tochemical step rather than *trans*-**14**, the ratio of the ht products **3** and **17** decreases from 2.9:1 to 1.7:1, while a 1:1 mixture of the two alkenes affords a product ratio of 2.2:1.[22]

In a sequence of related experiments, L-(+)-ethyl lactate (*S* configuration) has been converted to optically active (−)-sarracenin, mp 124–125 °C (lit.[4] 127–128 °C). The apparently low optical yield of this sequence ($([\alpha])^{23}_D - 20.9°$) is puzzling in light of the close correlation between the melting points of the synthetic and natural material but may be partially due to trace contaminants and concentration differences. However, the previously mentioned discrepancy concerning the specific rotation of the natural material makes a valid comparison difficult. This point, as well as an alternative synthesis of optically active dihydropyrans such as **14**, is under current investigation.

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(22) The ratios of the four products derived from pure *trans*-**14** pure *cis*-**14**, and as 1:1 mixture of the two was 12:4.2:2.8:1, 6.6:3.9:1.7:1, and 9.2:4.2:2.3:1, respectively.

Synthesis and Interconversions of Dinuclear Iron Complexes with μ-CH$_3$, μ-CH$_2$, and μ-CH Ligands

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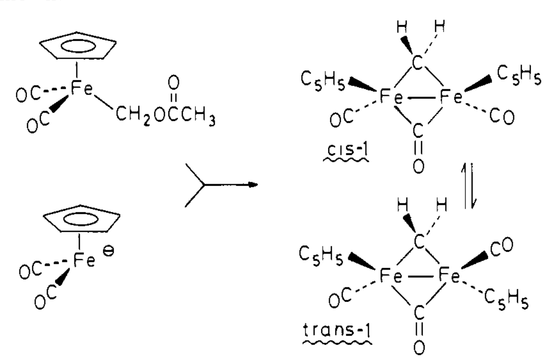
Received September 28, 1981

The increasing interest in the synthesis and chemistry of bimetallic bridged methylene complexes[1-7] stems from the demonstrated or proposed involvement of these and related species in carbon monoxide reduction chemistry,[2] olefin metathesis reactions,[3] alkyne polymerizations,[3] and methylene transfer reactions.[4] In this communication, we report the synthesis of the new iron complex[5,6] $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$(**1**)($Cp{=}\eta^5\text{-}C_5H_5$) and the facile conversion of **1** to the cationic bridging methyl and bridging methylidyne complexes $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_3)]^+$ (**2**) and $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH)]^+$ (**3**).[7] The reactions of compounds **1**, **2**, and **3** provide an additional example of the stepwise interconversion of μ-CH$_3$, μ-CH$_2$, and μ-CH ligands; only two other somewhat related examples of these interconversions are known.[1d,11,8]



Slow addition of a THF solution of $K[CpFe(CO)_2]$ to a refluxing THF solution of $CpFe(CO)_2CH_2O_2CCH_3$[10] produced a 1:2.1 mixture of $[CpFe(CO)_2]_2$ (**4**) and the bridging methylene complex **1** (50% crude yield, 3.4:1 mixture of *cis*-**1**:*trans*-**1**). The separation of **1** from **4** proved difficult but was accomplished by slow column chromatography (alumina:warm hexane) using a specialized apparatus (see supplementary material). Slow chromatography takes advantage of the fact that *cis*-**1** and *trans*-**1** equilibrate more rapidly than they are eluted and that *trans*-**1** elutes substantially faster than either *cis*-**1** or **4** which elute at very similar rates.[11] The yield of analytically pure **1** was greater

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(8) (a) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726–7727. (b) Calvert, R. B.; Shapley, J. R.; Schultz, A. J.; Williams, J. M.; Suib, S. L.; Stucky, G. D. *Ibid.* **1978**, *100*, 6240–6241. (c) Schultz, A. J.; Williams, J. M.; Calvert, R. B.; Shapley, J. R.; Stucky, G. D. *Inorg. Chem.* **1979**, *18*, 319–323. (d) Dimas, P. A.; Duesler, E. N.; Lawson, R. J.; Shapley, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 7787–7789.

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(11) The mixture of red *cis*-**1** and purple *trans*-**1** can be separated by thin layer chromatography (silica gel; 75:15:10 hexane–CH_2Cl_2–ether; *trans*-**1**, R_f 0.70; *cis*-**1**, R_f 0.44; **4**, R_f 0.40).

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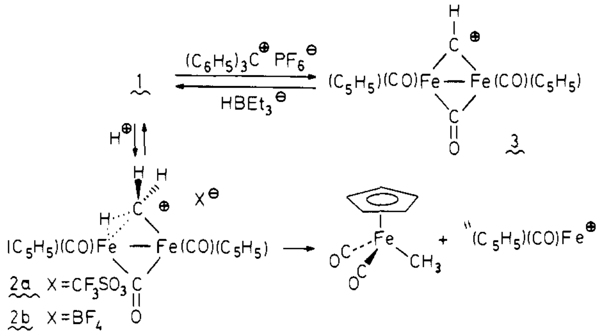
than 20%.

Enriched *trans*-**1** (67%) was obtained by fast K[CpFe(CO)$_2$]^9 chromatography on alumina. In C_6D_6, *trans*-**1** was converted to an equilibrium 3.4:1 mixture of *cis*-**1**–*trans*-**1** with a half-life of about 10 min at 36 °C. The cis–trans isomerization of **1** is much slower than that of **4**;^{12} this is probably due to the instability of an intermediate terminal methylene complex. A similar mechanism has been suggested by Knox and co-workers^{13} to explain the cis–trans isomerization of $Cp_2Ru_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(CH_3)_2]$.

In the ^1H NMR spectrum of an equilibrium mixture of *cis*-**1** and *trans*-**1** in C_6D_6,^{14} the nonequivalent protons of the μ-CH_2 group of *cis*-**1** appear as two doublets, each with 0.6-Hz splitting at δ 8.56 and 9.97, and the equivalent hydrogens of the μ-CH_2 group of *trans*-**1** appear as a singlet at δ 9.47. In the $^{13}C\{^1H\}$ NMR spectrum of *cis*-**1** and *trans*-**1**, the methylene carbon resonances appear at δ 138.5 and 141.7, respectively. The IR spectrum of **1** in CH_2Cl_2 has bands at 1986, 1942, and 1780 cm^{-1} for the terminal and bridging CO ligands. These spectral data are similar to those observed for complexes structurally related to **1**.^{5,7}



Protonation of **1** with either CF_3SO_3H or HBF_4 in diethyl ether at −78 °C followed by warming to room temperature leads to precipitation of the dark purple crystalline bridging methyl complexes, **2a** and **2b**, in 70% and 87% yield, respectively.^{15} The ^1H and ^{13}C NMR spectra of **2a** and **2b** establish that the two iron centers and the three protons of the methyl group are NMR equivalent at 0 °C. In contrast to **1** where both cis and trans isomers were observed, only a single isomer of **2** was observed by NMR spectroscopy. In the ^1H NMR spectrum of **2a** or **2b** in CH_2Cl_2 at 0 °C, the equivalent cyclopentadienyl groups appear at δ 5.41, and the methyl protons appear at δ −1.88. In the gated decoupled ^{13}C NMR spectrum of **2a**, the cyclopentadienyl groups appear as a doublet (J = 183 Hz) at δ 88.8, the methyl group gives rise to quartet (J = 120 Hz) at δ 23.4, and the terminal and bridging CO groups appear as singlets at δ 206.2 and 242.2. The large ^{13}C–^1H coupling constant of the methyl group is similar to that seen for other bridging methyl compounds^{16} and allows an unequivocal assignment of **2a** as a bridging methyl complex. The coupling constant expected for an alternative fluxional structure with a μ-CH_2 and protonated metal–metal bond would have been much smaller.^{17} The IR spectrum of **2a** (Nujol mull) has bands at 2025 and 1856 cm^{-1} for terminal and bridging CO groups.

While the average structure of the μ-CH_3 group shows symmetric bonding to the two iron atoms of **2a**, we have obtained evidence from the NMR spectra of monodeuterated **2a** that the μ-CH_3 is unsymmetrically bonded to the iron atoms and that there is a specific interaction of one iron atom with one CH bond of the μ-CH_3 group. A similar interaction of a bridging methyl group has been seen in $Os_3(CO)_{10}(\mu\text{-}CH_3)H$ (**5**)^{1d} and $\{Cp_2Fe_2(\mu\text{-}CO)[\mu\text{-}(C_6H_5)_2PCH_2P(C_6H_5)_2](\mu\text{-}CH_3)\}^+$ (**6**) in which the bridging H atom has been observed by Stone et al. using X-ray crystallography.^{7f} Treatment of **1** with 2 equiv of an ~3:1 mixture of CF_3SO_3D–CF_3SO_3H in diethyl ether followed by isolation of the solid gave a ~1:1 mixture of monodeuterated-**2a**–**2a**. In the ^1H NMR spectrum of this mixture in CD_2Cl_2 at −4 °C, the μ-CH_3 of **2a** appears at δ −1.85, and the μ-CH_2D group of deuterated-**2a** appears at δ −2.62. As in the case of Shapley's **5** and Stone's **6**, the large chemical shift difference between μ-CH_3 and μ-CH_2D is attributed to a large chemical shift difference between the hydrogen interacting with the metal and the two remaining hydrogens and to an equilibrium isotope effect that leads to a small preference for hydrogen in the bridging position. The chemical shift of the interacting hydrogen is expected to be at higher field than the remaining hydrogens, and this results in a shift of the μ-CH_2D resonance to 0.77 ppm higher field than μ-CH_3. As the temperature was lowered to −86 °C, the μ-CH_3 group shifts only 0.03 ppm to δ −1.88, but the μ-CH_2D group shifts 0.31 ppm to higher field (δ −2.93); this shift is attributed to a temperature dependence of the equilibrium constant which increasingly favors bridging hydrogen at lower temperatures. The signals for the μ-CH_3 and the μ-CH_2D broadened significantly^{18} upon cooling to −86 °C, apparently due to a slowing of the exchange process that interconverts the interacting hydrogen and the remaining two hydrogen atoms.

When either **2a** or **2b** is dissolved in slightly basic solvents such as acetone or acetonitrile, **1** is regenerated in nearly quantitative yield. While **2** is stable for days at −20 °C, it decomposes at room temperature over several days. Decomposition of **2** is much more rapid in CH_2Cl_2 ($t_{1/2}$ ~5 min at 25 °C) and gives $CpFe(CO)_2CH_3$ in nearly quantitative yield. No products derived from the remaining $CpFeCO^+$ fragment were directly observed, but insoluble material precipitated. Theopold and Bergman have reported a similar fragmentation upon protonation of $Cp_2Co_2(CO)_2(\mu\text{-}CH_2)$, but the intermediate μ-CH_3 complex was not detected.^{1q}

Reaction of **1** with $(C_6H_5)_3C^+PF_6^-$ in CH_2Cl_2 leads to hydride abstraction and formation of the cationic bridging methylidyne complex **3** which was isolated as a dull red crystalline material is 70–80% yield.^{19} Treatment of **3** with lithium triethylborohydride reforms **1** but only in about 10% yield. The air-sensitive complex **3** is thermally stable in the solid state but is unstable in CD_2Cl_2 solution at room temperature ($t_{1/2}$ ~ 2 h). The ^1H NMR spectrum of bridging methylidyne complex **3** in CD_2Cl_2 exhibits singlets at δ 5.39 (Cp) and at the very low field position of δ 22.8 (cf. δ 16.3 for $[Cp_3Rh_3(CO)_2\mu_3\text{-}CH]^{+11}$). In the $^{13}C\{^1H\}$ NMR spectrum of **3** the methylidyne carbon appears at the extreme down field position of δ 490.2. This is the lowest field ^{13}C chemical shift reported for a diamagnetic complex but is comparable to that found for the iron and ruthenium alkyl substituted analogues of **3** (cf. $[trans\text{-}Cp_2Fe_2(CO)_3(\mu\text{-}C(C_5H_7))]^+$, δ 448.3;^{7g} $[cis\text{-}Cp_2Ru_2(CO)_3(\mu\text{-}CCH_3)]^+$, δ 469.7^{7h}). Compound **3** is the only known example of a complex with a methylidyne ligand bridging two transition metals. An aluminium alkyl stabilized tantalum–

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(14) Compound **1**: IR (CH_2Cl_2) 1986, 1942, and 1780 cm^{-1}. *cis*-**1**: ^1H NMR (C_6D_6) δ 4.16 (10 H, s, Cp), 9.97 (1 H, d, $^2J_{HH}$ = 0.6 Hz, μ-CH_2), 8.56 (1 H, d, $^2J_{HH}$ = 0.6 Hz, μ-CH_2); ^{13}C $\{^1H\}$ (THF-d_8) δ 87.8 (Cp), 138.5 (μ-CH_2), 214.3 (CO), 271.3 (μ-CO). *trans*-**1**: ^1H NMR (C_6D_6) δ 4.36 (10 H, s, Cp), 9.47 (2 H, s, μ-CH_2); ^{13}C $\{^1H\}$ NMR (THF-d_8) δ 89.4 (Cp), 141.8 (μ-CH_2), 214.6 (CO), 272.2 (μ-CO). Anal. Calcd for $C_{14}H_{12}O_3Fe_2$: C, 49.47; H, 3.56; Fe, 32.86. Found: C, 49.51; H, 3.82; Fe, 33.22.

(15) Other μ-CH_3 transition metal and lanthanide complexes are known.^{8a,7f} (a) Edwards, P.; Mertis, K.; Wilkinson, G.; Hursthouse, M.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 334–344. (b) Masters, A. F.; Mertis, K.; Gibson, J. F.; Wilkinson, G. *Nouv. J. Chem.* **1977**, *1*, 389–392. (c) Krüger, C.; Sekutowski, J. C.; Berke, H.; Hoffmann, R. *Z. Naturforsch. B* **1978**, *33*, 1110–1115. (d) Jolly, P. W.; Mynott, R. *Adv. Organomet. Chem.* **1981**, *19*, 257–304. (e) Schmidt, G. F.; Muetterties, E. L.; Beno, M. A.; Williams, J. M. *Proc. Natl. Acad. Sci.* **1981**, *78*, 1318–1320. (f) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54–61.

(16) For $HOs_3(CO)_{10}(\mu\text{-}CH_3)$, J = 121.1 Hz.^{8a} For the related iron complex $\{Cp_2Fe_2(\mu\text{-}CO)[\mu\text{-}(C_6H_5)_2PCH_2P(C_6H_5)_2]\mu\text{-}CH_3\}^+$, J = 114 Hz.^{7f}

(17) The coupling constant for a bridging methylene–bridging hydride complex would be expected to be approximately $^2/_3$ the coupling constant for a μ-CH_2 complex. For *cis*-**1**, J_{CH} = 137 Hz.

(18) The line width at half-height of the μ-CH_3 resonance for **2a** broadens to 61 Hz at −86 °C compared to 10 Hz at −4 °C.

(19) Compound **3**: ^1H NMR (CD_2Cl_2) δ 5.39 (10 H, s, Cp); 22.8 (1 H, s, μ-CH); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 92.0 (Cp), 204.8 (CO), 252.7 (μ-CO), 490.2 (μ-CH); IR (CH_2Cl_2) 2052 and 1856 cm^{-1}. Anal. Calcd for $C_{14}H_{11}O_3PF_6Fe_2$: C, 34.75; H, 2.29; P, 6.40. Found: C, 34.51; H, 2.36; P, 6.18.

methylidyne complex has recently been reported,[20] and other binuclear alkylidyne species are known.[7g-i,21] A few metal cluster compounds containing triply and quadruply bridging methylidyne ligands have been synthesized.[11,8,22]

Extensions of the procedure employed for the synthesis of **1** are being explored as possible routes to other homo- and heterobimetallic bridging methylene complexes. In addition, the possibility that the cationic complex **3** might transfer CH^+ to organic substrates is under investigation.

Acknowledgment. Support from the Department of Energy, Division of Basic Energy Sciences, and the National Science Foundation is gratefully acknowledged.

Registry No. *cis*-**1**, 79839-80-8; *trans*-**1**, 79896-43-8; **2a**, 80461-96-7; **2b**, 80461-95-6; **3**, 80461-93-4; **4**, 12154-95-9; $K[CpFe(CO)_2]$, 60039-75-0; $CpFe(CO)_2CH_2O_2CCH_3$, 12244-91-6; $CpFe(CO)_2CH_3$, 12080-06-7.

Supplementary Material Available: Synthesis and purification of **1** (4 pages). Ordering information is given on any current masthead page.

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Thermodynamics of Acid–Base Reactions in Water. A Comment on the Eigen Mechanism

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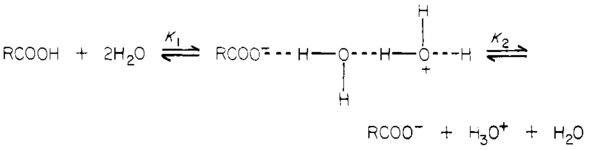
Received August 24, 1981

We have shown recently that the large negative heat capacity changes ($\Delta C_p^\ominus$) which characterize the ionization of carboxylic acids[1] and amines[2] in water can be understood by postulating that these reactions are not single-stage processes, i.e., they proceed in the sequence suggested by Eigen,[3] namely



$$RCOOH + 2H_2O \overset{K_1}{\rightleftharpoons} RCOO^- \cdots H{-}\overset{\displaystyle H}{\underset{}{O}}\cdots H{-}\overset{+}{O}H_2 \cdots \overset{K_2}{\rightleftharpoons} RCOO^- + H_3O^+ + H_2O \quad (1)$$

Table I. Data Related to the Ionization of Benzoic Acid at Various Temperatures

T, °C	$K_{ao} \times 10^5$, (m)[a]	$\Delta K \times 10^7$	K_a(calcd) $\times 10^5$ [b]
5	5.964	2.47	5.936
10	6.100	2.53	6.103
15	6.206	2.28	6.224
20	6.271	2.59	6.298
25	6.331	4.36	6.328
30	6.306	5.10	6.318
35	6.259	4.72	6.272
40	6.193	4.95	6.195
45	6.099	5.15	6.091
50	5.992	5.17	5.965
55	5.838	5.30	5.823
60	5.687	5.54	5.668
65	5.520	5.73	5.504
70	5.341	5.77	5.335
75	5.152	6.01	5.163
80	4.959	6.32	4.990

[a] Data in ref 5 reported on were the "C" scale; the conversion to the "m" scale was made in the usual way–see ref 10. [b] Calculated from eq 5 with values of $A + C$, $B + D$, C, and D given in Table III. The ΔT and ΔK quantities for the Wentworth regression followed the practices established in ref 2. See other references in that communication.

Table II. Data Related to the Autoprotolysis of Water at Various Temperatures[a]

T, °C	$K_{wo} \times 10^{15}$ [a]	K_w(calcd) $\times 10^{15}$	$K_{wo} \times 10^{15}$ [b]	K_w(calcd) $\times 10^{15}$
0	1.139	1.140	1.117	1.120
5	1.846	1.845	1.823	1.819
10	2.920	2.917	2.888	2.881
15	4.505	4.508	4.455	4.450
20	6.809	6.816	6.767	6.717
25	10.08	10.09	9.887	9.921
30	14.69	14.65	14.34	14.36
35	20.89	20.88	20.40	20.39
40	29.19	29.23	28.53	28.47
45	40.18	40.26	39.09	39.11
50	54.74	54.59	53.08	52.94
55	72.96	72.96	70.84	70.70
60	96.14	96.21	92.93	93.24

[a] Data from ref 6, but see also ref 10. [b] Data from ref 7. There is a considerable discrepancy between these two sets of data particularly at the high temperature end. See also footnotes to Table I.

Eigen and co-workers[3,4] have also argued that the rate constants for the diffusion-controlled separation and recombination of the ions in acid–base systems are comparable, and hence K_2 is approximately unity. For our analysis of the temperature dependence of the observed equilibrium constants (K_0) we derive for the coupled equilibria (reaction 1)

$$K_0 = K_1K_2/(1 + K_1) \qquad (2)$$

with

$$K_2 = \exp(A/T + B) \qquad (3)$$

and

$$K_1 = \exp(C/T + D) \qquad (4)$$

Combination of eq 2, 3, and 4 gives

$$K_0 = \exp([A + C)/T] + B + D)/[1 + \exp(C/T + D)] \qquad (5)$$

Here we extend the above analysis to fit the data from an extensive study of benzoic acid[5] and that for the autoprotolysis

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