

Equally surprising, the reaction is reversible; photolysis of 12 regenerates the carbene complex 11 as the primary product.

A reasonable mechanism for the interconversion of 11 and 12 is suggested in Scheme IV. The significant features and evidence to date for this mechanism are as follows: (1)The first step is a thermally induced reverse of the proposed 1,2-rearrangement, a reaction that must be occurring even in the absence of added CO since the only sensible role of the carbon monoxide is to trap 15. Evidence for this equilibrium is the finding that treatment of 11 with a trace of CD_3O^- in CD_3OD led to rapid exchange of four ring hydrogens (followed by slower exchange of methoxide) despite the fact that only the two at C3 should be acidic. Exchange of four hydrogens would be expected if 11 were in thermal equilibrium with 10 since C3 and C5 become equivalent in the latter. (2) If 11 and 10 equilibrate at room temperature (as suggested by the deuterium exchange) but not rapidly enough for 11 to show fluxionality in the ¹H NMR, the maximum energy separating 10 from 11 can be no more than about 25 kcal/mol nor less than about 15 kcal/mol. (3) The equilibrium between 10 and 15 must favor the latter and/or CO attack on 15 must be faster than on 10 because 12 was observed to the exclusion of 9 (probably for steric reasons). (4) This mechanism requires exclusive trans stereochemistry in 12 which is observed.

In conclusion it should be noted that conversion of 10 to 11 is the first example of rearrangement of alkyl from saturated carbon to metal in which the primary rearrangement product has been isolated. It also shows that the special bonding in the cyclopropane ring of 3 is not required for rearrangement to occur.

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Regiospecific Reactions of Cobait-Rhodium Mixed-Metal Clusters. Unprecedented, Facile and Reversible Tetranuclear-Dinuclear Transformations Involving Diphenylacetylene and/or Carbon Monoxide

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Summary: Co₂Rh₂(CO)₁₂ (1) reacts with alkynes (RC₂R, $R = C_6 F_5$ (2a), R = Ph (2b)) via specific insertion into the cobalt-cobalt bond to give $Co_2Rh_2(CO)_{10}(\mu_4-\eta^2-RC_2R)$ (3a,b). 3a was characterized by a single-crystal X-ray diffraction analysis: space group $P2_1/c$ (No. 14), a =11.286 (8) Å, b = 17.37 (1) Å, c = 16.65 (1) Å, $\beta =$ 126.32 (5)°, V = 2630 (5) Å³, Z = 4, $D_{calcd} = 2.43$ g/ cm³. A total of 2479 reflections ($I \ge 2\sigma$) of 3215 reflections were used to give $R_F = 5.2\%$ and $R_{F^2} = 5.6\%$. Reaction of 3a with CO and 2a results in regiospecific fragmentation to give CoRh(CO)₆(μ - η^2 -F₅C₆C₂C₆F₅) (4a) exclusively. 3b undergoes facile, reversible, and regiospecific fragmentation when treated with PhC₂Ph (2b) and carbon monoxide to give $\text{CoRh}(\text{CO})_6(\mu - \eta^2 - \text{PhC}_2\text{Ph})$ (4b). Medium-pressure in situ IR studies have revealed that 3b reacts with carbon monoxide in a reversible and regiospecific reaction to give the 1:1 mixture of $CoRh(CO)_7$ (5) and 4b.

The chemistry of mixed-metal cluster compounds is of current interest.¹ The reactions of mixed-metal clusters and alkynes can result in either substitution or degradation of the cluster to lower nuclearity complexes.² Two interesting questions arise. First, at which site does the substitution take place, and second, what is the metal distribution in the fragmentation products.

Reversible fragmentation of transition-metal clusters involving ligand addition and elimination is rarely observed, and the few studied examples are limited to clusters containing only carbonyl and hydride ligands.³ We now wish to report a facile, reversible, and regiospecific fragmentation of $\text{Co}_2\text{Rh}_2(\text{CO})_{10}(\mu_4 - \eta^2 - \text{PhC}_2\text{Ph})$ (3a) affected by diphenylacetylene and/or carbon monoxide.

The reaction of $Co_2Rh_2(CO)_{12}$ (1)⁴ and 1 equiv of alkyne

⁽²⁰⁾ Assignment of the trans stereochemistry is based on the known²¹ trans addition of nucleophiles to $Fp^+ \pi$ -complexes. However the cis isomer has not been synthesized for final confirmation.

⁽²¹⁾ Davies, S. G. "Organotransition Metal Chemistry: Applications to Organic Synthesis"; Pergamon Press: New York, 1982; pp 128-135. Lennon, P.; Madhavarao, M.; Rosan, A.; Rosenblum, M. J. Organomet. Chem. 1976, 108, 93.

⁽²²⁾ Careful examination of the ¹H NMR from photolysis of 8 reveals the growth and decline of a small resonance corresponding to the methoxy methyl of 12, which could also be isolated in small quantities as an impure sample from an incomplete reaction mixture.

⁽¹⁾ Gladfelter, W. L.; Geoffroy, G. L. Adv. Organomet. Chem. 1980, 18, 207. Roberts, D. A.; Geoffroy, G. L. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Elmsford, NY, 1982; Chapter 40.

Sappa, E.; Tiripicchio, A.; Braunstein, P. Chem. Rev. 1983, 83, 203.
Whyman, R. J. Chem. Soc., Dalton Trans. 1972, 1375. Whyman, R. J. Chem. Soc., Chem. Commun. 1970, 1194. Ungvary, F. J. Organomet. Chem. 1972, 36, 363. Oldani, F.; Bor, G. J. Organomet. Chem. 1983, 246, 309.



Figure 1. The molecular structure of 3a. Selected bond lengths (Å): Rh(1)-Rh(2), 2.700 (3); Rh(1)-Co(1), 2.539 (3); Rh(1)-Co(2), 2.513 (2); Rh(2)-Co(1), 2.515 (2); Rh(2)-Co(2), 2.541 (3); C-(11)-C(18), 1.369 (23); Co(1)-C(2), 1.820 (15); Rh(1)-C(2), 2.133 (11); Co(2)-C(4), 1.825 (16); Rh(2)-C(4), 2.123 (12); Co(1)-C(1), 1.723 (19); Rh(2)-C(1), 2.566 (12); Co(2)-C(6), 1.724 (19); Rh(1)-C(6), 2.561 (11). Selected bond angles (deg): Rh(1)-Co-(1)-Rh(2), 64.6 (1); Co(1)-Rh(1)-Co(2), 92.3 (1); C(11)-Co(1)-C(18), 37.2 (6); C(12)-C(11)-C(18), 127.9 (11); C(11)-C(18)-C(19), 126.1 (11); Co(1)-C(1)-O(1), 169.4 (10); Co(2)-C(6)-O(6), 165.6 (10). Dihedral angle (deg) between the Co(1)-Rh(1)-Rh(2) and Co(2)-Rh(1)-Rh(2) planes: 116.9.



 $(RC_2R', R = C_6F_5(2a), R = Ph(2b))$ in *n*-hexane resulted in formation of the purple clusters $Co_2Rh_2(CO)_{10}(\mu_4-\eta^2-RC_2R)$ (3a,b) in high yield (Scheme I).⁵ 3a,b were characterized by IR and NMR spectroscopic methods⁶ and

(5) Compounds **3a,b** are purple and were isolated by column chromatography (silica gel, *n*-hexane eluent) in 98 and 99% yield, respectively.

(6) For 3a: mp 178 °C dec; IR (ν (CO) in hexane) 2102 m, 2076 s, 2058 m, 2050 s, 1986 w, br, 1898 m cm⁻¹. For 3b: mp 192 °C dec; IR (ν (CO) in *n*-hexane) 2094.5 m, 2069 s, 2049 m, 2035 m, sh, 2029 s, 1978 w, br, 1889 m cm⁻¹; ¹H NMR (in CD₂Cl₂) 7.15-7.00 (m, 10 H) ppm; ¹³C NMR spectrum of ¹³CO-enriched 3b exhibits three resonances at 202.1 (s), 187.2 (d, $J_{\rm Rh-C} = 60$ Hz), and 176.8 (d, $J_{\rm Rh-C} = 62$ Hz) ppm of relative intensity 6:2:2 between 25 and -80 °C. This is in agreement with the structure of 3a and suggests that the rhodium-bonded terminal carbonyl ligands are still rigid at 25 °C and the cobalt-bonded terminal and the semibridging and bridging carbonyl ligands are exchanging evenly at -80 °C. Similar results have been reported for the analogous Co₄(CO)₁₀(μ_4 - η^2 -PhC₂Ph) compound: Evans, J.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W.; Norton, J. R. J. Chem. Soc., Dalton Trans. 1978, 626.





elemental analysis.⁷ The molecular structure of **3a** was determined by a single-crystal X-ray diffraction analysis,⁸ and its structure is shown in Figure 1. The molecule contains a butterfly cluster of two cobalt and two rhodium atoms with the cobalt atoms in the wing-tip position. The alkyne coordinates to all metal atoms to form a distorted *closo*-Co₂Rh₂C₂ octahedron. Overall, there are 10 carbonyl ligands; each cobalt atom and each rhodium atom is bonded to one linear terminal carbonyl ligand and two linear terminal carbonyl ligands, respectively. There are two semibridging and two bridging carbonyl ligands along the hinge-to-wing-tip cobalt-rhodium bonds. Structurally **3a** is very similar to the related Co₄(CO)₁₀(μ_4 - η^2 -RC₂R) (R = Et,⁹ H¹⁰) and to the analogous compounds containing a *closo*-M₄C₂ framework.^{11,12}

The formation of **3** has occurred apparently via specific insertion into a cobalt-cobalt bond accompanied by the loss of two carbonyl ligands. Although metal-specific insertion of alkynes have recently been reported for Co_2 -Ru₂(CO)₁₃¹² and Cp₂W₂Ir₂(CO)₁₀,¹³ this is the first example of metal specificity between metals of the same group in the periodic table.

Upon addition of another mole of 2a to 3a in the presence of carbon monoxide, highly regiospecific fragmentation occurs to give $\text{CoRh}(\text{CO})_6(\mu-\eta^2-F_5\text{C}_6\text{C}_2\text{C}_6\text{F}_5)$ (4a) in 98% yield.¹⁴ The structure of 4a was established by

(10) Gervasio, G.; Rossetti, R.; Stanghellini, P. L. Organometallics, 1985, 4, 1612.

(11) Johnson, B. F. G.; Lewis, J.; Reichter, B. E.; Schorpp, K. T.; Sheldrick, G. M. J. Chem. Soc., Dalton Trans. 1977, 1417. Fox, J. P.; Gladfelter, W. L.; Geoffroy, G. L.; Taranaiepour, I.; Abdel-Mequid, S.; Day, V. W. Inorg. Chem. 1981, 20, 3230.

(12) Roland, E.; Vahrenkamp, H. Organometallics 1983, 2, 183.

(13) Shapley, J. R.; McAteer, C. H.; Churchill, M. R.; Biondi, L. V. Organometallics 1984, 3, 1595.

(14) Compound **4a** is orange and was isolated by column chromatography (silica gel, n-hexane eluent).

⁽⁴⁾ Martinengo, S.; Chini, P.; Albano, V. G., Cariati, F.; Salvatori, T. J. Organomet. Chem. 1973, 59, 379.

⁽⁷⁾ All new compounds gave satisfactory elemental analysis.

⁽⁸⁾ Crystal data: $C_{24}Co_2F_{10}O_{10}Rh_2$, $M_r = 961.92$, monoclinic, space group pZ_1/c (No. 14), a = 11.286 (8) Å, b = 17.37 (1) Å, c = 16.65 (1) Å, $\beta = 126.32$ (5)°, V = 2630 (5) Å³, Z = 4, $D_{calcd} = 2.43$ g/cm³. Data were measured on a Syntex P3 diffractometer with graphite-monochromated Mo K_a ($\lambda = 0.71073$ Å) radiation using the ω scan technique. The structure was solved by direct methods. Solution and refinement were performed by using the SHELXTL system (Sheldrick, G. M. "Crystallographic Computing System", Revision, 1982, University of Göttingen, FRG). A total of 2479 reflections ($I \ge 2\sigma$) of 3215 reflections were used to give $R_F = 5.2\%$ and $R_{F^2} = 5.6\%$.

⁽⁹⁾ Dahl, L. F.; Smith, D. L. J. Am. Chem. Soc. 1962, 84, 2450.

single-crystal X-ray analysis¹⁵ and by spectroscopic analyses.16

3t reacts similarly with 1 mol of diphenylacetylene and 2 mol of carbon monoxide to form $CoRh(CO)_6(\mu-\eta^2-\eta^2-\eta^2)$ PhC_2Ph) (4b)¹⁷ according to Scheme II. Surprisingly, the reaction is fully reversible, such that upon bubbling N_2 into the reaction mixture 3b reforms quantitatively.¹⁸ Since 3b does not react with 2b in the absence of carbon monoxide, we have assumed that 3b reacts first with CO and then with 2b. This was evidenced by the reaction of 3b with CO, performed in a medium-pressure (2-16 bar) glass autoclave connected to a high-pressure IR cell¹⁹ using CO:N₂ (1:9).²⁰ At 0.3-bar partial CO pressure and 10 °C 3b reacts with CO to give an equilibrium mixture²¹ of 3b, 4b, and $CoRh(CO)_7$ (5).²² By increasing the partial pressure of CO to 2 bar, 3b disproportionates almost completely (>99.5%) to a 1:1 mixture of 4b and 5. Upon slowly removing the pressure and purging the solution with N_2 , 4b and 5 recombine to give 3b quantitatively (Scheme III).

To best of our knowledge the reversible fragmentation of 3b to 4b (Scheme II) is the first example for a reversible tetranuclear-dinuclear transformation involving an "alkyne cluster", free alkyne, and carbon monoxide. Mechanistically, it is clear that 3b reacts first with CO, which probably results in an unobserved intermediate such as $[Co_2Rh_2(CO)_{11}(PhC_2Ph)]$ (6). It is not apparent whether 6 is first attacked by CO or by free PhC_2Ph . However, if 6 is attacked first by carbon monoxide, 4b and 5 can be formed according to Scheme III; 5 can subsequently react with the free PhC_2Ph to result in the "second" mole of 4b. The most striking feature of Scheme II is the facile loss of the PhC₂Ph ligand and the regiospecific reformation of **3b.** Currently, there is no clear explanation for this unprecedented ligand loss.

Finally, it should be stressed that no spectroscopic evidence has been obtained for the existence of homonuclear cobalt or rhodium carbonyls in these reactions. This could mean that the heteronuclear metal-metal bond is stronger than the homonuclear bonds.

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(16) For 4a: MS, m/e 660 (M - CO)⁺ plus ions corresponding to the loss of five CO ligands; IR (ν (CO) in *n*-hexane) 2110 m, 2077 vs, 2063 s, 2053 s, 2053 m cm⁻¹; ¹⁹F NMR (in CDCl₃, in ppm from CFCl₃) -137.1 (q, 4 F), -154.5 (t, 2 F), -161.5 (m, 4 F).

(17) For 4b: IR (μ(CO) in *n*-hexane) 2095 m, 2060 vs, 2044 s, 2034.5 s, 2015 m, 2009.5 m cm⁻¹; ¹H NMR (in CD₂Cl₂) 7.60–7.25 (m, 10 H) ppm. (18) Repeating the reaction several times, 4b can be recovered in 100% yield.

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Supplementary Material Available: Tables of bond distances and angles, positional and thermal parameters, and observed and calculated structure factors and an ORTEP drawing of 4a (34 pages). Ordering information is given on any current masthead page.

Photolysis of Organopolysilanes. Photochemical **Behavior of**

3-Phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2tris(trimethylsllyl)-1-silacyclobut-2-ene and Molecular Structure of a Photoproduct

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Summary: The photolysis of 3-phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2-tris(trimethylsilyl)-1-silacyclobut-2-ene produced 4,5-benzo-1,3-bis(trimethylsilyl)-2-[1phenyl-2,2-bis(trimethylsilyl)ethenyl]-1-silacyclopenta-2,4diene (2), via a 1-silabicyclo [2.1.0] pent-3-ene intermediate, which could be trapped by methanol. Similar photolysis of 1,4,4-trimethyl-3,6-diphenyl-1,2,5-tris(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene also afforded compound 2. Preliminary results of an X-ray diffraction study of 2 are also described.

Small ring compounds involving one or two silicon atoms in the ring are interesting because of their high-strain energy.¹⁻⁵ In this communication, we report novel photochemical behavior of 3-phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2-tris(trimethylsilyl)-1-silacyclobut-2-ene (1), which can be prepared from the reaction of 3-phenyl-1,1,2-tris(trimethylsilyl)-1-silacyclopropene or (phenylethynyl)tris(trimethylsilyl)silane with phenyl(trimethylsilyl)acetylene in the presence of a nickel catalyst.^{6,7}

When a solution of 1 (0.8483 g, 1.62 mmol) in 100 mL of dry benzene was irradiated for 70 min, with a high-

⁽¹⁵⁾ Crystal data: $C_{20}CoF_{10}O_6Rh$, $M_7 = 688.04$, monoclinic, space group p_{2_1}/c (No. 14), a = 9.812 (6) Å, b = 15.582 (9) Å, c = 17.82 (1) Å, $\beta = 127.85$ (4)°, V = 2151 (5) Å³, Z = 4, $D_{calcd} = 1.83$ g/cm³. A total of 2121 reflections ($I \ge 2\sigma$) of 2578 reflections were used to give $R_F = 12.6\%$ and $R_{F^2} = 12.7\%$. During the refinement it became clear that the cobalt and rhodium atoms are mutually disordered within the CoRhC2 tetrahedron framework. The X-ray analysis cannot decide between the disorder of Co and Rh positions within the individual molecules in the crystal and a mixed-crystal containing Co₂C₂ or Rh₂C₂ cores. This later possibility was, however, ruled out by the significant differences between the spectroscopic data¹⁶ of **4a** and $\text{Co}_2(\text{CO})_6(\mu - \eta^2 \cdot F_5C_6C_2C_6F_5)$: Birchall, J. M.; Bowden, F. L.; Haszeldine, R. N.; Lever, A. B. P. J. Chem. Soc. A 1967, 747. Thus, the molecule of 4a consists of a sawhorse type of $CoRhC_2$ tetrahedral framework, and each metal atom is bonded to three linear terminal carbonyl ligands.

⁽¹⁹⁾ Dietler, U. K. Ph.D. Thesis, No. 5428, ETH-Zürich, 1974.

⁽²⁰⁾ Before each spectrum was scanned, the cell was flushed with 5-10 mL of a fresh solution from the autoclave by opening a discharge valve placed after the cell. The total pressure and temperature were kept constant.

⁽²¹⁾ $K = [3b][CO]^3/[4b][5] = 3.3 \times 10^{-4} \text{ mol}^2 \text{ L}^{-2} \text{ at } 10 \text{ }^{\circ}\text{C}.$

⁽²²⁾ Spindler, F.; Bor, G.; Dietler, U. K.; Pino, P. J. Organomet. Chem. 1981, 213, 303. Horvåth, I. T.; Bor, G.; Garland, M.; Pino, P. Organometallics, submitted for publication.

^{(1) (}a) Ishikawa, M.; Sugisawa, H.; Kumada, M.; Higuchi, T.; Matsui, K.; Hirotsu, K.; Iyoda, J. Organometallics 1983, 2, 174. (b) Ishikawa, M.; Sugisawa, H.; Kumada, M.; Kawakami, H.; Yamabe, T. Organometallics 1983. 2. 974.

⁽²⁾ Masamune, S.; Murakami, S.; Tobita, H. J. Am. Chem. Soc. 1983, 105, 7776.

^{(3) (}a) Seyferth, D.; Duncan, D. P.; Shannon, M. L. Organometallics 1984, 3, 579. (b) Seyferth, D.; Goldman, E. W.; Escudie, J. J. Organomet. Chem. 1984, 271, 337.

⁽⁴⁾ Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. Organometallics 1985, 4, 57.

⁽⁵⁾ Ishikawa, M.; Matsuzawa, S. J. Chem. Soc., Chem. Commun. 1985, 588

⁽⁶⁾ Ishikawa, M.; Matsuzawa, S.; Hirotsu, K.; Kamitori, S.; Higuchi, T. Organometallics 1984, 3, 1930. (7) Ishikawa, M.; Matsuzawa, S.; Higuchi, T.; Kamitori, S.; Hirotsu,

K. Organometallics 1985, 4, 2040.