Preferential Retainment of the Cobalt–Rhodium Bond in Some Reactions of Co$_2$Rh$_2$(CO)$_{12}$ and Its Triethylphosphine-Substituted Derivatives[1]

István T. Horváth

Department of Industrial and Engineering Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland
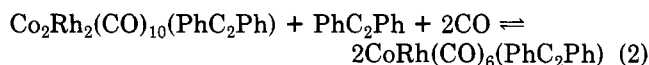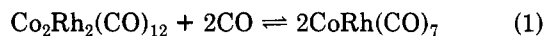
Co$_2$Rh$_2$(CO)$_{12}$ (1) reacts with PEt$_3$ to give CoRh(CO)$_5$(PEt$_3$)$_2$ (3); three intermediates, Co$_2$Rh$_2$(CO)$_{11}$(PEt$_3$) (4), Co$_2$Rh$_2$(CO)$_{10}$(PEt$_3$)$_2$ (5), and CoRh(CO)$_6$(PEt$_3$) (6), were separately isolated and characterized by IR and NMR spectroscopy. 4 reacts with CO in a reversible reaction to give an equilibrium mixture of 4, CoRh(CO)$_7$ (2), and 6. 5 undergoes facile and reversible fragmentation when treated with CO to give 6. Medium-pressure in situ IR studies have revealed that at higher CO pressure 6 is in equilibrium with CoRh(CO)$_7$(PEt$_3$) (7). 1 reacts with excess of MeCN to give CoRh(CO)$_6$(MeCN) (8), which undergoes heterolytic metal–metal bond cleavage when treated with PEt$_3$ to give [Rh(CO)(MeCN)(PEt$_3$)$_2$]$^+$[Co(CO)$_4$]$^-$. The treatment of 1 with 2 equiv of [PPN]Cl or [N(CH$_2$Ph)Et$_3$]Cl gives PPN[CoRh(CO)$_6$Cl] (9) and [N(CH$_2$Ph)Et$_3$][CoRh(CO)$_6$Cl] (10), respectively. 9 reacts with 2 equiv of PEt$_3$ to yield PPN[Co(CO)$_4$] and ClRh(CO)(PEt$_3$)$_2$.
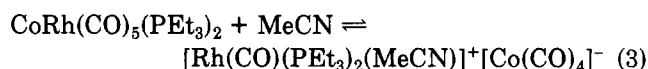
Introduction

There are important differences in the fundamental chemistry of cobalt and rhodium carbonyls, including the differences in their tendency to form coordinatively unsaturated (16-electron) species. Whereas the cobalt generally achieves the 18-electron configuration in its complexes,[2] a large number of compounds with square-planar (16-electron) rhodium centers are known.[3] When these two metals are combined in a mixed-metal compound, these differences could remain or give rise to some sort of structural compromise resulting in novel reactivity and catalytic activity.[4–9]

It has been found that Co$_2$Rh$_2$(CO)$_{12}$ (1)[5] reacts with carbon monoxide in a facile and reversible reaction to give CoRh(CO)$_7$ (2)[6] (eq 1).[7] Similar reversible fragmentation for Co$_2$Rh$_2$(CO)$_{10}$(PhC$_2$Ph) involving diphenylacetylene and carbon monoxide was recently described (eq 2).[8] In

$$Co_2Rh_2(CO)_{12} + 2CO \rightleftharpoons 2CoRh(CO)_7 \qquad (1)$$

$$Co_2Rh_2(CO)_{10}(PhC_2Ph) + PhC_2Ph + 2CO \rightleftharpoons$$
$$2CoRh(CO)_6(PhC_2Ph) \qquad (2)$$

contrast, CoRh(CO)$_5$(PEt$_3$)$_2$ (3) does not dimerize but easily undergoes reversible or irreversible heterolytic cleavage of its metal–metal bond (eq 3 and eq 4).[9] These

$$CoRh(CO)_5(PEt_3)_2 + MeCN \rightleftharpoons$$
$$[Rh(CO)(PEt_3)_2(MeCN)]^+[Co(CO)_4]^- \qquad (3)$$

$$CoRh(CO)_5(PEt_3)_2 + [PPN]Cl \rightarrow$$
$$ClRh(CO)(PEt_3)_2 + PPN[Co(CO)_4] \qquad (4)$$

results suggest that the nuclearity of the cobalt–rhodium system and the relative stability of the Co–Rh bond is strongly influenced by the nature of ligands present. Therefore, we have undertaken an investigation to understand the observed ligand dependence.

Results and Discussions

The reaction of Co$_2$Rh$_2$(CO)$_{12}$ (1) with 4 equiv of PEt$_3$ in *n*-hexane occurs rapidly at room temperature to yield CoRh(CO)$_5$(PEt$_3$)$_2$ (3), quantitatively (eq 5). Compound

$$Co_2Rh_2(CO)_{12} + 4PEt_3 \rightarrow 2CoRh(CO)_5(PEt_3)_2 + 2CO \qquad (5)$$
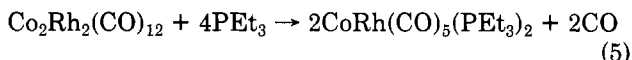
3 has been previously synthesized and structurally characterized.[9] When the successive addition of PEt$_3$ was followed by IR, the formation of three intermediates was observed: Co$_2$Rh$_2$(CO)$_{11}$(PEt$_3$) (4), Co$_2$Rh$_2$(CO)$_{10}$(PEt$_3$)$_2$ (5), and CoRh(CO)$_6$(PEt$_3$) (6). Compounds 4, and 5, and 6 were separately prepared and characterized by analytical and spectroscopical techniques.

At room temperature 1 reacts with 1 equiv of PEt$_3$ to form Co$_2$Rh$_2$(CO)$_{11}$(PEt$_3$) (4) in 96% yield. Its IR spectrum (Figure 1) is very similar to those of Co$_2$Rh$_2$(CO)$_{11}$P(OMe)$_3$[10] and Co$_4$(CO)$_{11}$PR$_3$ (R = alkyl, aryl),[11] suggesting a similar structure for 4. Since the two rhodium atoms could occupy different positions in the Co$_2$Rh$_2$ framework, different isomeric forms of 4 may be present in solution. However, the ν_1(CO) band at 2080 cm^{-1} does not show splitting[10] and only three bands are observed in the bridging carbonyl region, indicating that only one form of 4 is present. The PEt$_3$ ligand is attached to a rhodium atom as evidenced by ^{31}P NMR of 4 in toluene-d_8 (31.5 ppm (d, J_{Rh-P} = 116 Hz)). The ^{13}C NMR spectrum of a 90% ^{13}CO-enriched sample of 4 shows a broad singlet at 205 ppm at 25 °C in toluene-d_8. On cooling this peak

(1) This paper is dedicated to Professor Piero Pino on the occasion of his 65th birthday.

(2) Kemmitt, R. D. W.; Russell, D. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Elmsford, NY, 1982; Chapter 34.

(3) Hughes, R. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. Eds.; Pergamon Press: Elmsford, NY, 1982; Chapter 35.

(4) Labroue, D.; Poilblanc, R. *J. Mol. Catal.* 1977, *2*, 329. Ceriotti, A.; Garlaschelli, L.; Longoni, G.; Malatesta, M. C.; Strumolo, D.; Fumagalli, A.; Martinengo, S. *J. Mol. Catal.* 1984, *24*, 309. Pino, P.; von Bézard, D. A. Ger. Offen 2 807 251, 1978.

(5) Martinengo, S.; Chini, P.; Albano, V. G.; Cariati, F.; Salvatori, T. *J. Organomet. Chem.* 1973, *59*, 379.

(6) Spindler, F.; Bor, G.; Dietler, U. K.; Pino, P. *J. Organomet. Chem.* 1981, *213*, 303.

(7) Horváth, I. T.; Bor, G.; Garland, M.; Pino, P. *Organometallics* 1986, *5*, 1441.

(8) Horváth, I. T.; Zsolnai, L.; Huttner, G. *Organometallics* 1986, *5*, 180.

(9) Roberts, D. A.; Mercer, W. C.; Zaharuk, S. M.; Geoffroy, G. L.; DeBrosse, C. W.; Cass, M. E.; Pierpont, C. G. *J. Am. Chem. Soc.* 1982, *104*, 910. Roberts, D. A.; Mercer, W. C.; Geoffroy, G. L.; Pierpont, C. G. *Inorg. Chem.* 1986, *25*, 1439.

(10) Labroue, D.; Queau, R.; Poilblanc, R. *J. Organomet. Chem.* 1980, *186*, 101.

(11) Darensbourg, D. J.; Peterson, B. S.; Schmidt, R. E., Jr. *Organometallics* 1982, *1*, 306.
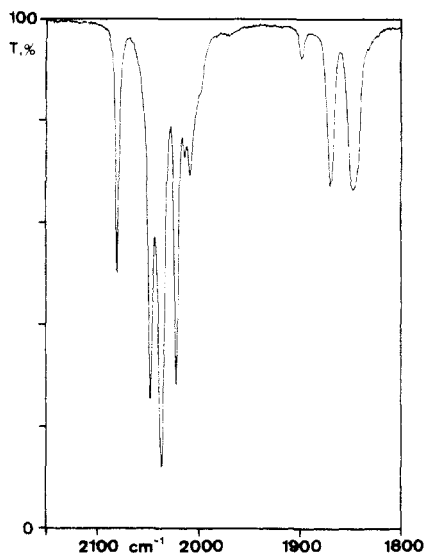
Figure 1. The IR spectrum of the $\nu(CO)$ region for $Co_2Rh_2(CO)_{11}(PEt_3)$ (**4**) in *n*-hexane.

Figure 2. Variable-temperature ^{13}C NMR spectra of the CO region for $Co_2Rh_2(CO)_{11}(PEt_3)$ (**4**) in toluene-d_8.

broadens, coalesces at –10 °C, and reforms into nine new resonances at –70 °C. These resonances can be unequivocally assigned to a structure shown in Figure 2. The two doublets at 244.5 (J_{Rh-C} = 35 Hz) and 237.7 ppm (J_{Rh-C} = 31 Hz) result from the two nonequivalent bridging

Figure 3. The IR spectrum of the $\nu(CO)$ region for $Co_2Rh_2(CO)_{10}(PEt_3)_2$ (**5**) in *n*-hexane.

carbonyl ligands between the cobalt and rhodium atoms in the basal plane and the broad triplet at 231.9 ppm (J_{Rh-C} = 38 Hz) from the bridging carbonyl between two basal rhodium atoms. The broad singlet at 199.8 ppm of relative intensity 3 is assigned to the three terminal carbonyls of the apical cobalt atom. The two singlet at 198.4 and 195.4 ppm is attributed to the equatorial and axial terminal carbonyl ligands of the basal cobalt atom, respectively.[12] The doublet of doublets at 188.7 ppm ($^1J_{Rh-C}$ = 73 Hz, $^2J_{P-C}$ = 19 Hz) results from the terminal carbonyl ligand on the basal rhodium atom bearing the PEt_3 ligand. Finally, the two doublets at 185.8 (J_{Rh-C} = 71 Hz) and 181.6 ppm (J_{Rh-C} = 65 Hz) are assigned to the equatorial and axial terminal carbonyl ligands on the basal rhodium atom, respectively.[12] Thus, the structure of **4** 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]

$Co_2Rh_2(CO)_{10}(PEt_3)_2$ (**5**) is prepared by the reaction of 1 and 2 equiv of PEt_3 in 92% yield. The IR spectrum of **5** (Figure 3) is very similar to those of $Co_2Rh_2(CO)_{10}(PR_3)_2$ (R = OMe,[10] F[14]). Although more than one isomeric form of **5** may be present in solution, the IR spectrum shows no splitting of the $\nu_1(CO)$ band at 2056 cm^{-1} and has only three bands in the bridging carbonyl region, indicating that only one form is present. Its ^{31}P NMR spectrum in toluene-d_8 shows a doublet at 27.0 ppm (J_{Rh-P} = 127 Hz) at 25 °C. On cooling this signal broadens and coalesces at –20 °C. Two doublets at 33.5 (J_{Rh-P} = 117 Hz) and 25.8 ppm (J_{Rh-P} = 136 Hz) of equal intensity were resolved on cooling to –90 °C. This indicates that the PEt_3 ligands are bonded to one or two rhodium atoms; however, the lack of P–P coupling suggests that each rhodium has one PEt_3 ligand. The ^{13}C NMR spectrum of a 90% ^{13}CO-enriched sample of **5** in toluene-d_8 shows a broad singlet at 211.9 ppm at 25 °C. Upon cooling this peak broadens, reaching the colescence point at –20 °C; at –90 °C the spectrum exhibits eight resonances. These resonances can be un-

(12) The assignment of the axial and equatorial carbonyl ligands is based on the generally observed treend that the axial carbonyls resonate at higher field. (a) Stuntz, G. F.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 607. (b) Heaton, B. T.; Strona, L.; Pergola, R. D.; Garlaschelli, L.; Sartorelli, U.; Sadler, I. H. *J. Chem. Soc., Dalton Trans.* **1983**, 173.

(13) Darensbourg, D. J.; Incoriva, M. *J. Inorg. Chem.* **1981**, *20*, 1911.

(14) Eshtiagh-Hosseini, H.; Nixon, J. F. *J. Organomet. Chem.* **1978**, *150*, 129.

(15) Johnson, B. F. G.; Benfield, R. E. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: Chichester, 1980; Chapter 7.
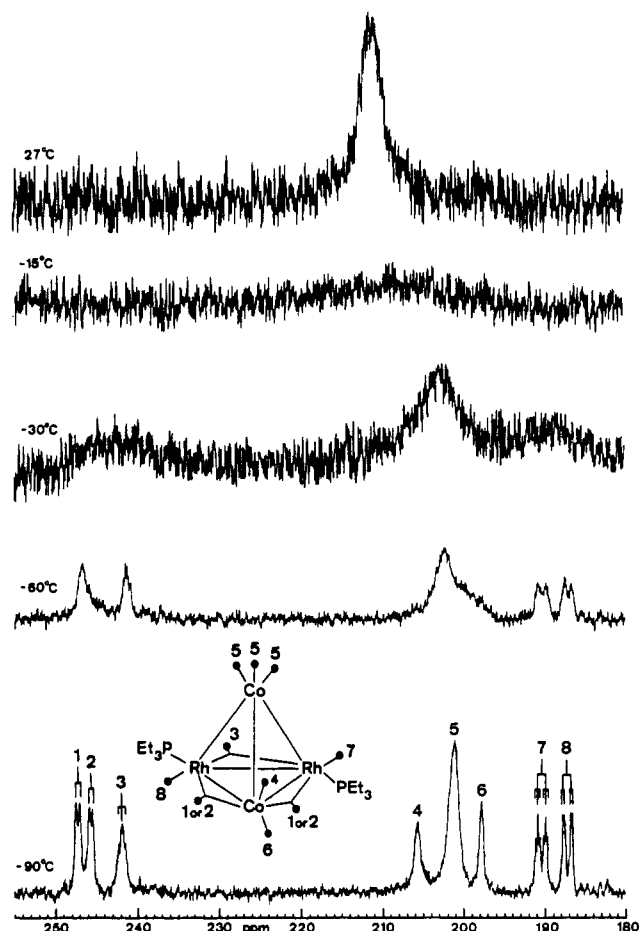
Figure 5. The IR spectrum of the ν(CO) region for CoRh-(CO)₆(PEt₃) (**6**) in *n*-hexane.

Figure 4. Variable-temperature ¹³C NMR spectra of the CO region for Co₂Rh₂(CO)₁₀(PEt₃)₂ (**5**) in toluene-d_8.

ambiguously assigned to a structure shown on Figure 4. The two doublets at 247.2 ($J_{\text{Rh-C}}$ = 37 Hz) and 245.7 ppm ($J_{\text{Rh-C}}$ = 37 Hz) are attributed to two nonequivalent bridging carbonyl ligands between the cobalt and rhodium atoms in the basal plane. The broad triplet at 241.8 ppm ($J_{\text{Rh-C}}$ = 40 Hz) results from the bridging carbonyl between two basal rhodium atoms. The broad singlet at 201 ppm of relative intensity 3 is assigned to the three terminal carbonyl ligands of the apical cobalt atom. The two singlets at 205.7 and 197.8 ppm result from the equatorial and the axial terminal carbonyl ligands of the basal cobalt atom, respectively.[12] The doublet of triplets at 190.5 ppm (¹$J_{\text{Rh-C}}$ = 73 Hz, ²J = 18.5 Hz) is assigned to the equatorial terminal carbonyl ligand of one of the basal rhodium atoms and the doublet of doublets at 187.2 ppm (¹$J_{\text{Rh-C}}$ = 70 Hz, ²$J_{\text{P-C}}$ = 17 Hz) to the axial terminal carbonyl ligand on the other basal rhodium atom.[12] Thus, the structure of **5** consists of a *closo*-Co₂Rh₂ tetrahedral cluster with two rhodium atoms in the basal plane. There are seven terminal carbonyl ligands and three bridging carbonyl ligands along the basal plane. Each rhodium atom has one PEt₃ ligand; one has it in an axial and the other in an equatorial position. Similar structure has been found for Ir₄(CO)₁₀-(PPh₃)₂.[16]

The variable-temperature NMR of **4** and **5** does not indicate any site selectivity in the scrambling process. Therefore a similar mechanism discussed in details for analogous tetranuclear clusters can be proposed.[15]

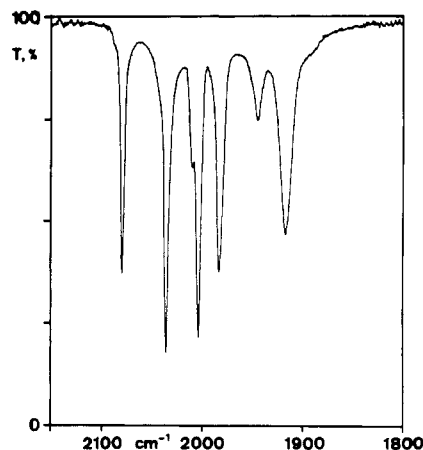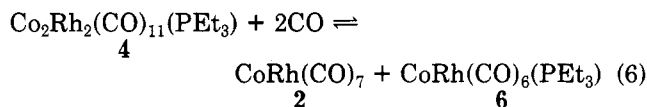In the reaction of **1** and 4 equiv of PEt₃ 2 mol of free carbon monoxide must be formed (eq 5) which can sub-

sequently react with **4** or **5**. It was interesting to see if Co₂Rh₂(CO)₁₁(PEt₃) (**4**) and Co₂Rh₂(CO)₁₀(PEt₃)₂ (**5**) do react with carbon monoxide as previously found for 1.[7] Indeed, facile and reversible reactions are observed.

Co₂Rh₂(CO)₁₁(PEt₃) (**4**) reacts with carbon monoxide at 1-bar pressure and room temperature to give an equilibrium mixture of **4**, CoRh(CO)₇ (**2**), and CoRh(CO)₆(PEt₃) (**6**) (eq 6). After the pressure was reduced and the solution was purged with N₂, **2** and **6** recombine to give **4** quantitatively.

$$\text{Co}_2\text{Rh}_2(\text{CO})_{11}(\text{PEt}_3) + 2\text{CO} \rightleftharpoons$$
$$\mathbf{4}$$

$$\text{CoRh(CO)}_7 + \text{CoRh(CO)}_6(\text{PEt}_3) \quad (6)$$
$$\mathbf{2} \qquad\qquad \mathbf{6}$$

When a solution of Co₂Rh₂(CO)₁₀(PEt₃)₂ (**5**) in *n*-hexane is stirred under 1 bar of carbon monoxide at room temperature, the color of the solution is slowly changed from dark reddish brown to light orange. After 12 h **5** is completely reacted and the quantitative formation of CoRh-(CO)₆(PEt₃) (**6**) is observed by IR (Figure 5). The reaction is fully reversible, such that upon removing the solvent in vacuo **6** reverts back quantitatively to **5** (Scheme I). The reversible reaction of **5** with CO can be repeated several times without loosing a noticeable amount of **5**. The formula CoRh(CO)₆(PEt₃) for **6** was established by the measurement of the amount of carbon monoxide needed for its formation (1.98 mol of CO/mol of **5**) and by freezing point molecular weight determination. The molecular weight measurements were carried out by the Beckman method in cyclohexane under a CO atmosphere: M_r-(measd) 454 ± 10 (M_r(calcd) 448). The ³¹P NMR spectrum of **6** in CD₂Cl₂ at 25 °C shows a doublet at 24.55 ppm ($J_{\text{Rh-P}}$ = 127.6 Hz). On cooling this resonance broadens reaching the coalescence point at -30 °C; at -90 °C the spectrum exhibits two doublets at 30.9 ($J_{\text{Rh-P}}$ = 143.2 Hz) and 18.5 ppm ($J_{\text{Rh-P}}$ = 114 Hz) of relative intensity ca. 5/95. The ¹³C NMR spectrum of a ¹³CO-enriched sample of **6** shows a broad singlet at 199.6 ppm, implying rapid exchange of the carbonyl ligands. On cooling this signal broadens and coalesces at -30 °C. Four resonances were resolved on cooling to -90 °C: δ_1 206.5 (s) for Co-bonded carbonyls, δ_2 193.1 (d, $J_{\text{Rh-C}}$ = 62 Hz), δ_3 188.0 (dd, ¹$J_{\text{Rh-C}}$ = 53 Hz, ²$J_{\text{P-C}}$ = 115 Hz), and δ_4 177.6 (dd, ¹$J_{\text{Rh-C}}$ = 78 Hz, ²$J_{\text{P-C}}$ = 19 Hz) for Rh-bonded carbonyls (Figure 6). The assignment of ²$J_{\text{P-C}}$ = 115 Hz and ²$J_{\text{P-C}}$ = 19 Hz is confirmed by ³¹P NMR of a 90% ¹³CO-enriched sample of **6**, when the doublet at 18.5 ppm (¹$J_{\text{Rh-P}}$ = 114 Hz) becomes a doublet of triplets. The relative intensity of the Co-bonded carbonyls to Rh-bonded carbonyls is ca. 4/2, which sug-

(16) Karel, K.; Norton, G. *J. Am. Chem. Soc.* **1974**, *96*, 6812.

Scheme I
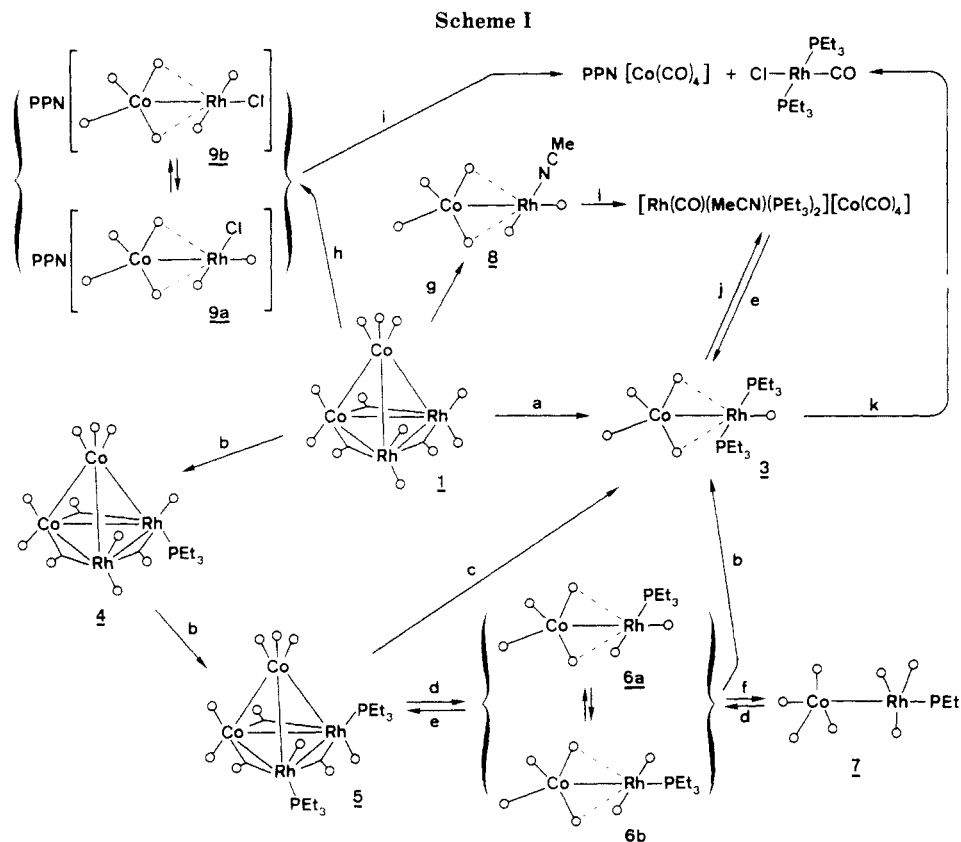
(a) 4 equiv of PEt_3/n-hexane/25 °C; (b) 1 equiv of PEt_3/n-hexane/25 °C; (c) 2 equiv of PEt_3/n-hexane/25 °C; (d) 1 bar of CO/n-hexane/25 °C; (e) slow evaporation/25 °C; (f) 15 bar of CO/n-hexane/5 °C; (g) 200 equiv of MeCN/CH_2Cl_2 or n-hexane/25 °C, or neat MeCN; (h) 2 equiv of [PPN]Cl/CH_2Cl_2/25 °C; (i) 2 equiv of PEt_3/CH_2Cl_2/25 °C; (j) neat MeCN/25 °C[9]; (k) 2 equiv of [PPN]Cl[9]

gests that in **6** a {$Co(CO)_4$} group is bonded to a coordinatively unsaturated {$Rh(CO)_2(PEt_3)$} fragment. The three resonances for Rh-bonded carbonyls arise from the presence of two isomers, **6a** (δ_3 and δ_4) and **6b** (δ_2) having a PEt_3 ligand cis and trans to the {$Co(CO)_4$} moiety (Figure 6); the ratio between **6a** and **6b** is ca. 95/5. Finally, the IR spectrum of **6** (Figure 5) shows six bands, and the bands at 1945 and 1917 cm^{-1} are at lower frequency values as it can be expected for linear terminal carbonyl ligands bonded to cobalt or rhodium atoms. The analogous bands have been also observed in the IR spectra of $CoRh(CO)_7$ (**2**)[7] and $CoRh(CO)_5(PEt_3)_2$ (**3**).[9] The regular shift of the bands to lower frequency values and the similar pattern of the two low-energy bands in the series **2 → 6 → 3** shows that the substitution of CO by PEt_3 results in the expected increase in electron density on the metals but does not change the overall geometry of these compounds. The structural characterization of compound **3**[9] revealed that two cobalt-bonded carbonyl ligands are slightly bent and directed toward the rhodium atom. This may indicate a weak interaction of these carbonyls with the rhodium atom or may only be a consequence of the distorted tetrahedral geometry at the cobalt atom. Although the later possibility cannot be ruled out entirely, the presence of two semibridging carbonyl ligands in these compounds seems to be plausible. Therefore, we propose a structure for **6** in which a distorted tetrahedral {$Co(CO)_4$} fragment with a local symmetry of C_{2v} is bonded to a square-planar {$Rh(CO)_2$-(PEt_3)} group through a Co–Rh bond and two semibridging carbonyl ligands. We postulate the presence of two isomers, **6a** and **6b**, in solution which interconvert rapidly at room temperature.

Before discussing the fluxionality of **6**, we report here an unexpectedly facile reaction of this compound. Because
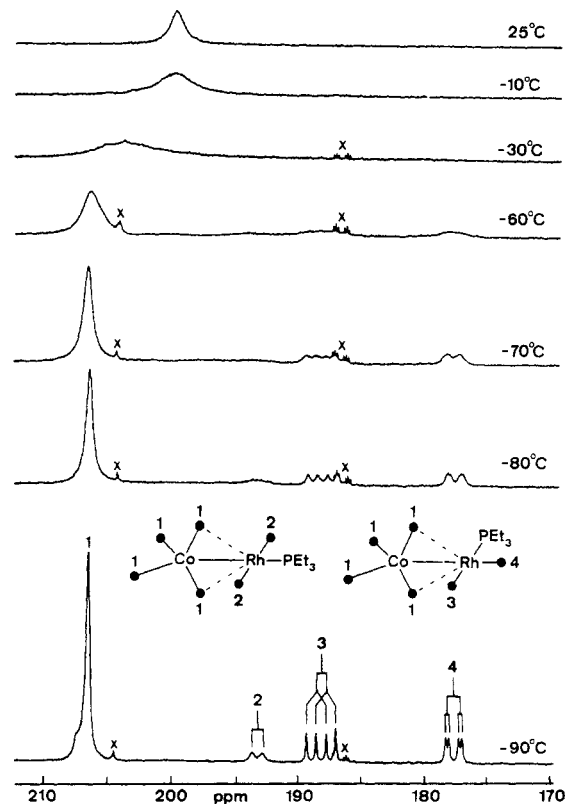

Figure 6. Variable-temperature ^{13}C NMR spectra of the CO region for $CoRh(CO)_6(PEt_3)$ (**6**) in toluene-d_8. The small peaks labeled with X are due to an unidentified trace impurities.

6 easily loses CO, its NMR sample generally was made in situ by the treatment of **5** with carbon monoxide in an
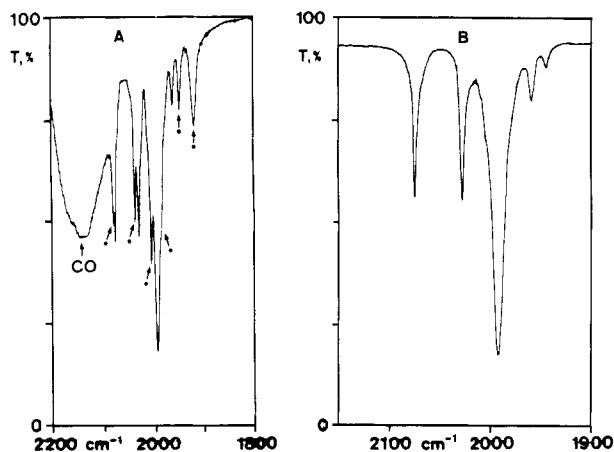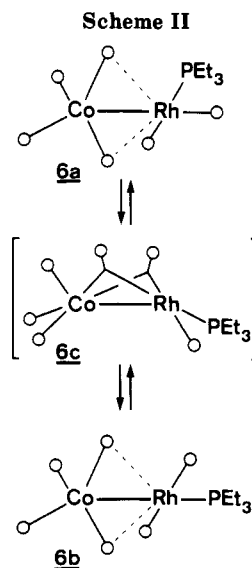
Figure 7. (A) IR spectrum of the ν(CO) region for the reaction mixture of CoRh(CO)₆(PEt₃) (6) under 15 bar of CO. The peaks labeled with asterisk are due to 6. (B) IR spectrum of CoRh-(CO)₇(PEt₃) (7) in *n*-hexane after subtracting the absorptions of dissolved CO and 6.

Scheme II

NMR tube. The 90% ¹³CO-enriched sample of 6 were prepared accordingly under 90% ¹³CO-enriched carbon monoxide. Although at 25 °C only one peak was observed, the ³¹P and ¹³C NMR spectra at –90 °C showed additional resonances at 53.8 (d, J_{Rh-P} = 94 Hz) and 198.2 ppm (d, J_{Rh-C} = 28 Hz), respectively. These resonances were first assigned for 6b; however, these peaks disappeared after the solution was purged with N₂ for a few minutes at –20 °C. Thus, a new species must have been formed by the reversible reaction of 6 and the dissolved carbon monoxide. Indeed, medium-pressure IR studies have revealed that 6 reacts with carbon monoxide when treated with 15 bar of CO at 5 °C to give the same species, for which we propose the formula CoRh(CO)₇(PEt₃) (7) based on the following strong evidences. Under these conditions 7 represents about 60% of the carbonyls in solution (based on the intensity of 6). New bands appear at 2075 m, 2020 m, 1992 s, 1960 w, and 1945 vw cm⁻¹, which was obtained by subtracting the spectral contributions of other components, solvent, CO, and 6 (Figure 7). The ratio between the intensities of the new bands do not change by changing the CO pressure, indicating that only one new compound is formed. The concentration of 7 increases by increasing the carbon monoxide pressure as expected for eq 7. The

$$CoRh(CO)_6(PEt_3) + CO \rightleftharpoons CoRh(CO)_7(PEt_3) \quad (7)$$
$$6 7$$
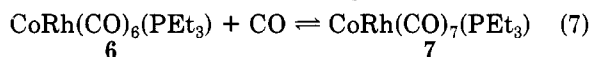
IR spectra of 7 and of Co₂(CO)₇PR₃[17] show a remarkable similarity. The absence of bands in the bridging carbonyl region and the NMR observations suggest that 7 is structurally analogous to Co₂(CO)₇(PEt₃), as is shown in Scheme I. After the pressure is decreased to 1 bar, 7 loses CO and 6 reforms quantitatively.

Since the variable-temperature NMR of 6 shows simultaneous broadening of all resonances upon cooling or warming, a localized carbonyl exchange process[18] between the cobalt and rhodium center involving the bridging intermediate 6c is proposed (Scheme II). 6c could form from 6a or 6b by shifting simultaneously two carbonyl ligands, one from the cobalt and the other from the rhodium atom, into a bridging position, respectively. A similar intermediate with bridging carbonyl ligands has been proposed for CpIrW(CO)₇.[19] It should be noted that if

(17) Szabó, P.; Fekete, L.; Bor, G.; Nagy-Magos, Z.; Markó, L. *J. Organomet. Chem.* **1968**, *12*, 245.
(18) Aime, S.; Milone, L. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 183.

6 loses CO by dimerization or decomposition, 7 could form, which may also be an intermediate between 6a and 6b. The variable-temperature NMR performed in the presence or in the absence of CO did not show a noticeable effect of carbon monoxide. However, this does not rule out the presence of a small amounts of 7 in solution. It appears that while CoRh(CO)₇ (2)[7] and CoRh(CO)₆(PEt₃) (6) are fluxional, CoRh(CO)₅(PEt₃)₂ (3) is rigid at room temperature. This could be explained by the absence of a carbonyl ligand in the cis position with respect to the {Co(CO)₄} group in 3, which seems to be essential for the carbonyl exchange between the cobalt and rhodium atoms.

Mechanistically, it is clear that at least five different types of reactions can occur in this system: (A) ligand substitution of the tetranuclear clusters 1 and 4; (B) reversible fragmentation reactions of 1,[7] 4, and 5 with carbon monoxide; (C) irreverisble fragmentation reaction of 5 with PEt₃; (D) reversible addition of carbon monoxide to 2[7] and 6; (E) ligand substitution of the coordinatively unsaturated dinuclear complexes 1 and 6. Although a dissociative mechanism for reaction A cannot be ruled out, it is proposed that reactions A, B, and C proceed through analogous intermeidates, which are formed by ligand addition accompanied by the cleavage of a metal–metal bond. These intermediates can undergo either CO elimination followed by the reformation of the metal–metal bond (reaction A) or further ligand addition resulting in fragmentation to dinuclear complexes (reactions B and C). With respect to a possible mechanism for the reformation of the teranuclear clusters in reaction B, the dinuclear complexes may lose CO and dimerize or first dimerize and then the formed intermediates undergo successive CO loss. There is an obvious mechanistic possibility for reaction E, involving the formation of a coordinatively saturated intermediate which easily undergoes CO elimination. In fact, reaction D indicates the existence of such species. It is clear that a thorough kinetic study is required to determine the mechanisms involved.

The observed facile and quantitative formation of CoRh(CO)₅(PEt₃)₂ (3) from 1 seemed to be in contrast to the results of Poilblanc and co-workers on the reaction of 1 and P(OMe)₃.[10] Although the preparation of the mono-, di-, and even the trisubstituted derivatives of 1 is reported, no indication could be found by these authors for the formation of {CoRh(CO)₅[P(OMe)₃]₂}, the analogue of 3.

(19) Einstein, F. W.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *Organometallics* **1985**, *4*, 250.
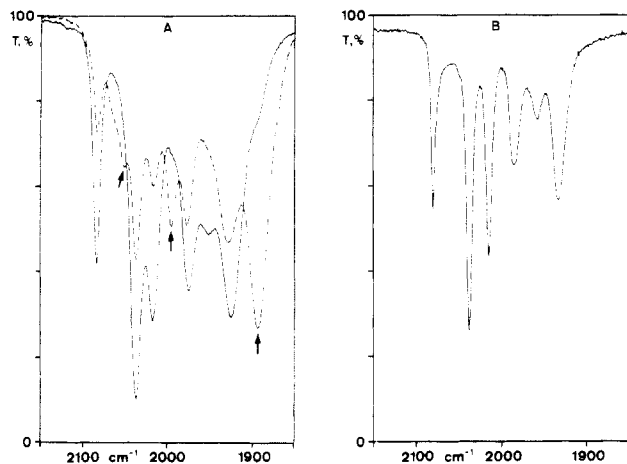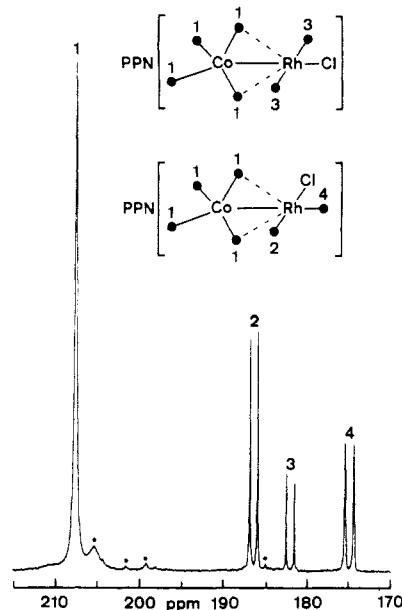
Figure 8. IR spectra of the $\nu(CO)$ region for the reaction-mixture of Co$_2$Rh$_2$(CO)$_{12}$ (1) and MeCN: (A) in neat MeCN, (—) after 2 minutes and (- - -) after 6 h; (B) in n-hexane after 5 min.

Therefore, the reaction of 1 with P(OMe)$_3$ was reinvestigated. To a n-hexane solution of 1 was added successively 10 equiv of P(OMe)$_3$. After the addition of the first equivalent, the formation of Co$_2$Rh$_2$(CO)$_{11}$P(OMe)$_3$ is observed. When the second equivalent is added, Co$_2$Rh$_2$(CO)$_{10}$[P(OMe)$_3$]$_2$ is formed. Further addition of P(OMe)$_3$, up to 10 equiv, *does not* result in {CoRh(CO)$_5$[P(OMe)$_3$]$_2$}. Besides the precipitation of some light yellow solid, the trisubstituted derivative Co$_2$Rh$_2$(CO)$_9$[P(OMe)$_3$]$_3$ is formed, confirming Poilblanc and co-workers' results.[10]

When the two systems are compared, it appears that the mono- and disubstituted derivatives of 1 with PEt$_3$ and P(OMe)$_3$ can be formed, but the reactivity of 5 differs significantly from that of Co$_2$Rh$_2$(CO)$_{10}$[P(OMe)$_3$]$_2$. Although PEt$_3$ has a slightly higher cone angle than P(OMe)$_3$, it is believed that the observed difference is primarily due to the lower basicity of the later.[20] The lower basicity could result in less polarization of the four Co–Rh bonds in Co$_2$Rh$_2$(CO)$_{10}$[P(OMe)$_3$]$_2$, thus making the two rhodium atoms less positive or, in other words, less attractive for the incoming next phosphite. Therefore, the third substitution may occur on a cobalt center rather than on the rhodium atom. Studies concerning this possibility as well as reactions of 1 with other phosphines are in progress.

Chini and co-workers reported almost 20 years ago that Co$_2$Rh$_2$(CO)$_{12}$ (1) reacts rapidly with weak Lewis bases as THF or Et$_2$O, but no details on these reactions were provided.[21] Therefore, we have first investigated the reaction of 1 and THF. When 1 is dissolved in THF, its dark color disappears and the solution become light orange. The IR spectrum after 2 min shows new bands at 2075 m, 2032 vs, 2002 s, 1975 m, 1950 w, and 1920 cm^{-1}. Since the new species is very unstable we decided to use MeCN instead of THF.

When Co$_2$Rh$_2$(CO)$_{12}$ (1) is dissolved in MeCN or excess MeCN is added to a n-hexane (or CH$_2$Cl$_2$) solution of 1 under N$_2$, the reddish brown color immediately turns to light orange and CoRh(CO)$_6$(MeCN) (8) is formed. This formula is based on the following observations: (1) no CO evolution could be detected after the addition of MeCN, (2) the IR spectra of the reaction mixture in MeCN and in n-hexane (Figure 8) show only six bands in both solvents, (3) no bands are observed in the bridging carbonyl region, (4) the overall patterns of these spectra are very

(20) Tollman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(21) Chini, P.; Martinengo, S.; Albano, V. "Proceedings of the First International Symposium on New Aspects of the Chemistry of Metal Carbonyls and Derivatives", Venice, Italy, Sept 2–4, 1968; p A3.

Figure 9. ^{13}C NMR spectrum of the CO region for PPN[Co-Rh(CO)$_6$Cl] (9) in CD$_2$Cl$_2$ at -90 °C. The small peaks labeled with asterisk are due to an unidentified trace impurities.

similar to those of 6. After further stirring, the color slowly changes to deep red and new IR bands appear at 2050, 1995, and 1894 cm^{-1} (Figure 8). The band at 1894 cm^{-1} indicates the formation of an ionic species in which [Co-(CO)$_4$]$^-$ is probably the anion. A 90% ^{13}CO-enriched sample of 8 is prepared in situ from a 90% ^{13}CO-enriched sample of 1 and MeCN in CD$_2$Cl$_2$. Since 8 is slowly fragmented to an ionic species, after the addition of MeCN the NMR tube had to be immediately cooled to -90 °C. At this temperature the ^{13}C NMR spectrum exhibits three intensive resonances, a singlet at 205 ppm and two doublets at 189.1 (J_{Rh-C} = 58 Hz) and 173.2 ppm (J_{Rh-C} = 73 Hz). Two doublets at 184.5 (J_{Rh-C} = 75 Hz) and 177.0 ppm (J_{Rh-C} = 65 Hz) in very low intensity are also present; their origin is not known. Although 8 has not been fully characterized, its spectral data indicate a structure similar to 6a (Scheme I).

1 undergoes facile and irreversible fragmentation when treated with 2 equiv of [PPN]Cl or [N(CH$_2$Ph)Et$_3$]Cl in CH$_2$Cl$_2$ at 25 °C to give PPN[CoRh(CO)$_6$Cl] (9) and [N-(CH$_2$Ph)Et$_3$][CoRh(CO)$_6$Cl] (10), respectively. An analogous compound, [N(C$_{12}$H$_{25}$)Me$_3$][CoRh(CO)$_6$Cl] (11), has recently been prepared, but only its proposed formula and IR spectra were reported.[22] Although compounds 9 and 10 are formed quantitatively, crystalline material for analysis could not been obtained. The IR spectra of 9, 10, and 11[22] are similar to those of compounds 6 and 8. The ^{13}C NMR spectrum of a 90% ^{13}CO-enriched sample of 9 in CD$_2$Cl$_2$ shows four resonances at -90 °C: δ_1 207.6 (s) for cobalt-bonded carbonyls and δ_2 186.3 (d, J_{Rh-C} = 69 Hz), δ_3 182.0 (d, J_{Rh-C} = 72 Hz), and δ_4 175.0 (d, J_{Rh-C} = 79 Hz) for rhodium-bonded carbonyls (Figure 9). The relative intensity of δ_1 and δ_2 + δ_3 + δ_4 is ca. 4:2, indicating that in 9 a {Co(CO)$_4$} group is bonded to a {Rh(CO)$_2$Cl} group. The three resonances for Rh-bonded carbonyls arise from the presence of two isomers, 9a (δ_2 and δ_4) and 9b (δ_3), having a chloride ligand cis and trans, respectively, to the {Co(CO)$_4$} moiety. The relative ratio between these two isomers is 4/1.

The addition of weak Lewis bases to 1 probably involves the formation of an unobserved intermediate such as

(22) Joó, F.; Alper, H. *Can. J. Chem.* **1985**, *63*, 1157.

{Co$_2$Rh$_2$(CO)$_{12}$Nu}, which easily undergoes subsequent ligand addition to yield CoRh(CO)$_6$Nu.

Finally, some preliminary experiments show that the relative stability of the Co–Rh bond is dependent of the ligands present on the rhodium atom. Addition of 2 equiv of PEt$_3$ to CoRh(CO)$_6$(MeCN) (8) results in heterolytic metal–metal bond cleavage and the heteronuclear ion pair [Rh(CO)(PEt$_3$)$_2$(MeCN)]$^+$[Co(CO)$_4$]$^-$ is formed. Its spectral data are identical with those reported by Roberts et al.[9] After the solvent and MeCN are removed, compound 3 is the only product present in agreement with eq 3. 9 undergoes heterolytic cleavage of its metal–metal bond when reacted with PEt$_3$ in CH$_2$Cl$_2$ to give PPN[Co(CO)$_4$] and *trans*-ClRh(CO)(PEt$_3$)$_2$.

Conclusions

The present study demonstrates that the combination of cobalt and rhodium does give rise to a structural compromise resulting in novel reactivity. The peculiarity of the observed tetranuclear–dinuclear transformations is the preferential retainment of the cobalt–rhodium bond. This may be explained by the higher "resistance" of the Co–Rh bond against metal–metal bond breaking than the Co–Co and Rh–Rh bonds. It is not clear if this is the characteristic feature of the Co$_2$Rh$_2$ framework itself, implying stronger Co–Rh bonds, or is the consequence of the nucleophilic attack occurring exclusively on a rhodium center.

It should be stressed that in the Co$_2$Rh$_2$(CO)$_{12-x}$L$_x$ (x = 0–2) clusters each metal atom achieves the 18-electron configuration, while the CoRh(CO)$_{7-x}$L$_x$ (x = 0–2) complexes are electronically unsaturated by the amount of two electrons. The formation of 3 and 6 from 5 and 2, 8, 9, and 10 from 1 involves only ligand addition and results in coordinatively unsaturated products. Such reactions may have an important implication in homogeneous catalysis when a cobalt–rhodium mixed-metal cluster is used as catalyst precursor. Although a coordinatively unsaturated dinuclear species can be the active catalyst, its further fragmentation to mononuclear species may result in mononuclear cycles involving one or both metals.

The relative stability of the Co–Rh bond in the dinuclear compounds is strongly dependent of the ligands present. The successive replacement of the carbonyl ligands by better donors like PEt$_3$[23] on the rhodium leads to heterolytic cleavage of the metal–metal bond.

Studies concerning the mechanism of these reactions and the possible role of the coordinatively unsaturated cobalt–rhodium compounds in homogeneous catalysis are in progress.

Experimental Section

General Data. All operations were performed under N$_2$ or CO atmosphere. High-purity carbon monoxide was prepared by catalytic dehydration of formic acid at 280 °C and stored in aluminum cylinders under pressure. The solvents (products of Fluka AG) were purified and dried by the usual methods. Co$_2$Rh$_2$(CO)$_{12}$[7] was prepared by a literature method. [^{13}C]Carbon monoxide (90% isotopic purity) was purchased from MSD Isotopes. PEt$_3$, P(OMe)$_3$, and [PPN]Cl were purchased from Strem Chemicals, Inc., Danvers, MA.

Medium-pressure (2–16 bar) experiments were carried out in a 150-mL glass autoclave equipped with magnetic stirring and jacketed cooling. Samples were withdrawn under pressure directly into a thermostated high-pressure IR cell. A pressure cell corresponding to the type published by Noack,[24] equipped with a heating/cooling mantle (connected to a thermostat), modified in some minor details according to the experience collected in this laboratory,[24] was used for IR spectral measurements.

IR spectra were recorded on a Perkin-Elmer Model 983 spectrometer. ^{13}C NMR spectra were recorded on a AM300WB Bruker spectrometer.

Reaction of Co$_2$Rh$_2$(CO)$_{12}$ (1) with 4 Equiv of PEt$_3$. A 100-mL, three-necked, round-bottomed flask was fitted with a pressure-equalizing dropping funnel. The flask was charged with 0.050 g (0.075 mmol) of 1 and 30 mL of *n*-hexane, and the dropping funnel was charged with a solution of 44 μL (0.3 mmol) of PEt$_3$ in 10 mL of *n*-hexane. The PEt$_3$ solution was added dropwise, and the mixture was stirred for 1 h at room temperature. After 20 min the IR spectrum revealed that 3 formed quantitatively. The solvent was removed in vacuo. The red residue was crystallized from *n*-pentane at −78 °C to give 0.079 g (0.146 mmol, 98%) of CoRh(CO)$_5$(PEt$_3$)$_2$ (3): IR (ν(CO), *n*-hexane) 2026 s, 1964.5 vs, 1954 vs, 1919.5 m, 1889.5 s cm^{-1}; ^{31}P NMR (in toluene-d_8) 16.65 ppm (d, J_{Rh-P} = 111 Hz).

Preparation of Co$_2$Rh$_2$(CO)$_{11}$(PEt$_3$) (4). A 100-mL, three-necked, round-bottomed flask was fitted with a pressure-equalizing dropping funnel. The flask was charged with 0.066 g (0.1 mmol) of 1 and 40 mL of *n*-hexane, and the dropping funnel was charged with a solution of 14.6 μL (0.1 mmol) PEt$_3$ in 10 mL of *n*-hexane. The PEt$_3$ solution was added dropwise, and the mixture was stirred for 2 h at room temperature. The reaction mixture was concentrated to 20 mL and chromatographed on a silica column. The reddish brown band eluted with *n*-hexane yielded 0.072 g (0.096 mmol, 96%) of Co$_2$Rh$_2$(CO)$_{11}$(PEt$_3$) (4): mp 122 °C; IR (ν(CO), *n*-hexane): 2080 m, 2047 s, 2037 vs, 2022 s, 2014 w, 2006 w, 1898 w, 1869 m, 1846 m cm^{-1}; ^{31}P NMR (toluene-d_8): 31.5 ppm (d, J_{Rh-P} = 116 Hz). Anal. Calcd for C$_{17}$H$_{15}$O$_{11}$PCo$_2$Rh$_2$: C, 27.22; H, 2.02. Found: C, 27.87; H, 2.23.

Preparation of Co$_2$Rh$_2$(CO)$_{10}$(PEt$_3$)$_2$ (5). A 100-mL, three-necked, round-bottomed flask was fitted with a pressure-equalizing dropping funnel. The flask was charged with 0.066 g (0.1 mmol) of 1 and 40 mL of *n*-hexane, and the dropping funnel was charged with a solution of 29.2 μL (0.2 mmol) of PEt$_3$ in 10 mL of *n*-hexane. The PEt$_3$ solution was added dropwise, and the mixture was stirred for 3 h at room temperature. The reaction mixture was concentrated to 20 mL and chromatographed on a silica column. The reddish brown band eluted with *n*-hexane yielded 0.077 g (0.092 mmol, 92%) of Co$_2$Rh$_2$(CO)$_{10}$(PEt$_3$)$_2$ (5), mp 65 °C. Anal. Calcd for C$_{24}$H$_{30}$O$_{10}$P$_2$Co$_2$Rh$_2$: C, 33.36; H, 3.50. Found: C, 31.50; H, 3.70. Freezing point molecular weight determination: first the freezing point of cyclohexane was measured under N$_2$ (5.36 °C). A solution of 0.119 g of 5 in 4.40 g of cyclohexane was placed in a 20-mL Schlenk tube under N$_2$. The freezing point was measured; 4.68 °C. The molecular weight was calculated from the freezing point depression: ΔT = 0.68 °C, M_r(measd) 828 ± 10 (M_r(calcd) 840). IR (ν(CO), *n*-hexane): 2055 s, 2019 vs, 2003 s, 1994 m, 1870 w, 1835 m, 1826 m cm^{-1}. ^{31}P NMR (toluene-d_8) 27 °C, 27.0 ppm (d, J_{Rh-P} = 127 Hz); at −90 °C, 33.5 (d, J_{Rh-P} = 117 Hz), 25.8 ppm (d, J_{Rh-P} = 136 Hz).

Reversible Reaction of Co$_2$Rh$_2$(CO)$_{11}$(PEt$_3$) (4) with Carbon Monoxide. 4 (0.075 g) was dissolved in 100 mL of *n*-hexane to give a 10^{-3} mol/L solution. The solution was transferred into a 150-mL glass autoclave under anaerobic conditions. The autoclave was thermostated to 25 ± 0.5 °C. The autoclave was charged with 2 bar of CO/N$_2$ (1:1) and stirred for 1 h. A sampling tube reaching the bottom of the autoclave was connected directly to a thermostated (T = 25 ± 0.5 °C) flow-through-type high-pressure IR cell. Before each spectrum was scanned, the cell was flushed with 5–10 mL of fresh solution from the autoclave by opening a discharge valve placed after the cell. The total pressure was maintained constant. The approximate equilibrium concentrations at 1 bar of CO and 25 °C are as follows: 4, 4 × 10^{-4} mol/L; 2 = 6, 6 × 10^{-4} mol/L.

Reversible Reaction of Co$_2$Rh$_2$(CO)$_{10}$(PEt$_3$)$_2$ (5) with Carbon Monoxide and Characterization of CoRh(CO)$_6$(PEt$_3$) (6). A 0.021-g (0.025-mmol) sample of 5 was dissolved in 30 mL of *n*-hexane in a Schlenk tube under N$_2$. The N$_2$ was changed to CO, and the solution was stirred for 12 h at room temperature. The reddish brown color slowly changed to light orange, and the IR spectrum showed new bands at 2078 m, 2035 vs, 2003 vs, 1983

(23) (a) Butler, I. S. *Acc. Chem. Res.* 1977, *10*, 359. (b) Yaneff, P. V. *Coord. Chem. Rev.* 1977, *23*, 183.

(24) Noack, K. *Spectrochim. Acta, Part A* 1968, *24A*, 1917. Dietler, U. K. Ph.D. Thesis, No. 5428, ETH-Zürich, 1974.

m, 1945 w, 1917 m cm^{-1}. Upon slow evaporation of the solvent the light orange color turned to reddish brown and the IR spectrum of the residue in *n*-hexane was identical with that of **5**. After the reeaction was repeated several times, **5** can be recovered quantitatively.

In some experiments the reaction was performed in a thermostated reaction vessel connected to a thermostated gas buret and the volume of the CO uptake was measured: 1.98 mol of CO/mol of **5** was found.

The molecular weight of **6** was determined by freezing point molecular weight determination. The measurements were performed by the Beckman method as described in the literature.[25] The sample was placed in a Schlenk tube equipped with a rubber septum and tied with a clamp. A thermocouple was led through the septum, and its end was placed just above the stirring magnetic bar. The freezing point of cyclohexane was measured under CO (5.36 °C). A solution of 0.119 g of **5** in 4.40 g of cyclohexane was placed in a 20-mL Schlenk tube and stirred under CO at 25 °C for 12 h. The freezing point was measured: 4.07 °C. The molecular weight was calculated from the freezing point depression. For CoRh(CO)$_6$(PEt$_3$) (**6**): $\Delta T = 1.29$ °C, M_r(measd) 454 ± 10 (M_r(calcd) 448).

Preparation of ^{13}CO-Enriched CoRh(CO)$_6$(PEt$_3$) (6). In a 10-mm NMR tube a solution of 0.02 g of 90% ^{13}CO-enriched sample of **5** in 4 mL of CD$_2$Cl$_2$ was shaken under 1.1 bar of a 90% ^{13}CO-enriched carbon monoxide at 5 °C for 12 h. The NMR tube was cooled with liquid N$_2$ and sealed. In some experiments the NMR tube was first cooled to -20 °C, and the solution was purged with N$_2$ for a few minutes.

Reaction of CoRh(CO)$_6$(PEt$_3$) (6) with Carbon Monoxide at 15 bar. A solution of 0.0224 g (0.05 mmol) of **6** in 100 mL of *n*-hexane was prepared in situ from **5** at 5 °C and 1 bar of CO in a glass autoclave. Then the autoclave was charged with 10 bar of CO and stirred for 2 h at 5 °C. The sample was transferred into the high-pressure IR cell. New bands appear at 2075 m, 2028 m, 1992 s, 1960 w, and 1945 vw cm^{-1}. After the pressure was degassed to 1 bar and the solution stirred for 3 h, the new bands disappeared and only **6** was present. Then the pressure was increased to 15 bar, and the solution was stirred for 1 h. The sample was transferred into the high-pressure IR cell. The same new bands were observed with higher intensity, but the relative intensity of these bands remained constant.

Reaction of Co$_2$Rh$_2$(CO)$_{12}$ (1) with THF. Freshly distilled THF (10 mL) was placed in a Schlenk tube under N$_2$. Solid **1** (0.011 g, 0.016 mmol) was added, and the solution was stirred intensively at room temperature. After the addition of **1** the color immediately became light orange and the IR spectrum showed bands at 2075 m, 2032 vs, 2002 s, 1975 m, 1950 w, and 1920 cm^{-1}. On further stirring rapid decomposition was observed.

Reaction of Co$_2$Rh$_2$(CO)$_{12}$ (1) with MeCN. (a) Freshly distilled MeCN (10 mL) was placed in a Schlenk-tube under N$_2$. Solid **1** (0.011 g, 0.016 mmol) was added, and the solution was stirred intensively at room temperature. After the addition of **1** the color immediately became light orange and the IR spectrum showed bands at 2083 m, 2036 vs, 2016 s, 1975 s, 1947 w, and 1926 s cm^{-1}. On further stirring the color slowly changed to a deep red, and after 6 h new IR bands appeared at 2050 m, 1995 m, and 1894 s cm^{-1}. (b) A solution of 0.033 g (0.05 mmol) of **1** in 30 mL of *n*-hexane (or CH$_2$Cl$_2$) was placed in a Schlenk tube under N$_2$. MeCN (400 μL) was added via syringe. The reddish brown color immediately changed to light orange, and the IR spectrum showed six bands at 2080 m, 2037 vs, 2014 s, 1984 m, 1957 w, and 1932 m cm^{-1} (or in CH$_2$Cl$_2$ at 2081 m, 2036 vs, 2014 s, 1976 m, 1952 w, and 1921 m cm^{-1}). Compound **8** was not isolated; its CH$_2$Cl$_2$ solution can be used as a stock solution without observable de-

composition within a few minutes. (c) For ^{13}C NMR measurements a 90% ^{13}CO-enriched sample of **8** was prepared from 0.016 g (0.024 mmol) of a 90% ^{13}CO-enriched **1** and 150 μL of MeCN in 3 mL of CD$_2$Cl$_2$ in an NMR tube under N$_2$. After the addition of MeCN the NMR tube was cooled to -80 °C.

Reaction of Co$_2$Rh$_2$(CO)$_{12}$ (1) with [PPN]Cl. A solution of 0.050 g (0.075 mmol) of **1** in 15 mL of CH$_2$Cl$_2$ was placed in a Schlenk tube under N$_2$. A sample of 0.087 g (0.15 mmol) of [PPN]Cl in 3 mL of CH$_2$Cl$_2$ was added via syringe. The solution was stirred intensively at room temperature for 2 h. A few minutes after the addition of [PPN]Cl the dark reddish brown color changed to light brownish red. The IR spectrum showed five bands at 2065 m, 2020 vs, 1985 s, 1948 m, and 1903 s cm^{-1}. Although the IR spectrum of the reaction mixture indicated the quantitative formation of one species, PPN[CoRh(CO)$_6$Cl] (**9**), crystalline material for analysis could not be obtained. Its 90% ^{13}CO-enriched sample was prepared in situ by the reaction of a 90% ^{13}CO-enriched sample of **1** (0.025 g) and [PPN]Cl (0.435 g) in 3 mL of CD$_2$Cl$_2$.

Reaction of Co$_2$Rh$_2$(CO)$_{12}$ (1) with [N(CH$_2$Ph)Et$_3$]Cl. A solution of 0.082 g (0.125 mmol) of **1** in 25 mL of CH$_2$Cl$_2$ was placed in a Schlenk tube under N$_2$. A sample of 0.057 g (0.25 mmol) of [N(CH$_2$Ph)Et$_3$]Cl in 5 mL of CH$_2$Cl$_2$ was added via syringe. The solution was stirred intensively at room temperature for 2 h. A few minutes after the addition of [N(CH$_2$Ph)Et$_3$]Cl the dark reddish brown color changed to light brownish red. The IR spectrum showed five bands at 2067 m, 2021 vs, 1990 s, 1950 m, and 1902 s cm^{-1}. Although the IR spectrum of the reaction mixture indicated the quantitative formation of one species, [N(CH$_2$Ph)Et$_3$][CoRh(CO)$_6$Cl] (**9**), crystalline material for analysis could not be obtained.

Reaction of CoRh(CO)$_6$(MeCN) (8) with PEt$_3$. A solution of **8** in 40 mL of CH$_2$Cl$_2$ was prepared in situ from 0.093 g (0.14 mmol) of **1** and 400 μL of MeCN in a Schlenk tube under N$_2$. After the quantitative formation of **8** (checked by IR), 82 μL (0.56 mmol) of PEt$_3$ was added by syringe. The color immediately changed to reddish yellow, and the band at 1896 cm^{-1} in the IR spectrum indicated the formation of [Rh(CO)(PEt$_3$)$_2$-(MeCN)]$^+$[Co(CO)$_4$]$^-$. The solvent and MeCN were removed in vacuo, and 25 mL of *n*-hexane was placed on the residue. The IR spectrum indicated that only CoRh(CO)$_5$(PEt$_3$)$_2$ (**3**) is present.

Reaction of PPN[CoRh(CO)$_6$Cl] (9) with PEt$_3$. A solution of **9** in 15 mL of CH$_2$Cl$_2$ was prepared in situ from 0.02 g (0.03 mmol) of **1** and 0.0348 g (0.06 mmol) of [PPN]Cl in a Schlenk tube under N$_2$. After the quantitative formation of **9** (checked by IR) 18 μL (0.124 mmol) of PEt$_3$ was added by syringe. The color immediately changed from light brown to light yellow. The solvent was removed in vacuo, and 25 mL of *n*-hexane was placed on the residue. The *n*-hexane solution became light yellow and contained some white precipitate. The white precipitate was filtered out and washed with *n*-hexane to give 0.042 g (0.059 mmol, 98.3%) of PPN[Co(CO)$_4$]: IR (ν(CO), CH$_2$Cl$_2$) 1889 cm^{-1}. The yellow *n*-hexane solution was evaporated in vacuo, and the residue was crystallized from *n*-hexane to give 0.024 g (0.0596 mmol, 99%) of *trans*-ClRh(CO)(PEt$_3$)$_2$: IR (ν(CO), *n*-hexane) 1957.5 cm^{-1}; ^{31}P NMR (toluene-d_8) 24.9 ppm (d, $J_{Rh-P} = 118$ Hz).

(25) Skau, E. L.; Arthur, J. C., Jr. In *Techniques of Chemistry*; Weissberger, A., Ed.; Wiley-Interscience: New York, 1971; Vol. I, Part V, pp 172–178.