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HETEROSITE REACTIVITY OF COBALT–RHODIUM MIXED-METAL CLUSTERS

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Abstract—It has been established that reactions of cobalt–rhodium mixed-metal clusters with nucleophiles such as PEt_3, THF, MeCN and Cl^- occur on the rhodium site, with alkynes on the cobalt site. Several reversible tetranuclear–dinuclear transformations were observed with preferential retainment of the cobalt–rhodium bond.

The application of multimetallic catalysts has attracted much interest since their catalytic activity and/or selectivity often differs significantly from that of the homometallic systems of the constituent metals.[1,2] Although synergism has been observed in various homogeneous catalytic reactions,[2] very little is known of the actual role of the different metals in the catalytic cycle. The synergetic effect is probably due to the presence of a mixed-metal species, which could form from homo- or heteronuclear catalyst precursors. Such species could exhibit novel reactivity compared to the homonuclear analogues.[3] For example, in a mixed-metal dinuclear complex three different coordination sites are available for ligand activation (Scheme 1). Incoming substrates can be activated on sites 1 and 2 (*heterosite ligand activation*), or on site 3 (*heteronuclear ligand activation*). Since the two metals possess different electronic structure and thus different reactivity, facile activation could occur preferentially at one of these sites.

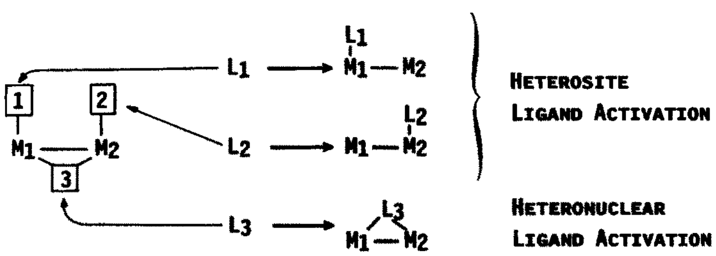
Cobalt–rhodium synergism has been reported for homogeneous catalytic hydrogenation,[4] hydroformylation[5] and hydrocarbonylation.[6] It was suggested by Pino and von Bezard that the synergetic effect, observed in the combined application of $Co_2(CO)_8$ (**1**) and $Rh_4(CO)_{12}$ (**2**) in the hydrocarbonylation of diketene, could arise from the presence of a cobalt–rhodium carbonyl complex.[6] It was later shown by Bor, Pino and coworkers that **1** and **2** are indeed in equilibrium with a new mixed-metal compound, formulated as $CoRh(CO)_7$ (**3**) [eq. (1)].[7]

$$\underset{\mathbf{1}}{2Co_2(CO)_8} + \underset{\mathbf{2}}{Rh_4(CO)_{12}} \rightleftharpoons \underset{\mathbf{3}}{4CoRh(CO)_7} \quad (1)$$

Complex **3** was recently isolated and its formula was established by analytical methods.[8] The proposed structure of $CoRh(CO)_7$ (**3**) contains a distorted tetrahedral $[Co(CO)_4]$ group bonded to a square-planar $[Rh(CO)_3]$ fragment through a Co—Rh bond and two semibridging carbonyl ligands.[8,9] It has also been found that $CoRh(CO)_7$ (**3**) is in equilibrium with two mixed-metal complexes: $CoRh(CO)_8$ (**4**)[8] and $Co_2Rh_2(CO)_{12}$ (**5**)[10] [eqs (2) and (3)].

$$\underset{\mathbf{3}}{CoRh(CO)_7} + CO \rightleftharpoons \underset{\mathbf{4}}{CoRh(CO)_8} \quad (2)$$

$$\underset{\mathbf{3}}{2CoRh(CO)_7} \rightleftharpoons \underset{\mathbf{5}}{Co_2Rh_2(CO)_{12}} + 2CO. \quad (3)$$



Scheme 1.

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In contrast, $CoRh(CO)_5(PEt_3)_2$ (**6**) does not dimerize to give a tetranuclear cluster but easily undergoes reversible or irreversible fragmentation when treated with MeCN and [PPN]Cl, respectively [eqs (4) and (5)].[11]

$$\underset{\mathbf{6}}{CoRh(CO)_5(PEt_3)_2} + MeCN \rightleftharpoons [Rh(CO)(PEt_3)_2(MeCN)]^+[Co(CO)_4]^- \quad (4)$$

$$\underset{\mathbf{6}}{CoRh(CO)_5(PEt_3)_2} + [PPN]Cl \rightarrow ClRh(CO)(PEt_3)_2 + PPN[Co(CO)_4] \quad (5)$$

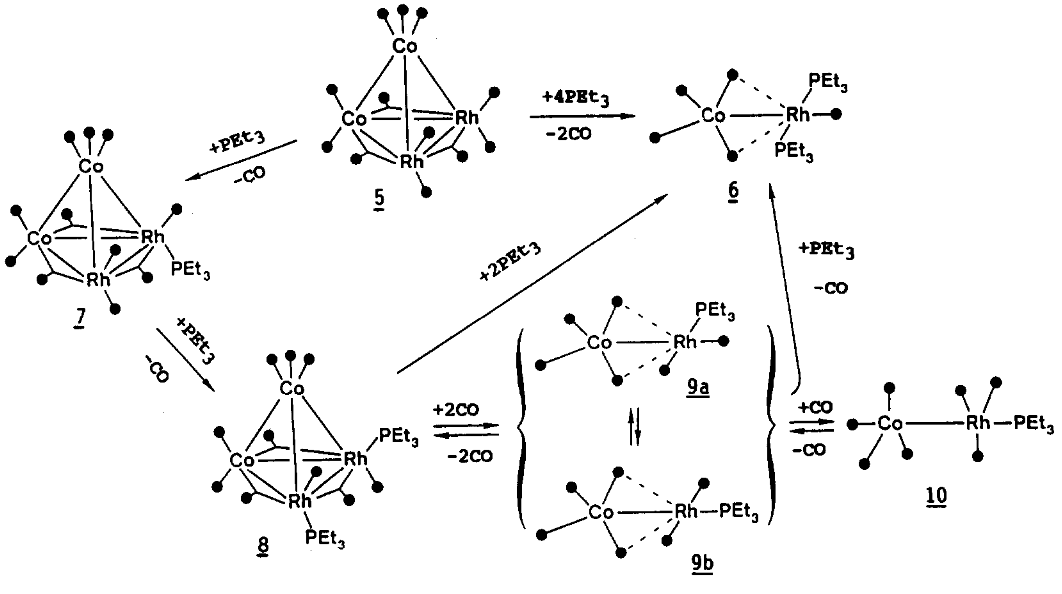
Furthermore, the reactions of **6** with nucleophiles showed preferential attack at the rhodium site. These results indicated that the reactivity of cobalt–rhodium clusters is strongly influenced by the nature of the ligands present. Therefore, we have undertaken a systematic study to develop a better understanding of the observed ligand dependence.

DISCUSSION

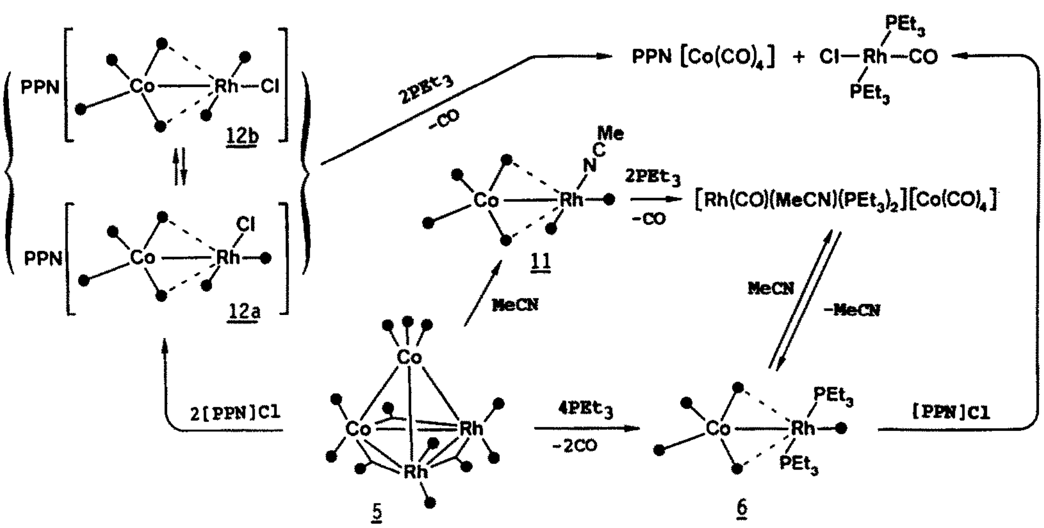
The reaction of $Co_2Rh_2(CO)_{12}$ (**5**) with four equivalents of PEt_3 results in the quantitative formation of $CoRh(CO)_5(PEt_3)_2$ (**6**) (Scheme 2).[12] Compound **6** has been previously isolated and structurally characterized.[11] When the reaction was followed by IR, the formation of three intermediates was observed: $Co_2Rh_2(CO)_{11}(PEt_3)$ (**7**), $Co_2Rh_2(CO)_{10}(PEt_3)_2$ (**8**), and $CoRh(CO)_6(PEt_3)$ (**9**). These compounds were separately isolated and their solution structures were established by spectroscopic methods. The structure of **7** consists of a *closo*-Co_2Rh_2 tetrahedral cluster with two rhodium atoms in the basal plane. There are eight terminal carbonyl ligands and three bridging carbonyl ligands along the basal plane. The PEt_3 ligand is bonded to a rhodium atom, and it probably occupies an axial position as was found for $Co_4(CO)_{11}(PPh_3)$.[13] The structure of $Co_2Rh_2(CO)_{10}(PEt_3)_2$ (**8**) is essentially the same as that of **7**, but each rhodium atom has one PEt_3 ligand; one has it in an axial and the other in an equatorial position. A similar structure was found for $Ir_4(CO)_{10}(PPh_3)_2$.[14] In the reaction of **5** and four equivalents of PEt_3, two moles of free carbon monoxide must be formed which can subsequently react with **7**, **8**, and **9**. It was interesting to see if $Co_2Rh_2(CO)_{11}(PEt_3)$ (**7**), $Co_2Rh_2(CO)_{10}(PEt_3)_2$ (**8**), and $CoRh(CO)_6(PEt_3)$ (**9**) do react with carbon monoxide as previously found for **3** and **5** [eqs (2) and (3)]. Indeed, facile and reversible reactions are observed. **7** reacts with carbon monoxide at atmospheric pressure and room temperature to give an equilibrium mixture of **7**, $CoRh(CO)_7$ (**3**), and $CoRh(CO)_6(PEt_3)$ (**9**) [eq. (6)].

$$\underset{\mathbf{7}}{Co_2Rh_2(CO)_{11}(PEt_3)} + 2CO \rightleftharpoons \underset{\mathbf{3}}{CoRh(CO)_7} + \underset{\mathbf{9}}{CoRh(CO)_6(PEt_3)} \quad (6)$$

Upon purging the equilibrium mixture with N_2, **3** and **9** recombine to give **7** quantitatively. Similarly, $Co_2Rh_2(CO)_{10}(PEt_3)_2$ (**8**) undergoes facile and reversible fragmentation when treated with 1 bar CO at room temperature to give $CoRh(CO)_6(PEt_3)$ (**9**)



Scheme 2.



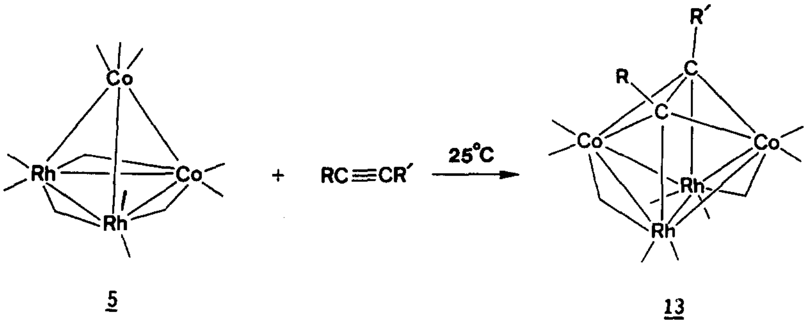
Scheme 3.

(Scheme 2). A structure has been proposed for **9**, in which a distorted tetrahedral $[Co(CO)_4]$ fragment is bonded to a square-planar $[Rh(CO)_2PEt_3]$ group through a Co—Rh bond and two cobalt-bonded semi-bridging carbonyl ligands.[9,12] The presence of two isomers, **9a** and **9b**, having a PEt_3 ligand *cis* and *trans*, respectively, to the $[Co(CO)_4]$ moiety, in solution was postulated. The relative ratio between **9a** and **9b** is 95 : 5. Medium-pressure IR studies have revealed that at higher carbon monoxide pressure $CoRh(CO)_6(PEt_3)_2$ (**9**) is in equilibrium with $CoRh(CO)_7(PEt_3)$ (**10**).[12] IR and NMR observations suggest that **10** is structurally analogous to $Co_2(CO)_7(PEt_3)$,[15] as shown in Scheme 2. The exact metal-site for the carbon monoxide addition to **4**, **8**, and **9** could not be determined. However, it is also believed to occur at the rhodium site(s), since the analogous $Co_2Ir_2(CO)_{12}$ cluster[10] does not react with CO at 15 bar and room temperature within 72 h.[16]

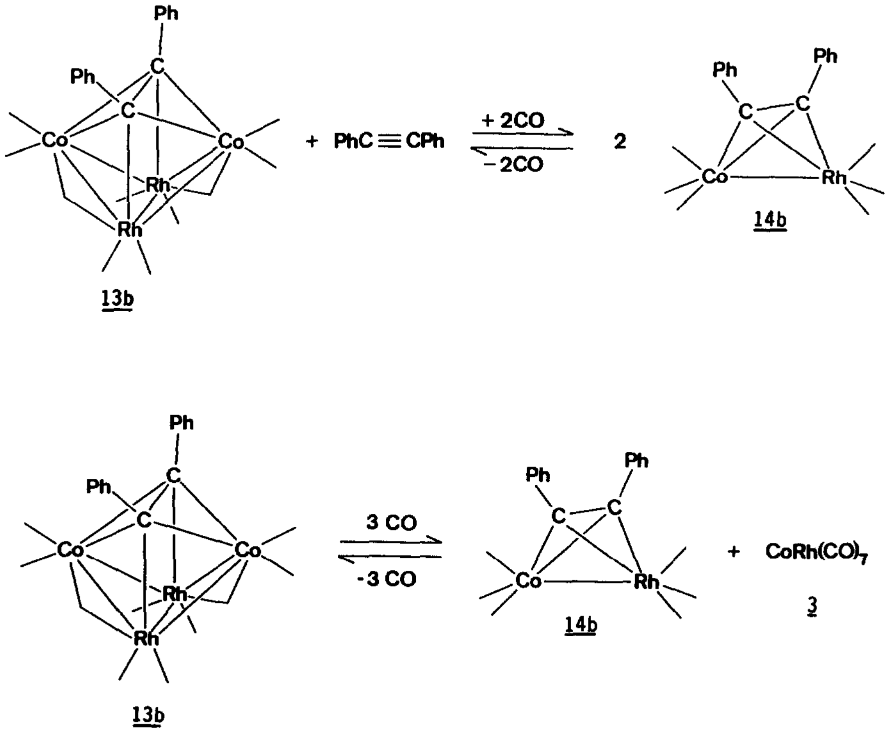
The reactivity of $Co_2Rh_2(CO)_{12}$ (**5**) towards other nucleophiles was also studied.[12] When **5** is dissolved in THF, its dark colour disappears and the solution becomes light orange. The IR spectrum of this solution indicates the transient formation of $CoRh(CO)_6(THF)$, which readily undergoes fragmentation to give an ionic species, probably $[Rh(CO)_2(THF)_2][Co(CO)_4]$.[16] **5** reacts similarly with excess or neat MeCN to give initially $CoRh(CO)_6(MeCN)$ (**11**) (Scheme 3). The solution structure of **11** was studied by IR and ^{13}C NMR, which indicate a structure analogous to **9a**. Although the stability of **11** is higher than that of $CoRh(CO)_6(THF)$, it slowly reacts further with the excess of MeCN to yield $[Rh(CO)_2(MeCN)_2][Co(CO)_4]$.[16] $Co_2Rh_2(CO)_{12}$ (**5**) undergoes irreversible fragmentation when treated with two equivalents of [PPN]Cl or $[N(CH_2Ph)Et_3]Cl$ to give $PPN[CoRh(CO)_6Cl]$ (**12**) and $[N(CH_2Ph)Et_3][CoRh(CO)_6Cl]$, respectively (Scheme 3).[12] An analogous compound, $[N(C_{12}H_{25})Me_3][CoRh(CO)_6Cl]$ has been previously prepared.[17] The solution structure of **12** was established by IR and ^{13}C NMR spectroscopy and is similar to **9**. The presence of two isomers, **12a** and **12b**, having a chloride ligand *cis* and *trans*, respectively, to the $[Co(CO)_4]$ moiety has been found. The relative ratio between these two isomers is 4 : 1.

It has been shown that $CoRh(CO)_5(PEt_3)_2$ (**6**) easily undergoes reversible or irreversible heterolytic cleavage of its metal–metal bond when treated with MeCN and [PPN]Cl [eqs (4) and (5)].[11] It was interesting to see if the same products form in the reaction of **11** and **12** with two equivalents of PEt_3, respectively. Indeed, the addition of PEt_3 to **12** results in the formation of the heteronuclear ion pair $[Rh(CO)(PEt_3)_2(MeCN)]^+[Co(CO)_4]^-$. After the solvent and MeCN are removed, compound **6** is the only product present, in agreement with eq. (4). The reaction of **12** with PEt_3 gives *trans*-$ClRh(CO)(PEt_3)_2$ and $PPN[Co(CO)_4]$, quantitatively (Scheme 3).

$Co_2Rh_2(CO)_{12}$ (**5**) reacts with alkynes via specific insertion into the Co—Co bond to give the butterfly cluster $Co_2Rh_2(CO)_{10}(\mu_4\text{-}\eta^2\text{-}RC_2R')$ [$R = R' = C_6F_5$ (**13a**), Ph (**13b**); R = H, R′ = Ph (**13c**); R = Me, R′ = Ph (**13d**)] (Scheme 4).[18] The molecular structure of **13a** was determined crystallographically, and it is very similar to related clusters containing a *closo*-M_4C_2 framework.[19] Upon addition of one equivalent of $F_5C_6C_2C_6F_5$ to **13a** in the presence of CO, highly regiospecific



Scheme 4.



Scheme 5.

fragmentation occurs to give $CoRh(CO)_6(\mu\text{-}\eta^2\text{-}F_5C_6C_2C_6F_5)$ (**14a**).

$Co_2Rh_2(CO)_{10}(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$ (**13b**) reacts similarly with diphenylacetylene and carbon monoxide to yield $CoRh(CO)_6(\mu\text{-}\eta^2\text{-}PhC_2Ph)$ (**14b**) (Scheme 5). Surprisingly, the reaction is fully reversible, such that upon bubbling N_2 into the reaction mixture **14b** reforms quantitatively. Since **13b** does not react with PhC_2Ph in the absence of carbon monoxide, it was assumed that **13b** reacts with CO and then with diphenylacetylene. Indeed, it was found that **13b** easily undergoes reversible fragmentation to give a 1 : 1 mixture of **14b** and $CoRh(CO)_7$ (**3**) at 2 bar CO pressure. In contrast, **13c,d** do not react with the corresponding alkynes in the presence of 1 bar CO at room temperature.[16] These results indicate that the nature of the substituents of the alkyne ligand has an opposite effect on the stability of **13** and **14**. Upon increasing the electronegativity of the substituents, the stability of the tetranuclear clusters decreases and that of the dinuclear complexes increases.

The present study has established that the combination of cobalt and rhodium in mixed-metal carbonyl complexes leads to regiospecific reactivity on rhodium or cobalt. Reactions of cobalt–rhodium mixed-metal clusters with nucleophiles such as PEt_3, THF, MeCN and Cl^- (and probably CO) occur on the rhodium site, with alkynes on the cobalt site. Several tetranuclear–dinuclear transformations are observed with the preferential retainment of the cobalt–rhodium bond. This indicates a higher "resistance" of the Co—Rh bond against metal–metal bond breaking than the Co—Co or Rh—Rh bonds. It is not clear if this is a characteristic feature of the Co_2Rh_2 framework itself, implying stronger Co—Rh bonds, or is a consequence of the attack of the substrates occurring exclusively on a rhodium or a cobalt centre. The facile formation of the coordinately unsaturated compounds $CoRh(CO)_{7-x}L_x$ (L = CO, THF, MeCN, Cl^-, PEt_3) could have an important role in homogeneous catalytic reactions. Studies concerning the mechanism of these reactions and the possible role of the coordinatively unsaturated cobalt–rhodium compounds in homogeneous catalytic hydroformylation are in progress.

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REFERENCES

1. J. H. Sinfelt, *Bimetallic Catalysts: Discoveries, Concepts, and Applications*. John Wiley, New York (1983).
2. P. Braunstein and J. Rose, in *Stereochemistry of Organometallic and Inorganic Compounds* (Edited by I. Bernal), Vol. 3. Elsevier, Amsterdam (in press).
3. W. L. Gladfelter and G. L. Geoffroy, in *Comprehensive Organometallic Chemistry* (Edited by G. Wilkinson, F. G. A. Stone and E. Abel), Chap. 40. Pergamon Press, Elmsford, NY (1982).
4. D. Labroue and R. Poilblanc, *J. Molec. Catal.* 1977, **2**, 329.
5. A. Ceriotti, L. Garlaschelli, G. Longoni, M. C. Malatesta, D. Strumolo, A. Fumagalli and S. Martinengo, *J. Molec. Catal.* 1984, **24**, 309.
6. P. Pino and D. A. von Bezard, Ger Offen 2 807 215, 1978.
7. F. Spindler, G. Bor, U. K. Dietler and P. Pino, *J. Organomet. Chem.* 1981, **213**, 303.
8. I. T. Horváth, G. Bor, M. Garland and P. Pino, *Organometallics* 1986, **5**, 1441.
9. I. T. Horváth and G. Bor, manuscript in preparation.
10. S. Martinengo, P. Chini, V. G. Albano, F. Cariati and T. Salvatori, *J. Organomet. Chem.* 1973, **59**, 379.
11. D. A. Roberts, W. C. Mercer, S. M. Zaharuk, G. L. Geoffroy, C. W. DeBrosse, M. E. Cass and C. G. Pierpont, *J. Am. Chem. Soc.* 1982, **104**, 910; D. A. Roberts, W. C. Mercer, G. L. Geoffroy and C. G. Pierpont, *Inorg. Chem.* 1986, **25**, 1439.
12. I. T. Horváth, *Organometallics* 1986, **5**, 2333.
13. D. J. Darensbourg and M. Incoriva, *Inorg. Chem.* 1981, **20**, 1911.
14. K. Karel and G. Norton, *J. Am. Chem. Soc.* 1974, **96**, 6812.
15. P. Szabó, L. Fekete, G. Bor, Z. Nagy-Magos and L. Markó, *J. Organomet. Chem.* 1968, **12**, 245.
16. I. T. Horváth, unpublished results.
17. F. Joó and H. Alper, *Can. J. Chem.* 1985, **63**, 1157.
18. I. T. Horváth, L. Zsolnai and G. Huttner, *Organometallics* 1986, **5**, 180.
19. L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc.* 1962, **84**, 2450; G. Gervasio, R. Rossetti and P. L. Stanghellini, *Organometallics* 1985, **4**, 1612; E. Sappa, A. Tiripicchio and P. Braunstein, *Chem. Rev.* 1983, **83**, 203.