Synthesis of M_2Rh_2 Bis(μ_3-carbon dioxide) Complexes from the Reaction between [Rh(OH)(η^4-COD)]$_2$ and Cationic Metal Carbonyls

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The M_2Rh_2 bis(μ_3-CO_2) complexes [Cp*(CO)(NO)Re(CO_2)Rh(η^4-cod)]$_2$ (**1**) and [Cp*(CO)$_2$-MCO_2Rh(η^4-cod)]$_2$, M = Fe (**2**) and Ru (**3**), were synthesized in moderate to high yields from treating [Rh(OH)(η^4-cod)]$_2$ (cod = 1,5-cyclooctadiene) with the carbonyl salts Cp*(L)(CO)$_2$M$^+$ (L = CO, M = Fe, Ru; L = NO, M = Re) and a base. [An alternative synthesis of **1** and its crystallographic structure determination has been reported.] Although details on using several bases in the synthesis of **2** are reported, the use of volatile $EtMe_2N$ in excess as the base is especially useful. IR and NMR spectral data are in accord with a M_2Rh_2 bis(μ_3-CO_2) core for **2** and **3**: they retain two μ_3-[η^1-C(M):η^1-O(Rh):η^1-O′(Rh′)] carboxylate ligands that resemble those that were found for **1** and the Rh(I) carboxylates [(RCO_2)Rh(diene)]$_2$. Complexes **2** and **3** with their “open-book” structures are not fluxional at room temperature. Complex **2**, its norbornadiene analogue, [Cp*(CO)$_2FeCO_2Rh$(η^4-nbd)]$_2$ (**4**), and their ^{13}C-labeled derivatives also are accessible from reactions of Cp*(CO)$_2FeCO_2K$ [or Cp*(CO)$_2$-Fe$^{13}CO_2$K] with [Rh(OSO_2CF_3)(η^4-cod)]$_x$. [Cp*(CO)$_2$Fe($^{13}CO_2$)Rh(η^4-diene)]$_2$ [diene = cod (**2-^{13}C**); nbd (**4-^{13}C**)] underwent carboxylate−carbonyl label shuttle to yield 1:1 mixtures of [Cp*(CO)(^{13}CO)$FeCO_2Rh$(diene)]$_2$ (**2a-C^{13}**) and **4a-C^{13}**. IR spectral assignments for the metallocarboxylate ν_{OCO} absorptions are also presented.

Introduction

We recently reported the synthesis and characterization of a new series of carbon dioxide complexes that retain a Re_2Rh_2(μ_3-CO_2)$_2$ structural motif in which each of the two rhenium metallocarboxylates bridge two rhodium(I) η^4-diene moieties.[1] The presence of the two μ_3-[η^1-C(Re):η^1-O(Rh):η^1-O′(Rh′)] carboxylate ligands was established by an X-ray crystallographic structure determination of [Cp*(CO)(NO)Re(CO_2)Rh(η^4-cod)]$_2$ (**1**). Its “open-book” structure, with a 85° angle between the two μ-CO_2Rh_2 carboxylate bridges and a (nonbonding) Rh, Rh separation of 3.24 Å, resembles the catalytically active Rh(I) carboxylates [(RCO_2)Rh(diene)]$_2$.[2]

These Re_2Rh_2 bis(μ_3-CO_2) complexes were synthesized by three synthetic routes starting with either a rhenium metallocarboxylate or its metallocarboxylic acid in the presence of a base. Treatment with the appropriate rhodium(I) precursor, [RhCl(η^4-cod)]$_2$, [Rh(OSO_2CF_3)(η^4-cod)]$_x$, or [Rh(OCH_3)(η^4-diene)]$_2$, provided the products in moderate yields. These syntheses resemble the procedures by which nearly all bi-, tri-, and tetrametallic carbon dioxide complexes[3] have been prepared: the μ-CO_2 ligand originates as a preformed monometal CO_2 complex or metallocarboxylic acid derivative. Exceptions include several examples of incorporating CO_2 into a metal−metal bond[4] or combining a metal oxo compound with a metal carbonyl complex.[5] We now report a new synthetic procedure for carbon dioxide complexes in which the μ-CO_2 ligand is assembled from a metal carbonyl complex plus a metal hydroxide in the presence of base.[6] Details are presented for combining [Rh(OH)(η^4-cod)]$_2$[7] with cationic metal carbonyl complexes and

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[6] Bimetallic μ-CO_2 complexes have been prepared by condensation of a metal hydroxide or alkoxide[1] and a metallocarboxylic acid: (a) Beck, W.; Raab, K.; Nagel, V.; Steimann, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 526. (b) Bennett, M. A.; Robertson, G. B.; Rokicki, A.; Wickramasinghe, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 7098. (c) Torresan, I.; Michelin, R. A.; Zanardo, A.; Pinna, F.; Strukul, G. *Organometallics* **1991**, *10*, 623.

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a base in the efficient syntheses of **1** and [Cp*(CO)$_2$MCO$_2$Rh(η^4-cod)]$_2$, M = Fe (**2**) and Ru (**3**). Complex **2**, its norbornadiene analogue, [Cp*(CO)$_2$FeCO$_2$Rh(η^4-nbd)]$_2$ (**4**), and their ^{13}C-labeled derivatives also are accessed from reactions of Cp*(CO)$_2$FeCO$_2$K [or Cp*(CO)$_2$Fe^{13}CO$_2$K] with [Rh(OSO$_2$CF$_3$)(η^4-cod)]$_x$.

Experimental Section

Synthetic manipulations were performed in a nitrogen atmosphere using a combination of standard Schlenk, glovebox, and vacuum line procedures.[8] Infrared spectra were recorded with a Perkin-Elmer model 1600 spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded in benzene-d_6 or toluene-d_8 (both dried over 3A molecular sieves) using a Varian Unity 500 or a Varian INOVA 300 spectrometer, and the data were reported relative to residual C$_6$D$_5$H (^{1}H, δ 7.15; ^{13}C, δ 128.00) or C$_6$D$_5$^{13}CD$_2$H (^{1}H, δ 2.09; ^{13}C, δ 20.4). Combustion microanalyses were done by Quantitative Technologies, Inc., Whitehouse, NJ.

Tetrahydrofuran (THF), hexane, ether, and toluene were distilled from sodium benzophenone ketyl; dichloromethane was distilled from phosphorus pentoxide. Acetone and acetonitrile were dried over 3A molecular sieves and deoxygenated by sparging with nitrogen prior to use. Ethanol was deoxygenated by sparging with nitrogen prior to use. Matheson "bone dry" carbon dioxide was dried further by passage through a 1 cm × 1 m glass column that was packed with a 25% P$_2$O$_5$ powder dispersion on activated silica gel (70−200 mesh) containing 1% Congo Red indicator. Before using, carbon dioxide and 99% ^{13}C-labeled CO$_2$ were frozen (−196 °C) and pumped on to remove noncondensable materials. All other reagents were purchased from commercial sources and used as received.

Silver triflate (AgOTf) was recrystallized from acetone and dried under vacuum at 95 °C. [Cp*(CO)$_2$Fe]$_2$,[9a,b] Fp*COPF$_6$,[9b] Cp*Ru(CO)$_3$PF$_6$,[9c] Cp*Re(NO)(CO)$_2$BF$_4$,[9d,e] [Rh(cod)Cl]$_2$, [Rh(nbd)Cl]$_2$,[10] [Rh(cod)OH]$_2$,[7] and [Rh(μ-CH$_3$CO$_2$)(cod)]$_2$[11] were prepared by literature procedures and judged pure by IR and ^{1}H NMR spectroscopy. IR spectra of Cp*(CO)$_2$FeK,[9b,12a] generated by sonication of [Cp*Fe(CO)$_2$]$_2$ with potassium,[13] routinely exhibited the presence of only negligible concentrations of hydride Cp*(CO)$_2$FeH[9a,12b,c] [ν(CO) 1993, 1932 cm^{-1}] or of [Cp*Fe(CO)$_2$]$_2$ [ν(CO) 1923, 1754 cm^{-1}]. The apparatus and vacuum line procedure for treating THF solutions of Cp*(CO)$_2$Fe$^-$ K$^+$ with 1.0 equiv of CO$_2$ or of 99% C^{13}-labeled CO$_2$ (−78 °C) have been described.[14]

Preparation of [(η^5-C$_5$Me$_5$)(CO)(NO)ReCO$_2$Rh(cod)]$_2$ (1). Cp*Re(NO)(CO)$_2$BF$_4$ (198 mg, 0.40 mmol) and [Rh(OH)(cod)]$_2$ (91 mg, 0.20 mmol) were mixed in 25 mL of THF (5 °C), and Me$_2$EtN (0.24 mL, 2.2 mmol) was injected. IR spectra after 10 min indicated that all of the starting Cp*Re(NO)(CO)$_2$BF$_4$ had been converted to **1**. The solvent and residual Me$_2$EtN were evaporated (10^{-2} mm, 30 min), and the red-brown solvent was solid was extracted with 3 × 5 mL of cold (5 °C) benzene. The combined red extracts were evaporated (10^{-2} mm, 1 h) [frozen immediately with an acetone−dry ice bath], re-extracted with 3 × 5 mL of cold benzene, and evaporated and dried on the vacuum line for 6 h. A brick red solid (252 mg) was obtained that corresponded to spectroscopically pure **1**[1] (99% yield).

Synthesis of [(η^5-C$_5$Me$_5$)(CO)$_2$FeCO$_2$Rh(cod)]$_2$ (1). Reaction between (η^5-C$_5$Me$_5$)Fe(CO)$_3$PF$_6$ and [Rh(OH)(cod)]$_2$ in the Presence of Dimethylethylamine. A suspension of Cp*Fe(CO)$_3$PF$_6$ (252 mg, 0.60 mmol) and [RhOH(cod)]$_2$ (137 mg, 0.30 mmol) in 50 mL of THF (5 °C) was treated with Me$_2$EtN (0.30 mL, 2.8 mmol). An IR spectrum of the clear orange solution after 10 min indicated that 85% of the starting Cp*Fe(CO)$_3$PF$_6$ had converted to [Cp*(CO)$_2$FeCO$_2$Rh(cod)]$_2$ (**2**), ν(CO) 1999, 1944 cm^{-1}. All subsequent operations were carried out at or below 5 °C. The solvent and excess Me$_2$EtN were evaporated, and the red-brown solid was extracted with 3 × 5 mL of cold benzene. The combined filtrates were frozen (−78 °C); then the benzene was evaporated at 5 °C. Another benzene extraction (3 × 5 mL) and removal of solvent on the vacuum line left 201 mg of a red-brown solid that was identified as [Cp*(CO)$_2$FeCO$_2$Rh(cod)]$_2$ (**2**) (67% yield): IR (THF) ν_{asym}(OCO) 1470 (br, m) cm^{-1}, ν_{sym}(OCO) 1262 (m), 1230 (m) cm^{-1}; ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 4.40 (br m, 4H, =CH), 4.24 (br m, 4H, =CH), 2.79 (mult, 4H, exo-CH*H*), 2.38 (mult, 4H, exo-CH*H*), 1.67 (mult, 4H, endo-C*H*H), 1.62 (s, 30H, C$_5$*Me*$_5$), 1.55 (br, 4H, endo-C*H*H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 217.39 (FeCO$_2$), 214.67 (FeCO), 96.18 (*C*$_5$Me$_5$), 80.59, 75.80 (br, =C), 31.56, 31.00 (allylic C), 9.78 (C$_5$*Me*$_5$). The ^{1}H NMR endo-CH$_2$ spectral assignments were made on the basis of a COSY NMR experiment. Anal. Calcd for C$_{42}$H$_{54}$Fe$_2$O$_8$Rh$_2$: C, 50.23; H, 5.42. Found: C, 49.98; H, 5.30.

Reaction of (η^5-C$_5$Me$_5$)Fe(CO)$_3$PF$_6$ and [RhOH(cod)]$_2$ with 2,6-Lutidine. A stirred suspension of Cp*Fe(CO)$_3$PF$_6$ (84 mg, 0.20 mmol) and [Rh(OH)(cod)]$_2$ (46 mg, 0.10 mmol) in 20 mL of THF (5 °C) was treated with 2,6-lutidine (0.022 g, 0.2 mmol). IR spectral monitoring of the clear red-brown solution that resulted within 1 h indicated 70% conversion of the reactants to [Cp*(CO)$_2$FeCO$_2$Rh(cod)]$_2$ (**2**) along with <2% [Cp*Fe(CO)$_2$]$_2$. The reaction was evaporated (5 °C), the red-brown residue was extracted with 3 × 3 mL of cold benzene, and the orange-brown filtrate was frozen (−78 °C). Removal of solvent on a vacuum line (5 °C) left 62 mg of a gummy brown solid, which by IR and ^{1}H NMR spectral examination consisted of 70% **1** and 30% [Cp*Fe(CO)$_2$]$_2$ [^{1}H NMR (C$_6$D$_6$): δ1.60 (s,Cp*)], 2−5% lutidine, and residual THF.

Reaction of [(η^5-C$_5$Me$_5$)(CO)$_2$FeCO$_2$Rh(cod)]$_2$ (2) with Ph$_3$SnCl. A solution of **2** (40 mg, 0.040 mmol) in 20 mL of THF (5 °C) that had been treated with Ph$_3$SnCl (31 mg, 0.080 mmol) changed from light brown to orange over 30 min. IR spectral monitoring indicated complete conversion of **2** to Cp*(CO)$_2$FeCO$_2$SnPh$_3$, ν(CO) 2013, 1960 cm^{-1}. The reaction was evaporated, the residue was extracted with 10 × 5 mL hexane, and the combined orange filtrates were evaporated. This left 42 mg of a brown solid that was identified by ^{1}H and ^{13}C NMR spectroscopy as Cp*(CO)$_2$FeCO$_2$SnPh$_3$[14b,15] (60%) admixed with unidentified organic residues. The remaining solid residue was extracted again with 3 × 3 mL of benzene, and the light yellow filtrates were evaporated. A light yellow solid was recovered (14 mg), which was identified as [RhCl(cod)]$_2$ (71% yield).

Synthesis of [(η^5-C$_5$Me$_5$)(CO)$_2$RuCO$_2$Rh(cod)]$_2$ (3). To a suspension of Cp*Ru(CO)$_3$PF$_6$ (186 mg, 0.40 mmol) and [RhOH(cod)]$_2$ (91 mg, 0.20 mmol) in 25 mL of THF (5 °C) was added Me$_2$EtN (0.24 mL, 2.2 mmol). After 10 min, IR spectral

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monitoring of the dark yellow solution indicated that all of the starting $Cp^*Ru(CO)_3PF_6$ had been consumed. Removal of solvent and excess Me_2EtN left a yellow-green solid, which was extracted with 3 × 5 mL of benzene (5 °C). The combined yellow-green filtrates were worked up as described for **2**. The resulting green solid (200 mg) was characterized as $[(\eta^5\text{-}C_5Me_5)(CO)_2RuCO_2Rh(cod)]_2$ (**3**), 91% yield: IR (THF) ν(CO) 2011, 1952 cm^{-1}, ν_{asym}(OCO) 1479 sh, 1467 (m) cm^{-1}, ν_{sym}(OCO) 1317 (w), 1256 (m), 1249 (sh) cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 4.39 (br m, 4H, =CH), 4.34 (br m, 4H, =CH), 2.80 (mult, 4H, exo-CH*H*), 2.43 (mult, 4H, exo-CH*H*), 1.70 (mult, 4H, endo-C*H*H), 1.61 (s, 30H, C_5*Me*$_5$), 1.59 (br, 4H, endo-CH*H*); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 100.46 (s, *C*$_5$ Me$_5$), 79.37, 72.52 (d$_{C-Rh}$, J = 14.3 Hz, =C), 31.68, 30.90 (allylic C), 10.29 (s, C_5*Me*$_5$)). Anal. Calcd for $C_{42}H_{54}O_8Rh_2Ru_2$: C, 46.08; H, 4.97. Found: C, 45.57; H, 4.78.

Reactions of $[(\eta^5\text{-}C_5Me_5)(CO)_2MCO_2Rh(cod)]_2$ (M = Fe, Ru) with Carbon Monoxide. Carbon monoxide was bubbled slowly through solutions of $[Cp^*(CO)_2MCO_2Rh(cod)]_2$ (**2**, M = Fe; **3**, M = Ru) (0.02 mmol) in 600 mg of C_6D_6 in an NMR tube (5 °C). Within 5 min, the solutions turned lighter brown. NMR spectra were consistent with complete release of the cod ligands leaving materials that were tentatively assigned as $[Cp^*(CO)_2FeCO_2Rh(CO)_2]_2$ (**5**) [^{1}H NMR δ 1.66 (s, 30 H, C_5*Me*$_5$); $^{13}C\{^1H\}$ NMR δ 9.79 (C_5*Me*$_5$), 96.43 (*C*$_5$Me$_5$)] and $[Cp^*(CO)_2RuCO_2Rh(CO)_2]_2$ (**6**) [^{1}H NMR δ 1.54 (s, 30 H, C_5*Me*$_5$); $^{13}C\{^1H\}$ NMR δ 10.15 (C_5*Me*$_5$), 100.93 (*C*$_5$Me$_5$)]. When kept in the original benzene solutions or in the presence of the CO atmosphere, these materials were stable for 2−3 h. Thereafter, these brown solutions degraded to unidentified materials.

Into cold (−78 °C) THF solutions containing **2** and **3** (0.02 mmol in 10 mL) CO was slowly bubbled. IR spectral monitoring indicated that **2** and **3** were transformed quantitatively within 5 min to products tentatively formulated as $[Cp^*(CO)_2FeCO_2Rh(CO)_2]_2$ (**5**) [IR ν(FeCO) 2008 (vs), 1956 (s), ν(RhCO) 2078 (s), 2054 (m), 2008 (vs) cm^{-1}, ν_{asym}(OCO) 1435 (br, m) cm^{-1}, ν_{sym}(OCO) 1261 (m), 1229 (m) cm^{-1}] and $[Cp^*(CO)_2RuCO_2Rh(CO)_2]_2$ (**6**) [IR ν(RuCO) 2020 (s), 1964 (s), ν(RhCO) 2079 (s), 2055 (m), 2002 (vs) cm^{-1}, ν_{asym}(OCO) 1436 (br, m) cm^{-1}, ν_{sym}(OCO) 1318 (w), 1259 (m), 1244 (m) cm^{-1}]. After being warmed above 0 °C, these solutions degraded to unidentified materials.

Preparation of $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe^{13}CO_2Rh(cod)]_2$ (2-C^{13}). A red solution of $Cp^*(CO)_2FeK$ was generated by sonication of a THF suspension (10 mL) of $[Cp^*Fe(CO)_2]_2$ (140 mg, 0.283 mmol) and potassium metal (130 mg, 3.32 mmol) in an ultrasonic cleaning bath (1 h). After centrifugation, the solution was transferred to a 100-mL round-bottom flask and treated with $^{13}CO_2$ (99% labeled, 13.4 mL, 0.60 mmol) at −196 °C and then at −78 °C. The resulting dark red-brown $Cp^*(CO)_2FeCO_2K$ solution[14] [IR 1974, 1904 cm^{-1} ν(CO)] was free of starting $Cp^*(CO)_2FeK$ and of contaminating $Cp^*(CO)_2FeH$ or $[Cp^*Fe(CO)_2]_2$. To this flask was added a filtered solution of "Rh(cod)(OTf)",[16] which was generated from a mixture of $[Rh(cod)Cl]_2$ (139 mg, 0.282 mmol) and AgOTf (144 mg, 0.562 mmol) in 10 mL of THF (−42 °C). An IR spectrum of the dark red solution after stirring for 10 min (−78 °C) was consistent with formation of a 2:1 mixture of $[Cp^*(CO)_2Fe^{13}CO_2Rh(cod)]_2$ (**2-C^{13}**) [1999, 1944 cm^{-1}, ν(CO)] and $[Cp^*(CO)(^{13}CO)FeCO_2Rh(cod)]_2$ (**2a-C^{13}**) [1983, 1913 cm^{-1}, ν(CO)]. The THF was evaporated, the remaining dark red residue was extracted with hexane (3 × 5 mL), and the combined extracts were evaporated. The resulting 60 mg of a dark red brown powder contained a 1:1:0.25:0.25 mixture of **2-C^{13}**, **2a-C^{13}**, $Cp^*_2Fe_2(CO)_2(^{13}CO)_2$, and $Cp^*_2Fe_2(CO)_4$, as determined by IR and ^{1}H NMR integration. IR spectral absorptions in the metallocarboxylate region appeared as broad envelopes 1475−1415 and 1255−1210 cm^{-1}.

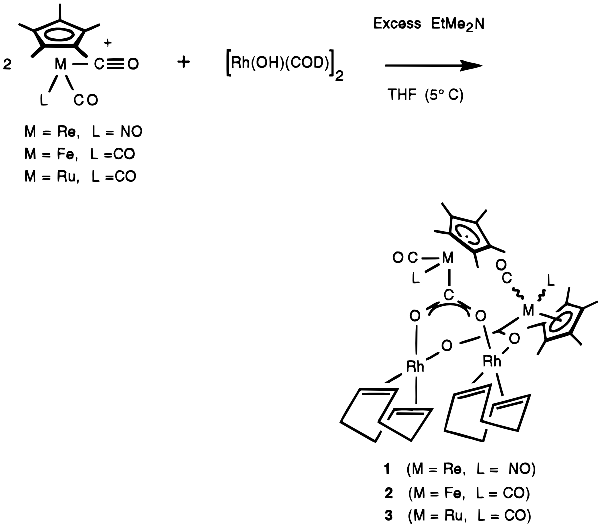
Attempts at purifying **2** by chromatography and by crystallization (hexane, acetonitrile, THF/hexane, toluene/hexane, ether/hexane, and CH_2Cl_2/hexane) invariably enriched the mixtures in $[Cp^*(CO)_2Fe]_2$.

Synthesis of $[(\eta^5\text{-}C_5Me_5)(CO)_2FeCO_2Rh(nbd)]_2$ (4) and of $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe^{13}CO_2Rh(nbd)]_2$ (4-C^{13}). $[Rh(nbd)Cl]_2$ (115 mg, 0.25 mmol) in 10 mL of THF at −42 °C was treated with AgOTf (128 mg, 0.50 mmol). After 20 min, the yellow suspension of "Rh(nbd)(OTf)"[16] was filtered and transferred to a THF solution of $Cp^*(CO)_2FeCO_2K$ (0.50 mmol, 10 mL) at −78° C. An infrared spectrum of the dark red solution (30 min) showed the presence of $[Cp^*(CO)_2FeCO_2Rh(nbd)]_2$ (**5**) [ν(CO) 1998, 1943 cm^{-1}] as the only $Cp^*(CO)_2Fe$ product. The THF was evaporated, the dark red residue was extracted with hexane (4 × 30 mL), and the combined extracts were evaporated. A dark red powder (180 mg) remained that was identified as **4** (75% yield) along with <5% $Cp^*_2Fe_2(CO)_4$. $[Cp^*(CO)_2FeCO_2Rh(nbd)]_2$ (**4**): IR (THF) ν(CO) 1998, 1943 cm^{-1}, ν_{asym} (OCO) 1466 (br, m), ν_{sym} (OCO) 1262 (m), 1229 (m) cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 3.95 (br m, 6H, =CH + $C_{5(6)}$H), 1.08 (mult, 2H, CH_2), 1.57 (s, 30H, C_5*Me*$_5$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 217.29 ($FeCO_2$), 212.82 (FeCO), 96.15 (*C*$_5$ Me$_5$), 59.46 (br, CH_2), 50.59 (=CH + $C_{5(6)}$H), 9.78 (C_5*Me*$_5$).

Substitution of $^{13}CO_2$ in place of CO_2 in the above procedure afforded 170 mg of a dark red powder. An infrared spectrum of the product in THF showed a mixture consisting of a 2:1:0.25:0.25 ratio of $[Cp^*(CO)_2Fe^{13}CO_2Rh(nbd)]_2$ (**4-C^{13}**), $[Cp^*(CO)(^{13}CO)FeCO_2Rh(nbd)]_2$ (**4a-^{13}C**), $Cp^*_2Fe_2(CO)_4$, and $Cp^*_2Fe_2(CO)_2(^{13}CO)_2$. IR (THF): **4-C^{13}**, ν(CO) 1997, 1942 cm^{-1}, ν_{asym} (OCO) 1417 (br, m), ν_{sym} (OCO) 1246 (m), 1213 (m) cm^{-1}; **4a-^{13}C**, ν(CO) 1983, 1912 cm^{-1}.

Results and Discussion

Treatment of the THF suspensions of the carbonyl salts $Cp^*Re(NO)(CO)_2BF_4$ or $Cp^*M(CO)_3PF_6$ with $[Rh(OH)(\eta^4\text{-cod})]_2$ and 5 equiv of $EtMe_2N$ in THF at 5 °C produced the bis(μ_3-CO_2) complexes depicted in eq 1.



(1)

These red to red brown solids **1**−**3** were isolated after evaporating excess amine and carrying out multiple extractions using cold benzene. We quantitatively isolated the previously reported[1a] Re_2Rh_2 bis(μ_3-CO_2) complex **1** as a 1:1 mixture of diastereomers that was characterized by ^{1}H and ^{13}C NMR spectroscopy. The analytically pure Fe_2Rh_2 and Ru_2Rh_2 products **2** and **3** were isolated in 67% and 91% yields, respectively. The reactions leading to and the workup procedures for **2** and **3** were conducted at 5 °C in order to minimize the

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[16] Aresta, M.; Quaranta, E.; Albinati, A. *Organometallics* **1993**, *12*, 2032.

Table 1. Infrared Spectral Data for M_2Rh_2 Bis(μ_3-CO_2) Complexes

compound[a]	ν(CO) (cm^{-1})[b]	$\nu_{OCO(asym)}$ (cm^{-1})	$\nu_{OCO(sym)}$ (cm^{-1})
$[Cp^*(CO)(NO)ReCO_2Rh(cod)]_2$[c] (**1**)	1960 1694 (NO)	1459 (br, m)	1304 (w), 1260 (m)
$[Cp^*(CO)_2FeCO_2Rh(cod)]_2$ (**2**)	1999, 1944	1470 (br, m)	1262 (w), 1230 (m)
$[Cp^*(CO)_2Fe^{13}CO_2Rh(cod)]_2$ (**2-C^{13}**)	1998, 1943	1475−1415[d]	1255−1210[d]
$[Cp^*(CO)_2RuCO_2Rh(cod)]_2$ (**3**)	2011 1952	1479 (sh, m) 1467 (m)	1317 (w), 1256 (m), 1249 (sh)
$[Cp^*(CO)_2FeCO_2Rh(nbd)]_2$ (**4**)	1998, 1943	1466 (br, m)	1262 (m), 1229 (m)
$[Cp^*(CO)_2Fe^{13}CO_2Rh(nbd)]_2$[e] (**4-C^{13}**)	1997, 1942	1417 (br, m)	1246 (m), 1213 (m)
$[Cp^*(CO)_2FeCO_2Rh(CO)_2]_2$ (**5**)	2008, 1956 2078, 2054, 2008	1435 (br, m)	1261 (m), 1229 (m)
$[Cp^*(CO)_2RuCO_2Rh(CO)_2]_2$ (**6**)	2020 s, 1964 s 2079 s, 2055 m, 2002 vs	1436 (br, m)	1318 (w), 1259 (m), 1244 (m)
$[Cp^*(CO)(NO)ReCO_2Rh(CO)_2]_2$[c]	1969, 1707 (NO) 2078, 2054, 2003	1454 (br, m) 1428 (br, m)	1260 (sh), 1254 (m)

[a] THF solutions. [b] ν(CO) relative intensities: s, strong, for Re, Fe, and Ru−CO and s-m, medium-strong for Rh−CO absorptions. Other relative intensities: m, medium; w, weak. [c] Reference 1. [d] Broad envelope due to 1:1 mixture of **2-^{13}C** and $[Cp^*(CO)(^{13}CO)FeCO_2Rh(cod)]_2$ (**2a-^{13}C**); ν(CO) bands 1983 and 1913 cm^{-1}. [e] Isolated as 2:1 mixture of **4-C^{13}** and $[Cp^*(CO)(^{13}CO)FeCO_2Rh(nbd)]_2$ (**4a-^{13}C**); ν(CO) bands 1983 and 1913 cm^{-1}.

amount of dimeric $[Cp^*M(CO)_2]_2$ that forms. Attempts to further purify **2** or **3** by crystallization or chromatography invariably enriched these mixtures in $[Cp^*M(CO)_2]_2$.

Once isolated, $[Cp^*(CO)_2FeCO_2Rh(cod)]_2$ (**2**) has a limited stability in benzene and THF solutions at room temperature. A 0.02 M solution in THF decomposed 15% over 2 h to give a darker brown solution containing $[Cp^*Fe(CO)_2]_2$ as the IR detectable product; its $t_{1/2} = 6$ h. ^1H NMR spectral monitoring of C_6D_6 solutions was consistent with 10% decomposition over 3 h to $[Cp^*Fe(CO)_2]_2$ as the only Cp*Fe species and a $t_{1/2} = 16$ h. $[Cp^*(CO)_2RuCO_2Rh(cod)]_2$ (**3**) is somewhat less stable. A 0.02 M solution of **2** in THF has a $t_{1/2}$ of 3 h, whereas in C_6D_6 15% of **2** decomposed over 3 h, $t_{1/2} = 9$ h. In both solvents, $[Cp^*Ru(CO)_2]_2$ was the only Cp*Ru species detected by IR and ^1H NMR spectral monitoring, respectively.[17]

Structures for the Fe_2Rh_2 and Ru_2Rh_2 products **2** and **3** were inferred from their IR, ^1H, and ^{13}C NMR spectra. The IR spectra are dominated with a pair of intense ν(CO) bands as well as medium-intensity metallocarboxylate ν_{OCO} absorptions, vide infra, between 1480 and 1230 cm^{-1} (Table 1). ^1H and ^{13}C NMR spectra for **2**, for example, exhibit single resonances for the CO, CO_2, and Cp* ligands. It was the NMR spectra of the cod ligands, however, that indicated the presence of the folded M_2Rh_2 structures illustrated.

^1H NMR spectra for **2** and **3** show the expected[18] upfield progression of the COD vinyl, exo, and endo methylene absorptions. The presence of two resonances for each of the vinyl, exo-, and endo-CH_2 hydrogens are consistent with the low C_{2v} symmetry of **2** and **3**. This doubling of ^1H NMR resonances for ligated cod represents the presence of "inside and outside" cod protons (inside hydrogens are juxtaposed in the region between the two cod rings). The results of COSY NMR experiments with **2** further allowed us to identify the two spin systems, δ 4.40, 2.38, 1.62 and δ 4.24, 2.79, 1.67, which correspond to "inside and outside" vinyl, exo-, and endo-methylene protons, respectively. (Inside hydrogens on each ligated cod are in the region between the two rhodium centers; cf. eq 1.) Each endo-H couples to one exo-H and a vinyl-H, each exo-H couples to a vinyl-H and an endo-H, and the vinyl-H also couples to the other vinyl-H. In the absence of definitive results of nOe experiments, we could not assign these spins systems as inside or outside, however. The same symmetry constraints—inside and outside cod sites—are manifested in the $^{13}C\{^1H\}$ NMR spectra of **2** and **3**, which show four cod resonances, two each for the vinyl and allylic carbons.

NMR spectra for **2** and **3** are less complex than the spectra for **1**,[1a] which are complicated by the presence of the stereogenic rhenium centers and the attendant formation of a 1:1 diastereomeric mixture. The relative simplicity of the present NMR spectra for **2** and **3** nevertheless are consistent with the illustrated folded structures (crystallographically established for **1**). The number of observed NMR absorptions are inconsistent with **2** and **3** in solution having either a planar structure or with a chelated η^2-O,O′ $Cp^*(CO)_2FeCO_2Rh(cod)$ structure.[19] Either structure would have half the number of NMR absorptions. In addition, any fluxional motion for **2** and **3** must be extremely slow with respect to the NMR time scale.[20]

The synthetic procedure outlined in eq 1 was optimized for maximum isolated yields of **1**−**3** by working at 5 °C and by using a large excess of a volatile tertiary amine. We optimized the conversion of $Cp^*Fe(CO)_3PF_6$

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[17] Solutions of $[Cp^*(CO)(NO)Re(CO_2)Rh(\eta^4\text{-cod})]_2$ (**1**) are more stable than those of **2** and **3** at 25 °C. In benzene, **1** degraded over 2 d to $Cp^*(CO)(NO)ReC_6H_5$ (37%) and low concentrations of unidentified rhenium and rhodium residues. Solutions of **1** are more stable in ether and THF.[1]

[18] (a) Rodman, G. S.; Mann, K. R. *Inorg. Chem.* **1988**, *27*, 3338; *J. Organomet. Chem.* **1989**, *378*, 255. (b) Ciriano, M. A.; Perez-Torrente, J. J.; Oro, L. A. *J. Organomet. Chem.* **1993**, *445*, 267.

[19] Monomeric bis(phosphine) rhodium(I) complexes bearing a chelating (η^2-O, O′) carboxylate ligand are known: Darensbourg, D. J.; Grotsch, G.; Wiegreffe, P.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3827. 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.

[20] One or more pathways for stereochemical nonrigidity are available for folded structures analogous to **1**−**3**.[18,21] The ^1H NMR spectrum of $[CH_3CO_2Rh(cod)]_2$ at room temperature, for example, exhibits three broadened absorptions at room temperature for the cod ligand vinyl and exo- and endo-methylene hydrogens plus a sharp methyl singlet. Cooling the toluene-d_8 solution to 0 °C and recording the NMR spectrum resolves each of the three broadened absorptions into two sharp absorptions, while having no effect on the methyl singlet. This temperature dependency can be accounted for by a tub−tub ring flipping of the eight-member ring that interconverts inside and outside sites but not the exo and endo hydrogens. The ^1H NMR spectrum of **2** in toluene-d_8 solution is independent of temperature between +25 and −65 °C.

and $[Rh(OH)(cod)]_2$ to **2** using a variety of bases and reaction conditions. It is worth noting that, in the absence of base, $[Rh(OH)(cod)]_2$ converted up to 40% of the $Cp^*Fe(CO)_3PF_6$ to **2** within 20 min at room temperature. Although this reaction consumed 60% of the $Cp^*Fe(CO)_3PF_6$ within 6 h, the concentration of **2** then remained constant and the excess iron appeared as $[Cp^*Fe(CO)_2]_2$. Carrying out the same reaction but in the presence of potassium hydride (1 equiv in THF at −20 °C) immediately consumed the $Cp^*Fe(CO)_3PF_6$ and gave **2** (85% yield) contaminated with $[Cp^*Fe(CO)_2]_2$.

Our best observation for the use of 1 equiv of an amine base corresponded to 2,6-lutidine at 5 °C. Under these conditions, lutidine converted 70% of the $Cp^*Fe(CO)_3PF_6$ plus $[Rh(OH)(\eta^4\text{-COD})]_2$ to **2** and less than 2% $[Cp^*Fe(CO)_2]_2$ after 1 h. Samples of **2** prepared by this procedure tended to be thermally unstable at room temperature. Attempts to purify this product by chromatography or by crystallization (hexane, acetonitrile, THF/hexane, toluene/hexane, ether/hexane, and CH_2Cl_2/hexane) invariably enriched the mixtures in $[Cp^*(CO)_2Fe]_2$. Moreover, excessive amounts of $[Cp^*Fe(CO)_2]_2$ were obtained upon scaling up this reaction.

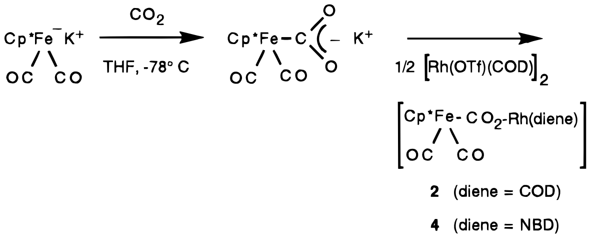
When this reaction with lutidine as the base was performed at room temperature, IR spectral monitoring also indicated that a maximum of 70% of the $Cp^*Fe(CO)_3PF_6$ converted to **2** within 15 min. After 6 h, no further $Cp^*Fe(CO)_3PF_6$ was consumed, but 15% of the **2** had degraded to $[Cp^*Fe(CO)_2]_2$. Substitution of 1 equiv of Me_2EtN, Et_3N, or $^iPr_2EtN$ for the lutidine converted at most 60% of the $Cp^*Fe(CO)_3PF_6$ to **2** after 1 h.[22] Thereafter, the remaining $Cp^*Fe(CO)_3PF_6$ decreased by an additional 20% over 6 h as the of amount of **2** dropped to 45% yield commensurate with building up of $[Cp^*Fe(CO)_2]_2$ (35% yield).

The use of amines in reaction 1 appears to involve equilibria analogous to that in eq 2. An excess of 5 equiv

$$2\ Cp^*(CO)_2FeCO^+\ PF_6^- \ +\ [Rh(OH)(\eta^4\text{-cod})]_2\ +\ 2\ EtMe_2N \rightleftharpoons 2\ EtMe_2NH^+\ PF_6^-\ +\ \underset{\textbf{2}}{[Cp^*(CO)_2Fe(CO_2)Rh(\eta^4\text{-cod})]_2} \quad (2)$$

of lutidine transformed 85% of the $Cp^*Fe(CO)_3PF_6$ to **2** in 15 min (IR spectral monitoring) while giving only traces of $[Cp^*Fe(CO)_2]_2$. Higher initial concentrations of Me_2EtN of up to 20 equiv at room temperature quantitatively generated **2**; slow evaporation of solvent and excess amine (room temperature at 10^{-2} mm) shifted the equilibrium to the left. Readdition of the THF and recording of the IR spectrum then indicated the presence of a 70:30 mixture of **2** and $Cp^*Fe(CO)_3PF_6$ plus traces of $[Cp^*Fe(CO)_2]_2$. The amine-promoted equilibrium leading to **2** also can be reversed with the presence of an excess of the amine salt conjugate acid. A THF solution of purified **2** upon treatment with 4 equiv of $Bu_3NH^+BF_4^-$ in THF solution at 5 °C afforded a 60:40 mixture of **2** and $Cp^*Fe(CO)_3BF_4$ within 1 h. The presence of $[RhOH(cod)]_2$ also was noted by its IR ν(OH) absorption at 3506 cm^{-1}.

We also generated samples of **2** and its norbornadiene analogue $[Cp^*(CO)_2Fe(CO_2)Rh(\eta^4\text{-nbd})]_2$ (**4**) by treating the metallocarboxylate $Cp^*(CO)_2FeCO_2K$ with a rhodium(I) η^4-diene triflate, eq 3. The $Cp^*(CO)_2FeCO_2K$ was



(3)

produced from the metalate $Cp^*(CO)_2FeK$ and CO_2 in THF at −78 °C,[13,14b] and the rhodium(I) triflates were obtained in situ from $[RhCl(\eta^4\text{-diene})]_2$ and silver triflate.[16] Rhodium(I) triflates were necessary since the starting $[RhCl(\eta^4\text{-diene})]_2$ complexes proved to be unreactive toward $Cp^*(CO)_2FeCO_2K$ (−78 °C)—only $[Cp^*Fe(CO)_2]_2$ was detected. In addition to evaluating an alternative synthesis of **2**, we wanted to obtain samples of C^{13}-labeled materials $[Cp^*(CO)_2Fe(^{13}CO_2)Rh(\eta^4\text{-diene})]_2$ [diene = cod (**2-^{13}C**) and nbd (**4-^{13}C**)] in order to help assign the carboxylate IR spectral absorptions.

Treatment of $Cp^*(CO)_2FeCO_2K$ with either of the rhodium(I) η^4-diene triflate intermediates (eq 3) quantitatively produced the Fe_2Rh_2 bis(μ_3-CO_2) complexes **2** and **4**, as judged by IR spectral monitoring. Samples of **2**, although obtained in low overall yields after benzene and hexane extraction, contained 90−95% pure **2** (IR, ^{1}H, and ^{13}C NMR spectroscopy), the remainder being the ubiquitous $[Cp^*Fe(CO)_2]_2$. These samples, however, decomposed more readily in solution at room temperature [$t_{1/2}$ (THF) = 76 min] than samples of **2** procured using the first route.

The nbd-containing **4** proved to be even less stable in solution. All attempted workup procedures degraded it to $[Cp^*Fe(CO)_2]_2$ as the only IR detectable species. The 75% isolated yield of **4** (with 5% $[Cp^*Fe(CO)_2]_2$ contamination) reported in the Experimental Section represents our best result. Although an elemental analysis for **4** was not obtained, its IR and NMR spectral data closely resemble that for **2**.

We repeated the preparations of **2** and **4** using 1.1 equiv of 99% labeled $^{13}CO_2$. Under the conditions reported, attempts to generate $[Cp^*(CO)_2Fe^{13}CO_2Rh(cod)]_2$ (**2-C^{13}**) instead provided 2:1 mixtures of **2-C^{13}** and $[Cp^*(CO)(^{13}CO)FeCO_2Rh(cod)]_2$ (**2a-C^{13}**). Alternatively, variable amounts of $\{Cp^*(CO)(^{13}CO)FeCO_2[Rh(cod)]_2O_2\text{-}^{13}CFe(CO)_2Cp^*\}$ if formed would have been indistinguishable from mixtures of **2-C^{13}** and **2a-C^{13}**. IR spectral monitoring of the cold reaction mixture nevertheless showed the expected ^{13}C label shift for the

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(21) (a) Sielisch, T.; Cowie, M. *Organometallics* **1988**, *7*, 707. (c) Tejel, C.; Villoro, J. M.; Ciriano, M. A.; López, J. A.; Eguizábal, E.; Lahoz, F. J.; Bakhumutov, V. I.; Oro, L. A. *Organometallics* **1996**, *15*, 2967. (d) Balley, J. A.; Grundy, S. L.; Stobart, S. R. *Organometallics* **1990**, *9*, 536. Bushnell, G. W.; Fjeldsted, D. O. K.; Stobart, S. R.; Wang, J. *Organometallics* **1996**, *15*, 3785.

(22) Other bases tried included 1 equiv of $(CH_3)_3COK$ or 1,8-bis(dimethylamino)naphthalene. The reaction between $Rh(OH)(\eta^4\text{-cod})]_2$ and $Cp^*Fe(CO)_3PF_6$ using the latter base was sluggish: After 2 h, 65% of the $Cp^*Fe(CO)_3PF_6$ converted to **2**. Thereafter further product formation was offset by increasing production of $[Cp^*Fe(CO)_2]_2$. Potassium *tert*-butoxide, on the other hand, rapidly gave **2** (even at −78 °C), but substantial concentrations of $[Cp^*Fe(CO)_2]_2$ also formed. The reaction at room temperature provided a 45:55 mixture of **2** and $[Cp^*Fe(CO)_2]_2$ within 15 min.

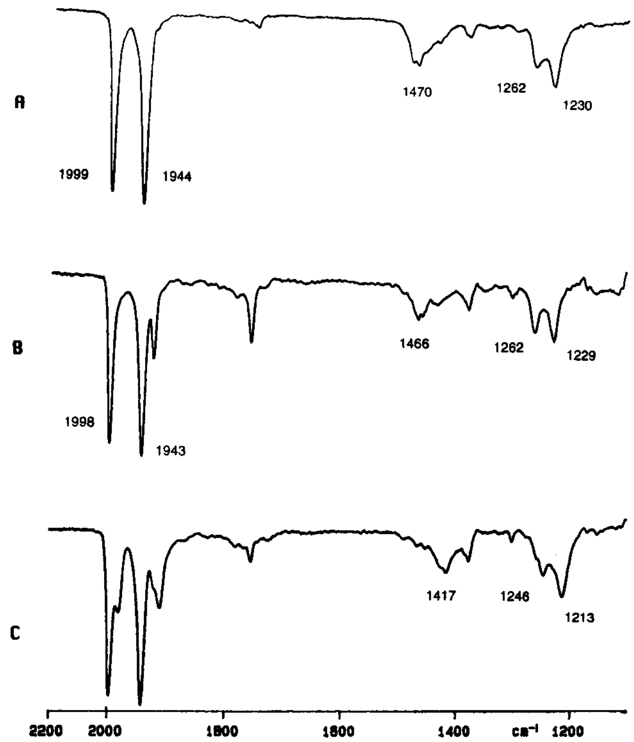
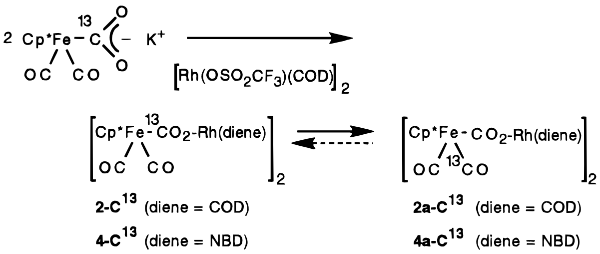


Figure 1. Infrared spectra in THF: (A) $[Cp^*(CO)_2FeCO_2Rh(cod)]_2$ (**2**), isolated material from reaction between $[Rh(OH)(\eta^4\text{-cod})]_2$ and $Cp^*Fe(CO)_3PF_6$; (B) $[Cp^*(CO)_2FeCO_2Rh(nbd)]_2$ (**4**), generated in THF from $Cp^*(CO)_2FeCO_2K$ and $[Rh(OSO_2CF_3)(\eta^4\text{-cod})]_x\}$ (peaks at 1924 and 1756 cm^{-1} correspond to the $[Cp^*(CO)_2Fe]_2$ impurity); (C) $[Cp^*(CO)_2Fe^{13}CO_2Rh(nbd)]_2$ (**4-C^{13}**) admixed with $[Cp^*(CO)(^{13}CO)FeCO_2Rh(nbd)]_2$ (**4a-^{13}C**) (1983, 1912 cm^{-1}).

$Cp^*(CO)(^{13}CO)Fe$ $\nu(CO)$ absorptions.[23] Further workup of the reaction was necessary in order to remove soluble triflate residues that absorbed in the carboxylate IR region. This workup—benzene or hexane extractions—engendered further carboxylate–carbonyl label shuttle[3,5a,23,24] that give a 1:1 mixture of **2-C^{13}** and **2a-C^{13}** along with labeled and unlabeled $[Cp^*Fe(CO)_2]_2$. This label shuttle is presumed to be an equilibrium process, eq 4.



(4)

Similar attempts to generate $[Cp^*(CO)_2Fe^{13}CO_2Rh(nbd)]_2$ (**4-C^{13}**) reaction were more promising in that we obtained a 2:1 mixture of **4-C^{13}** and **4a-C^{13}** after workup. Figure 1 presents IR spectra for **4-C^{13}** and **4a-C^{13}** in THF solution (scans B and C); scan A correponds to a THF solution of **2** that was prepared by the first procedure.

The carboxylate–carbonyl label shuttle observed in generating **2a-C^{13}** and **4a-C^{13}** originated from **2-C^{13}** and **4-C^{13}**, eq 4. An alternative prior equilibration of $Cp^*(CO)_2Fe^{13}CO_2K$ and $Cp^*(^{13}CO)(CO)FeCO_2K$[23a,24] followed by trapping with the rhodium(I) triflate was deemed less likely. The procedure reported here is identical to that previously used for cleanly transforming $Cp^*(CO)_2Fe^{13}CO_2K$ and either tin chloride R_3SnCl ($R = CH_3$, Ph) to $Cp^*(CO)_2Fe^{13}CO_2SnR_3$.[14b] The trimethyltin product subsequently underwent carboxylate–carbonyl label shuttle and competitive decarboxylation to give a mixture of $Cp^*(^{13}CO)(CO)FeCO_2Sn(CH_3)_3$ and $Cp^*(CO)_2FeSn(CH_3)_3/Cp^*(^{13}CO)(CO)FeSn(CH_3)_3$.

Table 1 collects solution IR spectral data for the M_2Rh_2 bis(μ_3-CO_2) complexes that were prepared in this study. Assignment of the medium-intensity carboxylate vibrational modes $\nu_{OCO(asym)}$ and $\nu_{OCO(sym)}$[3a] rests on comparison of these spectra with appropriate standards, typically $[Cp_2M(CO)_4]_2$ and $[RhCl(diene)]_2$, and on the label shift for the carboxylate bands for **4** and **4-C^{13}**. Note that carboxylate IR spectral band assignments are collected as $\nu_{OCO(asym)}$ and $\nu_{OCO(sym)}$ regions in this table due to the existence of several bands that appear as two distinct groups. It is important to note that the number of these bands and their relative intensities—their overall appearance—is independent of the sample history, the temperature (−15 to +25 °C), and the method of preparation. Moreover, the IR spectra in the carboxylate region of the iron and ruthenium complexes **2**–**6** resemble that of **1**, which also exhibits the same spectrum in the solid state as a KBr pellet.

The appearance of several bands in the carboxylate region rather than one band each for the $\nu_{OCO(asym)}$ and $\nu_{OCO(sym)}$ vibrational modes is unexpected. Thus far, metallocarboxylates have been treated analogous to organic carboxylate ligands[25] in that their IR spectra were expected to exhibit single $\nu_{OCO(asym)}$ and $\nu_{OCO(sym)}$ bands, perhaps augmented by a δ bending vibrational mode.[26] This analogy clearly breaks down for the present M_2Rh_2 bis(μ_3-CO_2) complexes. The rhodium(I) acetates $[Rh(\mu\text{-}CH_3CO_2)(cod)]_2$[11] and $[Rh(\mu\text{-}CH_3CO_2)(CO)_2]_2$,[27a,b] in contrast, exhibit just two acetate carboxylate absorptions, 1580, 1426 cm^{-1} and 1570, 1436 cm^{-1}, respectively, in THF. These rhodium acetates

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[23] For similar IR spectral $\nu(CO)$ assignments, see those for $Cp(^{13}CO)(CO)MCO_2ZrClCp_2$ [M = Fe, Ru],[4b,14a,23a] $Cp^*(^{13}CO)(CO)FeCO_2SnMe_3$,[14b] and $Cp(^{13}CO)(CO)MCO_2M'$ [M = Fe, Ru; M′ = Na, K].[13] (a) Steffey, B. D.; Vites, J. C.; Cutler, A. R. *Organometallics* **1991**, *10*, 3432.

[24] (a) Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 1467. (b) Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 794.

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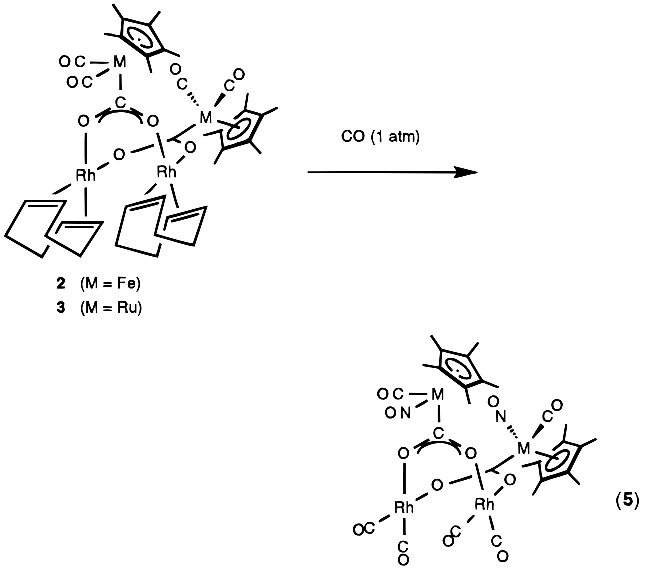
should have structures[28] similar to that of **1**, which presumably resembles those of **2**–**6**.

The presence of the carboxylate–carbonyl label shuttle for **2-C^{13}** and **4-C^{13}** allowed us to assign the ^{13}C NMR resonances for the carbonyl and carboxylate ligands, which appear as two singlets near δ 213–215 and δ 217. Although ^{13}C NMR spectra for these complexes exhibited intense resonances in both regions due to the presence of **2a-C^{13}** and **4a-C^{13}**, the downfield singlet initially was up to twice as intense. Hence, we assign the downfield absorption to the carboxylate ligand. These carbonyl and carboxylate chemical shift assignments are consistent with those that we reported for the related tin esters $Cp^*(CO)_2Fe^{13}CO_2SnR_3$: R = Ph, δ 218 (CO_2), 216 (CO); R = Me, δ 216.5 (CO_2), 212 (CO).[14b]

We further characterized **2** and **3** by carbonylation and by the reaction of **2** with Ph_3SnCl. One atmosphere of carbon monoxide promptly carbonylated the rhodium centers, eq 5. IR spectra of the reaction solutions confirmed the presence of the iron or ruthenium metallocarboxylates and the rhodium dicarbonyl moiety; NMR spectra confirmed the release of 1,5-cycloctadiene and the presence of one set of Cp* resonances. The three IR ν_{CO} bands for the rhodium, moreover, closely resemble those observed for $[Rh(\mu\text{-}CH_3CO_2)(CO)_2]_2$,[11] the analogous carbonylation product of $[Rh(\mu\text{-}CH_3CO_2)(cod)]_2$.[27] Taken togeather, the spectral data for **5** and **6** are consistent with the illustrated "open-book" Rh_2 structures. Solutions of **5** and **6** in benzene or THF were unstable at room temperature, behavior reminiscent of $[Rh(\mu\text{-}CH_3CO_2)(CO)_2]_2$.[11b]

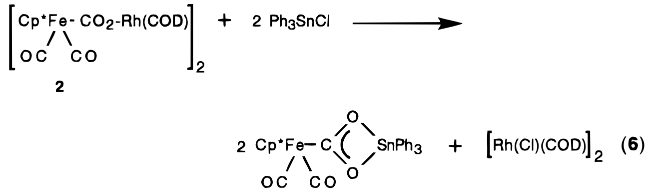


2 (M = Fe)
3 (M = Ru)

5 (M = Fe)
6 (M = Ru)

(**5**)

The rapid reaction with 1 equiv of Ph_3SnCl (eq 6) conveniently derivatized **2** as the known FeSn ester.[14b,15]



2

(**6**)

This FeSn ester retains the original CO_2 ligand. IR spectral monitoring of this reaction confirmed that it occurred quantitatively within 0.5 h, and subsequent workup afforded 60–70% isolated yields of the FeSn ester and $[Rh(Cl)(cod)]_2$.

Conclusions

In this article we document the synthesis of three M_2Rh_2 bis(μ_3-CO_2) complexes $[Cp^*(CO)(NO)Re(CO_2)Rh(\eta^4\text{-}cod)]_2$ (**1**) and $[Cp^*(CO)_2MCO_2Rh(\eta^4\text{-}cod)]_2$, M = Fe (**2**) and Ru (**3**), from the reaction between $[Rh(OH)(\eta^4\text{-}cod)]_2$ and a carbonyl salt $Cp^*(L)(CO)_2M^+$ (L = CO, M = Fe, Ru; L = NO, M = Re) and a base. The resulting μ_3-CO_2 ligands thus originate from condensation of a metal carbonyl plus a metal hydroxide with loss of a proton, a reaction with little precedent.[6] The more common synthetic procedure[3] of treating a metallocarboxylate $[Cp^*(CO)_2FeCO_2K$ or $Cp^*(CO)_2Fe^{13}CO_2K]$ with a metal electrophile $\{[Rh(OSO_2CF_3)(\eta^4\text{-}cod)]_x\}$ also was used to prepare **2** and $[Cp^*(CO)_2Fe^{13}CO_2Rh(diene)]_2$ [diene = cod (**2-^{13}C**) and nbd (**4-^{13}C**)]. These ^{13}C-labeled compounds readily exchanged the ^{13}C-label between the carboxylate and carbonyl ligands. The IR and NMR spectroscopy of these Re_2Rh_2 and Fe_2Rh_2 bis(μ_3-CO_2) complexes are consonant with the presence of two μ_3-$[\eta^1\text{-}C(M)\text{:}\eta^1\text{-}O(Rh)\text{:}\eta^1\text{-}O'(Rh')]$ carboxylate groups and an overall structure that resembles the Rh(I) carboxylates $[(RCO_2)Rh(diene)]_2$.

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