to oxidize but harder to reduce than when R = CF_3. In contrast, irrespective of the thermodynamic stability, all of the anionic, cationic, and neutral complexes are kinetically more stable in the presence of the sterically bulky *t*-Bu group than with R = CF_3. The ability of the bridged carbonyl configuration to be retained during electron-transfer reactions of dirhodium complexes may be significant in their potential role as catalysts since the bridging format has been postulated to be essential in this role in other studies.[10] The ability of $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}R_2C_2R)]^{1-/0/+1/2+}$ complexes to participate in catalytic processes will be investigated in future work in these laboratories.

Acknowledgment. Experimental assistance from R. N. Bagchi and D. L. Luscombe in obtaining the ESR data contained in this report is gratefully acknowledge as is financial assistance from the Australian Research Grant Scheme and the Deakin University Research Committee.

Registry No. 1, 84897-47-2; 2, 71844-53-6.

Cobalt–Rhodium Heptacarbonyl: A Coordinatively Unsaturated Dinuclear Metal Carbonyl

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$CoRh(CO)_7$ (**3**) was prepared by the reaction of $Na[Co(CO)_4]$ with $[Rh(CO)_2Cl]_2$ under a continuous purge of carbon monoxide at −78 °C or by the treatment of $Co_2Rh_2(CO)_{12}$ (**4**) with 2.5 bar of CO at 0 °C. The $CoRh(CO)_7$ formula for **3** was established on the basis of its decomposition with Br_2/CH_2Cl_2 and I_2/pyridine followed by atomic emission analysis of the metals and freezing point molecular weight determination under carbon monoxide pressure. Its yellow crystals or its *n*-hexane solutions are stable only below −65 °C under N_2. Under carbon monoxide the existence of two pseudoequilibria is observed: between $CoRh(CO)_7$ (**3**) and $Co_2Rh_2(CO)_{12}$ (**4**) ($-65\ °C < T < 15\ °C$ and $0 < p_{CO} < 2.5$ bar) and between $CoRh(CO)_7$ (**3**) and $CoRh(CO)_8$ (**5**) ($T = 0\ °C$ and $130 < p_{CO} < 160$ bar), respectively. At room temperature and under 10 bar of CO pressure **3** disproportionates very slowly to $Co_2(CO)_8$ (**1**) and $Rh_4(CO)_{12}$ (**2**).

Introduction

Neutral dinuclear metal carbonyls containing only carbonyl ligands are the simplest models for understanding metal–metal interactions and subsequent reactions, which involve the participation of two metal centers. Whereas the chemistry of homodinuclear carbonyls is well documented,[1] the field of mixed-metal dinuclear carbonyls is not as extensively studied.[2]

First, $CoMn(CO)_9$[3] and subsequently the other $CoM(CO)_9$ compounds (M = Re,[4] Tc[5]) were prepared. Furthermore, all three $MM'(CO)_{10}$ species (M or M′ = Mn, Tc, Re)[6,7] have been obtained and characterized.[6–8] It is striking that although several higher nuclearity mixed-metal carbonyls, $M_3M'(CO)_{12}$ and $M_2M'_2(CO)_{12}$ (M or M′ = Co, Rh, Ir), within the cobalt triad had been reported,[9] no dinuclear M–M′ carbonyls were known in this group until recently.

The existence of a $Co_xRh_y(CO)_z$ species, different from those known hitherto, was first suggested by the synergism observed in the combined application of $Co_2(CO)_8$ (**1**) and $Rh_4(CO)_{12}$ (**2**) as catalyst precursors in the hydrocarbonylation of diketene.[10] During the search for the origin of the synergetic effect it was shown that **1** reacts with **2** under carbon monoxide pressure, in the temperature range between 40 and 85 °C to form a mixed-metal carbonyl formulated as $CoRh(CO)_7$ (**3**).[11] Although **3** had not been isolated in that study, its formula and possible structure were proposed on the basis of the stoichiometry of its formation and its IR spectrum and solubility. The $CoRh(CO)_7$ formula implied a coordinative unsaturation in this molecule, which was assumed to be related mainly to the relative stability of the square-planar 16-electron configuration of the rhodium atom.[11]

Considering the unprecedented structural feature for a nonsubstituted metal carbonyl like **3** and its possible role in cobalt–rhodium catalytic systems, a more detailed study was aimed at the preparation, isolation, and characteri-

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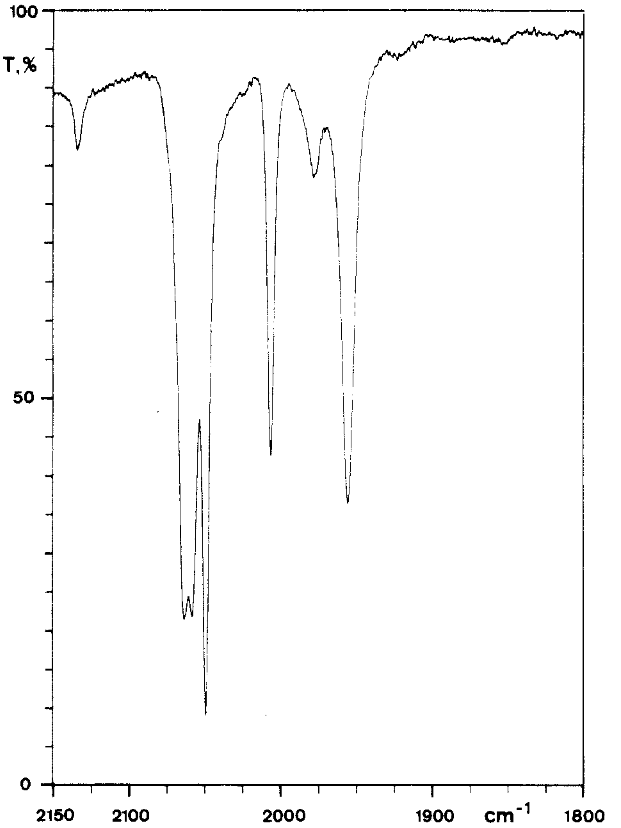

Figure 1. IR spectrum of $CoRh(CO)_7$ (3) in *n*-hexane at -65 °C.

zation of $CoRh(CO)_7$ (**3**) as well as to some aspects of its chemical reactivity.

Results

Synthesis of $CoRh(CO)_7$ (3). Two equivalents of $Na[Co(CO)_4]$ react slowly with $[Rh(CO)_2Cl]_2$ in *n*-hexane at -78 °C under a continuous purge of carbon monoxide to give a light yellow solution containing a white precipitate (NaCl) (eq 1). The low-temperature IR spectrum of this

$$2Na[Co(CO)_4] + 2[Rh(CO)_2Cl]_2 \rightarrow \underset{\mathbf{3}}{2CoRh(CO)_7} \quad (1)$$

solution is shown in Figure 1. The observed bands correspond to those which were reported for the postulated species $CoRh(CO)_7$ (**3**).[11] Upon warming to -60 °C under carbon monoxide (1 bar) the color of the solution slowly changed to light orange. At this point the IR spectrum indicated the presence of some $Co_2Rh_2(CO)_{12}$ (**4**).[9] After the solution was further warmed to 15 °C under 1 bar of CO and repeatedly cooled to 0 °C, it became apparent that **4** formed in a reversible reaction from **3**. At room temperature after N_2 purge the only compound present in the solution is **4** (99% isolated yield).

Following the observation of the reversibility of the reaction between **3** and **4** under carbon monoxide, this approach was elaborated for the preparation of **3**. We observed, by the application of in situ IR spectroscopy, that with 2.5 bar of CO pressure at 0 °C **4** is almost completely (~98%) converted to **3**. Cooling the solution of -78 °C, yellow crystals of **3** formed which could be separated and dried in a CO stream.

$$\underset{\mathbf{3}}{2CoRh(CH)_7} \rightleftharpoons \underset{\mathbf{4}}{Co_2Rh_2(CO)_{12}} + 2CO \quad (2)$$

Characterization of $CoRh(CO)_7$ (3). Since the yellow crystals of **3** or its *n*-hexane solutions are stable only below -65 °C under N_2 or below 15 °C under 2.5 bar of CO, the determination of its formula was carried out as follows. The Co/Rh/CO ratio was determined by the combined application of Br_2/CH_2Cl_2 (-78 °C) and I_2/pyridine (25 °C) decomposition followed by atomic emission analysis of the metals. The Co/Rh/CO ratio found was 1:1:6.8. As the thermal lability of **3** did not allow the application of MS, we determined the molecular weight by means of freezing point depression measurements under carbon monoxide pressure. After a series of solvents were considered, *p*-xylene was found to be chemically inert and to have the appropriate freezing point temperature, dissolving powder, and cryoscopic constant. First the freezing points of *p*-xylene and of a solution of CO in *p*-xylene (p_{CO} = 2.55 bar) were determined. The freezing point depression with respects to *p*-xylene (curve b, Figure 2) corresponds to a solution of CO in *p*-xylene of 0.008 mol/L in the range of the solubility expected for CO in an aromatic solvent.[12] Then the freezing point depression of a solution of **4** in *p*-xylene was measured under N_2, and a molecular weight of 634 ± 50 was found (curve c). After the solution was pressurized to 2.55 bar of CO and stirred at 14 °C for 3 h, the freezing point depression was measured (curve d) and a molecular weight of 350 ± 50 was found which is in very good agreement with the molecular weight of 358 calculated for $CoRh(CO)_7$ (**3**). Finally CO was removed and the solution was stirred under N_2 for 1 h at 14 °C, and the freezing point was measured again (curve e). From the freezing point depression a molecular weight of 634 ± 50 was found again, indicating that no decomposition of **4**

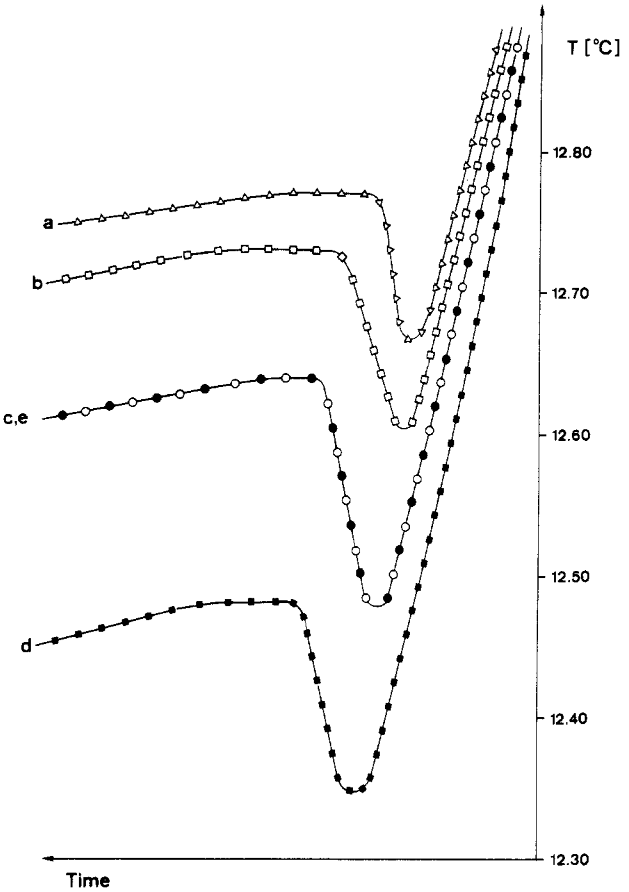

Figure 2. Freezing point depression curves: (a) *p*-xylene, (b) *p*-xylene under 2.55 bar of carbon monoxide, (c) $Co_2Rh_2(CO)_{12}$ (**4**) in *p*-xylene under N_2, (d) $Co_2Rh_2(CO)_{12}$ (**4**) in *p*-xylene under 2.55 bar of carbon monoxide after 3 h of stirring at 14 °C, (e) $Co_2Rh_2(CO)_{12}$ (**4**) in *p*-xylene under N_2.

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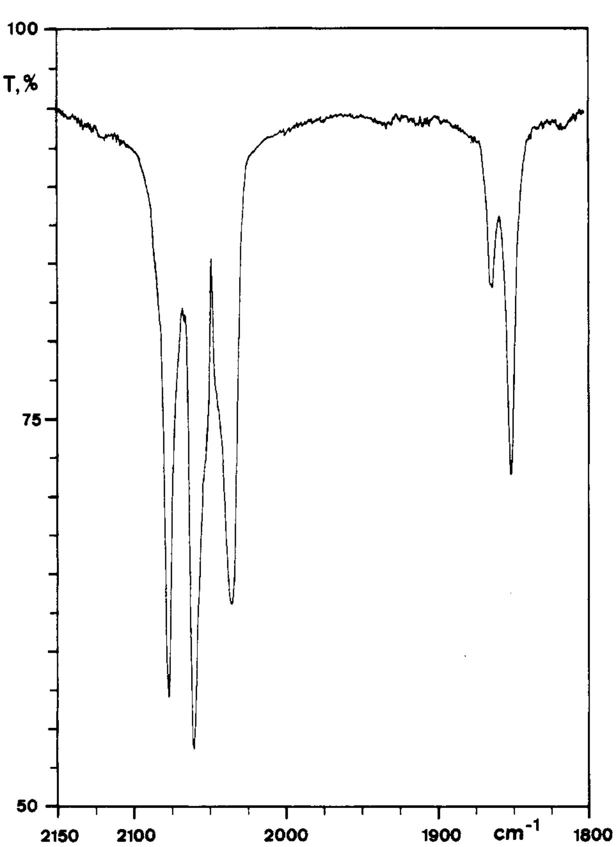


Figure 3. IR spectrum of **5** in *n*-hexane after subtracting the absorptions of dissolved carbon monoxide and CoRh(CO)$_7$ (**3**).

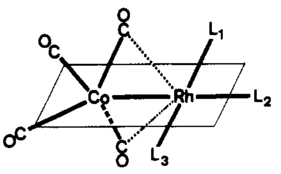
and/or **3** occurred during the measurements.

The IR spectrum of **3** shows seven bands at 2134 (w), 2064 (s), 2058 (s), 2049 (vs), 2006 (m), 1977 (w), and 1955 (m) cm^{-1} which are consistent with our previous report.[11] ^{13}C NMR spectrum of ^{13}CO-enriched **3** exhibits two resonances at 199 and 198 ppm of relative intensity 3.8:3.2 at −120 °C. Upon warming each signal broadens and reaches a coalescence point at about −80 °C. On further warming the spectrum shows a single sharp absorption at 195 ppm.[13]

Reactivity of CoRh(CO)$_7$ (3). When **3** in *n*-hexane at 0 °C is treated with 130 bar of carbon monoxide, we observe significant reversible changes in the in situ IR spectra. Under these conditions the new species represent about 40% of the carbonyls in solution (based on the intensity of **3**). New bands appear at 2076 (s), 2060 (vs), 2044 (sh), 2034.5 (s), 1863.5 (w), and 1850 (m) cm^{-1}, which was obtained by subtracting the spectral contributions of other components, solvent, CO, and **3** (Figure 3). The ratio between the intensities of the new bands do not change by changing the carbon monoxide pressure. This indicates that only one new compound is formed. The fact that the concentration of the new species increases by increasing the carbon monoxide pressure as expected for eq 3 indicates that the new compound has a CO/Co + Rh ratio larger then 3.5. When the CO pressure is decreased to 3 bar, **3** is reformed. Finally, similarities in the IR spectra to Co$_2$(CO)$_8$ (**1**)[14] and Rh$_2$(CO)$_8$,[15] particularly the relative intensities and the intermediate frequency values of the two bands at 1863.5 and 1850 cm^{-1}, halfway between the corresponding bands of **1** and Rh$_2$(CO)$_8$,[15] suggest that the new compound is CoRh(CO)$_8$ (**5**).

$$\underset{\mathbf{3}}{\mathrm{CoRh(CO)_7}} + \mathrm{CO} \rightleftharpoons \underset{\mathbf{5}}{\mathrm{CoRh(CO)_8}} \qquad (3)$$

Chart I



	L$_1$	L$_2$	L$_3$
3 :	CO	CO	CO
7 :	PEt$_3$	CO	CO
6 :	PEt$_3$	CO	PEt$_3$

At room temperature and under 10 bar of carbon monoxide **3** very slowly (50% transformed in 5 days) disproportionates to **1** and **2** (eq 4). In a previous study equilibrium 4 starting from **1** and **2** was reached after 4–5 h at 70 °C and p_{CO} between 50 and 150 bar.[11]

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

Between −65 and 15 °C and under a low CO partial pressure the pseudoequilibrium[16] between **3** and **4** (eq 2) is easily reached (about 1 h at 10 °C). According to quantitative IR analysis based on the bands at 1955 and 1886 cm^{-1} no significant amount of other products are present. We determined the equilibrium concentrations of **3** and **4** at 10 °C by in situ IR spectroscopy at various CO pressure using the bands at 1955 and 1886 cm^{-1}, respectively. Preliminary data show that the equilibrium constant $K = [\mathrm{Co_2Rh_2(CO)_{12}}][\mathrm{CO}]^2/[\mathrm{CoRh(CO)_7}]^2$ is $\sim 6 \times 10^{-3}$ mol/L at 10 °C.

Discussion

Although **3** can be isolated, we have not succeeded up to now obtaining crystals suitable for X-ray diffractometric study. However, its previously suggested composition and molecular formula has now been determined unequivocally as CoRh(CO)$_7$. Moreover, we are quite confident, on the basis of the following arguments, that **3** has the molecular geometry as shown in Chart I. The IR spectrum of **3** shows, besides five bands between 2140 and 2000 cm^{-1}, a medium intensity band at 1955 cm^{-1} and a weaker one at 1977 cm^{-1}, which indicate an unusual structural feature present in the molecule. In our first paper[11] on the occurrence of **3** we proposed a structure with a single unsupported Co–Rh bond between a Co(CO)$_4$ and a coordinatively unsaturated Rh(CO)$_3$ group. We ascribed the low-energy shift of the mentioned bands to the influence of this unusual unsaturation. After our first paper, Roberts et al.[17] found in the analogous compound CoRh(CO)$_5$(PEt$_3$)$_2$ (**6**) the presence of two cobalt-bonded semibridging carbonyl ligands. We recently isolated compound **6** from Co$_2$Rh$_2$(CO)$_{12}$ (**4**) and in addition also the monosubstituted phosphine derivative CoRh(CO)$_6$(PEt$_3$) (**7**).[18] The comparative study of their IR spectra[19a,b] furnished a strong indication for the presence of the same structural char-

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[13] Different explanations are possible for the low-temperature ^{13}C NMR results. The problem is under investigation.

[14] (a) Bor, G. *Spectrochim. Acta* **1963**, *19*, 1209. (b) Noack, K. *Spectrochim. Acta* **1963**, *19*, 1925. (c) Bor, G. *Spectrochim. Acta* **1963**, *19*, 2065.

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[16] Reaction 4 can be considered as pseudoequilibrium; see Discussion.

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[19] (a) For **6**: IR (ν (CO) in *n*-hexane) 2026 (m), 1964 (vs), 1954 (vs), 1919 (w), 1889 (m) cm^{-1}. For **7**: IR (ν (CO) in *n*-hexane): 2078 (m), 2035 (vs), 2003 (vs), 1983 (m), 1945 (w), 1917 (m) cm^{-1}. (b) The analogous IR bands: **3**, 1977 (w), → **7**, 1945 (w), → **6**, 1919 (w), and **3**, 1955 (m), → **7**, 1917 (m), → **6**, 1889 (m) cm^{-1}.

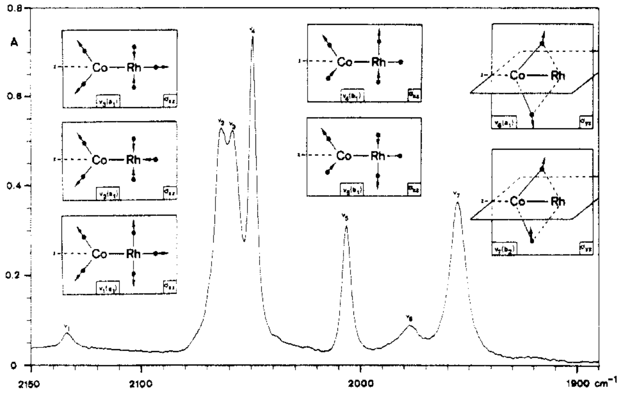


Figure 4. Assignment of the C–O stretching frequencies to the various vibrational modes in the IR spectrum of $CoRh(CO)_7$ (**3**).

acteristics (Chart I) in compounds **3**, **6**, and **7**. Therefore, our previous interpretation should now be completed with the existence of some sort of interaction between the Rh atom and two of the cobalt-bonded carbonyls resulting in two semibridging[20] carbonyl ligands. Even the extent of deviation from linearity of the two semibridging carbonyls having some sort of interaction with the rhodium atom seems to be essentially constant in this series (i.e., ca. 170°, reported for **6**), as indicated by the rather regular shift of the analogous IR bands[19b] upon increasing phosphine substitution in the series **3** → **7** → **6** (Chart I).

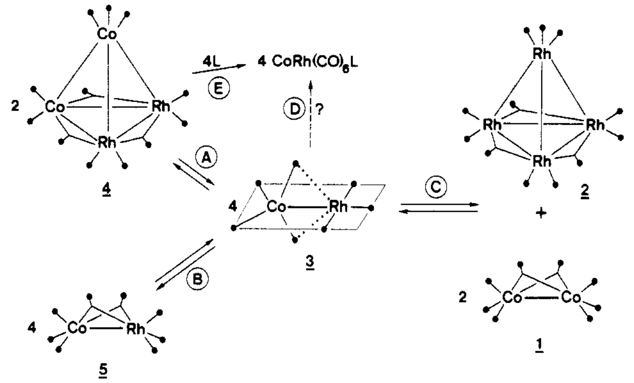
Hence we propose for $CoRh(CO)_7$ (**3**) a structure in which a square-planar $Rh(CO)_3$ fragment is coupled with a $Co(CO)_4$ group of distorted tetrahedral geometry through a Co–Rh bond and two semibridging carbonyl ligands. The assignment of the C–O stretching frequencies to the various vibrational modes are shown, in a qualitative way, on Figure 4. The idealized geometry of the proposed structure of the molecule is C_{2v}.

The heterobimetallic nature of **3** is combined with the known tendency of the rhodium atom to assume a planar, 16-electron configuration, as is well-known from the chemistry of Wilkinson's catalysts, $XRhL_3$. This asymmetry might give rise to a considerable polarity of the molecule in the sense $Co(\delta-)$–$Rh(\delta+)$.

Good evidence for the existence of a coordinatively saturated mixed-metal carbonyl, $CoRh(CO)_8$ (**5**), has been obtained by investigating the reaction of **3** with CO at high pressure.

The reactivity of $CoRh(CO)_7$ (**3**) is expected to involve dimerization, disproportionation, addition, and substitution reactions (Scheme I).

Scheme I



Considering the system at low temperature ($T < 10$ °C), it appears that the reactions A and B occur rapidly, reaching a constant composition in few hours. At low carbon monoxide pressure ($p_{CO} < 0.2$ bar) the prevailing species is **4**, and between $0.2 < p_{CO} < 2.5$ bar the predominant species is **3**. Only at much higher pressures ($p_{CO} > 10$ bar) does **5** become observable by IR. Since even at 10 bar of CO **5** is still not observable by IR, equilibrium B is also largely displaced toward **3** at low p_{CO}. Equilibrium C, which is reached after 4–5 h at 70 °C (p_{CO} = 50–150 bar),[11] has not been reached even in 2 days at 10 °C (p_{CO} = 10 bar). In fact, only a trace amount of **1** and **2** could be detected after 1 day at room temperature and 10 bar of CO pressure. These data suggest to two interesting conclusions. (1) The thermodynamic stability of the species in the system at 10 °C and p_{CO} = 1 bar varies in the order $Co_2(CO)_8/Rh_4(CO)_{12} > CoRh(CO)_7 > Co_2Rh_2(CO)_{12} > CoRh(CO)_8$. (2) The activation energy for reaction C is large enough to prevent substantial formation of **1** and **2** from **3** at 10 °C in 1 day. Therefore reactions A and B can be considered as pseudoequilibria and studied independently. Furthermore, reaction B is so highly displaced toward **3** at 10 °C and $p_{CO} < 2.5$ bar that it can also be neglected in the calculation of the equilibrium constant for reaction A.

There are two obvious mechanistic possibilities for the dimerization of **3** (reaction A): a, **3** loses carbon monoxide to form an even more unsaturated species $\{CoRh(CO)_6\}$ which then dimerizes to **4**; b, first **3** dimerizes to yield $\{Co_2Rh_2(CO)_{14}\}$, which could then undergo successive CO loss to $\{Co_2Rh_2(CO)_{13}\}$ and **4**, respectively. From preliminary experiments it seems that the activation energy for dimerization is low. Studies are in progress to determine the mechanism involved.

The rate of the disproportionation of **3** (reaction C) rapidly increases between 10 and 70 °C, and this implies a high activation energy. With respect to a possible mechanism for reaction C the homolytic cleavage of the Co–Rh bond in the first step can be considered, followed by a recombination of the fragments $\{Co(CO)_4\}$ and $\{Rh(CO)_3\}$, respectively, to yield **1** and **2**.

Among the addition reactions only the carbon monoxide addition is described here which occurs at low temperature probably involving a low activation energy. Other addition reactions, e.g., H_2 addition, are under investigation.

Concerning substitution reactions, monosubstituted derivatives of **3** (e.g., $CoRh(CO)_6L$ on Scheme I) have been obtained starting from **4** with use of nucleophiles such as PEt_3, MeCN, and *t*-BuNC.[18] The possibility of obtaining the same substitution products directly from **3** has not been explored up to now. Since **3** is in equilibrium with **4**, the distinction between path D and path (A + E) may require a thorough kinetic study.

Experimental Section

General Information. 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. $Na[Co(CO)_4]$[21] and $[Rh(CO)_2Cl]_2$[22] were prepared by a literature method. [^{13}C]carbon monoxide (90% isotopic purity) was purchased from MSD Isotopes.

High-pressure experiments were performed in a 150-mL stainless-steel rocking autoclave cooled in a dry ice/isobutyl alcohol bath. 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 cor-

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(21) Edgell, W. F.; Lyford, J. *Inorg. Chem.* **1970**, *9*, 1932.

(22) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.

responding to the type published by Noack,[23] 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. A thick-wall Schlenk tube closed with a rubber septum and clamp was used for preparative experiments up to 2.5 bar.

IR spectra were recorded on a Perkin-Elmer Model 983G spectrometer. ^{13}C NMR spectra were recorded on a AM300WB Bruker spectrometer. Atomic emission analyses were performed on an Instrumentation Laboratory, plasma 200 instrument.

Reaction of $Na[Co(CO)_4]$ with $[Rh(CO)_2Cl]_2$. A 500-mL, three-necked, round-bottomed flask was fitted with a gas dispersion tube and a pressure equalizing funnel connected to a bubbler. The flask was charged with 0.0388 g (0.2 mmol) of $Na[Co(CO)_4]$ and 250 mL of *n*-hexane, and the dropping funnel was charged with a solution of 0.0388 g (0.1 mmol) of $[Rh(CO)_2Cl]_2$ in 200 mL of *n*-hexane. The flask was cooled to −78 °C, and the solution was purged continuously with carbon monoxide. The $[Rh(CO)_2Cl]_2$ solution was added dropwise, and the heterogeneous mixture was stirred vigorously. After 6 days of stirring the solution became light yellow and contained some white precipitate. The white insoluble material, which consists, after completion of the reaction, of NaCl (containing only trace amount of unreacted $Na[Co(CO)_4]$) was filtered out at −78 °C under CO atmosphere. The solution contains only $CoRh(CO)_7$ (**3**). Upon evaporation or warming above −65 °C, the solution slowly turns to light orange and $Co_2Rh_2(CO)_{12}$ (**4**) starts to form as indicated by IR. When the orange solution was warmed to room temperature and purged with N_2, it turned to dark reddish brown and contained only **4**. After evaporation of the solvent an analytically pure sample of **4** can be obtained by recrystallization from *n*-hexane at −78 °C: yield 0.0653 g (0.099 mmol, 99%); IR (ν(CO) in *n*-hexane): 2106 (vw), 2064 (vs), 2058 (vs), 2038 (m), 2030 (m), 1922 (w), 1986 (m), 1973 (m), 1855 (w) cm^{-1}.

Preparation of $CoRh(CO)_7$ (3). A solution of 0.011 g (0.017 mmol) of **4** in 15 mL of *n*-hexane was placed in a 20-mL thick-wall Schlenk tube under N_2. The solution was cooled to 0 °C, then the N_2 was changed to CO, and the flask was charged with 2.5 bar of CO. The solution was stirred at 0 °C for 3 h. The dark reddish brown color changed to yellow. When the solution was cooled to −78 °C, yellow crystals formed. After 5 h at −78 °C the pressure was released and the solvent was removed via syringe. The yellow crystals were dried in a CO stream at −78 °C. The crystals can be stored below −65 °C for a long time. Above −65 °C the crystals slowly became light orange and then brownish black. The IR spectrum of the *n*-hexane solution of the brownish black crystals showed that only **4** was present. The yellow crystals of **3** can be dissolved in CO saturated and precooled ($T < -65$ °C) *n*-hexane.

Analysis of $CoRh(CO)_7$ (3). Cobalt/Rhodium/Carbon Monoxide Ratio. A 0.358-g (1×10^{-3} mol) sample of **3** and 100 mL of *n*-hexane were placed in a 100-mL Schlenk tube at −78 °C connected to a thermostated (25 °C) gas buret. A 0.5-g sample of Br_2 in 2 mL of CH_2Cl_2 was added and the mixture stirred for 3 h at −78 °C. The solution was warmed up to room temperature, and 0.5 g of I_2 in 5 mL of pyridine was added and stirred for 24 h. Then the solution was cooled again to −78 °C, and the total amount of CO evolved was 152 NmL (6.8×10^{-3} mol). The solvent was removed in vacuo, and the residue was worked up and dissolved in 100 mL of 1 M HCl for atomic emission analysis. The analysis gave 0.059 g (1×10^{-3} mol) of cobalt and 0.103 g (1×10^{-3} mol) of rhodium. Thus the Co/Rh/CO ratio found was 1:1:6.8.

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 thick-wall Schlenk tube equipped with a high-vacuum stopcock connected to a calibrated Bourdon type manometer (accuracy ±1%) and a pressure regulator. The Schlenk tube was closed 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. This equipment was capable to withstand overpressure up to ca. 3 bars. The freezing point of *p*-xylene was measured under N_2 (12.77 °C) and then under 2.55 bar of CO (12.73 °C). A solution of 0.0659 g (0.099 mmol) of **4** in 3.44 g of *p*-xylene was placed in a 20-mL Schlenk tube under N_2. The freezing point was measured: 12.64 °C. Then the N_2 was changed to CO, and the flask was charged with 2.55 bar of CO. The solution was stirred at 14 °C for 3 h. The freezing point was measured: 12.48 °C. The CO pressure was released and the solution stirred under N_2 for 1 h to ensure the reformation of **4**. The freezing point was measured again: 12.64 °C. The molecular weights were calculated from the freezing point depression. For $Co_2Rh_2(CO)_{12}$ (**4**): $\Delta T = 0.13$ °C, $M_{measd} = 634 \pm 50$ ($M_{calcd} = 660$). For $CoRh(CO)_7$ (**3**): $\Delta T = 0.25$ °C, $M_{measd} = 350 \pm 50$ ($M_{calcd} = 358$).

Preparation of ^{13}CO-Enriched $CoRh(CO)_7$ (3). In a 10-mm NMR tube a solution of 0.022 g of **4** in 3 mL of CD_2Cl_2 was shaken under 1.5 bar of 90% enriched ^{13}CO at −10 °C for 6 h. The NMR tube was cooled to −78 °C, and 1 mL of $CDCl_3$ was added. Then the NMR tube was cooled with liquid N_2 and sealed.

Reaction of $CoRh(CO)_7$, 3 with Carbon Monoxide at 130 bar. A solution of 0.0358 g (0.1 mmol) of **3** in 100 mL of *n*-hexane was prepared in situ from **4** at 0 °C and 10 bar of CO in a stainless-steel autoclave. Then the autoclave was charged with 130 bar of CO and shaken for 1 h. Sample was transferred into the high-pressure IR cell. New bands appear at 2076 (s), 2060 (vs), 2044 (sh), 2034.5 (s), 1863.5 (w), and 1850 (m) cm^{-1}. After the pressure was decreased to 3 bar and the autoclave was shaken for 3 h, the new bands disappeared and only **3** was present. Then the pressure was increased to 160 bar, and the autoclave was shaken 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 $Co_2Rh_2(CO)_{12}$ (4) with Carbon Monoxide. A 0.066-g sample of **4** 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 10 ± 0.5 °C. The autoclave was charged with 2 bar of $CO:N_2$ (1:9) and stirred for 3 h. A sampling tube reaching the bottom of the autoclave was connected directly to a thermostated ($T = 10 \pm 0.5$ °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. Samples were taken until the equilibrium point was definitely reached.

Disproportionation of $CoRh(CO)_7$ (3) at 25 °C and 10 bar of CO. A solution of 0.066 g (0.1 mmol) of **4** in 100 mL of *n*-hexane was transferred to a low-pressure glass autoclave at 5 °C. It was charged with 10 bar of CO and stirred for 3 h to yield **3** (~98%). This was confirmed by IR. The temperature was raised to 25 °C, and the solution was stirred continuously. Periodic IR spectra showed the formation of **1** and **2**. The reaction was not complete after 2 weeks. Compounds **1** and **2** were not isolated.

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