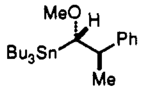
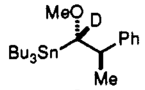
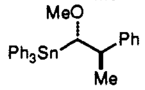
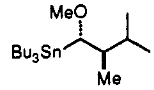
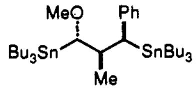
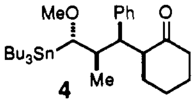
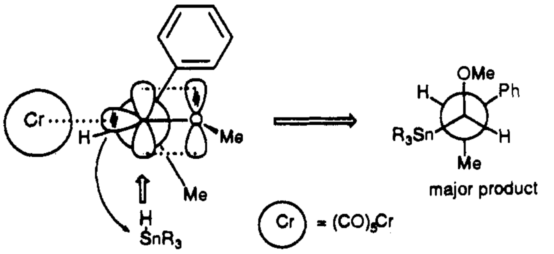
Table I. Stereoselective Sn–H Insertion Reaction[a]

entry	1	diastereo ratio[b]	% yield	major product
1	**1a**	77:23	69	
2	**1a**	77:23	66	
3	**1a**	74:26	73	
4	**1b**	79:21	82	
5	**1c**	88:12	43	
6	**1d**	93:7	81	 **4**

[a] The reaction was carried out with 1.5–3 equiv of a tin hydride and 2–5 equiv of pyridine in hexane at 60 °C for 5–10 h. Tin hydride reagents: Bu_3SnH in entries 1 and 4–6; Bu_3SnD in entry 2; Ph_3SnH in entry 3. [b] The ratios were determined by ^1H NMR analysis (e.g., of MeO signals).

Scheme I



crucial feature is that the bulky $Cr(CO)_5$ group severely restricts the conformation of the 1-phenylethyl side chain and allows only a hydrogen atom to be located (approximately) in the plane defined by O–C(carbene)–C(α). The selectivity of the reaction can thus be rationalized on the basis of the following three assumptions: (1) the approach of the tin hydride reagent takes place from the less hindered bottom side; (2) the reagent approaches with hydride projecting toward the carbene;[3b,8] and (3) the Cr–carbene bond is cleaved with retention of configuration to form a tin–carbon bond as indicated by the arrow.

Despite the accumulated knowledge on face-selective trigonal-to-tetrahedral transformations,[11] there is little information on digonal-to-tetrahedral conversions. The present results shed the first light on the potential utility of the latter type of transformation, which will be the subject of future studies in our laboratory.

Acknowledgment. We thank the Ministry of Education, Science, and Culture of Japan (Grant-in-Aid 04217207) and the Nissan Foundation for financial support.

Supplementary Material Available: Listings of physical data for the insertion products (4 pages). Ordering information is given on any current masthead page.

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(10) Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. *Adv. Mol. Model.* **1990**, *2*, 65. While parameterization is poor for Cr, the steric bulk of the $Cr(CO)_5$ may be reasonably estimated.

(11) For other aspects of this problem, see: Arai, M.; Nemoto, T.; Ohashi, Y.; Nakamura, E. *Synlett* **1992**, 309. Isaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **1990**, *112*, 7428. Nakamura, E. *Synlett* **1991**, 539.

Synthesis and Characterization of μ_2-η^2- and μ_2-η^3-CO_2 Complexes of Iron and Rhenium

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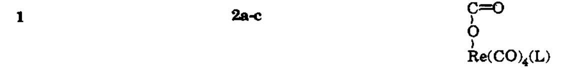
There is current interest in finding ways to activate CO_2 and to use it as a building block for organic synthesis.[1] The possibility for thermal activation of CO_2 was outlined by Floriani,[2] who suggested that bifunctional systems, having a highly basic metal to bind carbon and an acidic one to bind one or both oxygens, might be effective in sequestering CO_2 and in activating it. Floriani characterized a cobalt metallocarboxylate anion with a potassium counterion.[2] Since then, several μ_2-η^2- and μ_2-η^3-CO_2-bridged complexes have been reported[3] and a few other μ_2-η^3 complexes have been structurally characterized. We report here the synthesis of three μ_2-η^2-CO_2 complexes, the structural characterization of one, and the conversion of all to the corresponding μ_2-η^3-CO_2 complexes.

We reported the characterization of **1**, $CpFe(CO)(PPh_3)$-$CO_2^-K^+$ (Cp = η^5-C_5H_5), previously.[3i,r] Reactions of **1** with a series of rhenium cations[4,5] having a weakly coordinated BF_4 anion yield μ_2-η^2-CO_2 complexes as shown below:



$$\underset{\mathbf{1}}{CpFe(CO)(PPh_3)CO_2^-K^+} + \underset{\mathbf{2a\text{-}c}}{Re(CO)_4(L)(F{-}BF_3)} \xrightarrow{-KBF_4} \underset{\mathbf{3a\text{-}c}}{\begin{array}{l}CpFe(CO)(PPh_3)\\ \quad C{=}O\\ \quad O\\ \quad Re(CO)_4(L)\end{array}}$$

a, L=PPh_3
b, L=$P(OPh)_3$
c, L=CO

Compound **3a** is the most stable and has been fully characterized;[6,7]

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(1) (a) *Catalytic Activation of Carbon Dioxide*; Ayers, W. M.; ACS Symposium Series 363; American Chemical Society: Washington, DC, 1988. (b) Behr, A. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; D. Reidel Publ. Co.: Dordrecht, 1988; Vol. 6, p 59. (c) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (d) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661. (e) *Carbon Dioxide Activation by Metal Complexes*; Behr, A., Ed.; VCH Publishers: Weinheim, Federal Republic of Germany, 1988. (f) Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135.

(2) (a) Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *100*, 7405. (b) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082.

(3) (a) Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1627. (b) Maher, J. M.; Lee, G. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 6797. (c) Audett, J. D.; Collins, T. J.; Santarsiero, B. D.; Spies, G. H. *J. Am. Chem. Soc.* **1982**, *104*, 7352. (d) Forschner, T.; Menard, K.; Cutler, A. *J. Chem. Soc., Chem. Commun.* **1984**, 121. (e) Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 794. (f) Barrientos-Penna, C. F.; Gilchrist, A. B.; Klahn-Oliva, H.; Hanlan, A. J. L.; Sutton, D. *Organometallics* **1985**, *4*, 478. (g) Tso, C. T.; Cutler, A. R. *J. Am. Chem. Soc.* **1986**, *108*, 6069. (h) Giuseppetti, M. E.; Cutler, A. R. *Organometallics* **1987**, *6*, 970. (i) Gibson, D. H.; Ong, T.-S. *J. Am. Chem. Soc.* **1987**, *109*, 7191. (j) Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2956. (k) Senn, D. R.; Gladysz, J. A.; Emerson, K.; Larsen, R. D. *Inorg. Chem.* **1987**, *26*, 2737. (l) Bennett, M. A.; Robertson, G. B.; Rokicki, A.; Wickramasinghe, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 7098. (m) Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1287. (n) Pilato, R. S.; Housmekerides, C. E.; Jernakoff, P.; Rubin, D.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 2333. (o) Gibson, D. H.; Richardson, J. F.; Ong, T.-S. *Acta. Crystallogr.* **1991**, *C47*, 259. (p) Torreson, I.; Michelin, R. A.; Marsella, A.; Zanardo, A.; Pinna, F.; Strukul, G. *Organometallics* **1991**, *10*, 623. (q) Vites, J. C.; Steffey, B. D.; Giuseppetti-Dery, M. E.; Cutler, A. R. *Organometallics* **1991**, *10*, 2827. (r) Gibson, D. H.; Ong, T.-S.; Ye, M. *Organometallics* **1991**, *10*, 1811.

(4) Reactions were done in an argon-filled glovebox at –40 °C in dry CH_2Cl_2 (**3a,b**) or dry THF (**3c**). Compounds **2a,c** have been prepared previously by Beck.[5] Compound **2b** was prepared in the same way; acceptable elemental analyses have been obtained for **2a,b**.

(5) (a) See: Beck, W. *Inorg. Synth.* **1990**, *28*, 1 and references cited therein. (b) Schweiger, M.; Beck, W. *Z. Anorg. Allg. Chem.* **1991**, *595*, 203.

(6) **3a**: IR ν_{OCO} (neat, DRIFTS) 1505 (m) and 1135 (m) cm^{-1}; ^{13}C NMR (carbonyl and carboxyl only: CD_2Cl_2, –10 °C) δ 221.54 (d, J_{PC} = 33.0 Hz), 211.91 (dd, J_{PC} = 32.6 Hz, 3.9 Hz), 190.33 (d, J_{PC} = 9.9 Hz), 190.13 (d, J_{PC} = 9.0 Hz), 188.65 (d, J_{PC} = 4.6 Hz), 186.79 (d, J_{PC} = 61.2 Hz); ^{31}P NMR (THF, –35 °C) δ 80.37 (s) and 8.61 (s).

(7) Characterization data are contained in the supplementary material.

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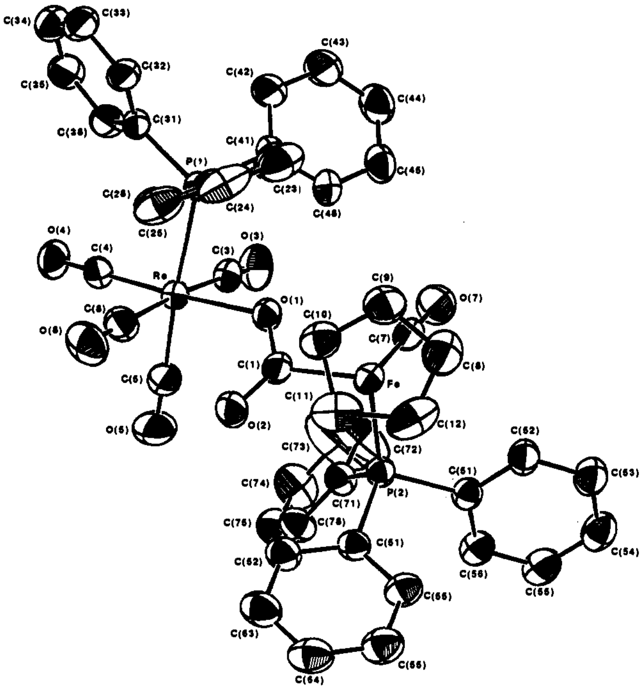
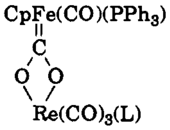


Figure 1. ORTEP drawing of **3a**, with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and bond angles (deg) are as follows: Fe–C(1), 1.994 (3); C(1)–O(1), 1.298 (3); C(1)–O(2), 1.226 (3); O(1)–Re, 2.154 (2); O(2)–Re, 3.178 (2); O(1)–C(1)–O(2), 121.9 (3), Fe–C(1)–O(1), 115.8 (2); Fe–C(1)–O(2), 122.2 (2); Re–O(1)–C(1), 121.7 (2).

the crystallographic structure[8] is illustrated in Figure 1. Compounds **3b** and **3c** were characterized by spectral data only.[7] DRIFTS spectra are helpful in identifying **3a–c** as μ_2-η^2-CO_2 complexes; all three show bands at 1491 ± 14 cm^{-1} for the carboxyl carbonyl group. Also, compounds **3a** and **3c** show $\nu_{C\text{-}O}$ at 1138 ± 3 cm^{-1}; this band in **3b** is obscured. Similar IR spectral bands have been reported[31] previously for CO_2-bridged complexes which were formulated as μ_2-η^2 complexes. The ^{13}C NMR spectrum of **3a**[6] shows low-field resonances for the carbonyl and carboxyl carbons attached to iron; one of these is a pair of doublets and is assigned to the carboxyl carbon. Terminal carbonyls bound to rhenium appear as four doublets at slightly higher field. X-ray crystallographic data for **3a** show that the carboxyl "carbonyl", C(1)–O(2), is unusually long [1.226 (3) Å], accounting for the very low $\nu_{C=O}$ observed in IR spectra of this compound and in **3b**,**c**. X-ray data show that O(2) is not bonded to rhenium. Reaction of **3a** with excess $HBF_4 \cdot Et_2O$ yields $CpFe(CO)_2(PPh_3)^+BF_4^-$ and *cis*-$Re(CO)_4(PPh_3)(F\text{–}BF_3)$; these products are expected from reactions initiated by either carboxyl C–O bond breaking or O–Re bond breaking. Use of 1 equiv of the electrophile resulted in an incomplete reaction. Reaction of **3a** with 1 equiv of trimethylsilyl triflate gave $CpFe(CO)_2(PPh_3)^+SO_3CF_3^-$ and *cis*-$(CH_3)_3SiORe(CO)_4(PPh_3)$.[9] Thus, reaction with the electrophile is initiated by C–O bond cleavage in the manner of the lithium salt of **1**.[3r]

Thermolysis of solid **3a** afforded a new compound, **4a** (L = PPh_3). Elemental analysis and spectral data[7,10] for **4a** are in agreement with its formulation as a μ_2-η^3-CO_2-bridged complex as illustrated below:



$CpFe(CO)(PPh_3)=C(O)_2Re(CO)_3(L)$

4a, L=PPh_3
4b, L=$P(OPh)_3$
4c, L=CO

Formulation of this product with a carbene-like carboxylate carbon is based on a comparison of the ^{13}C NMR chemical shift of this carbon (245.88 ppm, dd) with that in the μ_2-η^3-CO_2-bridged complexes reported by Geoffroy.[3m,n] The rhenium–tungsten complex prepared by Geoffroy was structurally characterized and shows a shortened rhenium–carboxyl carbon bond as expected for a carbene; also, it shows nearly equal carboxyl C–O bond lengths [1.32 (4) and 1.34 (4) Å]. This and all of the other μ_2-η^3 complexes reported by Geoffroy show extremely low field ^{13}C NMR resonances for the carboxyl carbons. DRIFTS data for **4a** differ from those of **3a**; bands at 1435 and 1247 cm^{-1} are assigned to the fully chelated carboxyl group (ν_{asym} and ν_{sym}, respectively). DRIFTS data[3r] for the structurally characterized[3o] μ_2-η^3 complex $CpFe(CO)(PPh_3)(CO_2)SnPh_3$ (**5**; 1432 and 1174 cm^{-1}) are quite similar to those for **4a**, but the chemical shift of the carboxyl carbon is not unusually low (228.16 ppm). The carboxyl C–O bond lengths in **5** are unequal [1.270 (6) and 1.305 (6) Å], as they are in a related rhenium–tin complex.[3k] Also, the Fe—C bond length in **5** is shortened as compared to **3a**, but it is longer than in the carbene complex $CpFe(CO)(PPh_3)({=}CF_2)^+BF_4^-$ [1.724 (9) Å].[11] Compound **3b** is converted to **4b** after 1 h at 85 °C; **3c** is converted to **4c** after 4 h at 50 °C. The spectral properties of **4b**,**c** are very similar to those of **4a**.[7] These conversions are the first in which μ_2-η^2-CO_2-bridged compounds have been converted to μ_2-η^3 complexes.

Comparisons of our compounds with related ones prepared by others suggest that there are two structurally distinct μ_2-η^3-CO_2-bridged compound types, as illustrated below:

A B

Compounds of type A have been characterized by Geoffroy;[3m,n] the spectral properties of **4a–c** place them in the same class. Compound **5**, its rhenium–tin analog,[3k] and the CO_2-bridged compounds characterized by Cutler[3g,q] appear to fit into class B. Structural data place Floriani's cobalt–potassium complex[2] in class B since the carboxyl C–O bond lengths differ by 0.04 Å but the Co–C bond is not significantly shortened; ^{13}C NMR data were not reported.

Compound **4a** is stable to further thermolysis at 85 °C (20 h), but thermolysis of **4b**,**c** results in destruction of the bridging CO_2 ligand. Efforts to characterize the thermolysis products are in progress. From the thermolysis studies of **3a–c** and **4a–c** it is clear that the ligand L on rhenium exerts a very large effect on the thermal stability of **3a–c** and **4a–c**. Reactivity is in the order CO > $P(OPh)_3$ ≫ PPh_3, clearly indicating that replacement of a single CO by an electron-donating ligand on rhenium can stabilize the CO_2 bridge.

Acknowledgment. Support of this work by the United States Department of Energy, Division of Chemical Sciences (Office of Basic Energy Sciences), Office of Energy Research, is gratefully acknowledged. The X-ray equipment was purchased with assistance from the National Science Foundation (CHE 9016978).

Supplementary Material Available: Tables of data collection and refinement parameters, anisotropic thermal parameters, hydrogen atom parameters, bond distances, bond angles, and torsional angles for **3a** and characterization data for **3a–c** and **4a–c** (20 pages); tables of structure factor amplitudes for **3a** (31 pages). Ordering information is given on any current masthead page.

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(8) Crystallographic data for **3a** (at 23 °C): $a = 12.264$ (2) Å, $b = 16.398$ (3) Å, $c = 11.189$ (2) Å, $\alpha = 98.98$ (2)°, $\beta = 113.26$ (2)°, $\gamma = 83.30$ (2)°, $V = 2038.2$ Å^3 with $Z = 2$ in triclinic space group $P\bar{1}$. Data were collected on an Enraf-Nonius CAD4 diffractometer using the ω–2θ scan technique to a maximum $2\theta = 53°$. The structure was refined using full matrix least squares to final agreement factors of $R(F) = 0.021$, $R_w(F) = 0.025$ for 7664 observed reflections [$I > 3\sigma(I)$].

(9) Satisfactory elemental analysis and spectral data have been obtained for this compound.

(10) **4a**: IR ν_{OCO} (neat, DRIFTS) 1435 (m) and 1247 (s) cm^{-1}; ^{13}C NMR (carbonyls and carboxyl only; CD_2Cl_2) δ 245.88 (dd, J_{PC} = 33.1 Hz, 2.7 Hz), 219.72 (d, J_{PC} = 30.2 Hz), 197.90 (d, J_{PC} = 7.9 Hz), 197.50 (d, J_{PC} = 6.9 Hz), 191.70 (d, J_{PC} = 78.4 Hz): ^{31}P NMR (THF-d_8, −20 °C) δ 75.24 (s) and 21.14 (s).

(11) Crespi, A. M.; Shriver, D. F. *Organometallics* **1985**, *4*, 1830.