presented in Table I. Structurally, **6c** closely resembles Cp_2TiS_5[13] and S_5CH_2.[14] In contrast, the most stable conformer of **2** in solution and as a solid[15] is the twist boat which is stabilized by minimization of unfavorable transannular S···S contacts.[16] In **6c** the transannular S···S distances are longer as the result of the Ti–S bonds being ca. 0.6 Å longer than typical C–S bonds offsetting the effect of the S–Ti–S angle (91°) which is 26° more acute than for typical S–C–S angles.[17]

The pathway for insertion of CR_2 unit into the *cyclo*-TiS_5 moiety is proposed to proceed via initial cleavage of the TiS_5 ring by an anionic sulfur nucleophile. The intermediate $Cp_2TiS_x^{2-}$ species would be capable of nucleophilic addition to ketones or alkyl halides (Scheme I). We have previously shown that **1** is reactive toward phosphine nucleophiles,[7,20] and it is well-known that S–S bonds are readily cleaved by RS^- reagents.[21] It should be noted that our procedures work optimally with aqueous $(NH_4)_2S$; aqueous Na_2S and anhydrous Li_2S (in THF) were found not to be useful.

The TiS_4CR_2 ring inversion barriers for **3a**, **6a**, and **7a** were measured in toluene-d_8 by DNMR spectroscopy.[22] The results reveal the following ordering in the free energies of activation for ring inversion: $Cp_2TiS_4CMe_2$ (83.6 kJ/mol) > Cp_2TiS_5[24] (76 kJ/mol) > 1,4-$Cp_2TiS_4CH_2$ (59.2 kJ/mol) ≈ 3-$(C_5H_5)_2TiS_4CH_2$ (57 kJ/mol). We suggest that the lone pair–methyl and lone pair–lone pair repulsions strongly influence the ease of TiS_4X ring inversion.

In summary, the reactivity of **1** toward sulfur nucleophiles establishes a route to novel Ti–S–C rings. By virtue of the stability of the Ti–S bonds toward nucleophiles, **1** reacts in a more controlled manner with S^{2-} than S_8 itself. It will be of interest to test the generality of this reaction with other polysulfide chelates and to examine the utility of these compounds in organic synthetic applications.

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Registry No. **1a**, 12116-82-4; **1b**, 78614-86-5; **1c**, 88510-17-2; **2**, 4475-72-3; **3a**, 88510-18-3; **3b**, 88510-19-4; **3c**, 88510-20-7; **4a**, 88510-21-8; **4b**, 88510-22-9; **5a**, 88510-23-0; **6a**, 88510-24-1; **6b**, 88510-25-2; **6c**, 88510-26-3; **7a**, 88510-27-4; **7b**, 88524-89-4; **7c**, 88510-28-5; $(NH_4)_2S$, 12135-76-1; CH_2Br_2, 74-95-3; methyl ethyl ketone, 78-93-3; cyclohexanone, 108-94-1.

Supplementary Material Available: A full structure analysis report, including tables of atomic coordinates, anisotropic thermal parameters, bond lengths, bond angles, intramolecular contacts, and observed and calculated structure factor amplitudes (31 pages). Ordering information is given on any masthead page.

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(13) Muller, E. G.; Peterson, J. L.; Dahl, L. F. *J. Organomet. Chem.* **1976**, *111*, 91. Epstein, E. F.; Bernal, I. *J. Organomet. Chem.* **1971**, *26*, 229.

(14) Fehér, R.; Lex, J. *Z. Anorg. Allg. Chem.* **1976**, *423*, 103.

(15) Fredga, A. *Acta Chem. Scand.* **1958**, *12*, 891.

(16) Bushweller, C. H. *J. Am. Chem. Soc.* **1969**, *91*, 6019.

(17) The average C–S distance and S–C–S angle for 3,3:6,6-bis(pentamethylene)-*s*-tetrathiane,[18] pentathiane, and 1,4-$(i\text{-PrCp})_2TiS_4CH_2$ are 1.82 Å and 114°, respectively. The average Ti–S distance for Cp_2TiS_5, 1,4-$(i\text{-PrCp})_2TiS_4CH_2$, 1,4-$(i\text{-PrCp})_4Ti_2S_4$[19] and 1,5-$(MeCp)_4TiS_6$[20] is 2.40 Å.

(18) Bushweller, C. H.; Bhat, G.; Letendre, L. J.; Brunelle, J. A.; Bilofsky, H. S.; Ruben, H.; Templeton, D. H.; Zalkin, A. *J. Am. Chem. Soc.* **1975**, *97*, 65.

(19) Giolando, D. M.; Rauchfuss, T. B.; Wilson, S. R., unpublished results.

(20) Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 5620.

(21) Davis, R. E. In "Survey of Progress in Chemistry"; Scott, A., Ed.; Academic Press: New York, 1964; Vol. II, pp 189–238.

(22) Values were calculated from[23] $k = \pi\delta\nu^2/[2(W^* - W_0)]$ and $\Delta G^* = 1.914 \times 10^{-2})T[10.319 + \log (T/k)]$. Assuming an uncertainty of 4 K in the coallescence temperature, ΔG^* will differ by 0.5 kJ/mol.

(23) Sandstrom, J. "Dynamic NMR Spectroscopy"; Academic Press: New York, 1982.

(24) Abel, E. W.; Booth, M.; Orrell, K. G. *J. Organomet. Chem.* **1978**, *160*, 75.

Mechanistic and Synthetic Implications of the Reactions of Aroyl Chlorides with Chlorocarbonylbis(triphenylphosphine)rhodium(I). A Catalytic Procedure for the Preparation of Carbonyl-Labeled Aroyl Chlorides

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Summary: The reaction of chlorocarbonylbis(triphenylphosphine)rhodium, $RhCl(CO)(PPh_3)_2$, with aroyl chlorides in the presence of free ^{13}CO in $CDCl_3$ or C_6H_6 solvent at 100 °C gives a statistical distribution of the label over all of the "CO" sites in the system. The reaction is catalytic in rhodium complex and constitutes a simple synthesis of aroyl chlorides labeled with ^{13}C in the carbonyl position. $Ph^{13}COCl$, 2-$ClC_6H_4{}^{13}COCl$, 3-$NO_2C_6H_4{}^{13}COCl$, 4-$NO_2C_6H_4{}^{13}COCl$, 4-$Cl^{13}COC_6H_4{}^{13}COCl$, 4-$CH_3OC_6H_4{}^{13}COCl$, 4-$CH_3COC_6H_4{}^{13}COCl$, and *trans*-$C_6H_5CH{=}CH^{13}COCl$ were successfully prepared by this procedure. $Ph^{14}COCl$ was prepared by exchange with $CH_3{}^{14}COCl$ in the presence of $RhCl(CO)(PPh_3)_2$. Control experiments show that the labeling does not proceed via aryl chlorides. The labeling, by equilibrium of organometallic intermediates, shows that $RhCl(CO)(PPh_3)_2$ reacts with aroyl chlorides at 100 °C and that the equilibration reactions are faster than formation of aryl chlorides.

Acid chlorides are decarbonylated to give aryl chlorides by catalytic amounts of chlorotris(triphenylphosphine)rhodium, **1**, at temperatures of the order of 180 °C.[1] At temperatures of the order of 100 °C, the reaction of aroyl chlorides with complex **1** is stoichiometric and was thought[2] to give aryl chlorides and chlorocarbonylbis(triphenylphosphine)rhodium, **4**. The difference between the catalytic and stoichiometric reactions was attributed to a high barrier to further reaction of complex **4** with the aroyl chloride.[3]

We recently reported[4] that the stoichiometric decarbonylation of aroyl chlorides by $RhCl(PPh_3)_3$ does not give aryl chlorides[5] and that the actual decarbonylation product is $RhCl_2(Ar)(PPh_3)_2$, **5**. We also presented evidence for

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(1) The literature has been summarized and reviewed several times, most recently and thouroughly by Baird (Baird, M. C. In "The Chemistry of Acid Derivatives"; Patai, S., Ed., Wiley: New York, 1979, Supplement B, part 2, pp 825–857. See also: Tsuji, J. In "Organic Synthesis by Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley: New York, 1977, Vol. 2, pp 595–654.

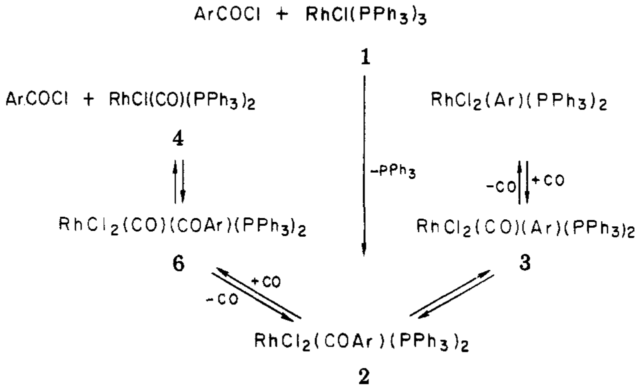
(2) (a) Blum, J. *Tetrahedron Lett.* **1966**, 1605–1608. (b) Stille, J. K.; Regan, M. T. *J. Am. Chem. Soc.* **1974**, *96*, 1508–1514.

(3) (a) Ohno, K.; Tsuji J. J. Am. Chem. Soc. **1968**, *90*, 99–107. (b) Stille, J. K.; Huang, F.; Regan, M. T. *Ibid.* **1974**, *96*, 1518–1522. (c) Strohmeier, W.; Pfohler, P. *J. Organomet. Chem.* **1967**, *89*, 2338–2341.

(4) Kampmeier, J. A.; Rodehorst, R. M.; Philip, J. B., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 1847–49.

(5) Ehrenkaufer, R. E.; MacGregor, R. R.; Wolf, R. P. *J. Org. Chem.* **1982**, *47*, 2489–91, subsequently reported that benzoyl fluoride is not converted to fluorobenzene as claimed in the literature.[6]

Scheme I



an interlocking set of equilibria which accommodate the observed chemistry at moderate temperatures (see Scheme I).[7] The net equilibration is ArCOCl + $RhCl(CO)(PPh_3)_2 \rightleftarrows 2CO + RhCl_2(Ar)(PPh_3)_2$. This reaction leads to the prediction that the carbonyl of the aroyl chloride should exchange with the carbonyl ligand of $RhCl(CO)(PPh_3)_2$ and that both should scramble with free CO. We now report[9] experiments in the presence of ^{13}CO that are consistent with the proposed equilibria. These experiments show clearly that acid chlorides react with $RhCl(CO)(PPh_3)_2$ at moderate temperatures, in contrast to previous assumptions. These experiments also demonstrate a new, catalytic procedure for the preparation of $Ar^{13}COCl$.

In a typical experiment, benzoyl chloride (2.6 mmol) and $RhCl(CO)(PPh_3)_2$ (0.10 mmol) were dissolved in 4 mL of $CDCl_3$ in a 10-mm NMR tube. The mixture was deoxygenated by two freeze–pump–thaw cycles and the evacuated tube opened to a reservoir of ^{13}CO (90%) at approximately atmospheric pressure; the volume above the reaction mixture corresponded to ~0.2 mmol of ^{13}CO. The tube was sealed and heated at 90 ± 10 °C; ^{13}C NMR spectra were recorded periodically at room temperature using fixed instrument parameters. The initial spectrum, before heating, showed a strong singlet[11] at 186 ppm due to the $RhCl(^{13}CO)(PPh_3)_2$ and a very weak peak at 168 ppm due to natural abundance $Ph^{13}COCl$. After 6 h of heating, the spectrum showed absorptions of roughly comparable intensity at 186 and 168 ppm. The heating was continued until the relative intensities of the 186 and 168 ppm absorptions showed no further change; after 24 h of heating the intensity of the 168 ppm peak was several times that of the 186 ppm peak. No other absorptions were observed in the carbonyl region of the ^{13}C NMR spectra. The tube was opened and the "organic" fraction separated either by bulb to bulb distillation at reduced pressure or by evaporation of the solvent and extraction with 1:1 ether–pentane. The "inorganic" residue was identified as $RhCl(CO)(PPh_3)_2$ [IR absorptions at 1975 (^{12}CO) and 1925 (^{13}CO)[11] cm^{-1} and no other absorptions in the region 1500–2200 cm^{-1}; ^{13}C NMR showed the characteristic doublet of triplets pattern[11] of 4]. Benzoyl chloride was characterized in the "organic" fraction by the carbonyl absorptions at 1775 and 1735 cm^{-1}; chlorobenzene was not detected by GC analysis.[14] Hydrolysis of the organic phase gave benzoic acid, mp 121–122 °C, in 99% yield. The benzoic acid was analyzed by mass spectrometry at 20 eV; the observed enrichment factor, $10^2(m^+ + 1)/[(m^+) + (m^+ + 1)]$, was 12.8%. The observed enrichment factor (ef) for natural benzoic acid obtained from the starting benzoyl chloride was 7.4%. The theoretical change in ef, $(ef)_{product} - (ef)_{starting\ material}$, calculated from the composition of the reaction mixture by assuming statistical distribution of the label over all of the carbonyl sites (4 + PhCOCl + free CO) was ~6% (observed 5.4%).

In a separate experiment, a highly enriched sample of $Ph^{13}CO_2H$ was prepared by reacting PhCOCl (0.48 mmol), $RhCl(CO)(PPh_3)_2$ (0.083 mmol), and ^{13}CO (~1 mmol) in 5 mL of C_6H_6 at 100 °C for 36 h. The recovered $RhCl(CO)(PPh_3)_2$ (86%) was analyzed by IR; the ratio of the integrated intensity of the 1925 cm^{-1} absorption to the sum of the integrated intensities of the 1925 + 1975 cm^{-1} absorptions corresponded to ef = 66%. The mass spectrum of the isolated benzoic acid gave ef = 63%.

With use of the "typical conditions" described above for benzoyl chloride, 2-chloro-, 3-nitro-, 4-nitro-, 4-methoxy-, and 4-acetylbenzoyl chlorides and terephthaloyl chloride[15] were all successfully labeled. The acids were recovered in good yields (70–99%; ef = 13–15%), and aryl chlorides were not produced.[14] Crossover experiments rigorously excluded a decarbonylation–recarbonylation pathway via the corresponding aryl chlorides. Thus, benzoyl chloride was reacted in the typical manner in the presence of 1 equivalent of added 1,2-dichlorobenzene. The ^{13}C NMR spectrum showed the formation of $C_6H_5{}^{13}COCl$ (168 ppm), but even after 40 h at 90–100 °C, $2\text{-}ClC_6H_4{}^{13}COCl$, (165 ppm) was not observed. The ^{13}C NMR spectra of the inverse experiment, 2-chlorobenzoyl chloride doped with chlorobenzene, showed the formation of $2\text{-}ClC_6H_4{}^{13}COCl$, but no $C_6H_5{}^{13}COCl$. This experiment was worked up to give recovered $RhCl(CO)(PPh_3)_2$ (90%) and recovered chlorobenzene (94%). The carboxylic acid fraction was precipitated from the hydrolysis mixture and analyzed without purification. The mass spectrum corresponded to that of 2-chlorobenzoic acid (ef = 14.5%) and showed no peak corresponding to benzoic acid at *m/e* 122.

These experiments are in good agreement with predictions based on Scheme I. The observed labeling is approximately that expected for a statistical distribution of the ^{13}CO over all of the "CO" sites in the reaction mixture. The process is clearly catalytic since $[ArCOCl]/[RhCl(CO)(PPh_3)_2] \geq 25$. Aryl chlorides are not produced nor are they intermediates in the labeling. Since other carbonyl complexes do not build up, the equilibria in Scheme I must favor ArCOCl + $RhCl(CO)(PPh_3)_2$ under these conditions. As a result, *the final reaction mixtures contain only the labeled starting materials*. It is, of course, important to note that the reaction is tolerant of a variety of functional groups, several of which are incompatible with the classical Grignard route to labeled aromatic acids.

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(6) Olah, G. A.; Krienbuehl, P. J. *J. Org. Chem.* **1967**, *32*, 1614–5.

(7) Complex 6, in Scheme I, has not been isolated and characterized. There is good analogy for this intermediate; similar complexes are known.[8]

(8) Baird, M. C.; Mague, J. T.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 1347–1360. Chatt, J.; Shaw, B. L.; *J. Chem. Soc. A* **1966**, 1437–1442.

(9) This work was reported, in part: Kampmeier, J. A.; Mahalingam, S. 185th National Meeting of the American Chemical Society, Seattle, WA, Mar 1983; American Chemical Society: Washington, DC, 1983; Abstract ORGN-32.

(10) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711–32.

(11) $RCl(CO)(PPh_3)_2$ normally shows a doublet of triplets (*J* = 73, 16 Hz) centered at 187 ppm[12] but is known to exchange "instantaneously" with free CO.[13]

(12) Bresler, L. S.; Buzina, N. A.; Varshavsky, Y. S.; Kieseleva, N. V.; Cherkasova, T. G. *J. Organomet. Chem.* **1979**, *171*, 229–235.

(13) Wojcicki, A.; Basolo, F. *J. Am. Chem. Soc.* **1961**, *83*, 525–528.

(14) Conversion of the aroyl chloride to aryl chloride in 1% yield would have been detected.

(15) The procedure failed with phthaloyl chloride; $RhCl(CO)(PPh_3)_2$ was consumed to give a stable adduct of unknown structure.

The procedure described above must also work to introduce ^{14}CO into the carbonyl position. To avoid handling ^{14}CO, we tried $CH_3{}^{14}COCl$[16] as an in situ source of ^{14}CO. Thus, $RhCl(CO)(PPh_3)_2$ (0.10 mmol), benzoyl chloride (2.7 mmol), and $CH_3{}^{14}COCl$ (3.3 mmol, 13 mCi/mol) were reacted in benzene (5 mL) for 22 h at 100 °C. The normal workup gave benzoic acid (97%) with a specific activity of 8 mCi/mol (theoretical for statistical distribution = 7 mCi/mol). The recovered $RhCl(CO)(PPh_3)_2$ was also radioactive. The success of this exchange experiment suggests that nonaromatic acid chlorides might also be successfully labeled under our "typical" conditions. In fact, *trans*-cinnamoyl chloride[18] was smoothly labelled in 11 h at 100 °C (recovered acid, 96% yield, ef = 21%). We are actively pursuing experiments with simple aliphatic substrates.

Several observations suggest that the slow step in the labeling mechanism is the initial reaction of $RhCl(CO)(PPh_3)_2$ with the acid chloride. Thus, the rate of the labeling depends qualitatively on the concentration of 4 and on the structure of the acid chloride. For example, a simple competition experiment revealed that 4-nitrobenzoyl chloride is labeled more rapidly than benzoyl chloride. The time courses of the ^{13}C NMR spectra show that cinnamoyl chloride labels more rapidly than does benzoyl chloride. The most important mechanistic conclusions follow from the success of these labeling experiments; the barrier to product formation (**3** or **5** → ArCl) must be greater than the barriers $\mathbf{5} \rightleftarrows \mathbf{3} \rightleftarrows \mathbf{2} \rightleftarrows \mathbf{6} \rightarrow \mathbf{4}$ (see Scheme I). The labeling reaction shows that the aroyl chlorides react with $RhCl(CO)(PPh_3)_2$ at 100 °C. The "activation" of $RhCl(CO)(PPh_3)_2$ is, therefore, not the reason that the catalytic decarbonylation of aroyl chlorides requires high temperatures. Rather, the high temperature is required to form the aryl chloride product. The most important synthetic conclusion is that these reactions provide a simple, one-pot, catalytic procedure for preparing aroyl chlorides labeled with ^{13}C or ^{14}C in the carbonyl group.

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Registry No. 4, 13938-94-8; ^{13}C-4, 88548-50-9; PhCOCl, 98-88-4; ^{13}CO, 1641-69-6; $Ph^{13}COCl$, 52947-05-4; $Ph^{13}CO_2H$, 3880-99-7; 2-ClC_6H_4COCl, 609-65-4; 3-$NO_2C_6H_4COCl$, 121-90-4; 4-$NO_2C_6H_4COCl$, 122-04-3; 4-$CH_3OC_6H_4COCl$, 100-07-2; 4-$CH_3COC_6H_4COCl$, 31076-84-3; 4-$ClCOC_6H_4COCl$, 100-20-9; 2-$ClC_6H_4{}^{13}COCl$, 88525-75-1; 3-$NO_2C_6H_4{}^{13}COCl$, 88525-76-2; 4-$NO_2C_6H_4{}^{13}COCl$, 88525-77-3; 4-$CH_3OC_6H_4{}^{13}COCl$, 88525-78-4; 4-$CH_3COC_6H_4{}^{13}COCl$, 88525-79-5; 4-$Cl^{13}COC_6H_4{}^{13}COCl$, 88525-80-8; $CH_3{}^{14}COCl$, 676-77-7; $Ph^{14}CO_2H$, 1589-66-8; *trans*-$C_6H_5CH{=}CHCOCl$, 17082-09-6; *trans*-$C_6H_5CH{=}CH^{13}COCl$, 88525-81-9.

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[16] Prepared from commercial $CH_3{}^{14}CO_2Na$ (Amersham) by reaction with phthaloyl chloride.[17]

[17] Koltai, E.; Esses-Reiter, K.; Banfi, D. *J. Labelled Compd. Radiopharm.* **1982**, *19*, 13–18.

[18] Kampmeier, J. A.; Harris, S. H.; Rodehorst, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 1478–1485.

A Facile Equilibrium Involving CO and H_2. The Fe–H–Fe Bond Energy in $(\mu_2\text{-}H)_3Fe_3(CO)_9(\mu_3\text{-}CCH_3)$

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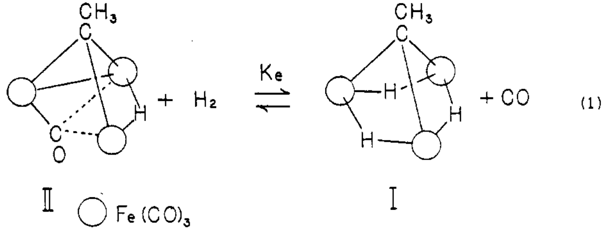
Summary: The reaction $H_2 + (\mu_2\text{-}H)Fe_3(CO)_{10}(\mu_3\text{-}CCH_3) = CO + (\mu_2\text{-}H)_3Fe_3(CO)_9(\mu_3\text{-}CCH_3)$ is shown to be an equilibrium process with an equilibrium constant of 0.66 at 60 °C in benzene. This measurement allows an estimate of the enthalpy change of the same reaction of 4 kcal/mol. By utilization of known thermochemical information and this reaction enthalpy, the bond energy for a FeHFe three-center interaction is calculated to lie between 81 and 85 kcal/mol. This number is significantly larger than that for an FeCO interaction and suggests an energetic preference for bridging over terminal FeH bonds.

We have found that the reduction of certain iron carbonyl anions with $BH_3{\cdot}THF$ leads to the formation of $(\mu_2\text{-}H)_3Fe_3(CO)_9(\mu_3\text{-}CCH_3)$ (I)[1,2] as well as other iron clusters containing hydrocarbon fragments.[3] One of these products, $(\mu_2H)Fe_3(CO)_{10}(\mu_3\text{-}CCH_3)$ (II),[4] is converted in the presence of H_2 into I, and I, in the presence of CO, is converted into II (eq 1). Although a number of instances



of the addition of H_2 to metal cluster compounds, with or without the displacement of another ligand, are known,[5,6]

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[1] Wong, K. S.; Fehlner, T. P. *J. Am. Chem. Soc.* **1981**, *103*, 966.

[2] Wong, K. S., Haller, K. J.; Dutta, T. K.; Chipman, D. M.; Fehlner, T. P. *Inorg. Chem.* **1982**, *21*, 3197. DeKock, R. L.; Wong, K. S.; Fehlner, T. P. *Ibid.* **1982**, *21*, 3203.

[3] Fehlner, T. P.; Vites, J., unpublished work.

[4] This molecule has been characterized spectroscopically. NMR: ^1H ($C_6D_5CD_3$, −45 °C) δ 4.05 (d, 3 H, $J = 1.2$ Hz), −19.98 (q, 1 H, $J = 1.2$ Hz); $^{13}C[^1H]$ ($C_6D_5CD_3$, −70 °C) δ 310.0 (1 C, μ_3-C), 224–205 (10 C, CO), 46.1 (1 C, CH_3). The assignment of for the quaternary carbon was proved by ^{13}CO reaction with I. At higher temperatures the ^{13}CO resonances coalesce at 209.3 and the 310.0 resonance in the ^{13}C spectrum and the −19.98 resonance in the ^1H spectrum undergo broadening. MS: p^+ = 475.785 calcd, 475.786 measd; loss of 9 CO's observed. IR (hexane, cm^{-1}): 2108 (w), 2053 (s), 2045 (s), 2020 (s), 2005 (m, sh), 1988 (w), 1890 (w, br). In Nujol mull bands at 1630 (vw, br) and 1550 (w, br) are also observed. The postulated structure is indicated in eq 1. Note that the deprotonated anion of II $(Fe_3(CO)_{10}(\mu_3CCH_3)^-]$, has been reported as two isomers, one with a μ_2-CO and one with a μ_3-CO (Lourdichi, M.; Mathieu, R. *Nouv. J. Chim.* **1982**, *6*, 231). Also note that a compound having the same molecular formula as II has been reported recently but has significantly different spectroscopic properties from the compound characterized here. (Wong, W. K.; Chiu, K. W.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 1557). Finally, the structure of $[Fe_3(CO)_9(\mu_2\text{-}CO)(\mu_3\text{-}CH)^-]$ has been published (Kolis, J. W.; Holt, E. M.; Drezdzon, M.; Whitmire, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 6134). The spectroscopic properties of II compare favorably with those reported recently for $HFe_3(CO)_{10}CH$ (Kolis, J. W.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 7307).

[5] Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 477. Roland, E.; Vahrenkamp, H. *Organometallics* **1983**, *2*, 183. Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7255. Keister, J. B.; Payne, M. W.; Muscatella, M. J. *Organometallics* **1983**, *2*, 219. Farrugia, L. J.; Green, M.; Hankey, D. R.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1983**, 310. DuBois, M. R. *J. Am. Chem. Soc.* **1983**, *105*, 3710. L'Eplattenier, F.; Calderazzo, F. *Inorg. Chem.* **1968**, *7*, 1290. Hill, R. H.; Puddephatt, R. J., *J. Am. Chem. Soc.* **1983**, *105*, 5797.

0276-7333/84/2303-0491$01.50/0