

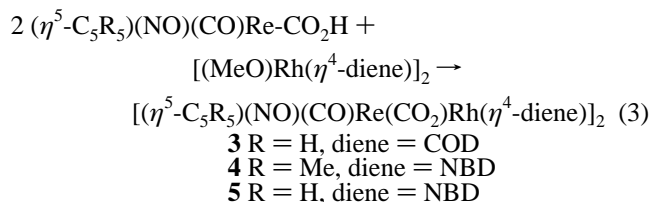
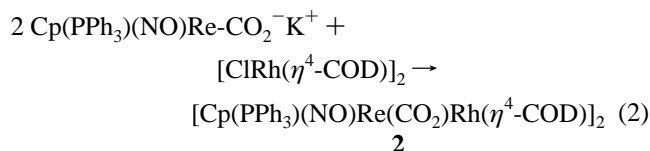
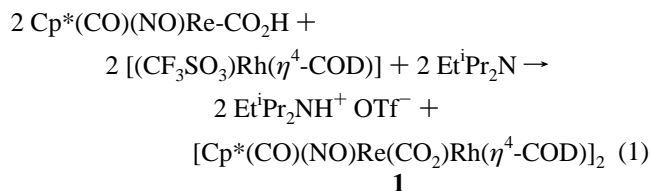
Re₂Rh₂ μ_3 -[η^1 -C(Re): η^1 -O(Rh): η^1 -O'(Rh')] Bis(carbon dioxide) Complexes [(η^5 -C₅R₅)(L)(NO)Re(CO₂)Rh(η^4 -diene)]₂ That Are Structurally Related to Rhodium(I) Carboxylate Dimers [Rh(O₂CR)(η^4 -diene)]₂

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Transition metal complexes in which carbon dioxide bridges two or more metal centers are plausible models for the binding, activation, and potentially the (catalytic) reduction of CO₂. Most of these are bimetallic with either μ -(η^1 -C: η^1 -O) or chelating μ -(η^1 -C: η^1 -O,O') carboxylate ligands.¹ We now report the synthesis and characterization of five heterobimetallic Re₂Rh₂-(μ_3 -CO₂)₂ complexes, [(η^5 -C₅R₅)(L)(NO)Re(CO₂)Rh(η^4 -diene)]₂ (**1–5**, eq 1–3). These retain two μ_3 -[η^1 -C(Re): η^1 -O(Rh): η^1 -O'(Rh')] carboxylate ligands² and structurally resemble the catalytically active Rh(I) carboxylates, [(RCO₂)Rh(diene)]₂.^{3,4}



We synthesized **1–5** from the rhenium acids (η^5 -C₅R₅)(NO)

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(2) A related trimetallic CO₂ complex, (PMe₂Ph)₃Os(μ -H)₂(μ_3 -CO₂)-[Rh(COD)]₂, with μ_3 -[η^1 -C(Os): η^1 -O(Rh): η^1 -O'(Rh')] bound CO₂ has the Os carboxylate bridging two Rh(I)(COD) moieties in the presence of two Os–H–Rh linkages (Lundquist, E. G.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1986**, *108*, 8309. Lundquist, E. G.; Huffman, J. C.; Folting, K.; Mann, B. E.; Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 128). Several other examples of μ_3 - η^3 CO₂ complexes are known.^{1a}

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(4) Rhodium formate complexes have been implicated in Rh(I)-catalyzed hydrogenation of CO₂ to formic acid^{1b,3g} and in hydroformylation catalysis.^{4c} (a) Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207. (b) Suss-Fink, G.; Soulie, J.-M.; Rheinwald, G.; Stoeckli-Evans, H.; Sasaki, Y. *Organometallics* **1996**, *15*, 3416. (c) Mieczynska, E.; Trzeciak, A. M.; Ziolkowski, J. J.; Lis, T. *J. Chem. Soc., Dalton Trans.* **1995**, 105.

(L)ReCO₂H (R = H, L = CO, PPh₃; R = Me, L = CO)⁵ and one of three rhodium precursors⁶ (eq 1–3). Treatment of Rh-(I) (1,5- η^4 -COD, COD = cyclooctadiene) triflate^{6a} with Cp*(CO)(NO)ReCO₂H^{5d} (Cp* = pentamethylcyclopentadiene) and base gave **1** (65–70%) as an analytically pure red solid.⁷ Reaction of [CIRh(η^4 -COD)]₂ with Cp(PPh₃)(NO)ReCO₂K^{5c} (Cp = cyclopentadiene) afforded analytically pure, yellow microcrystalline **2** (49%) from ether or THF/pentane at –20 °C. Oro's Rh(I) COD or norbornadiene μ -methoxides^{6b,c} served as convenient precursors to **3** (48% yield) and to the less stable Rh(I) norbornadiene congeners **4** and **5** (25–35% yields), which formed orange solids (**3** and **4** were procured analytically pure).

Solid samples of **1–3** are stable at 25 °C; their solution stability in C₆D₆ varies, **2** \gg **1** (2 d) $>$ **3** (2–4 h) \gg **4**, **5** (unstable above 0 °C). Solutions of **1** and **3** are more stable in ether and THF. In C₆H₆, **1** degraded over 2 d to Cp*(CO)(NO)ReC₆H₅⁸ (37%) and low concentrations of unidentified rhenium and rhodium residues. Other more plausible degradation products such as Cp*(CO)(NO)ReH,⁹ Cp*(CO)(NO)ReC(O)OC₆H₅,⁸ and the Rh(I) compounds [(X)Rh(η^4 -COD)]₂ [X = HCO₂,^{3d,g} PhCO₂,^{3a,c} HO,^{6b} PhO^{6c}] and [(HRh(η^4 -COD)]₄¹⁰ were not detected by IR or ¹H and ¹³C NMR spectroscopies.

Spectral data for **1–5** are consistent with Re₂Rh₂(μ_3 -CO₂)₂ cores. In addition to IR ν (CO) and ν (NO) absorptions, **1–5** show intense $\nu_{\text{OCO(asy)}}$ and $\nu_{\text{OCO(sym)}}$ bands at 1460 and 1260 cm⁻¹ (1408 and 1232 cm⁻¹ for **2**). Their relatively high $\Delta\nu = [\nu_{\text{OCO(asy)}}] - [\nu_{\text{OCO(sym)}}]$ values of 176–206 cm⁻¹ imply the presence of bridging Re carboxylates.^{1a} NMR spectra of **1–5** are influenced by the stereogenic rhenium centers, which afford *RR(SS)* enantiomers and a *meso* diastereomer. Two sets of resonances (1:1)¹¹ were observed by ¹H and/or ¹³C NMR spectroscopy for the CO, CO₂, and Cp (or Cp*) ligands.¹² ¹H NMR spectra for **1–3** show the upfield progression^{3,13} of the

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(7) Synthesis of **1**: [Rh(COD)Cl]₂ (161 mg, 0.326 mmol) and AgOTf (162 mg, 0.632 mmol) in 3 mL of THF were stirred for 30 min at 25 °C and centrifuged. The orange centrifugate was added to Cp*Re(CO)(NO)-(COOH)^{5d} (265 mg, 0.625 mmol) and NEtⁱPr₂ (720 μ L, 0.674 mmol) in 30 mL of pentane (–78 °C). After 40 min (25 °C), an orange precipitate was collected and washed with ether; the combined filtrates were evaporated and crystallized from CH₂Cl₂/pentane (yield of **1** 255 mg, 64%).

(8) This compound was independently synthesized and characterized (Supporting Information).

(9) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 2811. (10) Kulzick, M. A.; Price, R. T.; Muetteries, E. L.; Day, V. E. *Organometallics* **1982**, *1*, 1256. Marciniak, B.; Krzyzanowski, P. *J. Organomet. Chem.* **1995**, *493*, 261.

(11) Isoelectronic [Cp*(CO)₂FeCO₂Rh(COD)]₂ was synthesized according to eq 2, except that the Cp*(CO)₂FeCO₂⁻ was generated from ligating CO₂ to Cp*(CO)₂Fe⁻. ¹H and ¹³C NMR spectra of [Cp*(CO)₂FeCO₂Rh(COD)]₂ exhibit single resonances for the CO, CO₂, and Cp* ligands. The COD ligands have six ¹H NMR resonances (two each for the vinyl, exo, and endo methylene hydrogens), as observed for [CH₃CO₂Rh(COD)]₂ at 0 °C. Pinkes, J. R.; Tetrick, S. M.; Xu, C.-F.; Cutler, A. R. Submitted.

(12) Only **2** forms unequal amounts (4:1 ratio) of diastereomers. The phosphine ligand on the major diastereomer induces substantial ¹H NMR chemical shift dispersion: 11 COD resonances (12 possible) were observed; ¹H NMR (500 MHz, C₆D₆) δ 5.60 (s, 5H, Cp), 5.25 (s, Cp, minor diastereomer, 1:4 ratio); ¹³C{¹H} NMR (C₆D₆) δ 93.79 (Cp), 93.26 (Cp, minor diastereomer, 1:4 ratio); ³¹P{¹H} NMR (C₆D₆) δ 22.64, 22.12 (4:1 ratio). We assign the major diastereomer as *RR(SS)* due to the presence of extensive vicinal methylene ³J_{H,H} spin interactions. Thus, 2D COSY NMR experiments map 12 interconnected hydrogens: every hydrogen atom on each COD is unique and is related by the C₂ axis to its equivalent hydrogen on the other COD ligand.

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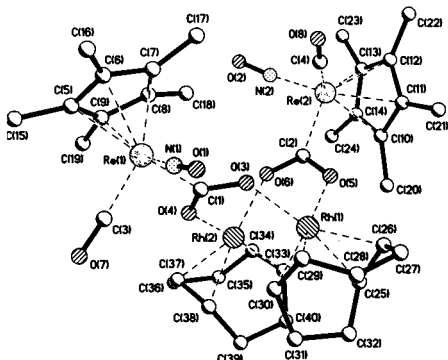


Figure 1. Ball and stick view of $[\text{Cp}^*(\text{CO})(\text{NO})\text{Re}(\text{CO})_2\text{Rh}(\eta^4\text{-COD})]_2 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{C}_5\text{H}_{12}$ (**1**). Selected interatomic distances (Å) and angles (deg): Rh–Rh 3.245(1), Re–Re 6.893(1), Re–CO₂ 2.127(7), 2.132(7), C–O₂ 1.267(9), 1.274(8), 1.296(9), 1.237(9), Rh–O 2.082(5), 2.090(5), 2.092(5), 2.085(5); O–C–O 123.1(6), 122.8(7), [Rh(1), Rh(2), C(1), O(3), O(4)] and [Rh(1), Rh(2), C(2), O(5), O(6)] 85.3(1), [Rh(1), O(3), O(5), C(56A), C(90B)] and [Rh(2), O(4), O(6), C(34C), C(78D)] 57.0; C(56A), C(90B), C(34C), C(78D) represent the midpoints of C(25)–C(26), C(29)–C(30), C(33)–C(34), and C(37)–C(38).

COD vinyl CH, *exo*-CH₂, and *endo*-CH₂ absorptions; the number of resonances are consistent with the low *C*₂ [*RR(SS)*] and *C_i* [*RS*] symmetry. Thus, **1** shows four *exo*-CH₂ multiplets⁷ vs a possible maximum of four per diastereomer.

The Re₂Rh₂(μ₃-CO₂)₂ core of **1** was established by an X-ray structure determination (Figure 1)¹⁴ as two square-planar Rh centers, each of which incorporates a chelating COD ligand and one oxygen atom from each of the two μ-(η¹-O, η¹-O') Re carboxylate ligands. This structure resembles other dimeric Rh(I)(η⁴-diene)(μ-carboxylate) complexes that also lack rhodium–rhodium bonding.^{3b,f,g,15} The “open-book” structure of **1** maintains a 57.0° dihedral angle between the best coordination planes, although the Rh atoms reside above these planes (0.166 and 0.135 Å) and closer to one another.

Complex **1** crystallized as a single *meso* diastereomer.¹⁶ The Re–C(carboxyl) bond is 0.03–0.09 Å longer than similar bonds

(14) Crystal data for **1**: C₄₀H₅₄N₂O₈Re₂Rh₂·2CH₂Cl₂·C₅H₁₂, *M_r* = 1426.14, orthorhombic, *Pbca*; *a* = 16.094(1) Å, *b* = 17.659(2) Å, *c* = 35.517(3) Å; *V* = 10 094(2) Å³; *Z* = 8; *D_c* = 1.877 g/cm³; red prism (0.32 × 0.60 × 0.62 mm); 9502 reflections (7933 independent); 198 K; Siemens P4 diffractometer (*ω* – 2θ scan, 3 ≤ 2θ ≤ 48°). The full-matrix least-squares refinement was based on 7932 reflections [*I* > 2σ(*I*)] and 605 parameters and converged with *R* = 0.0380 (*R_w* = 0.0859). Data were processed using the SHELXTL version 5.03 package (Siemens).

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(16) (a) Explanations for crystallization of a single diastereomer of **1** include the following: (1) *SR* and *SS(RR)* equilibrate via carbonyl–carboxylate ligand interchange¹⁷ and *meso*-**1** preferentially crystallizes. (2) Ring opening via monomeric Cp*(CO)(NO)Re(CO)₂Rh(COD), conproportionates enantiomeric *SS/RR* to (selectively crystallized) *meso*-**1**. Varying mixtures of **1** and [(COD)Rh(OAc)]₂ equilibrate in C₆D₆ (confirmed by EXSY NMR experiments) with the tentatively identified [Cp*(CO)(NO)Re(CO)₂][OAc][Rh(η⁴-COD)]₂, *K_{eq}* = 15. (b) For analogous conproportionation reactions,^{13a} see: Oro, L. A.; Teresa Pinillos, M.; Tejel, C.; Apreada, M. C.; Foces-Foces, C.; Cano, F. H. *J. Chem. Soc., Dalton Trans.* **1988**, 1927. (c) Monomeric bis(phosphine) Rh(I) complexes bearing a chelating (η²-O,O') carboxylate ligand are known. Werner, H.; Schäfer, M.; Nürnberg, O.; Wolf, J. *Chem. Ber.* **1994**, 127, 27. Schäfer, M.; Wolf, J.; Werner, H. *J. Organomet. Chem.* **1994**, 476, 85. Kukla, F.; Werner, H. *Inorg. Chim. Acta.* **1995**, 235, 253.

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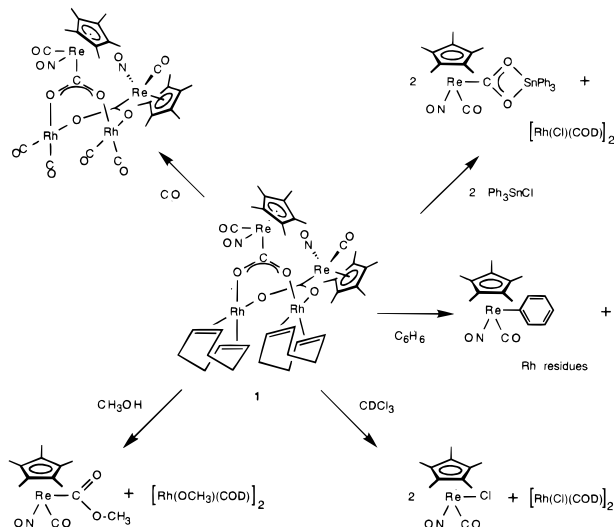


Figure 2.

for Cp*(CO)(NO)Re[μ-(η¹-C:η²-O,O') CO₂]ML_x [ML_x = Re(CO)₃PPh₃, ZrCl(Cp)₂, Mo(CO)₂Cp].¹⁸ Although the average carboxylate C–O bond length on **1** of 1.27 Å is comparable, its 123° O–C–O angles exceed those previously recorded (113–114°),¹⁸ as well as the 116° O–C–O angle for (PMe₂-Ph)₃Os(μ-H)₂(μ₃-CO₂)[Rh(COD)]₂.² Rh–O bond lengths of 2.09 Å on **1** likewise resemble those on [Rh(diene)(O₂CR)]₂ complexes (R = H, CH₃),^{3b,g,15b} but are less than the 2.06 Å on the OsRh₂(μ₃-CO₂) complex.²

Some preliminary results with the prototypical **1** underscore the high reactivity of these Re₂Rh₂ bis(μ₃-CO₂) adducts (Figure 2). Treatment of **1** with Ph₃SnCl quantitatively produced Cp*(CO)(NO)Re(CO)₂SnPh₃^{18a} plus [ClRh(COD)]₂; dissolution of **1** in CHCl₃ gave [(COD)RhCl]₂ (96% by NMR) and Cp*(CO)(NO)ReCl¹⁹ (98%). Methanolysis of **1**, however, yielded Cp*(CO)(NO)Re(CO)₂CH₃⁸ (71%) plus [CH₃ORh(COD)]₂^{6b} (64%). Attempts to discern if Cp*(CO)(NO)ReCO₂H or [HORh(COD)]₂ are intermediates have been unsuccessful. Although inert toward ¹³CO₂ (1 atm), **1** immediately absorbed CO (1 atm) and quantitatively generated a material formulated as [Cp*(CO)(NO)Re(CO)₂Rh(CO)]₂. Its IR spectrum resembles that obtained after carbonylation of [(CH₃CO₂)Rh(η⁴-COD)]₂ to [(CH₃CO₂)Rh(CO)]₂.^{3d–f,20} Studies in progress are focusing on the facile reactions of hydrosilanes and of H₂ with **1** and **2**.

Acknowledgment. Support from the National Science Foundation, Grant CHE-9108591, is gratefully acknowledged.

Supporting Information Available: Spectroscopic and characterization data and tables of crystallographic parameters, hydrogen atom parameters, and thermal parameters for **1** (22 pages). See any current masthead page for ordering and Internet access instructions.

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