions in the 1880–1950 cm^{-1} region indicates the absence of the several known Rh species

(30) Hancock, R. D.; Howell, I. V.; Pitkethly, R. C.; Robinson, P. J. In "Catalysis: Heterogeneous and Homogeneous"; Elsevier: Amsterdam, 1975; p 361.

(31) Knozinger, H.; Thornton, E. W.; Wolf, M. *J. Chem. Soc., Faraday Trans.* 1979, 7, 75.

(32) Prepared from Biosil A silica and $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{NMe}_2$ (see Experimental Section). Our thanks to J. Linowski, Dow Chemical, Midland, MI, for preparing this material.

(29) Identified by the extractive separation and plasma emission techniques described earlier. Also see Experimental Section.

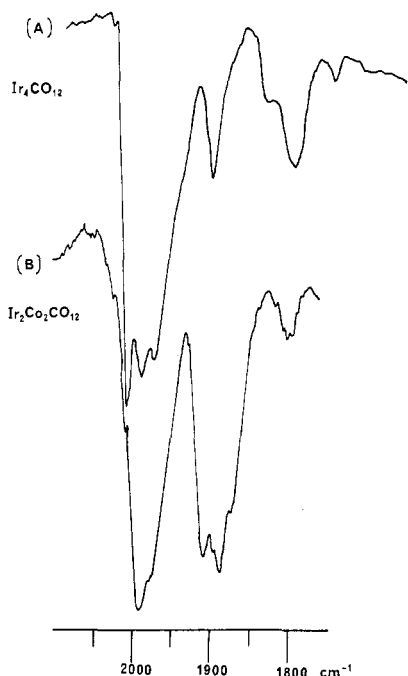


Figure 5. Interaction of $\text{Ir}_4(\text{CO})_{12}$ (A) and $\text{Ir}_2\text{Co}_2(\text{CO})_{12}$ (B) with Dowex MWA-1.

mentioned previously, and the absorptions present at ~ 1995 and $1830\text{--}1840\text{ cm}^{-1}$ could indicate the presence of large Rh carbonyl clusters. The reaction product of the amine-functionalized silica with $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ reveals a spectrum similar in $\nu(\text{CO})$ intensities in the 2030, 2000, and 1790 cm^{-1} regions but lacking any absorptions in the $1830\text{--}1840\text{ cm}^{-1}$ region. One should also notice the decrease in intensity of the 1900 cm^{-1} $\text{Co}(\text{CO})_4^-$ absorption²⁹ vs. the rest of the spectrum when compared to Figure 1.

An alternate interpretation would involve the interaction of the clusters with the silica surface. Basset et al.³³⁻³⁵ have studied the interaction of $\text{Rh}_6(\text{CO})_{16}$ and $\text{Rh}_4(\text{CO})_{12}$ with silica surfaces. $\text{Rh}_6(\text{CO})_{16}$ adsorbed on dry silica exhibits bands at 2080 (s) and 1800 (s) cm^{-1} which are similar in position although not in intensity to the absorptions of $\text{Rh}_6(\text{CO})_{16}$ itself. When $\text{Rh}_4(\text{CO})_{12}$ is adsorbed on dry silica, one does not observe IR absorptions similar to those of $\text{Rh}_4(\text{CO})_{12}$ but rather $\nu(\text{CO})$ absorptions similar to those of $\text{Rh}_6(\text{CO})_{16}$. In fact after adsorption $\text{Rh}_6(\text{CO})_{16}$ could be desorbed from the catalyst, indicating the $\text{Rh}_4(\text{CO})_{12}$ was rapidly transformed to $\text{Rh}_6(\text{CO})_{16}$ on the silica surface. Treatment of the adsorbed species with O_2 (300 torr) for 2 h at $50\text{ }^\circ\text{C}$ resulted in a transformation of the " $\text{Rh}_6(\text{CO})_{16}$ " Rh species to a *cis*- $\text{Rh}(\text{CO})_2$ species having $\nu(\text{CO})$ absorptions at 2091 and 2035 cm^{-1} . In our case we feel we can rule out such interactions since $\text{Rh}_4(\text{CO})_{12}$ reacts with the amine-functionalized silica to produce Rh-containing species with no 2080 (s) or 2091 (s) cm^{-1} absorptions, precluding "adsorbed" $\text{Rh}_6(\text{CO})_{16}$ and or the *cis*- $\text{Rh}(\text{CO})_2$ species observed by Basset.

Interaction of $\text{Ir}_x\text{Co}_{4-x}(\text{CO})_{12}$ ($x = 0, 2, 4$) with MWA-1. Unlike Co and Rh, the chemistry of polynuclear iridium carbonyl species has not been studied in as much

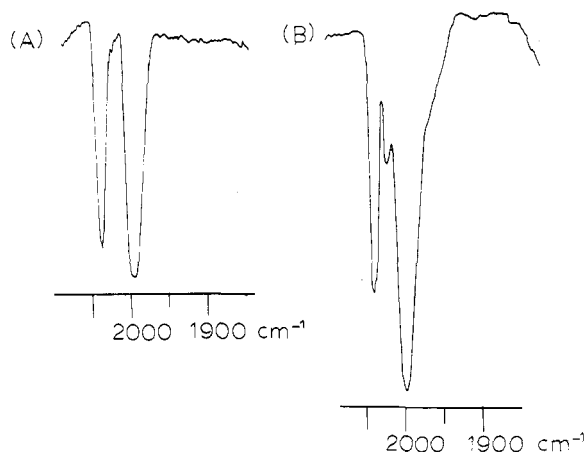


Figure 6. Interaction of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ with Dowex MWA-1: (A) initial interaction; (B) after 3 h at $100\text{ }^\circ\text{C}$ under 1:1 CO/H_2 .

detail.¹⁴ The species that have been observed are analogous to Rh in terms of their stoichiometry and stereochemistry.^{14,36} Interaction of $\text{Ir}_4(\text{CO})_{12}$ with MWA-1 proceeds similarly to $\text{Rh}_4(\text{CO})_{12}$ in that no $\text{Ir}(\text{CO})_4^-$ is observable in its IR spectrum (1895 cm^{-1}). In contrast to $\text{Rh}_4(\text{CO})_{12}$ however, the Ir-containing species present are not easy to deduce from analysis of the infrared spectrum. Absorptions are present at 2080 (vw), 2010 (s), 1995 (s), 1950 (sh), 1910 (m), 1830 (sh), 1795 (m), and 1745 (w) cm^{-1} . One can speculate by comparison to the analogous Rh spectra that little if any $\text{Ir}(\text{CO})_2\text{Cl}_2^-$ is present and that major quantities of $\text{Ir}_x(\text{CO})_y^{n-}$ anions are present. The weak absorption at 1745 cm^{-1} may be indicative of minor amounts of $\text{Ir}_6(\text{CO})_{16}^{2-}$ by comparison to spectra reported previously.³⁶

Although we cannot speculate on the exact nature of the Ir anions present in this system, it is useful nevertheless to compare their spectra to the spectra obtained from the material produced by the interaction of $\text{Ir}_2\text{Co}_2(\text{CO})_{12}$ with MWA-1 (Figure 5). In this case one observes an envelope in the $2020\text{--}1975\text{ cm}^{-1}$ region as well as bands at 1910 , 1890 , 1870 (sh), and 1790 (w) cm^{-1} . Again the mixed cluster fragments to $\text{Co}(\text{CO})_4^-$, $\nu(\text{CO}) = 1890\text{ cm}^{-1}$.²⁹ The lack of intensity in the $1850\text{--}1750\text{ cm}^{-1}$ bridged carbonyl region indicates the absence of large amounts of high nuclearity clusters.¹⁴ Extractive separation and subsequent plasma emission analysis of the species having $\nu(\text{CO})$ absorptions in the $2020\text{--}1975\text{ cm}^{-1}$ region revealed mainly (>95%) Ir, analogous to the $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ results.

Interaction of Polymer-Supported $\text{Rh}_x\text{Co}_{4-x}(\text{CO})_{12}$ with CO and CO/H_2 Atmospheres. Rollman et al.²⁰ have shown that $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ reacts with amine resins to give $\text{Rh}(\text{CO})_2\text{Cl}(\text{A})$. They also observed that such mono-substituted amine complexes, when exposed to synthesis gas, give anionic $\text{Rh}_x(\text{CO})_y^{n-}$ clusters. Figure 6 verifies these results. After 3 h at $100\text{ }^\circ\text{C}$ under 1:1 CO/H_2 one observes the relative intensities of the 2088 and the 2003 cm^{-1} absorptions changing and a $\nu(\text{CO})$ absorption at 2030 cm^{-1} ($\text{Rh}_{12}(\text{CO})_{30}^{2-}$) emerging. Figure 7 depicts the spectrum obtained after $\text{Rh}_2\text{Co}_2(\text{CO})_{12}/\text{MWA-1}$ (2% metal) was reacted with CO (1 atm) for 2 h in toluene. Again we note the formation of $\text{Rh}_{12}(\text{CO})_{30}^{2-}$ at the expense of the *cis*- $\text{Rh}(\text{CO})_2$ species. Similar results are obtained when one examines $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ or $\text{RhCo}_3(\text{CO})_{12}$ on Amberlite or amine-functionalized silica. Figure 8 depicts a sample of $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ used for >200 h at $\sim 130\text{ }^\circ\text{C}$ in a hydro-

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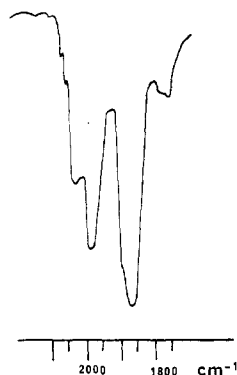


Figure 7. Interaction of $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ /MWA-1 (2% Rh) with 1 atm CO for 2 h in toluene.

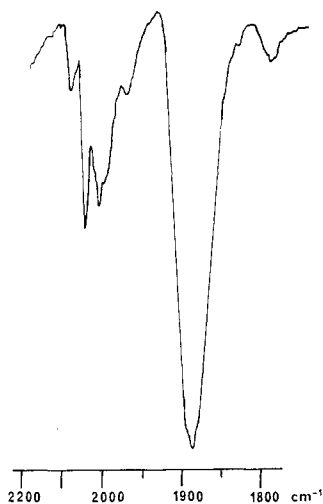


Figure 8. $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ on IRA-68 MWA-1 (2% Rh) after ~ 200 h at 130°C under 3000 psig 1:2 CO/H_2 .

formylation reaction. We notice a definite loss of intensity in the 2000 cm^{-1} region and again the appearance of an absorption at 2030 cm^{-1} ($\text{Rh}_{12}(\text{CO})_{30}^{2-}$) as described previously.

Conclusions

From these studies we can conclude that interaction of the mixed-metal Co/Rh and Co/Ir carbonyl clusters with tertiary amine-functionalized support materials results in fragmentation and or disproportionation of the clusters. Homogeneous model experiments have revealed that Cl⁻, acting as a nucleophile, is one source of cluster degradation reactions. Careful analysis of *all* the amine-functionalized support materials reveals chloride ion contamination that could cause catalytic cluster degradation even in such minor amounts.

Extractive separation and subsequent plasma emission metal analysis reveals segregation of M (M = Rh or Ir) from Co in the products. Initially formed *cis*- $\text{Rh}(\text{CO})_2$ species transform, after heating under CO/H_2 , into higher nuclearity Rh anionic clusters consistent with the studies of previous workers. Future publications will describe the use of such supported cluster catalysts in typical synthesis gas reactions such as hydroformylation.

Experimental Section

Unless otherwise indicated, all operations were conducted under purified argon or nitrogen, using standard inert atmosphere techniques. Solvents were dried and deaerated prior to use.

Infrared spectra were recorded on a Beckman IR 4240 spectrometer. Metal analysis was performed on a SMI IV plasma emission spectrometer using the 3396.85 and 3453.5 Å emission

Table I

resin	cluster	% Rh	% Co	% Ir
Dowex MWA-1	$\text{Rh}_4(\text{CO})_{12}$	1.08		
	$\text{Rh}_2\text{Co}_2(\text{CO})_{12}$	1.19	0.67	
	$\text{RhCo}_3(\text{CO})_{12}$	0.64	1.09	
	$\text{Co}_4(\text{CO})_{12}$		0.80	
	$\text{Ir}_4(\text{CO})_{12}$			1.10
Amberlite IRA-68 amine-functionalized silica	$\text{Ir}_2\text{Co}_2(\text{CO})_{12}$		0.28	0.19
	$\text{Rh}_2\text{Co}_2(\text{CO})_{12}$	1.40	0.80	
	$\text{Rh}_4(\text{CO})_{12}$	1.05		
	$\text{Rh}_2\text{Co}_2(\text{CO})_{12}$	1.24	0.70	
	$\text{Co}_4(\text{CO})_{12}$		1.15	

Table II

extract	molar ratio Co/Rh	IR absptns obsd, cm^{-1}			
		2075	1995	1895	1840-
1	4.9	vw	vw	s	
2	1.0	w	s	s	m
3	0.29	s	s	m	w
4	0.08	s	s	vw	
5	<0.01	s	s		
6	<0.01	s	s		
resin after six extractions	8.6	vw	vw		

lines for Rh and Co, respectively.

$\text{Ir}_4(\text{CO})_{12}$, $\text{Rh}_4(\text{CO})_{12}$, and $\text{Co}_4(\text{CO})_{12}$ were purchased from Strem Chemical Co. $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ and $\text{RhCo}_3(\text{CO})_{12}$ were prepared by the method of Chini.³⁷

Resin Preparation. Dowex MWA-1 and Amberlite IRA-68. Typically the resin (25 g) was washed four times with 100-mL portions of methanol in a Schlenk filtration apparatus and then dried in an oven at 100°C and 25 mm pressure overnight. At this point no water could be observed by IR and/or thermogravimetric analysis. Typical analyses follow: Dowex MWA-1: C, 83.72 ± 0.75 ; H, 9.04 ± 0.11 ; N, 6.31 ± 0.06 ; Cl, 0.47 ± 0.27 . Amberlite IRA-68: N, 7.84; Cl, 2.09. The resins were stored in a drybox until they were used.

Dechlorination Procedure for Amberlite IRA-68. The beads, 150 g, were placed in a column and washed with water (3 L), 1 N NH_4OH (3 L), and then water until the washings were neutral to litmus. The beads were then dried as previously described: initial chloride analysis 2.09%; chloride analysis after treatment 0.03%.

Amine-Functionalized Silica. Biosil-A (42 g) was reacted at reflux with 7.0 mL of $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NMe}_2$ in 200 mL of toluene for 3 h. The solid material was filtered, washed 3 times with 500 mL of acetone, and vacuum dried as described above. Analysis revealed 2.1% N and 0.02% Cl.

Metal Loading Procedure. The cluster (0.1–0.2 g) and the resin (5.0 g) were stirred together in 50 mL of toluene overnight. After filtration the loaded resin was vacuum dried. Analyses are given in Table I.

Preparation of $\text{Ir}_2\text{Co}_2(\text{CO})_{12}$. CO was bubbled through a solution of $\text{Ir}_2\text{Cl}_2(\text{C}_8\text{H}_{14})_4$ (0.30 g) in toluene, (10 mL) to give 0.18 g of a deep navy blue precipitate.³⁸ This "iridium blue" (0.32 g) was then reacted with $\text{NaCo}(\text{CO})_4 \cdot 2\text{THF}$ (0.27 g) in 40 mL of hexane overnight. After 16 h the solution was filtered and the filtrate stripped down to give $\text{Ir}_2\text{Co}_2(\text{CO})_{12}$ (0.22 g). This is a 53.6% yield based on $\text{Ir}_2\text{Cl}_2(\text{C}_8\text{H}_{14})_4$: IR $\nu(\text{CO})$ 2070 (s), 2060 (s), 2035 (m), 1863 (s) cm^{-1} . Anal. Calcd: Ir, 45.9; Co, 14.0. Found: Ir, 44.7; Co, 13.7.

Typical Extractive Separation. A sample of Amberlite IRA-68 (6 g) loaded with $\text{RhCo}_3(\text{CO})_{12}$ (1.4% Rh) was reacted with Bu_4NClO_4 (1.0 g) in CH_2Cl_2 (50 g) and stirred for 2 h. The reaction

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(38) This "iridium blue" complex reveals $\nu(\text{CO})$ absorptions at 2075 (s) and 1990 (s) cm^{-1} and is soluble in ketones. Complete details on the preparation of this material and its reaction chemistry will be described elsewhere. To our surprise the Ir analogue of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ is not known in the literature.

was filtered, the resin was washed with CH_2Cl_2 (two times, 50 mL), and the washings and filtrate were combined for IR and plasma emission analysis. The recovered resin was treated five times in an analogous manner. The resin that was left after six such treatments was washed with CH_2Cl_2 and analyzed for Rh and Co. Analyses are given in Table II.

Registry No. $\text{Co}_4(\text{CO})_{12}$, 17786-31-1; $\text{Co}(\text{CO})_4^-$, 14971-27-8; $\text{Rh}_2(\text{CO})_{30}^{2-}$, 12775-50-7; $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$, 50696-78-1; $\text{Rh}_4(\text{CO})_{12}$, 19584-30-6; $\text{Rh}_4(\text{CO})_2\text{Cl}_2^-$, 15550-00-2; $\text{Rh}(\text{CO})_4^-$, 44797-04-8; $[(\text{Bu}_4\text{N}^+)_2(\text{Co}(\text{CO})_4^-)]^+$, 87739-34-2; $[(\text{Bu}_4\text{N}^+)_2(\text{Rh}(\text{CO})_2(\text{Cl})_2^-)]^+$, 87739-35-3; $\text{Ir}_2\text{Co}_2(\text{CO})_{12}$, 50696-80-5; $\text{Ir}_2\text{Cl}_2(\text{C}_8\text{H}_{14})_4$, 12246-51-4; $\text{NaCo}(\text{CO})_4$, 14878-28-5; Cl^- , 16887-00-6.

Cluster Chemistry. 27.¹ The Synthesis and Structural Characterization of Three Mixed Gold-Cobalt-Ruthenium Carbonyl Clusters $\text{Ph}_3\text{PAuCoRu}_3(\text{CO})_{13}$, $(\text{Ph}_3\text{PAu})_2\text{CoRu}_3(\text{H})(\text{CO})_{12}$, and $(\text{Ph}_3\text{PAu})_3\text{CoRu}_3(\text{CO})_{12}$

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A unique series of mixed gold-cobalt-ruthenium carbonyl clusters has been prepared and structurally characterized. Reaction of $[(\text{Ph}_3\text{PAu})_3\text{O}]\text{BF}_4$ with $\text{HCoRu}_3(\text{CO})_{13}$ gives the three clusters $\text{Ph}_3\text{PAuCoRu}_3(\text{CO})_{13}$ (1), $(\text{Ph}_3\text{PAu})_2\text{CoRu}_3(\text{H})(\text{CO})_{12}$ (2), and $(\text{Ph}_3\text{PAu})_3\text{CoRu}_3(\text{CO})_{12}$ (3). An alternative specific route to 3 is via $[(\text{Ph}_3\text{PAu})_3\text{O}]\text{BF}_4$ and $[\text{CoRu}_3(\text{CO})_{13}]^-$, while Ph_3PAuCl and $[\text{CoRu}_3(\text{CO})_{13}]^-$ give exclusively 1. For 1 [$\text{C}_{31}\text{H}_{15}\text{O}_{13}\text{AuCoPrRu}_3$, $a = 9.345$ (3) Å, $b = 14.217$ (4) Å, $c = 14.721$ (3) Å, $\alpha = 114.83$ (2)°, $\beta = 93.16$ (2)°, $\gamma = 92.44$ °, triclinic, $\bar{P}1$, $Z = 2$] a trigonal-bipyramidal core is found, with the Ph_3PAu group triply bridging a CoRu_2 triangle. For 2 [$\text{C}_{48}\text{H}_{31}\text{Au}_2\text{CoO}_{12}\text{P}_2\text{Ru}_3 \cdot 0.5\text{CH}_2\text{Cl}_2$, $a = 35.173$ (9) Å, $b = 13.548$ (9) Å, $c = 23.193$ (4) Å, $\beta = 102.27$ (2)°, monoclinic, $C2/c$, $Z = 8$] a capped trigonal-bipyramidal core exists with the second Ph_3PAu group capping an AuRu_2 face of 1 and the hydride ligand bridging an Ru-Ru bond. The structures are rationalized in terms of the maximum number of face-sharing tetrahedra; the isolobality of H and Ph_3PAu is not valid in the context of polygold clusters.

Introduction

Development of the burgeoning field of mixed-metal clusters is limited by some practical difficulties. First, specific syntheses of the higher nuclearity clusters are not commonly available. Secondly, there are very few series of closely related clusters differing in nuclearity so that the effects of increasing size cannot be readily measured.

A number of groups have recently reported syntheses of mixed-metal clusters containing gold atoms by (i) the addition of R_3PAu^+ to appropriate cluster anions³⁻¹⁰ and

(ii) by the elimination of CH_4 between R_3PAuMe and cluster hydrides.¹¹ For (i) only one or two Au atoms have been introduced since most cluster anions are only mono- or dinegatively charged, although Ellis has reported $\text{V}(\text{AuPPh}_3)_3(\text{CO})_5$ via the $[\text{V}(\text{CO})_5]^{3-}$ anion.¹² We have adopted a different approach in our current efforts, namely, the use of the strong aurating agent $(\text{Ph}_3\text{PAu})_3\text{O}^+$ first reported by Nesmeyanov et al.,¹³ which we have found can add up to three gold atoms to a cluster substrate.^{14,15}

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