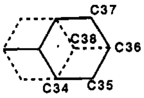
was modelled as shown in the diagram below with occupancy factors of $^1/_2$ for C35, C37, and C38. Temperature factors and a list of F_o vs. F_c are in Tables VI and VII (supplementary material), respectively. The largest shift/error on the last cycle for any parameter was less than 1.5. The largest residual in the final difference map was 0.7 e/Å^3.



(b) Compound 7. Single crystals were grown from a toluene solution of 7 at −23 °C. Lattice parameters were determined and intensity data collected as described above. The structure was solved and refined with the SHELX package of crystallographic programs.[25] The final difference map was featureless. Scattering factors were taken from ref 24. Tables VIII and IX (supplementary material) contain the temperature factors and lists of F_o vs. F_c, respectively.

Acknowledgment. This work was supported by the National Science Foundation (CHE-8206153) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. 1, 56200-27-2; 1′, 69140-73-4; 4, 1972-28-7; 5, 84624-70-4; 5·1/2PhMe, 109585-15-1; 5 (Ar = Ph), 84624-68-0; 5 (Ar = *p*-tolyl), 84624-69-1; 7, 109585-16-2; $Cp_2W_2(CO)_4$, 62853-03-6; $Cp_2Cr_2(CO)_4$, 54667-87-7; $Cp_2Mo_2(CO)_6$, 12091-64-4; $CpFe(CO)_2N_3$, 42765-82-2; NaN_3, 26628-22-8; LiN_3, 19597-69-4; *p*-$(O_2N)C_6H_4N_3$, 1516-60-5; $PhCoN_3$, 582-61-6; *p*-$(CH_3)C_6H_4SO_2N_3$, 941-55-9; *p*-(*t*-Bu)$C_6H_4N_3$, 18522-89-9; *p*-$(CH_3)C_6H_4N_3$, 2101-86-2; PhN_3, 622-37-7; 4-phenyl-1,2,4-triazoline-3,5-dione, 4233-33-4.

Supplementary Material Available: Tables of temperature factors for 5·$^1/_2$PhMe and 7 (2 pages); listings of F_o vs. F_c for 5·$^1/_2$PhMe and 7 (21 pages). Ordering information is given on any current masthead page.

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[25] Sheldrick, C. M. *SHELX-76*, 1976, "Package for Crystal Structure Determination", University of Cambridge, Cambridge, England.

Reaction of Diiron μ-Alkylidyne Complexes with Diazo Compounds

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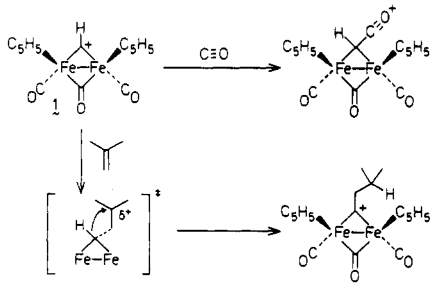
The reaction of μ-methylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (1) with ethyl diazoacetate gave the ester-substituted μ-alkenyl complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHCO_2Et)^+PF_6^-$ (2) in 86% yield. 1 also reacted with diazomethane, diazoethane, methyl 2-diazopropionate, and (trimethylsilyl)diazomethane to give similar μ-alkenyl products. μ-Alkenyl complex 2 reacted with the nucleophiles $NEt_4^+[HFe(CO)_4]^-$ and lithium diethyl malonate to give the carbene complexes $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_2CO_2Et)$ (17) and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH(CO_2Et)CH(CO_2Et)_2)$ (16). Reductive dimerization of 2 gave the tetrairon carbene complex $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCHCO_2Et)\}_2$ (25). The structure of 25 was determined by X-ray crystallography, monoclinic space group $P2_1/c$, with unit cell constants a = 12.318 (2) Å, b = 16.443 (2) Å, c = 17.679 (2) Å, β = 105.20 (1)°, and Z = 4.

Introduction

The diiron μ-methylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (1) forms 1:1 adducts with nucleophiles such as NMe_3 and CO.[1] 1 also adds the C–H bond of the methylidyne group across the double bond of alkenes in a carbon–carbon bond forming reaction that involves an initial nucleophilic interaction of the alkene and the methylidyne carbon.[2,3]



In a search for new carbon–carbon bond forming reactions of diiron-bridging complexes, we have explored the reactivity of μ-alkylidyne complexes with diazo compounds. We envisioned a process in which nucleophilic attack of a diazo compound on a μ-alkylidyne complex would generate an intermediate that could lose dinitrogen and form a μ-alkenyl complex.

Here we report that this process works efficiently for the μ-methylidyne complex 1 but fails for alkyl- and aryl-substituted μ-alkylidyne complexes. In addition, a novel reductive dimerization of a diiron μ-alkenyl complex to a tetrairon carbene complex was discovered.

Results and Discussion

Reaction of μ-Methylidyne Complex 1 with Diazo Compounds. The diiron methylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (1) reacts rapidly with a variety of diazo compounds to produce new μ-alkenyl diiron complexes. When ethyl diazoacetate was added to

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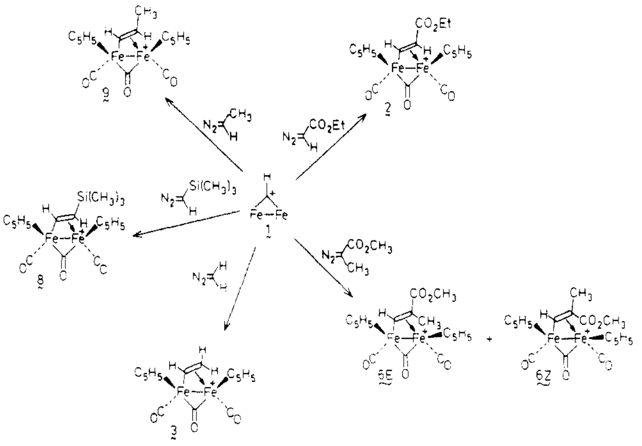
[1] Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 7360–7361.
[2] Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4950–4951.
[3] Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Marder, S. R.; Austin, E. A. *J. Am. Chem. Soc.* **1986**, *108*, 4043–4053.

a slurry of μ-methylidyne complex **1** in CH_2Cl_2 at −78 °C, gas evolution occurred smoothly over 10 min as the reaction mixture was allowed to warm. The resulting solution was recooled to −78 °C, and diethyl ether was added to precipitate the deep red μ-alkenyl complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHCO_2Et)^+PF_6^-$ (**2**) which was isolated in 86% yield.



The structure of **2** was readily established from IR and ^1H NMR spectra. In the IR spectrum of **2**, two strong bands at 2030 and 2013 cm^{-1} and a strong band at 1883 cm^{-1} were observed for the two terminal and one bridging CO ligands, respectively. A band at 1724 cm^{-1} was seen for the carbonyl group of the α,β-unsaturated ester.

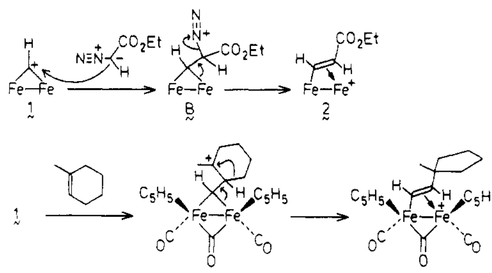
In the ^1H NMR, the trans vinyl protons of **2** appear as a pair of doublets (J = 11.6 Hz) at δ 12.90 and 3.16. For the related μ-$CH{=}CH_2$ complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}COp)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CH_2)^+PF_6^-$ (**3**) the α-vinyl hydrogen appears far downfield at δ 12.7 while the β-vinyl hydrogens appear at δ 5.2 (J_{cis} = 7.4 Hz) and 3.0 (J_{trans} = 13.2 Hz).[4] The appearance of two cyclopentadienyl resonances at δ 6.07 and 5.60 demonstrates that the fluxional process which exchanges the environment of the C_5H_5 rings in μ-alkenyl complexes is slow in the case of **2** at −72 °C. This fluxional process was previously correlated with the electron-donating ability of β-substituents on the μ-alkenyl group.[5] The static NMR of **2** is consistent with the electron-withdrawing nature of the carbethoxy group.

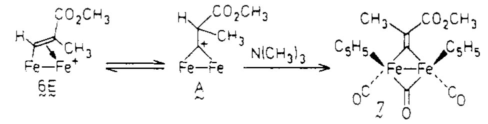
μ-Alkenyl complex **2** is unstable in coordinating solvents such as acetone or THF. In a variable-temperature ^1H NMR experiment in acetone-d_6, **2** decomposed above −20 °C to a mixture of the monoiron complex $(C_5H_5)Fe(CO)_2$(*trans*-$CH{=}CHCO_2Et$) (**4**) (32%), the μ-alkenylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCO_2Et)$ (**5**) (23%), ferrocene (17%), the cationic iron complex $[(C_5H_5)Fe(CO)_3]^+PF_6^-$ (16%), and the bridging carbonyl dimer $[(C_5H_5)(CO)_2Fe]_2$ (11%). The stability of **2** was much greater in CH_2Cl_2; $t_{1/2}$ = 2 days at 50 °C.

μ-Alkenyl complex **2** did not undergo further reaction with ethyl diazoacetate. When an isolated sample of **2** was treated with diazo ester at low temperature and slowly warmed, ^1H NMR showed no new products from the reaction of **2** with ethyl diazoacetate. The only products observed were from the decomposition of **2** in acetone-d_6.

μ-Methylidyne complex **1** reacted with methyl 2-diazopropionate to produce a 6:1 mixture of double-bond isomers of the μ-alkenyl complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C(CH_3)CO_2CH_3)^+PF_6^-$ (**6E** and **6Z**) in 66% yield. In the ^1H NMR of **6**, the α-vinyl protons of the two isomers appear at δ 14.51 and 12.93. **6** is even more thermally unstable than **2** in acetone and THF and decomposed above −50 °C to give mixtures of the monoiron complex $(C_5H_5)Fe(CO)_2(CH{=}C(CH_3)CO_2CH_3)$ and ferrocene.

Scheme I





Treatment of a solution of **6E** and **6Z** in CH_2Cl_2 with $N(CH_3)_3$ gave the μ-alkenylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CO_2CH_3)$ (**7**) in 40% yield. This result was somewhat unexpected since stable μ-alkenyl complexes such as $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHCH_2CH_2CH_3)^+PF_6^-$ are deprotonated to produce vinyl carbene complexes such as $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH{=}CHCH_2CH_3)$.[3,6] Previously we found that β-dialkyl-substituted μ-alkenyl complexes such as $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C(CH_3)CH_2CH_3)^+PF_6^-$ (**23**) are in rapid equilibrium with μ-alkylidyne complexes such as $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH(CH_3)CH_2CH_3)^+PF_6^-$ and that kinetic deprotonation of the μ-alkylidyne complex produces μ-alkenylidene complexes such as $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CH_2CH_3)$ (**24**).[3] Because of this later reaction we suggest that μ-alkenyl complex **6** is in rapid equilibrium with an unobserved μ-alkylidyne complex A and that A is kinetically deprotonated to produce μ-alkenylidene complex **7**.

μ-Methylidyne complex **1** reacts with (trimethylsilyl)diazomethane to produce the μ-alkenyl complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHSi(CH_3)_3)^+PF_6^-$ (**8**) in 49% yield. In the ^1H NMR of **8**, the trans vinyl protons appear as two doublets (J = 12.9 Hz) at δ 12.97 and 2.81 while the trimethylsilyl group appears as a singlet at δ 0.29. Compound **8** is the first diiron complex we have synthesized with a silyl group on the μ-alkenyl ligand.

μ-Methylidyne complex **1** reacts rapidly with diazomethane in CH_2Cl_2 at −78 °C. Recrystallization of the reaction mixture from CH_2Cl_2–diethyl ether led to the isolation of the known μ-vinyl complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CH_2)^+PF_6^-$ (**3**)[4] in 42% yield contaminated with 5% of $[(C_5H_5)Fe(CO)_3]^+PF_6^-$. Similarly, reaction of **1** with diazoethane gave a 43% yield of μ-alkenyl complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHCH_3)^+PF_6^-$ (**9**).[5]

The formation of μ-alkenyl complexes from the reaction of μ-methylidyne complex **1** with diazo compounds can be rationalized as shown in Scheme I. Nucleophilic attack of the diazo carbon at the methylidyne center is proposed to lead to intermediate B. The μ-methylidyne complex **1** is readily attacked by nucleophiles such as CO, NMe_3, and

---

(4) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911–918.

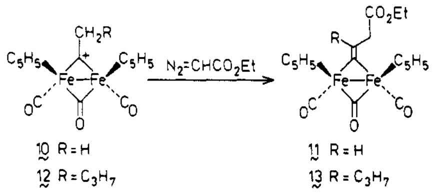
(5) Casey, C. P.; Marder, S. R.; Adams, B. R. *J. Am. Chem. Soc.* **1985**, *107*, 7700–7705.

(6) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Colborn, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 4053–4059.

tert-butyl isocyanide to form stable 1:1 adducts.[1,7] Iron-assisted loss of dinitrogen from B leads directly to μ-alkenyl complexes. Electron donation from iron was suggested in the formation of μ-alkenyl complexes via rearrangement of an intermediate carbocation formed from reaction of 1 with some alkenes.[6]

The reaction of diazo compounds with 1 provides a new route to μ-alkenyl compounds. Other routes to diiron μ-alkenyl complexes include thermal rearrangement of μ-alkylidyne complexes,[5] electrophilic addition of 1 to selected alkenes,[6] and hydride abstraction from μ-alkylidene complexes.[4,8]

Reaction of Other μ-Alkylidyne Complexes with Diazo Compounds. Alkyl- and aryl-substituted μ-alkylidyne complexes failed to react with diazo compounds to produce μ-alkenyl complexes. For example, the μ-ethylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_3)^+BF_4^-$ (**10**) failed to react with excess ethyl diazoacetate at room temperature. When the reaction mixture was refluxed in CH_2Cl_2 for a day, most of **10** was destroyed and chromatography of the reaction mixture led to the isolation of the ester-substituted μ-alkenylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2CO_2Et)$ (**11**).

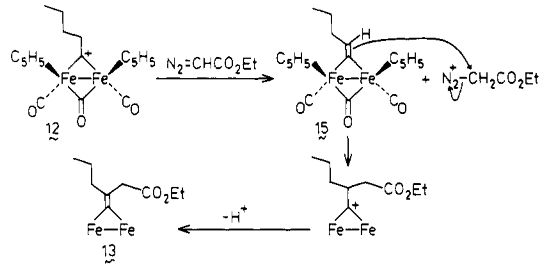


Similarly, when a solution of μ-pentylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_2CH_2CH_3)^+PF_6^-$ (**12**) and ethyl diazoacetate in CH_2Cl_2 was refluxed for 3 h, ^1H NMR showed that all the starting μ-pentylidyne complex **12** was destroyed. The μ-alkenylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_2CH_2CH_3)CH_2CO_2Et)$ (**13**) was isolated in 10% yield by chromatography. The *p*-tolyl-substituted μ-alkylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C\text{-}C_6H_4\text{-}p\text{-}CH_3)^+BF_4^-$ (**14**) survived 5-h refluxing with ethyl diazoacetate in CH_2Cl_2. Neither **14** nor μ-propylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_3)^+PF_6^-$ (**18**) reacted with solutions of diazomethane.

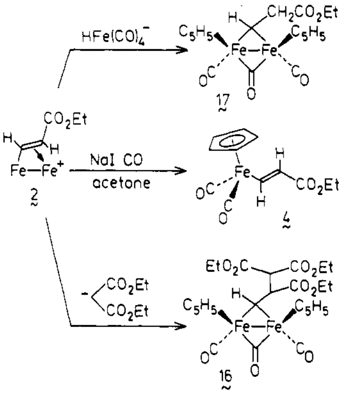
The failure of these substituted μ-alkylidyne complexes to react with diazo compounds is probably due to steric hinderance by the substituent on the μ-alkylidyne carbon. While μ-methylidyne complex 1 reacts readily with CO,[1] alkenes,[2] RLi,[9] and RMgBr[9] to form new carbon–carbon bonds, it is very difficult to prepare $\mu\text{-}CR_2$ complexes. We have succeeded in making $\mu\text{-}CR_2$ complexes only by the addition of $Li(CH_3CuCN)$ to 10[7] and 14[10] to give μ-alkylidene complexes $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C(CH_3)_2)$ in 20% yield and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C(CH_3)C_6H_4\text{-}p\text{-}CH_3)$ in 62% yield.

The reaction of μ-alkylidyne complexes such as 12 with ethyl diazoacetate which produces low yields of ester-substituted μ-alkenylidene complexes such as 13 can be explained as shown in Scheme II. Proton transfer from the μ-pentylidyne complex to ethyl diazoacetate would produce μ-pentenylidene complex 15 and protonated diazo ester. The μ-pentylidyne complex 12 is approximately as acidic as trifluoroacetic acid as established by studying the equilibrium between 12 and 15 in the presence of trifluoroacetic acid.[11] The electron-rich double bond of pentenylidene complex 15 is then proposed to nucleophilically displace dinitrogen from the protonated diazo ester. Related electrophilic attacks on the double bond of μ-alkenylidene complexes have been observed in the reactions of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ with $Ph_3C^+PF_6^-$,[9] and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)_2)$ (**22**) with $Me_3O^+BF_4^-$[7] and in the condensation of aldehydes with diiron μ-alkylidyne complexes.[12]

Scheme II



Reaction of Ester-Substituted μ-Alkenyl Complex 2 with Nucleophiles. The addition of nucleophiles to the β-carbon of the bridging alkenyl complex 2 proved to be a facile, high-yield route to new bridging carbene complexes. Reaction of lithium diethyl malonate with 2 led to the formation of the triester-substituted bridging carbene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH(CO_2Et)CH(CO_2Et)_2)$ (**16**) in 97% yield. In the 500-MHz ^1H NMR of **16**, three distinct AB quartets for the diastereotopic methylene protons of the three different ester groups were observed at δ 4.26, 4.22, and 4.17. Hydride addition to 2 from NEt_4^+ $[HFe(CO)_4]^-$ produced the neutral diiron carbene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_2CO_2Et)$ (**17**) in 85% yield. In these reactions, the regiochemistry of nucleophilic addition to the complexed double bond is clearly controlled by the diiron moiety and not by the ester function.



Previously, we have shown that cationic diiron μ-alkenyl complexes can be converted to neutral monoiron vinyl compounds by treatment with NaI and CO in acetone.[13] These conditions worked well in the case of the ester-substituted μ-alkenyl complex 2 and led to the formation of the monoiron vinyl compound $(C_5H_5)Fe(CO)_2$(*trans*-$CH{=}CHCO_2Et$) (**4**) in 66% yield along with $(C_5H_5)Fe(CO)_2I$.

Reaction of μ-Vinyl Complex 3 with Diazomethane. μ-Methylidyne complex 1 reacted readily with diazomethane to give μ-vinyl complex 3. When 1.5 equiv of

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[7] Casey, C. P.; Crocker, M., unpublished results.

[8] Casey, C. P.; Roddick, D. M. *Organometallics* **1986**, *5*, 436–438.

[9] Marder, S. R. Ph.D. Dissertation, University of Wisconsin—Madison, 1985.

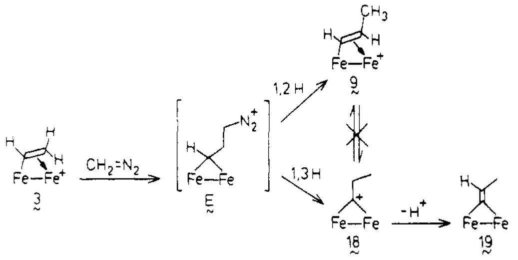
[10] Casey, C. P.; Vosejpka, P. C., unpublished results.

[11] Casey, C. P.; Austin, E. A., unpublished results.

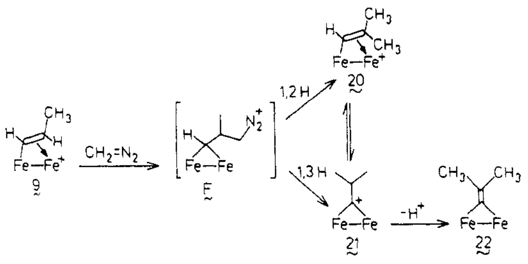
[12] Casey, C. P.; Konings, M. S.; Palermo, R. E.; Colborn, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 5296–5297.

[13] Casey, C. P.; Marder, S. R.; Colborn, R. E.; Goodson, P. A. *Organometallics* **1986**, *5*, 199–203.

Scheme III



Scheme IV



diazomethane were used in the reaction with 1, only μ-vinyl complex 3 was observed by ^{1}H NMR. However since we found that some nucleophiles add to the μ-CH=CHR group of μ-alkenyl complexes 2 and 3,[4,5,10] we decided to investigate whether nucleophilic addition of diazomethane to 3 might occur.

The μ-vinyl complex 3 was treated with 10 equiv of diazomethane in CH_2Cl_2 at 0 °C. The reaction mixture was filtered and concentrated. Diethyl ether was added which led to the precipitation of a mixture of the cationic μ-alkenyl compound $[(C_5H_5)(CO)Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHCH_3)^+PF_6^-$ (**9**) (31% yield) and starting material **3** (31% recovery). Workup of the filtrate gave a mixture of the neutral μ-alkenylidene compounds $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_3)$ (**19**)[3] (16% yield) and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)_2)$ (**22**)[14] (16% yield). When μ-vinyl complex **3** was treated with a huge excess of diazomethane (40 equiv) in CH_2Cl_2 at room temperature, ^{1}H NMR showed that **3** had been destroyed and no cationic products remained. Chromatography of the crude material on alumina led to the isolation of the μ-alkenylidene complexes **19** (19%), **22** (6%), and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CH_2CH_3)$ (**24**)[15] (19%).

The formation of the one-carbon addition compounds **9** and **19** can be rationalized as shown in Scheme III. Initial nucleophilic attack of diazomethane on μ-vinyl complex **3** is suggested to generate the intermediate diazonium ion E, which then decomposes via two routes. A 1,2 hydrogen shift converts E to μ-alkenyl complex **9** while a 1,3 hydrogen shift yields μ-alkylidyne complex **18** which is subsequently deprotonated to give μ-alkenylidene complex **19**. Since cations **9** and **18** do not interconvcert at the temperature of this reaction,[5] the occurrence of both 1,2 and 1,3 hydride shifts is required to explain the formation of **9** and **18**. We have previously observed related 1,2 hydride shifts in the reaction of alkenes with **1** that lead directly to μ-alkenyl complexes.[6] The hydrocarbation reaction involves a net 1,3 hydride shift similar to that proposed here.[3]

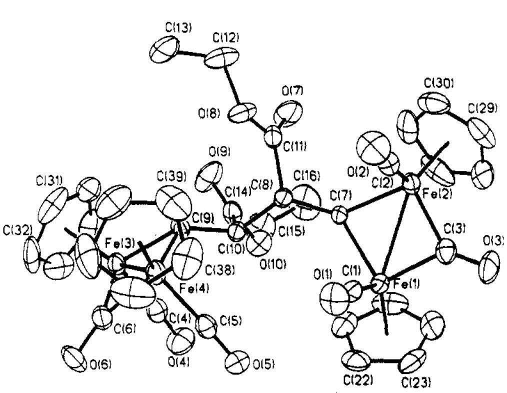
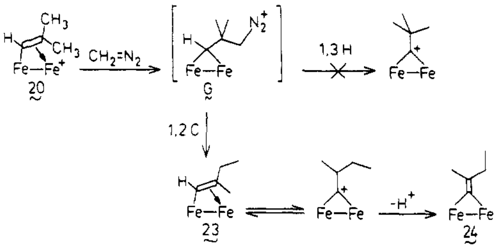


Figure 1. ORTEP of **25**.

Scheme V

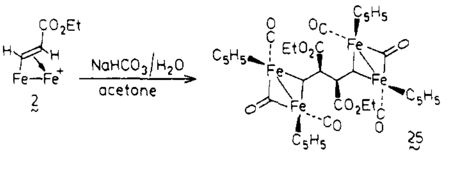


The formation of μ-alkenylidene complex **22**, which contains two additional carbon atoms, is suggested to arise by nucleophilic addition of diazomethane to μ-alkenyl complex **9**, which generates the diazonium intermediate F (Scheme IV). A 1,2 or 1,3 hydrogen shift converts F to μ-alkenyl complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C(CH_3)_2)^+PF_6^-$ (**20**) or μ-alkylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH(CH_3)_2)^+PF_6^-$ (**21**), respectively. These two complexes readily equilibrate by a 1,2 hydride shift.[14] Deprotonation of μ-alkylidyne complex **21** would produce the observed μ-alkenylidene **22**.

The formation of μ-alkenylidene complex **24**, which contains three new carbon atoms, can be rationalized as shown in Scheme V. A third intermediate diazonium ion G could result from the reaction of μ-alkenyl complex **20** with diazomethane. Decomposition of G via a 1,2 carbon shift leads to μ-alkenyl complex **23** which is in rapid equilibrium with μ-alkylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C\text{-}CH(CH_3)CH_2CH_3)^+PF_6^-$.[15] Deprotonation of this μ-alkylidyne complex would produce μ-alkenylidene product **24**.

The reaction of μ-vinyl complex **3** with diazomethane produces a number of neutral and cationic products. In each case, we believe the reaction begins by initial nucleophilic attack of diazomethane on the β-carbon of a μ-alkenyl complex. The large excess of diazo compound required to completely destroy starting μ-vinyl complex **3** clearly shows how unreactive this compound is toward diazomethane compared to μ-methylidyne complex **1**.

Reductive Dimerization of Ester-Substituted μ-Alkenyl Complex 2. A very unusual reductive dimerization of ester-substituted μ-alkenyl complex **2** occurred upon treatment with aqueous bicarbonate in acetone. A single diastereomer of the tetrairon carbene complex $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCHCO_2Et)\}_2$ (**25**) was isolated in 60% yield following chromatography on alumina. The ^{1}H NMR **25** in acetone-d_6 showed a distinctive AA′XX′ pattern at δ 11.57 and 4.46 for the four protons along the carbon chain connecting the diiron units.



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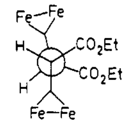
[14] Hoel, E. L. *Organometallics* **1986**, *5*, 587–588.

[15] Casey, C. P.; Meszaros, M. W.; Marder, S. R.; Bly, R. K.; Fagan, P. J. *Organometallics* **1986**, *5*, 1873–1879.

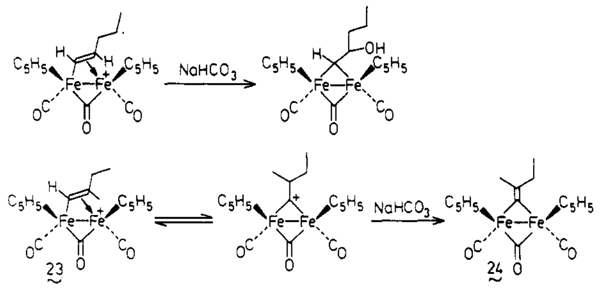
Table I. Selected Bond Distances and Angles for $\langle[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCHCO_2Et)\rangle_2$

	(a) Bond Distances (Å)		
Fe(1)-Fe(2)	2.533 (1)	C(10)-C(8)	1.577 (6)
Fe(3)-Fe(4)	2.531 (1)	C(7)-C(8)	1.542 (6)
Fe(1)-C(1)	1.759 (5)	C(9)-C(10)	1.539 (6)
Fe(2)-C(2)	1.750 (6)	C(8)-C(11)	1.524 (7)
Fe(3)-C(4)	1.745 (6)	C(10)-C(14)	1.525 (6)
Fe(4)-C(5)	1.743 (6)	C(11)-O(7)	1.201 (7)
Fe(1)-C(3)	1.943 (5)	C(14)-O(9)	1.191 (7)
Fe(2)-C(3)	1.912 (5)	C(11)-O(8)	1.383 (7)
Fe(3)-C(6)	1.906 (5)	C(14)-O(10)	1.349 (7)
Fe(4)-C(6)	1.928 (5)	O(8)-C(12)	1.454 (9)
Fe(1)-C(7)	1.988 (5)	O(10)-C(15)	1.450 (7)
Fe(2)-C(7)	1.984 (4)	C(12)-C(13)	1.462 (11)
Fe(3)-C(9)	1.983 (4)	C(15)-C(16)	1.450 (7)
Fe(4)-C(9)	1.977 (4)		
	(b) Bond Angles (deg)		
Fe(1)-C(1)-O(1)	176.3 (4)	C(7)-C(8)-C(11)	110.5 (4)
Fe(2)-C(2)-O(2)	177.8 (4)	C(9)-C(10)-C(14)	109.8 (3)
Fe(3)-C(4)-O(4)	178.1 (4)	C(7)-C(8)-C(10)	111.9 (4)
Fe(4)-C(5)-O(5)	176.2 (4)	C(9)-C(10)-C(8)	113.5 (4)
Fe(1)-C(3)-O(3)	137.6 (4)	C(10)-C(8)-C(11)	109.0 (3)
Fe(2)-C(3)-O(3)	140.1 (4)	C(8)-C(10)-C(14)	109.7 (4)
Fe(3)-C(6)-O(6)	138.8 (4)	C(8)-C(11)-O(7)	125.3 (6)
Fe(4)-C(6)-O(6)	138.6 (4)	C(10)-C(14)-O(9)	124.8 (5)
Fe(1)-C(7)-C(8)	123.3 (3)	C(8)-C(11)-O(8)	111.6 (4)
Fe(2)-C(7)-C(8)	124.3 (3)	C(10)-C(14)-O(10)	111.8 (4)
Fe(3)-C(9)-C(10)	123.2 (3)	O(7)-C(11)-O(8)	123.0 (6)
Fe(4)-C(9)-C(10)	123.7 (3)	O(9)-C(14)-O(10)	123.4 (5)
Fe(1)-C(3)-Fe(2)	82.2 (2)	C(11)-O(8)-C(12)	116.7 (5)
Fe(3)-C(6)-Fe(4)	82.6 (2)	C(14)-O(10)-C(15)	117.1 (5)
Fe(1)-C(7)-Fe(2)	79.3 (1)	O(8)-C(12)-C(13)	108.0 (6)
Fe(3)-C(9)-Fe(4)	79.5 (2)	O(10)-C(15)-C(16)	112.1 (5)

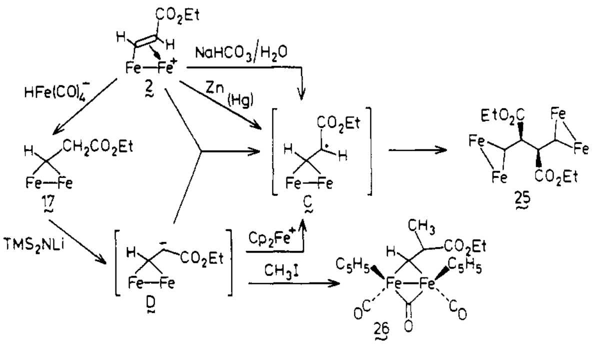
The structure of **25** was established by X-ray crystallography (Figure 1, Table I).[16] A Newman projection down the central carbon–carbon bond formed in the dimerization shows the anti relationship between the two large CFe_2 groups (166° dihedral angle) and the gauche relationship between the two ester groups. The dihedral angle between the large CFe_2 groups and the medium-sized ester units is expanded to 72° at the expense of compression of the dihedral angle between the ester units to 51°.



This reductive dimerization was completely unexpected. We had anticipated either nucleophilic addition of hydroxide as we had seen in the reaction of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHCH_2CH_2CH_3)^+PF_6^-$ or rearrangement to a μ-alkylidyne complex followed by deprotonation as we had seen in the case of the reaction of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C(CH_3)CH_2CH_3)^+PF_6^-$ (**23**)[17] with $NaHCO_3$.



The reductive dimerization of **2** to **25** occurs in the apparent absence of any reducing agent. However, addition of hydroxide to the μ-alkenyl group or a carbonyl of the cationic complex **2** could generate a neutral diiron complex that could serve as a reducing agent. Electron transfer to **2** from this putative reducing agent would generate a radical species C that could dimerize to produce **25**.



In support of this hypothesis, several attempts to generate radical C have led to formation of dimer **25**. Treatment of **2** in THF at −78 °C with 0.6% Zn–Hg amalgam gave tetrairon compound **25** in 39% yield. The diiron carbene complex **17** was deprotonated with lithium hexamethyldisilazide to give a solution of the anion $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCHCO_2Et)^-Li^+$ (D). This anionic iron complex was characterized by quenching with excess CH_3I which gave the methylated carbene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH(CH_3)CO_2Et)$ (**26**) in 83% yield. When the anion was oxidized with $[(C_5H_5)_2Fe]^+BF_4^-$ in THF, the tetrairon compound **25** was isolated in 72% yield. The best yield of **25** (92%) came from the direct reaction of anion D with cationic complex **2**. All three of these reactions can be explained by generation and dimerization of radical C.

The reductive dimerization of **2** to **25** is certainly not a general reaction. Even the ester-substituted μ-alkenyl complex **6** which differs from **2** only by a methyl substituent failed to produce a tetrairon complex upon treatment with aqueous sodium bicarbonate; only products from the normal decomposition of **6** in acetone were observed.

Experimental Section

General Data. ^1H NMR were obtained on a Brucker WP200, WP270, or AM500 spectrometer. ^{13}C NMR were obtained on JEOL FX-200 (50.1 MHz) or Brucker AM500 (126 MHz) spectrometers using 0.07 M $Cr(acac)_3$ as a shiftless relaxation agent. Infrared spectra were measured on a Beckman 4230 infrared spectrometer. Mass spectra were determined on a Kratos MS-80.

Air-sensitive materials were manipulated in an inert-atmosphere glovebox or by standard high-vacuum and Schlenk techniques. Diethyl ether, THF, and hexane were distilled from purple solutions of sodium and benzophenone. CH_2Cl_2 and acetone were dried over P_2O_5 and B_2O_3, respectively.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHCO_2Et)^+PF_6^-$ (2). Ethyl diazoacetate (80 μL, 86.8 mg, 0.76 mmol) was added to a slurry of **1** (210 mg, 0.43 mmol) in CH_2Cl_2 (30 mL) at −78 °C. The cold bath was removed, and the solution was stirred until bubble formation had ceased (15–20 min). The solution was cooled to −78 °C, and diethyl ether (30 mL) was added. The resulting deep red solid was isolated by filtration, washed with diethyl ether (2 × 4 mL), and dried under high vacuum to give **2** (213 mg, 86%): ^1H NMR (acetone-d_6, −72 °C, 270 MHz) δ 12.90 (d, J = 11.6 Hz, μ-CH=), 6.07 (s, C_5H_5), 5.60 (s, C_5H_5), 4.19 (m, CH_2), 3.16 (d, J = 11.6 Hz, μ-CH=C*H*), 1.23 (t, J = 7.2 Hz, CH_3); ^{13}C NMR

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[16] We originally reported (Casey, C. P.; Austin, E. A. *Abstracts of Papers*, 190th National Meeting of the American Chemical Society, Chicago, IL; American Chemical Society: Washington, DC, 1985; INOR 394.) an incorrect structure for **25** which contained an additional oxygen atom.

[17] Casey, C. P.; Fagan, P. J.; Miles, W. H.; Marder, S. R. *J. Mol. Catal* **1983**, *21*, 173–188.

(acetone-d_6, −68 °C, 50.1 MHz, 0.07 M Cr(acac)$_3$) δ 237.2 (μ-CO), 213.4 (CO), 207.7 (CO), 185.7 (d, *J* = 165 Hz, μ-CH=), 169.8 (CO$_2$), 93.5 (d, *J* = 186 Hz, C_5H_5), 90.1 (d, *J* = 183 Hz, C_5H_5), 67.5 (d, *J* = 164 Hz, μ-CH=*C*H), 62.1 (t, *J* = 150 Hz, CH$_2$), 14.2 (q, *J* = 126 Hz, CH$_3$); IR (Nujol) 2030 (s), 2013 (s), 1883 (s), 1724 (s) cm^{-1}.

Anal. Calcd for $C_{18}H_{17}F_6Fe_2O_5P$: C, 37.93; H, 3.01. Found: C, 37.81; H, 3.15.

$(C_5H_5)(CO)_2Fe(CH{=}CHCO_2Et)$ (4). **2** (100 mg, 0.18 mmol) and NaI (43 mg, 0.29 mmol) were stirred in acetone (25 mL) under a CO (0.65 atm) atmosphere for 10 min at −78 °C and then 90 min at room temperature. Solvent was evaporated under vacuum, and diethyl ether (20 mL) was added. Filtration, evaporation of solvent, and flash chromatography (alumina, 2:5 diethyl ether/hexane) gave green CpFe(CO)$_2$I (40 mg, 73%) identified by ^{1}H NMR and IR and the yellow oil 4 (33 mg, 66%). For **4**: ^{1}H NMR (acetone-d_6, 200 MHz) δ 9.14 (d, *J* = 16.4 Hz, μ-CH=), 6.11 (d, *J* = 16.4 Hz, μ-CH=C*H*), 5.17 (s, C_5H_5), 4.03 (q, *J* = 7.2 Hz, CH$_2$), 1.19 (t, *J* = 7.2 Hz, CH$_3$); ^{13}C NMR (acetone-d_6, 126 MHz, 0.07 *M* Cr(acac)$_3$) δ 215.8 (CO), 170.3 (d, *J* = 145 Hz, μ-CH=), 162.2 (CO$_2$), 134.9 (d, *J* = 161 Hz, μ-CH=*C*H), 87.4 (d, *J* = 181 Hz, C_5H_5), 59.3 (t, *J* = 146 Hz, CH$_2$), 14.8 (q, *J* = 125 Hz, CH$_3$); IR (CH$_2$Cl$_2$) 2028 (s), 1982 (vs), 1711 (s), 1554 (m) cm^{-1}; HRMS calcd for $C_{12}H_{12}O_4Fe$ 276.0085, found 276.0080.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCO_2Et)$ (5). Flash chromatography (alumina, 1:1 CH$_2$Cl$_2$/hexane) of the products from the decomposition of **2** in acetone gave a small amount of **5**: ^{1}H NMR (acetone-d_6, 200 MHz) δ 7.79 (s, =CH), 5.09 (s, C_5H_5), 5.04 (s, C_5H_5), 4.17 (dq, *J* = 7.0, 12.3 Hz, CH$_2$), 1.30 (t, *J* = 7.0 Hz, CH$_3$); ^{13}C NMR (acetone-d_6, 126 MHz, 0.07 M Cr(acac)$_3$) δ 304.5 (μ-C), 267.4 (μ-CO), 211.9 (CO), 211.7 (CO), 164.0 (CO$_2$), 133.3 (d, *J* = 163 Hz, =CH—), 89.9 (d, *J* = 181 Hz, C_5H_5), 89.4 (d, *J* = 183 Hz, C_5H_5), 59.1 (coupling not resolved, CH$_2$), 15.0 (q, *J* = 127 Hz, CH$_3$); IR (CH$_2$Cl$_2$) 1998 (s), 1970 (m), 1802 (m) cm^{-1}; HRMS calcd for $C_{18}H_{16}O_5Fe_2$ 423.9697, found 423.9697.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C(CH_3)CO_2CH_3)^+PF_6^-$ (6E and 6Z). Methyl 2-diazopropionate[18] (45 μL, 0.43 mmol) was added to a slurry of **1** (206 mg, 0.43 mmol) in CH$_2$Cl$_2$ (25 mL) at −78 °C. The solution was stirred without a cold bath until bubble formation ceased (15 min). Solvent volume was reduced by 8 mL, and diethyl ether (30 mL) was added at −78 °C. The resulting solid was isolated by filtration, washed with diethyl ether (5 × 3 mL), and dried under high vacuum. Recrystallization from CH$_2$Cl$_2$/diethyl ether gave **6** (162 mg, 66%): ^{1}H NMR (acetone-d_6, −65 °C, 270 MHz) major isomer, δ 14.51 (s, μ-CH), 5.50 (s, C_5H_5), 5.34 (s, C_5H_5), 3.30 (s, OCH$_3$), 1.85 (s, CH$_3$), minor isomer, δ 12.93 (s, μ-CH), 5.80 (s, C_5H_5), 5.17 (s, C_5H_5), 3.54 (s, OCH$_3$), 2.90 s, (CH$_3$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −70 °C, 126 MHz, 0.07 M Cr(acac)$_3$) δ 235.2 (μ-CO), 211.9 (CO), 203.8 (CO), 184.1 (μ-CH=), 171.8 (CO$_2$), 92.0 (C_5H_5), 90.4 (μ-CH=*C*), 87.8 (C_5H_5), 52.4 (CH$_3$), 31.3 (CH$_3$); IR (CH$_2$Cl$_2$) 2069 (m), 2020 (s), 1870 (m) cm^{-1}.

Anal. Calcd for $C_{18}H_{17}F_6Fe_2O_5P$: C, 37.93; H, 3.01. Found: C, 37.83; H, 3.15.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CO_2CH_3)$ (7). A solution of **6E** and **6Z** in CH$_2$Cl$_2$ (25 mL) was prepared from **1** (200 mg, 0.41 mmol) and methyl 2-diazopropionate (50 μL, 0.48 mmol), N(CH$_3$)$_3$ (0.072 atm, 530 mL, 17 mmol) was added at −78 °C, and the solution was warmed to room temperature. Solvent was evaporated under high vacuum, diethyl ether (25 mL) was added, and the solution was filtered. Flash chromatography (alumina, 1:1 hexane/CH$_2$Cl$_2$) and trituration with pentane gave red solid **7** (69 mg, 40%): mp (open capillary) 155–157 °C dec; ^{1}H NMR (acetone-d_6, 270 MHz) δ 5.09 (s, C_5H_5), 5.03 (s, C_5H_5), 3.74 (s, CH$_3$), 2.68 (s, CH$_3$); ^{13}C NMR (acetone-d_6, 126 MHz, 0.07 M Cr(acac)$_3$) δ 295.2 (μ-C), 268.4 (μ-CO), 212.2 (CO), 212.1 (CO), 166.2 (CO$_2$), 137.7 (=C), 89.9 (d, *J* = 179 Hz, C_5H_5), 88.8 (d, *J* = 176 Hz, C_5H_5), 51.0 (q, *J* = 146 Hz, CO$_2$*C*H$_3$), 25.2 (q, *J* = 130 Hz, CH$_3$); IR (CH$_2$Cl$_2$) 2006 (s), 1974 (m), 1800 (s) cm^{-1}; HRMS calcd for M–CO, $C_{17}H_{16}O_4Fe_2$, 395.9747, found 395.9719.

Reaction of 1 with Diazomethane. A dry solution of diazomethane[19] (2.0 mL, 0.26 M, 0.52 mmol) in CH$_2$Cl$_2$ at −78 °C was added via pipet to a slurry of **1** (210 mg, 0.43 mmol) in CH$_2$Cl$_2$ (25 mL) at −78 °C. The solution was stirred for 30 min at −78 °C and then allowed to warm to room temperature. Gas formation began within 5 min at −78 °C. Solvent was evaporated under vacuum, and the residue was recrystallized from CH$_2$Cl$_2$/diethyl ether to give brown solid **3**[5] (98 mg, 42%) contaminated with 5% of $[(C_5H_5)Fe(CO)_3]^+PF_6^-$: ^{1}H NMR (acetone-$d_6$, 270 MHz) δ 12.70 (m, μ-CH=), 5.83 (s, C_5H_5), 5.62 (s, C_5H_5), 5.19 (d, J_{cis} = 7.4 Hz, =CH$_2$), 3.01 (d, J_{trans} = 13.2 Hz, =CH$_2$).

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHSi(CH_3)_3)^+PF_6^-$ (8). A dry, degassed solution of (trimethylsilyl)diazomethane (1.0 mL, 10% in hexane, 0.58 mmol) was added to a solution of **1** (210 mg, 0.43 mmol) in CH$_2$Cl$_2$ (45 mL) at −78 °C, and the solution was stirred at 0 °C for 30 min. The solution was filtered, solvent volume was reduced to 10 mL by evaporation, and diethyl ether (25 mL) and hexane (10 mL) were added. The resulting black solid was isolated by filtration, washed with diethyl ether (3 × 3 mL), and dried under high vacuum to give **8** (118 mg, 49%): ^{1}H NMR (acetone-d_6, −68 °C, 270 MHz) δ 12.97 (d, *J* = 12.9 Hz, μ-CH=), 5.90 (s, C_5H_5), 5.68 (s, C_5H_5), 2.81 (d, *J* = 12.9 Hz, μ-CH=C*H*), 0.29 (s, (CH$_3$)$_3$); ^{13}C{^{1}H} NMR (acetone-d_6, −50 °C, 126 MHz, 0.07 M Cr(acac)$_3$) δ 241.1 (μ-CO), 214.6 (CO), 208.3 (CO), 190.4 (μ-CH=), 92.8 (C_5H_5), 88.2 (C_5H_5), 80.9 (μ-CH=*C*H), −1.2 (Si(*C*H$_3$)$_3$); IR (CH$_2$Cl$_2$) 2033 (s), 2010 (m), 1867 (m) cm^{-1}.

Anal. Calcd for $C_{18}H_{21}F_6Fe_2O_3PSi$: C, 37.92; H, 3.71. Found: C, 37.97; H, 3.83.

Reaction of 1 with Diazoethane. A dry solution of diazoethane[19] (6 mL, 0.27 M, 1.6 mmol) in CH$_2$Cl$_2$ at −78 °C was added via pipet to a slurry of **1** (260 mg, 0.54 mmol) in CH$_2$Cl$_2$ (30 mL) at −78 °C, and the solution was warmed to room temperature. Solvent was evaporated under vacuum, and the residue was recrystallized from CH$_2$Cl$_2$/diethyl ether to give $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHCH_3)^+PF_6^-$ (**9**)[5,20] (116 mg, 43%): ^{1}H NMR (acetone-d_6, 270 MHz) δ 12.02 (d, *J* = 10.6 Hz, μ-CH=), 5.66 (s, C_5H_5), 3.86 (m, μ-CH=C*H*–), 2.13 (d, *J* = 6.0 Hz, CH$_3$).

Reaction of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_2CH_2CH_3)^+PF_6^-$ (12) with Ethyl Diazoacetate. **12** (300 mg 0.56 mmol) and ethyl diazoacetate (300 μL, 2.8 mmol) in CH$_2$Cl$_2$ (25 mL) were refluxed for 2 h. Additional diazo ester (140 μL, 1.3 mmol) was added and the solution refluxed an additional 30 min. Flash chromatography (alumina, 3:2 hexane/diethyl ether) followed by preparative TLC (silica gel, 2:1 diethyl ether/hexane) gave $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_2CH_2CH_3)CH_2CO_2CH_2CH_3)$ (**13**) (34 mg, 82% pure, 10% yield) as a red solid. Further purification by preparative TLC gave a small amount of pure **13** for characterization: ^{1}H NMR (acetone-d_6 200 MHz) δ 5.04 (s, C_5H_5), 4.98 (s, C_5H_5), 4.19 (q, *J* = 7.1 Hz, OCH$_2$), 3.86 (d, J_{AB} = 14.6 Hz, CH*H*), 3.65 (d, J_{AB} = 14.6 Hz, C*H*H), 2.91 (m,CH$_2$), 1.68 (m, CH$_2$), 1.28 (t, *J* = 7.1 Hz, CH$_3$), 0.98 (t, *J* = 7.4 Hz, CH$_3$); ^{13}C {^{1}H} NMR (acetone-d_6, 50.1 MHz, 0.0 M Cr(acac)$_3$) δ 270.9 (μ-CO), 265.9 (μ-C), 213.0 (CO), 212.7 (CO), 173.8 (CO$_2$), 141.5 (μ-C=*C*), 88.5 (C_5H_5), 88.4 (C_5H_5), 60.6 (CO$_2$*C*H$_2$), 45.1 (*C*H$_2$CO$_2$) 43.4 (*C*H$_2$CH$_2$CH$_3$), 22.8 (CH$_2$*C*H$_2$CH$_3$), 14.6 (CO$_2$CH$_2$*C*H$_3$), 14.3 (CH$_3$); IR (CH$_2$Cl$_2$) 1993 (s), 1957 (m), 1787 (s), 1723 (m) cm^{-1}; HRMS calcd for M − 2CO, $C_{20}H_{24}O_3Fe_2$, 424.0417, found 424.0424.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CHCH(CO_2Et)CH(CO_2Et)_2)$ (16). **2** (220 mg, 0.39 mmol) in THF (45 mL) at −78 °C was added to a solution of lithium diethyl malonate (78 mg, 0.49 mmol) in THF (15 mL) at −78 °C. The solution was stirred at room temperature for 45 min. Evaporation of solvent and flash chromatography (alumina, 5% acetone in CH$_2$Cl$_2$) gave **16** (219 mg, 97%): mp (open capillary) 159–161 °C dec; ^{1}H NMR (acetone-d_6, 500 MHz) δ 11.07 (d, *J* = 12.2 Hz, μ-CH), 4.97 (s, C_5H_5), 4.82 (s, C_5H_5), 4.27 (dq, *J* = 7.1, 10.7 Hz, C*H*H), 4.26 (dq, *J* = 7.1, 10.8 Hz, C*H*H), 4.25 dq, *J* = 7.1, 10.9 Hz, C*H*H), 4.17 (dq, *J* = 7.1, 10.8 Hz, CH*H*), 4.11 (dq, *J* = 7.1, 10.9 Hz, CH*H*), 3.92 (dd, *J* = 6.2, 12.2 Hz, CHC*H*CH), 1.31 (t, *J* = 7.1 Hz, CH$_3$), 1.309 (t, *J* = 7.1 Hz, CH$_3$), 1.20 (t, *J* = 7.1 Hz, CH$_3$); ^{13}C{^{1}H} NMR (acetone-d_6, 126 MHz, 0.07 M Cr(acac)$_3$ δ 270.7 (μ-CO), 213.4 (CO), 212.9 (CO), 174.1 (CO$_2$), 168.7 (CO$_2$), 168.5 (CO$_2$), 164.6 (CH), 89.0 (C_5H_5), 88.7 (C_5H_5), 67.4 (CH), 61.8 (CH$_2$), 61.7 (CH$_2$), 60.8 (CH$_2$), 60.5 (CH), 14.4 (CH$_3$), 14.3 (CH$_3$), 14.2 (CH$_3$); IR (CH$_2$Cl$_2$) 1992 (s), 1951 (m), 1787 (m), 1731 (m) cm^{-1}; HRMS calcd for M − CO, $C_{24}H_{28}O_8Fe_2$, 556.0482, found 556.0482.

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Table II. Crystal Data for $\langle[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCHCO_2Et)\rangle_2$

	(a) Crystal Parameters		
formula	$C_{36}H_{34}Fe_4O_{10}$	V, Å^3	3455.5 (8)
cryst system	monoclinic	Z	4
space group	$P2_1/c$	temp, K	293
a, Å	12.318 (2)[a]	color	deep red
b, Å	16.443 (2)	size, mm	0.26 × 0.33 × 0.40
c, Å	17.679 (2)	μ, cm^{-1} (Mo Kα)	17.02
β, deg	105.20 (1)		
	(b) Data Collection		
diffractometer	Nicolet R3m/μ	scan speed, deg min^{-1}	var 4–20
radiation	Mo Kα	data collected	6547
wavelength, Å	0.71073	indepnt data, system. present	6093
monochromator	graphite		
scan technique	Wyckoff	obsd data ($3\sigma(F_o)$)	4432
scan limits, deg	$4 \le 2\theta \le 50$	R(int), %	1.76
std rflns	3 std/97 rflns	T_{max}/T_{min}	0.398/0.330
var in std rflns	+1% to −2%		
	(c) Structure Refinement		
$R(F)$, %	4.88	N_o/N_v	9.81
$R(wF)$, %	5.54	$\Delta(\rho)$, e Å^{-3}	0.44
GOF	1.095	Δ/σ, final	0.08

[a] Unit cell parameters from the angular settings of 25 reflections (21° ≤ 2θ ≤ 27°).

Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)

	x	y	z	u
Fe(1)	5581 (1)	7008 (1)	3482 (1)	34 (1)
Fe(2)	5210 (1)	7926 (1)	4538 (1)	38 (1)
Fe(3)	626 (1)	5639 (1)	1649 (1)	38 (1)
Fe(4)	1884 (1)	4943 (1)	2835 (1)	38 (1)
C(1)	5318 (4)	6073 (3)	3884 (3)	42 (2)
C(2)	4788 (4)	7198 (3)	5125 (3)	49 (2)
C(3)	6495 (4)	7279 (3)	4524 (3)	43 (2)
C(4)	1638 (4)	5865 (3)	1150 (3)	47 (2)
C(5)	3161 (4)	4990 (3)	2585 (3)	42 (2)
C(6)	1220 (4)	4563 (3)	1783 (3)	46 (2)
C(7)	4154 (4)	7522 (3)	3561 (3)	33 (2)
C(8)	3074 (4)	7037 (3)	3536 (3)	34 (2)
C(9)	1545 (4)	6111 (3)	2643 (3)	36 (2)
C(10)	2450 (4)	6766 (3)	2676 (3)	37 (2)
C(11)	2271 (4)	7540 (3)	3871 (3)	50 (2)
C(12)	780 (5)	7469 (4)	4482 (5)	86 (3)
C(13)	−108 (5)	6867 (6)	4432 (5)	129 (5)
C(14)	1923 (4)	7506 (3)	2199 (3)	44 (2)
C(15)	2227 (6)	8555 (4)	1342 (4)	83 (3)
C(16)	2789 (7)	9261 (4)	1759 (6)	117 (5)
O(1)	5210 (3)	5461 (2)	4154 (2)	63 (2)
O(2)	4542 (4)	6726 (3)	5529 (3)	75 (2)
O(3)	7398 (3)	7134 (3)	4915 (2)	64 (2)
O(4)	2294 (4)	5999 (3)	804 (2)	73 (2)
O(5)	4009 (3)	4978 (2)	2436 (3)	61 (2)
O(6)	1194 (3)	3964 (2)	1412 (2)	63 (2)
O(7)	2138 (4)	8262 (3)	3797 (3)	86 (2)
O(8)	1696 (3)	7079 (2)	4243 (2)	59 (2)
O(9)	1033 (3)	7789 (2)	2196 (3)	81 (2)
O(10)	2587 (3)	7806 (2)	1767 (2)	56 (1)
C(21)	5209 (5)	7125 (4)	2247 (3)	64 (2)
C(22)	5880 (5)	6452 (4)	2495 (3)	60 (2)
C(23)	6900 (5)	6709 (4)	2974 (4)	66 (3)
C(24)	6867 (5)	7529 (4)	3032 (4)	73 (3)
C(25)	5811 (7)	7793 (4)	2588 (4)	73 (3)
C(26)	4439 (6)	9088 (3)	4420 (5)	79 (3)
C(27)	5392 (9)	9121 (3)	4127 (4)	84 (4)
C(28)	6322 (6)	8932 (4)	4745 (6)	86 (4)
C(29)	5962 (7)	8784 (4)	5396 (4)	80 (3)
C(30)	4822 (6)	8879 (4)	5202 (4)	76 (3)
C(31)	−993 (5)	5541 (5)	1859 (4)	90 (3)
C(32)	−989 (5)	5134 (4)	1160 (7)	99 (4)
C(33)	−774 (5)	5717 (7)	649 (4)	91 (3)
C(34)	−628 (5)	6446 (4)	1058 (4)	76 (3)
C(35)	−791 (4)	6331 (4)	1764 (4)	69 (3)
C(36)	995 (8)	4023 (5)	3255 (4)	88 (3)
C(37)	2128 (7)	3848 (4)	3468 (4)	86 (3)
C(38)	2655 (6)	4482 (5)	3954 (4)	77 (3)
C(39)	1848 (7)	5029 (4)	4027 (4)	79 (3)
C(40)	831 (6)	4748 (4)	3591 (4)	82 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Anal. Calcd for $C_{25}H_{28}O_9Fe_2$: C, 51.40; H, 4.83. Found: C, 51.17; H, 4.96.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_2CO_2Et)$ (17). A solution of $NEt_4^+[HFe(CO)_4]^-$[21] (1.25 g, 4.2 mmol) in CH_2Cl_2 (20 mL) was added to freshly prepared **2** (from 1.00 g, 2.07 mmol of **1** and 250 μL, 2.4 mmol of diazo ester in 50 mL of CH_2Cl_2) at −78 °C. The solution was stirred at room temperature for 15 min. Solvent was removed under vacuum, and the resulting red solid was washed four times with diethyl ether and triturated with pentane to give **17** (750 mg, 85%): mp (open capillary) 107 °C dec; ^1H NMR (acetone-d_6, 200 MHz) δ 11.51 (t, J = 8.4 Hz, μ-CH), 4.87 (s, 10 H, C_5H_5), 4.22 (q, J = 7.0 Hz, OCH_2), 3.99 (d, J = 8.4 Hz, CH_2), 1.31 (t, J = 7.0 Hz, CH_3); $^{13}C\{^1H\}$ NMR (acetone-d_6, 50.1 MHz, 0.07 M $Cr(acac)_3$) δ 271.7 (μ-CO), 214.1 (CO), 173.4 (CO_2), 163.4 (μ-CH), 88.7 (C_5H_5), 60.7 (CH_2), 59.8 (CH_2), 15.1 (CH_3). IR (CH_2Cl_2) 1983 (s), 1943 (m), 1780 (s), 1725 (s) cm^{-1}; HRMS calcd for M − CO, $C_{17}H_{18}O_4Fe_2$, 397.9903, found 397.9898.

Anal. Calcd for $C_{18}H_{18}O_5Fe_2$: C, 50.75; H, 4.26. Found: C, 50.89; H, 4.04.

$\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCHCO_2Et)\}_2$ (25). Method A. **2** (80 mg, 0.14 mmol) was stirred in acetone (20 mL) at −78 °C. A deoxygenated solution of aqueous saturated $NaHCO_3$ (5 mL) was added, and the solution was stirred at room temperature for 40 min. Solvent was evaporated under vacuum, and the residue was dissolved in CH_2Cl_2. The resulting solution was filtered and evaporated to dryness. Flash chromatography (alumina, 3:1 CH_2Cl_2/hexane) gave red **25** (36 mg, 60%).

Method B. **2** (102 mg, 0.18 mmol) in THF (25 mL) was stirred over a 0.6% amalgam of Zn (39 mg, 0.60 mmol) in Hg (6.86 g) at 0 °C for 5 min. The solution was decanted via cannula and filtered. Evaporation of solvent and flash chromatography (alumina, 2:1 CH_2Cl_2/hexane) gave **25** (30 mg, 39%).

Method C. **17** (85 mg, 0.20 mmol) and lithium hexamethyldisilazide (42 mg, 0.25 mmol) were stirred in THF (50 mL) at −20 °C for 1 h and then cooled to −78 °C. A solution of **2** (102 mg, 0.18 mmol) in THF (20 mL) at −78 °C was added via cannula. The reaction mixture was stirred at room temperature for 1 h and filtered. Solvent was evaporated, and the residue was purified by chromatography (alumina, CH_2Cl_2) to give **25** (141 mg, 92%).

Method D. **17** (107 mg, 0.25 mmol) and lithium hexamethyldisilazide (49 mg, 0.29 mmol) in THF (40 mL) were stirred at −20 °C for 40 min and then cooled to −78 °C. A solution of $[(C_5H_5)_2Fe]^+BF_4^-$ (80 mg, 0.29 mmol) in THF (25 mL) at −78 °C was added via cannula, and the combined solutions were stirred at room temperature for 1 h. Workup as in method C gave **25** (77 mg, 72%): mp (open capillary) 185–187 °C dec; ^1H NMR (acetone-d_6, 500 MHz) δ 11.57 (XX′ of AA′XX′ system, J_{AX} = 12.3 Hz, $J_{AA'}$ = 2.7 Hz, μ-CH), 4.90 (s, C_5H_5), 4.88 (s, C_5H_5), 4.48 (dq, J = 7.1, 10.9 Hz, OC*H*H), 4.46 (AA′ of AA′XX′ system, μ-CHC*H*), 4.34 (dq, J = 7.1, 10.9 Hz, OCH*H*), 1.47 (t, J = 7.1 Hz, CH_3); ^{13}C NMR (acetone-d_6, 50.1 MHz, 0.07 M $Cr(acac)_3$) δ 271.8 (μ-CO), 213.8 (CO), 213.4 (CO), 173.8 (CO_2), 167.9 (d, J = 139 Hz, μ-CH), 89.2 (d, J = 176 Hz, C_5H_5), 88.9 (d, J = 184 Hz, C_5H_5), 76.9 (d, J = 136 Hz, CH), 60.6 (t, J = 146 Hz, CH_2), 14.9 (q, J = 124 Hz, CH_3); IR (CH_2Cl_2) 1982 (vs), 1946 (m), 1833 (m), 1779 (s), 1735 (m), 1716 (m) cm^{-1}.

Anal. Calcd for $C_{36}H_{34}O_{10}Fe_4$: C, 50.87; H; 4.03. Found: C, 50.60; H, 4.28.

Crystal Structure Determination of 25. An irregularly shaped crystal of **25**, obtained by slow evaporation of a pentane–CH_2Cl_2 solution at −20 °C, was mounted on a glass fiber and found unambiguously to belong to the monoclinic space group $P2_1/c$. Crystal, data collection, and refinement parameters are collected in Table II. Atomic coordinates and isotropic thermal

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[21] Cole, T. E.; Pettit, R. *Tetrahedron Lett.* **1977**, 781.

parameters are collected in Table III. Corrections to the intesity data for absorption were applied empirically (ψ scan method, seven reflections, 252 data, six-parameter pseudoellipsoid model).

The direct methods routine SOLV successfully located the four Fe atoms, and the structure was completed from subsequent different maps. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized, updated contributions (d(H–H) = 0.96 Å).

All software is contained in the P3 and SHELXTL libraries (Nicolet Corp., Madison, WI). Additional crystallographic data are available as supplementary material.

[$(C_5H_5)(CO)Fe]_2(\mu$-CO)(μ-CHCH(CH$_3$)CO$_2$Et) (26). 17 (102 mg, 0.24 mmol) and lithium hexamethyldisilazide (44 mg, 0.26 mmol) were stirred in THF (30 mL) at −20 °C for 45 min. The solution was cooled to −78 °C, and CH_3I (0.028 atm, 530 mL, 0.65 mmol) was added. The solution was stirred at room temperatue for 1 h, solvent was removed, and diethyl ether (20 mL) was added. Filtration, evaporation of solvent, and flash chromatography (alumina, 2:1 CH_2Cl_2/hexane) gave **26** (87 mg, 83%): mp (open capillary) 155–156 °C dec; ^1H NMR (acetone-d_6 270 MHz) δ 11.27 (d, J = 11.8 Hz, μ-CH), 4.93 (s, C_5H_5), 4.80 (s, C_5H_5), 4.22 (dq, J = 3.8, 7.1 Hz, C*H*H), 4.21 (dq, J = 3.8, 7.1 Hz, CH*H*), 3.39 (dq, J = 6.5, 11.8 Hz, CH), 1.70 (d, J = 6.5 Hz, CH_3), 1.30 (t, J = 7.1 Hz, CH_3), ^{13}C NMR (acetone-d_6, 126 MHz, 0.07 M Cr(acac)$_3$) δ 271.5 (μ-CO), 214.1 (CO), 213.2 (CO), 177.0 (CO_2), 173.4 (d, J = 131 Hz, μ-CH), 88.5 (d, J = 181 Hz, C_5H_5), 88.3 (d, J = 179 Hz, C_5H_5), 63.7 (d, J = 136 Hz, CH), 60.3 (t, J = 148 Hz, CH_2), 25.0 (q, J = 132 Hz, CH_3), 14.7 (q, J = 117 Hz, CH_3); IR (CH_2Cl_2) 1987 (s), 1944 (m), 1782 (s), 1716 (m) cm^{-1}; HRMS calcd for M − CO, $C_{18}H_{20}O_4Fe$, 412.0060, found 412.0047.

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Registry No. 1, 82660-14-8; 2, 109864-35-9; 3, 87858-04-6; 4, 109956-78-7; 5, 109864-36-0; 6E, 109864-38-2; 6Z, 109956-80-1; 7, 109864-39-3; 8, 109864-41-7; 9, 87711-26-0; 10, 67378-10-3; 11, 99326-81-5; 12, 87711-12-4; 13, 109864-33-7; 14, 109864-43-9; 16, 109864-44-0; 17, 109864-45-1; 18, 82621-29-2; 19, 99923-10-1; 22, 99923-12-3; 24, 87711-31-7; 25, 109889-33-0; 26, 109864-46-2; CpFe(CO)$_2$I, 12078-28-3; [$(C_5H_5)Fe(CO)_3]^+PF_6^-$, 38834-26-3; $Net_4^+[HFe(CO)_4]^-$, 25879-01-0; [$(C_5H_5)_2Fe]^+BF_4^-$, 1282-37-7; lithium diethyl malonate, 34727-00-9; ethyl diazoacetate, 623-73-4; methyl 2-diazopropionate, 34757-14-7; (trimethylsilyl)diazomethane, 18107-18-1; lithium hexamethyldisilazide, 4039-32-1.

Supplementary Material Available: Tables of bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates (5 pages); a structure factor table (calculated vs. observed) (27 pages). Ordering information is given on any current masthead page.

X-ray Crystal Structures of Bis(dichlorophenyltelluro)methane and Bis(trichlorotelluro)methane

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X-ray crystal structures are reported for bis(dichlorophenyltelluro)methane (1) [$(C_6H_5TeCl_2)_2CH_2$; monoclinic; space group $C2/c$; a = 24.90 (1) Å, b = 5.464 (2) Å, c = 18.158 (4) Å, β = 138.37 (3)°; Z = 4; R_F = 0.017 for 1176 observed reflections, T = −75 °C] and for bis(trichlorotelluro)methane (2) [$(TeCl_3)_2CH_2$; monoclinic; space group $P2_1/c$; a = 9.025 (3) Å, b = 6.677 (4) Å, c = 17.480 (4) Å, β = 106.16 (2)°; Z = 4; R_F = 0.042 for 2042 observed reflections, T = −74 °C]. The Te–CH$_2$–Te linkage in these compounds favors intramolecular Te–Cl–Te bridging interactions, resulting in unimolecular rather than oligomeric structures. In 1 the CH$_2$ bridge is supported by a pair of asymmetric Te···Cl–Te contacts involving one of the two chlorine atoms on each Te atom. For 2, the interactions are stronger to the point of becoming a nearly symmetrical triple bridge. The unusual ^{125}Te quadrupole couplings, previously reported for these compounds, are attributed to the constraints imposed by these bridging systems.

Introduction

The large number of crystallographic structural studies of R_2TeX_2 and $RTeX_3$ compounds, where X is a halogen, have demonstrated the stereochemical preferences of Te(IV) in such systems. In the solid state, R_2TeX_2 molecules usually adopt the distorted ψ-trigonal-bipyramidal geometry predicted by VSEPR.[1] The halogen atoms occupy the axial positions while the organic groups and the nonbonding pair of electrons occupy the equatorial positions. These molecules are weakly interconnected by secondary bonds[2] between tellurium and halogen atoms of neighboring molecules.

The $RTeX_3$ compounds, in contrast, associate in the solid state through the formation of symmetrical Te–X–Te bridges to form dimers or polymers. Each Te atom is in an irregular square-pyramidal environment in which two terminal halogen atoms and two bridging halogen atoms occupy the basal plane. The apical organic group is presumably trans to the nonbonding pair of electrons while each terminal halogen is trans to one of the bridging halogen atoms.

The preferred stereochemistry in these compounds may be altered in a variety of ways. For example, where the organic groups of an R_2TeX_2 species are replaced by a single bidendate group,[3-10] this may place a restriction on the C–Te–C bond angle. Moreover, for either $RTeX_3$ or R_2TeX_2, donor atoms, included as part of the organic

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