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Chemistry of Heterobimetallic Cobalt-Rhodium Complexes

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Summary: The complex [CoRh(CO)$_3$(μ-dppm)$_2$] (**1**), formed directly from Co(II) and Rh(III), reacts with CHCl$_3$ or HgCl$_2$ to give [CoRh(μ-Cl)(CO)$_2$(μ-CO)(μ-dppm)$_2$]$^+$ (**3a**), with I$_2$ to give [CoRh(μ-I)(CO)$_2$(μ-CO)(μ-dppm)$_2$]$^+$ (**3b**), with sulfur to give [CoRh(μ-S)(CO)$_2$(μ-CO)(μ-dppm)$_2$] (**3c**), with H$^+$ to give [CoRh(μ-H)(CO)$_3$(μ-dppm)$_2$]$^+$ (**4**), and with Ph$_2$PH to give [CoRh(μ-H)(μ-PPh$_2$)(CO)$_2$(μ-dppm)$_2$] (**5**), all with retention of the heterobimetallic unit. The complexes have been characterized by spectroscopy and, for **1** and **5**, by X-ray structure analysis.

Mixed cobalt-rhodium carbonyls may be responsible for the synergism observed in some reactions catalyzed by mixtures of [Co$_2$(CO)$_8$] and [Rh$_4$(CO)$_{12}$],[2] and this has encouraged research on such compounds. The parent complex [CoRh(CO)$_7$], which is stable only at low temperature, can add CO reversibly to give [CoRh(CO)$_8$], dimerize with loss of CO to give [Co$_2$Rh$_2$(CO)$_{12}$], or disproportionate under CO to give [Co$_2$(CO)$_8$] and [Rh$_4$(CO)$_{12}$].[2] The triethylphosphine derivative [CoRh(CO)$_5$(PEt$_3$)$_2$] is thermally stable, but it undergoes remarkably easy heterolysis to give [Rh(CO)(PEt$_3$)$_2$L]$^+$ and [Co(CO)$_4$]$^-$, e.g. with L = CH$_3$CN; consequently few of its reactions occur with retention of the Co-Rh bond.[3] This communication reports an easy synthesis of the stable complex [CoRh(CO)$_3$(μ-dppm)$_2$] (1; dppm = Ph$_2$PCH$_2$PPh$_2$), in which the μ-dppm ligands prevent fragmentation and so allow the chemistry of the cobalt-rhodium bond to be studied for the first time in a systematic way.

Complex 1 is isolated in up to 40% yield in a single experimental step by rapid addition of NaBH$_4$ to a solution containing RhCl$_3$·xH$_2$O, CoCl$_2$·6H$_2$O, and dppm with an excess of CO.[4] As in some related reductions,[5] the rate of addition of NaBH$_4$ is important in determining the product; slow addition gives 1 along with the homobimetallic complex [Rh$_2$(CO)$_3$(μ-dppm)$_2$].[6]

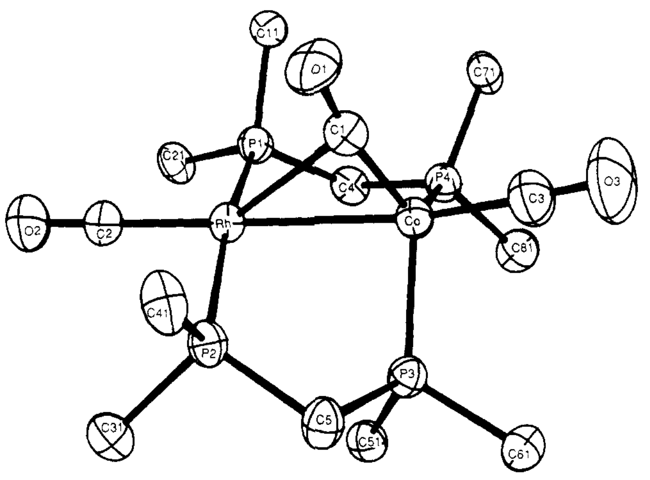

Figure 1. Perspective view of the structure of [CoRh(CO)$_2$(μ-CO)(μ-dppm)$_2$] (1), in which the phenyl groups are omitted for clarity.

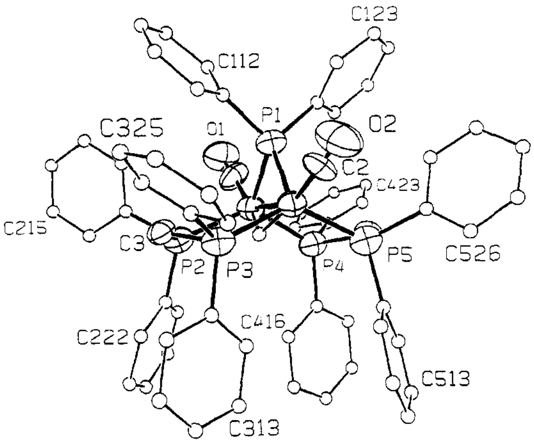

Figure 2. View of the structure of [CoRh(μ-H)(μ-PPh$_2$)(μ-dppm)$_2$] (5). The hydride ligand was not refined, and its position is tentative (see text).

The structure of 1, determined by a single-crystal X-ray study,[7] is shown in Figure 1. It is isostructural with [Rh$_2$(CO)$_3$(μ-dppm)$_2$][6] (2) and cocrystallizes with 2 when both compounds are formed in the synthesis (in Figure 1, the Rh center is common to both 1 and 2 and is labeled Rh^1, while the Co center in 1 becomes Rh in 2 and is labeled M^2). The chief structural differences between 1 and 2 appear to arise because of increased steric hindrance at the smaller cobalt center in 1, which leads to opening of $\angle$P^{3}M^{2}P^4 from 104.39 (3)° when M^2 = Rh[6] to 108.88 (4)° when M^2 = Co. This effect and the shorter Rh^1–M^2 bond

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(1) (a) Lakehead University. (b) University of Western Ontario. (c) University of Guelph. (d) University of Minnesota, Duluth.

(2) Horvath, I. T.; Bor, G.; Garland, M.; Pino, P. *Organometallics* **1986**, *5*, 1441. Horvath, I. T.; Zsolnai, L.; Huttner, G. *Organometallics* **1986**, *5*, 180. Horvath, I. T. *Polyhedron* **1988**, *7*, 2345. Spindler, F.; Bor, G.; Dietler, U. K.; Pino, P. *J. Organomet. Chem.* **1981**, *213*, 303.

(3) Roberts, D. A.; Mercer, W. C.; Geoffroy, G. L.; Pierpoint, C. G. *Inorg. Chem.* **1986**, *25*, 1439.

(4) A suspension of NaBH$_4$ in ethanol was added over 1–2 min to an equimolar mixture of Co(II), Rh(III), and dppm in 1:1 C$_6$H$_6$/EtOH solution at room temperature under N$_2$. The complex [Rh(CO)(dppm)$_2$]$^+$ was identified by ^{31}P NMR spectroscopy (δ = −24, ^1J(Rhp) = 97.4 Hz) at intermediate stages of the reaction, and it is likely that 1 is formed by reaction of this complex with [Co(CO)$_4$]$^-$ with loss of CO. This reaction is reversible: James, B. R.; Mahajan, D. *Can. J. Chem.* **1980**, *58*, 996. Complex 1 has been prepared and studied independently by: Antonelli, D. M.; Cowie, M. *Organometallics*, in press.

(5) Elliot, D. J.; Hughes, A. N.; Mirza, H. A.; Thompson, J. D. *Inorg. Chim. Acta* **1987**, *126*, L7. Elliot, D. J.; Holah, D. G.; Hughes, A. N. *Inorg. Chim. Acta* **1988**, *142*, 195. Elliot, D. J.; Holah, D. G.; Hughes, A. N.; Mirza, H. A.; Zawada, E. *J. Chem. Soc., Chem. Commun.*, in press.

(6) Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1985**, *24*, 1285.

(7) Crystal data for C$_{53}$H$_{44}$CoO$_3$P$_4$Rh: fw 1014.31; monoclinic, space group $P2_1/a$; a = 18.924 (6) Å, b = 12.1550 (18) Å, c = 20.295 (3) Å, β = 95.663 (21)°; V = 4645.5 Å^3; Z = 4; calculated density 1.451 g cm^{-3}; ambient temperature; crystal dimensions 0.20 × 0.30 × 0.55 mm; graphite monochromated Mo Kα radiation; μ(Mo Kα) = 8.8 cm^{-1}; ω-scan technique for 0° ≤ 2θ ≤ 50°; octants measured $h,k,\pm l$, total reflections 8161; R = 0.034, R_w = 0.050, goodness of fit 0.789 for 559 parameters varied and 5910 reflections with $I \geq 3\sigma(I)$. All calculations were carried out on a AT&T 6386 WGS computer using a PC version of NRCVAX. NRCVAX: Gabe, E. J.; Lee, F. L.; Le Page, Y. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Data Bases*; Sheldrick, G. M., Kruger, C., Eds.; Clarendon Press: Oxford, England, 1985; p 167. Atomic scattering factors were taken from: Cromer, D. T.; Waber, J. T. *International Tables* for *X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.4. Cromer, D. T. *Ibid.*, Table 2.3.1.

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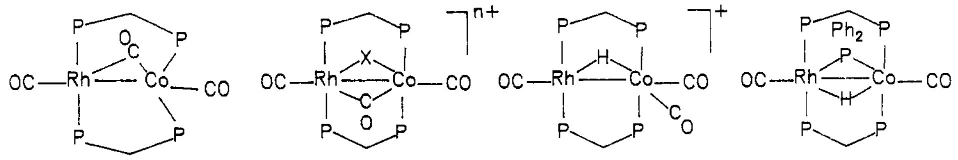
Chart I



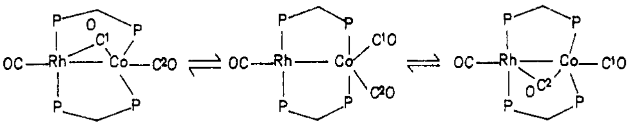
1

3a, X=Cl, n=1
3b, X=I, n=1
3c, X=S, n=0

4

5

when M^2 = Co (2.6852 (7) Å) than when M^2 = Rh (2.739 (1) Å)[6] lead to the shorter distance $Rh^1\cdots C^1$ = 2.420 (4) Å and the more cute angle $\angle Rh^1M^2C^1$ = 62.06 (13)° for **1** compared to corresponding values of 2.533 (3) Å and 63.5 (1)° for **2**. The semibridging CO ligand in **1** is characterized by ν(CO) = 1815 cm^{-1} compared to 1835 cm^{-1} in **2**. The complex **1** is fluxional at room temperature in the sense that the two carbonyl ligands on cobalt are effectively equivalent in the ^{13}C NMR spectrum, but there is no evidence for exchange of carbonyls between metal centers as appears to occur for **2**.[6] The fluxionality, which can be frozen out at −45 °C, is illustrated in eq 1.[4,8]



(1)

Complex **1** is readily oxidized. For example, reaction with $HgCl_2$ or $CHCl_3$, followed by precipitation with $NaBPh_4$, gave **3a**, reaction with iodine and $NaBPh_4$ gave **3b**, and reaction with sulfur gave **3c**.[9] Complex *1* was protonated by HBF_4 at the Co–Rh bond to give, after precipitation with $NaBPh_4$, complex **4**. Complex **4** differs from $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]^+$ in that it has no μ-CO group.[6,10] This is consistent with the tendency of cobalt to adopt a higher coordination number than rhodium, as is also seen in the structure of **1**. Complex **4** is fluxional, since the ^1H NMR spectrum gives a singlet for the CH_2P_2 protons and the ^{13}C NMR spectrum gives a single CoCO resonance; in this case, inversion of the RhCo(μ-H) group must occur.[10]

Complex **1** reacts easily with Ph_2PH to give complex **5**, which has been characterized crystallographically.[11] The structure is shown in Figure 2. The structure is disordered with 0.5 occupancy by Co and Rh in each metal position, and so bond distances, other than *d*(Co–Rh) = 2.795 (3) Å, involving the metal centers are average values. Nevertheless, a peak corresponding to the expected position of the hydride ligand was observed and the position is shown in Figure 2. The Rh–Co bond in **5** (2.795 (3) Å) is significantly longer than in **1** (2.6852 (7) Å). In both **4** and **5** the RhCo(μ-H) interaction is a 3c–2e bond only and so the longer metal–metal bond is expected.

These reactions clearly illustrate that the bimetallic Rh–Co core can be stabilized by μ-dppm ligands, and the organometallic and catalytic reactivity of the complex **1** is being studied.

Acknowledgment. We thank the NSERC (Canada) for financial support.

Registry No. 1, 125782-10-7; **3a**, 125782-11-8; **3b**, 125782-12-9; **3c**, 125782-13-0; **4**, 125801-23-2; **5**, 125782-14-1; **5**·$2C_2H_5OH$, 125782-15-2; $CHCl_3$, 67-66-3; Co, 7440-48-4; Rh, 7440-16-6.

Supplementary Material Available: Listings of crystal data, positional and thermal parameters, and bond distances and angles for **1** and positional and thermal parameters, bond distances and angles, least-squares planes, and torsion angles for **5** (29 pages); a listing of observed and calculated structure factors for **5** (25 pages). Ordering information is given on any current masthead page.

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[8] NMR data for **1**: ^{31}P, δ 31.5 [br s, *P*Co], 20.1 [dt, $^2J(PP)$ = 72 Hz, $^1J(RhP)$ = 129 Hz, *P*-Rh]; ^{13}C (−45 °C), δ 214.7 [br s, Co*C*O], 214.4 [br s, Co*C*O], 180.7 [dt, $^2J(PC)$ = 15 Hz, $^1J(RhC)$ = 71 Hz, Rh*C*O]. IR: ν(CO) 1965 (s), 1922 (s), 1815 (s) cm^{-1}.

[9] Spectroscopic data for **3a**: ^{31}P NMR, δ 46.1 [t, $^2J(PP)$ = 39 Hz, *P*Co], 26.5 [dt, $^2J(PP)$ = 39 Hz, $^1J(RhP)$ = 104 Hz, *P*Rh]; IR, ν(CO) 1986 (m), 1962 (s), 1850 (m) cm^{-1}. Spectroscopic data for **3b**: ^{31}P NMR, δ 47.9 [t, $^2J(PP)$ = 47 Hz, *P*Co], 29.3 [dt, $^2J(PP)$ = 47 Hz, $^1J(RhP)$ = 100 Hz, *P*Rh]; IR (Nujol), ν(CO) 1997 (m), 1990 (m), 1970 (s), 1849 (m) cm^{-1}. Spectroscopic data for **3c**: ^{13}C NMR, δ 197.7 [dt, $^1J(RhC)$ = 73 Hz, $^2J(PC)$ = 14 Hz, Rh*C*O], 211.0 rt, $^2J(PC)$ = 56 Hz, μ-*C*O], 222.6 [s, Co*C*O]; ^{31}P NMR, δ 25.3 [dt, $^1J(RhP)$ = 134 Hz, $^2J(PP)$ = 32 Hz, Rh*P*], 38.4 [t, $^2J(PP)$ = 32 Hz, Co*P*]; IR (Nujol), ν(CO) 1971 (s), 1958 (s), 1796 (m) cm^{-1}.

[10] Spectroscopic data for **4**: ^1H NMR, δ −13.3 [br, CoRh(μ-*H*)], 3.80 [s, CH_2P_2]; ^{31}P NMR, δ 44.8 [t, $^2J(PP)$ = 56.5 Hz, *P*Co], 25.5 [dt, $^2J(PP)$ = 56.5 Hz, $^1J(RhP)$ = 111 Hz, *P*Rh]; ^{13}C NMR, δ 206.9 [*s*, 2 C, Co*C*O], 182.0 [dt, 1 C, $^1J(RhC)$ = 60.7 Hz, $^2J(PC)$ = 14.5 Hz, Rh*C*O]; IR, ν(CO) 1981 (s), 1946 (sh), 1933 (m) cm^{-1}.

[11] Crystal data for **5**·$2C_2H_5OH$: $C_{68}H_{67}CoO_4P_5Rh$; fw 1265.00; monoclinic, space group $P2_1/c$; a = 12.241 (5) Å, b = 20.459 (4) Å, c = 25.394 (5) Å, β = 96.48 (3)°; V = 6319 (6) $Å^3$; Z = 4; calculated density 1.33 g cm^{-3}; T = 21 °C; Mo Kα radiation (λ = 0.710<<mt73 Å); μ(Mo Kα) = 6.9 cm^{-1}; unique reflections 7231 with 2θ up to 43°; Lorentz, polarization, linear decay, and a numerical absorption correction applied; R = 0.075, R_w = 0.092 for 358 variable parameters and 2464 observations with $I \geq 3\sigma(I)$. ^1H NMR data for **5**: δ −15.49 [br s, CoRh(μ-H)]. ^{31}P NMR data for **5**: δ 28.7 [m, 2 P, Rh*P*], 46.4 [m, 2 P, CoP], 213.0 [m, 1 P, μ-*P*Ph_2].

Rotational Isomerism in Bis(carbon dioxide) Complexes of Molybdenum Generated by Conrotatory Motion of the CO_2 Ligands

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Summary: The existence of rotational isomers in $(CO_2)_2$ complexes of molybdenum and their interconversion by a concerted rotation, in which the two CO_2 ligands rotate in the same direction, have been demonstrated with the aid of variable-temperature NMR studies carried out with complexes of the type *trans*-$[Mo(CO_2)_2(PMe_3)_2(P\text{-}P)]$ and *trans*-$[Mo(CO_2)_2(P\text{-}P)_2]$ (P-P = chelating diphosphine).

We have recently described the formation of *trans*-$[Mo(CO_2)_2(PMe_3)_4]$ (**1**) and *trans*-$[Mo(CO_2)_2(PMe_3)_3(CNR)]$ (**2**), the first bis(carbon dioxide) adducts of a transition metal.[1] Although these compounds were fully

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[1] Alvarez, R.; Carmona, E.; Marín, J. M.; Poveda, M. L.; Gutierrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* **1986**, *108*, 2286.

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