reduced in volume to about 5 cm^3. At −20 °C microcrystals of 2 (15 mg or 75% yield) were obtained after 2 days.

Characterization. The IR and FABS mass spectrum were identical with those of the electrochemically synthesized material. ^1H NMR (in CD_2Cl_2 at room temperature): δ 7.42–7.85 (m, 30 H). Microanal. Calcd for $C_{122}H_{60}O_{48}Hg_2Os_{20}N_2P_4$: C, 21.8; H, 0.90; N, 0.42. Found: C, 21.52; H, 0.93; N, 0.56. The PPh_3Me^+ and Ph_4As^+ salts of 2 were prepared in a similar yield.

Preparation of $[N(PPh_3)_2]_2[Os_{20}Hg(C)_2(CO)_{48}]$ (3). $[N(PPh_3)_2]_2[Os_{20}(C)_2(CO)_{48}Hg_2]$ (2) (20 mg, 0.0029 mmol) was dissolved in 10 cm^3 of CH_2Cl_2 and allowed to stand under N_2 for 1 week. The solution changed from brown to deep red, and crystals of 3 (17 mg, 89% yield) were deposited along with metallic mercury.

Characterization. IR (cm^{-1} in CH_2Cl_2): v(CO) 2072 m, 2057 s, 2005 s. FAB mass spectrum: m/z 5408 corresponds to $[Os_{20}(C)_2(CO)_{48}Hg]$ using ^{192}Os. Microanal. Calcd for $C_{122}H_{60}O_{48}HgOs_{20}N_2P_4$: C, 22.6; H, 0.93; N, 0.43. Found: C, 22.39; H, 1.04; N, 0.55. The PPh_3Me^+ and Ph_4As^+ salts of 3 were prepared in a similar yield.

Chemical Preparation of $[Os_{10}C(CO)_{24}]^{3-}$ (4). $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (1) (200 mg, 0.055 mmol) is dissolved in 60 cm^3 of thoroughly freeze–thaw–degassed THF. To this solution is added 1 cm^3 of a freshly prepared solution of sodium benzyl ketyl in THF (made from 13 mg of Na (0.55 mmol) and 105 mg of benzophenone (0.55 mmol) in 100 cm^3 of THF) over a period of 2–3 min (1 equiv of Na/benzophenone in THF) which results in a darkening of the solution. Careful monitoring of the IR of the reaction mixture (using spectroscopic cells flushed with argon) showed that the reaction was complete after about 5 min with near quantitative formation of 4. On standing a mixture of 1 and 5 forms so crystals of 4 could not be obtained. The chemically prepared sample was characterized by IR spectroscopy (ν(CO) 2009 s, 1966 s cm^{-1} in CH_2Cl_2).

Electrochemical Preparation of $[Os_{10}C(CO)_{24}]^{4-}$ (5). $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (1) (20 mg, 0.0055 mmol) is added to 20 cm^3 of degassed CH_3CN–0.1 M TBAF. Controlled potential electrolysis of this solution at a Pt mesh at a potential of −1.40 V yields a new species (5) quantitatively as judged by IR. Crystals of this new osmium cluster could not be obtained due to the presence of electrolyte and the *extreme* oxygen sensitivity of 5. However, repeating this preparation in CH_2Cl_2–0.1 M tetraethylammonium perchlorate caused deposition of microcrystals. This solid gave satisfactory microanalysis for $[TEA]_2[PPN]_2$–$[Os_{10}C(CO)_{24}]$, and on dissolving in THF-d_8 NMR signals consistent with the presence of both PPN^+ and TEA^+ were observed. This solid or its solution readily regenerated 1 in quantitative yield on standing in moist air for a matter of minutes. All this evidence supports the formulation of the reduced cluster as a tetraanion.

Characterization. IR (cm^{-1} in CH_3CN); ν(CO) 1989 s, 1941 s. FAB mass spectrum: m/z 2604 corresponds to $[Os_{10}C(CO)_{24}]$ using ^{192}Os. Microanal. Calcd for $C_{101}H_{80}O_{24}Os_{10}N_4P_4$ ($[NEt_4]_2[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$): C, 32.09; H, 2.12; N, 1.48. Found: C, 32.31; H, 2.17; N, 1.53. ^1H NMR data recorded in THF-d_8 at room temperature: δ +1.62 (t), +3.04 (q), +7.36–7.64 (m).

Chemical Preparation of $[Os_{10}C(CO)_{24}]^{4-}$ (5). $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (1) (20 mg, 0.0055 mmol) is dissolved in 10 cm^3 of thoroughly freeze–thaw–degassed THF. To this solution is added, over a period of 30 min, 2 equiv of Na/benzophenone in THF. The solution changed from red-brown to black. Careful monitoring of the IR of this solution (using spectroscopic cells flushed with argon) showed that the reaction was complete after about 30 min with quantitative formation of 5. Attempts to prepare crystals from this solution failed as in all cases 1 was regenerated. The chemically prepared sample was characterized by IR spectroscopy (ν(CO) 1988 s, 1940 s cm^{-1} in CH_2Cl_2). Attempts to obtain ^{13}C NMR data on this tetraanion (5) were frustrated by difficulties in the preparation of the ^{13}C-labeled $[Os_{10}C(CO)_{24}]^{2-}$.

Acknowledgment. We are grateful to the SERC for financial support (S.R.D. and M.H.B.) and to Dr. R. C. S. McQueen for assistance with some of the electrochemistry.

Registry No. 1, 75026-12-9; 1·$[N(PPh_3)_2]_2$, 75117-74-7; 2, 112548-69-3; 2·$[N(PPh_3)_2]_2$, 112595-82-1; 3, 106466-56-2; 4, 112352-96-2; 5, 112326-42-8; 5·$(NEt_4)_2[N(PPh_3)_2]_2$, 112533-53-6; $AgBF_4$, 14104-20-2; Hg, 7439-97-6; O_3, 7440-04-2; Pt, 7440-06-4; Au, 7440-57-5.

Organolithium Reagents in Metal Carbonyl Reduction Reactions. Syntheses of $HFe_3(\mu_2\text{-}COMe)(CO)_{10}$, $Fe_3(\mu_3\text{-}COMe)_2(CO)_9$, and $Fe_3(\mu_3\text{-}C{=}CH_2)(CO)_{10}$

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n-Butyllithium reduces the $Fe_3(CO)_{12}$ cluster, and on subsequent treatment with Me_3OBF_4 the compounds $HFe_3(\mu_2\text{-}COMe)(CO)_{10}$ (2), $Fe_3(\mu_3\text{-}COMe)_2(CO)_9$ (3), and $Fe_3(\mu_3\text{-}C{=}CH_2)(CO)_{10}$ (1) are formed. Similar reductions are possible with t-BuLi and PhLi. Compound 2 is thus obtained more simply and less dangerously than in a previously published procedure. Complex 3 is the first example where two μ_3-methylidyne methyl ether groups are symmetrically bound to a trinuclear cluster. Synthesis of 3 from 2 is also demonstrated. Similarly, compound 3 can be converted to 1. The photochemical reactivity of 1 with H_2 and with (E)-cyclooctene is described. Compounds 1 and 3 have been characterized by an X-ray structure analysis. (1: $C_{12}H_2O_{10}Fe_3$, orthorhombic, space group $Pna2_1$, a = 21.129 (2) Å, b = 9.079 (1) Å, c = 8.599 (1) Å, Z = 4. 3: $C_{13}H_6O_{11}Fe_3$, monoclinic, space group $P2_1/n$, a = 8.606 (1) Å, b = 13.955 (2) Å, c = 14.899 (1) Å, β = 92.117 (9)°, Z = 4.)

Introduction

Trinuclear cluster compounds of the nature $H_mM_3(CO)_nCX$ (M = Fe, Ru, Os, Co; X = H, Me, OMe, etc.; m = 1–3, n = 9–11) are rapidly gaining importance as model compounds for mechanistic studies on reactions of CO involving (1) C–C and C–H bond formations and (2) C–O

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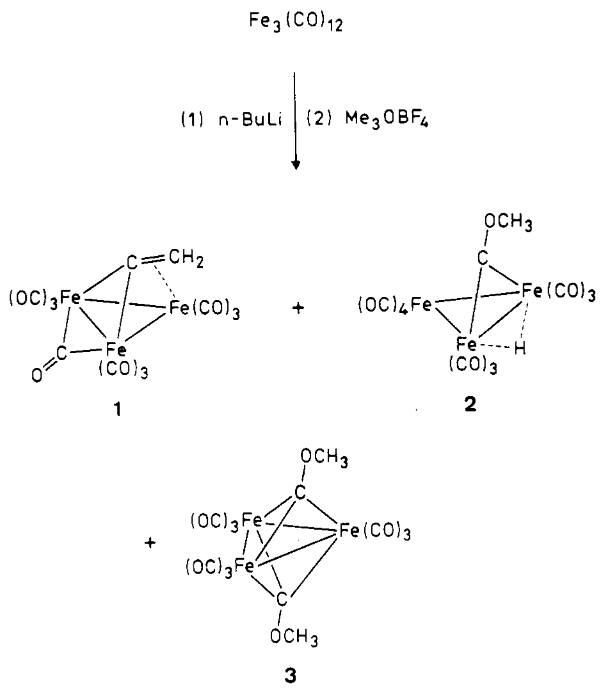
Scheme I



bond cleavages on metal cluster systems.[1] This is of interest in syngas conversion to hydrocarbons.[2]

We now wish to report on a new and convenient access to this class of compounds through reduction of $Fe_3(CO)_{12}$ by lithium reagents such as *n*-BuLi, *t*-BuLi, PhLi, and $LiAlH_4$. This is the first reported application of organolithium reagents in this type of metal carbonyl reduction.

Results and Discussion

Treatment of $Fe_3(CO)_{12}$ in diethyl ether with *n*-BuLi produces a red solution. Solvent removal and addition of water/hexane and then Me_3OBF_4 give a mixture of compounds in the organic phase from which the following compounds are separated by column chromatography (see Scheme I): $Fe_3(\mu_3\text{-}C{=}CH_2)(CO)_{10}$ (**1**), green, ca. 2%; $HFe_3(\mu_2\text{-}COMe)(CO)_{10}$ (**2**), red, 34%; $Fe_3(\mu_3\text{-}COMe)_2(CO)_9$ (**3**), brown, 15%. *t*-BuLi reacts likewise, but in this case an additional new compound of the formula $Fe_2[\mu_2\text{-}C(OMe)\text{-}t\text{-}C_4H_9](\mu_2\text{-}CO)_2(CO)_6$ (**7**) is isolated in a trace amount. Since the R_f factor of this compound on silica gel is very close to that of **1**, separation is achieved by both chromatography and fractional recrystallization. This yellow complex appears to be a Fischer-type adduct[3] of $Fe_2(CO)_9$ and *t*-BuLi. PhLi reacts to give the highest yields of **1** (4.6%), and $LiAlH_4$, on the other hand, reacts very inefficiently with $Fe_3(CO)_{12}$ to give **2** and Fehlner's compound $H_3Fe_3(\mu_3\text{-}CCH_3)(CO)_9$[2d] (**5**) in yields of 13 and 3.5%, respectively. In all the reactions above the known tetranuclear compound $HFe_4(COMe)(CO)_{12}$[4] is a byproduct that appears in trace amounts and elutes very slowly in hexane.

Table I. Selected Interatomic Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for 3

Bond Distances			
Fe(1)-Fe(2)	2.562 (1)	Fe(3)-C(32)	1.790 (3)
Fe(1)-Fe(3)	2.534 (1)	Fe(3)-C(33)	1.826 (3)
Fe(1)-C(1)	1.933 (2)	O(1)-C(1)	1.337 (3)
Fe(1)-C(3)	1.942 (2)	O(1)-C(2)	1.406 (4)
Fe(1)-C(11)	1.818 (3)	O(3)-C(3)	1.338 (3)
Fe(1)-C(12)	1.807 (3)	O(3)-C(4)	1.440 (4)
Fe(1)-C(13)	1.780 (3)	O(11)-C(11)	1.130 (4)
Fe(2)-Fe(3)	2.542 (1)	O(12)-C(12)	1.146 (4)
Fe(2)-C(1)	1.898 (2)	O(13)-C(13)	1.140 (4)
Fe(2)-C(3)	2.034 (3)	O(21)-C(21)	1.139 (4)
Fe(2)-C(21)	1.789 (3)	O(22)-C(22)	1.133 (4)
Fe(2)-C(22)	1.823 (3)	O(23)-C(23)	1.136 (4)
Fe(2)-C(23)	1.792 (3)	O(31)-C(31)	1.131 (4)
Fe(3)-C(1)	2.057 (2)	O(32)-C(32)	1.133 (4)
Fe(3)-C(3)	1.892 (3)	O(33)-C(33)	1.135 (4)
Fe(3)-C(31)	1.810 (3)		
Bond Angles			
Fe(2)-Fe(1)-Fe(3)	59.8 (1)	Fe(2)-Fe(3)-C(3)	52.1 (1)
Fe(2)-Fe(1)-C(1)	47.4 (1)	C(1)-Fe(3)-C(3)	82.0 (1)
Fe(2)-Fe(1)-C(3)	51.5 (1)	C(1)-O(1)-C(2)	120.0 (2)
Fe(3)-Fe(1)-C(1)	52.8 (1)	C(3)-O(3)-C(4)	119.1 (2)
Fe(3)-Fe(1)-C(3)	47.8 (1)	Fe(1)-C(1)-Fe(2)	84.0 (1)
C(1)-Fe(1)-C(3)	84.0 (1)	Fe(1)-C(1)-Fe(3)	78.8 (1)
Fe(1)-Fe(2)-Fe(3)	59.5 (1)	Fe(1)-C(1)-O(1)	126.6 (2)
Fe(1)-Fe(2)-C(1)	48.6 (1)	Fe(2)-C(1)-Fe(3)	79.9 (1)
Fe(1)-Fe(2)-C(3)	48.3 (1)	Fe(2)-C(1)-O(1)	137.2 (2)
Fe(3)-Fe(2)-C(1)	52.8 (1)	Fe(3)-C(1)-O(1)	130.0 (2)
Fe(3)-Fe(2)-C(3)	47.2 (1)	Fe(1)-C(3)-Fe(2)	80.2 (1)
C(1)-Fe(2)-C(3)	82.4 (1)	Fe(1)-C(3)-Fe(3)	82.8 (1)
Fe(1)-Fe(3)-Fe(2)	60.6 (1)	Fe(1)-C(3)-O(3)	127.5 (2)
Fe(1)-Fe(3)-C(1)	48.4 (1)	Fe(2)-C(3)-Fe(3)	80.6 (1)
Fe(1)-Fe(3)-C(3)	49.5 (1)	Fe(2)-C(3)-O(3)	129.5 (2)
Fe(2)-Fe(3)-C(1)	47.3 (1)	Fe(3)-C(3)-O(3)	136.4 (2)

The above synthesis of **2** gives the same yield, based on $Fe_3(CO)_{12}$, as the previously published procedure[5] but offers the following advantages: (1) it is a one-pot synthesis using easily available reagents such as *t*-BuLi or *n*-BuLi, (2) the required reagents are fewer, and (3) methylation with the highly volatile and therefore exceptionally toxic $MeSO_3F$ is avoided.

The novel compound **3** is also accessible from **2** (eq 1) by addition of *t*-BuLi or *n*-BuLi to a frozen solution of **2** at liquid-nitrogen temperature,[6] allowing the mixture to thaw and then methylating with Me_3OBF_4 at room temperature conditions. The pure compound is obtainable

$$\mathbf{2} \xrightarrow[2.\ Me_3OBF_4]{1.\ BuLi} \mathbf{3} \qquad (1)$$

in yields of up to 34% after column chromatography. As a byproduct of this reaction, a new green compound, **8**, is obtained in yields up to 12%. In the mass spectrum the molecular ion (M^+ 560) of this compound loses 11 CO ligands in succession. The proton NMR spectrum of **8** shows a highly shielded hydrogen resonating at δ 7.90, indicative of a proton connected to a carbyne-like carbon. This carbon atom is identified through distortionless en-

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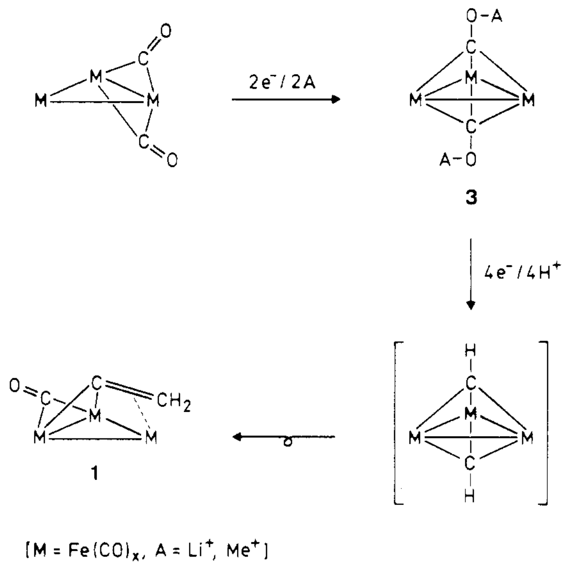
(6) For an example of this procedure, see: Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1981**, *213*, 126.

Scheme II



hancement by polarization transfer (DEPT) in the ^{13}C NMR spectrum and resonates at 128.87 ppm. A second proton signal is located at δ 3.84 and is characteristic of a methyl group. The corresponding carbon atom is found at 60.21 ppm in the ^{13}C NMR spectrum. From this data and the IR spectrum, the compound appears to have the chemical formula $Fe_4(\mu_3\text{-}CHCH_3)(\mu_2\text{-}CO)_2(CO)_9$ (8).

Compound 3 shows five bands in the ν(CO) region of the infrared spectrum. The $^{13}C\{^1H\}$ NMR spectrum is rather simple with three singlets for the methyl, CO, and carbyne carbon atoms. The CO groups remain equivalent down to 173 K, as evidenced by one sharp resonance signal, suggesting a structure where the two μ_3-methylidyne methyl ether groups bind symmetrically above and below the Fe_3 plane. This has been confirmed by X-ray crystallography (Figure 1, Table I). The iron triangle is bicapped by two almost equivalent carbon atoms that are nearly equidistant to one of the metal atoms [C(1)–Fe(1) = 1.933 (2), C(3)–Fe(1) = 1.942 (2) Å] but exhibit alternating distances to the other two: C(1)–Fe(2) = 1.898 (2), C(1)–Fe(3) = 2.057 (2), C(3)–Fe(2) = 2.034 (3), and C(3)–Fe(3) = 1.892 (3) Å. This deviation from threefold symmetry is also reflected by the Fe–C–OR angles: those at Fe(1) are identical within experimental error [Fe(1)–C(1)–O(1) = 126.6 (2)°, Fe(1)–C(3)–O(3) = 127.5 (2)°] whereas those at Fe(2) and Fe(3) are alternating [Fe(2)–C(1)–O(1) = 137.2 (2)°, Fe(2)–C(3)–O(3) = 129.5 (2)°, Fe(3)–C(1)–O(1) = 130.0 (2)°, Fe(3)–C(3)–O(3) = 136.4 (2)°]. The O–R methyl groups point toward gaps between carbonyl groups.

Although the mechanistic details have not yet been investigated, the reduction of $Fe_3(CO)_{12}$ up to compound 3 (see Scheme II) could be visualized either in terms of single electron transfer (SET) steps or via dialkylated intermediate species. Organolithium reagents are known to serve as single electron donor sources through a radical mechanism,[7] and $Fe_3(CO)_{12}$ has been shown to undergo consecutive one-electron reductions to the dianion, through a radical anion intermediate.[8] Thus, direct reduction of the cluster compound through a SET type of mechanism[9] seems possible. Alternatively, indirect reduction could occur through dialkylation of a metal center by the organolithium reagent, followed by β-hydride transfer to the metal with concomitant olefin elimination. The resulting cluster–hydride–alkyl species could undergo reductive elimination to give an alkane and the reduced cluster dianion[10] that is the direct precursor of 3.

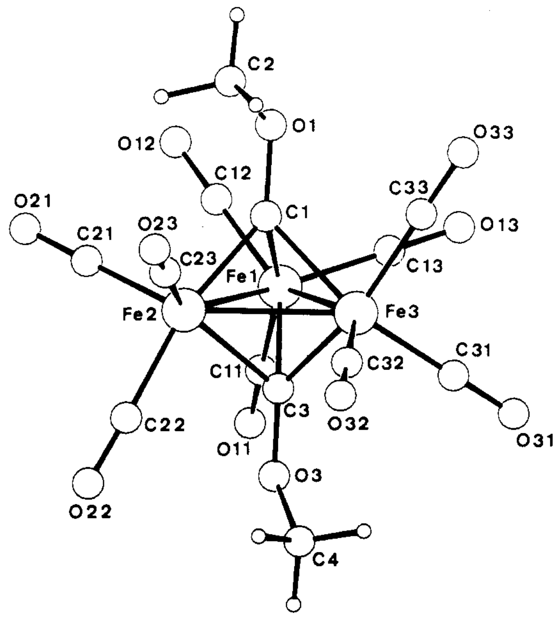


Figure 1. Structure of 3 in the crystal.

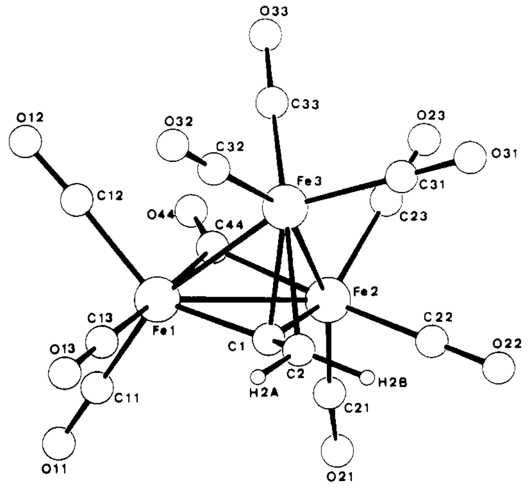


Figure 2. Structure of 1 in the crystal.

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Table II. Selected Interatomic Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for 1

Bond Distances

Fe(1)-Fe(2)	2.547 (1)	Fe(3)-C(31)	1.833 (9)
Fe(1)-Fe(3)	2.611 (1)	Fe(3)-C(32)	1.814 (8)
Fe(1)-C(1)	1.877 (6)	Fe(3)-C(33)	1.782 (6)
Fe(1)-C(11)	1.833 (8)	O(11)-C(11)	1.13 (1)
Fe(1)-C(12)	1.830 (7)	O(12)-C(12)	1.11 (1)
Fe(1)-C(13)	1.789 (7)	O(13)-C(13)	1.13 (1)
Fe(1)-C(44)	2.009 (6)	O(21)-C(21)	1.124 (8)
Fe(2)-Fe(3)	2.595 (1)	O(22)-C(22)	1.14 (1)
Fe(2)-C(1)	1.901 (6)	O(23)-C(23)	1.12 (1)
Fe(2)-C(21)	1.816 (6)	O(31)-C(31)	1.12 (1)
Fe(2)-C(22)	1.773 (9)	O(32)-C(32)	1.13 (1)
Fe(2)-C(23)	1.839 (8)	O(33)-C(33)	1.131 (8)
Fe(2)-C(44)	2.027 (7)	O(44)-C(44)	1.147 (7)
Fe(3)-C(1)	1.966 (6)	C(1)-C(2)	1.399 (9)
Fe(3)-C(2)	2.194 (6)		

Bond Angles

C(44)-Fe(1)-C(1)	99.0 (3)	C(2)-Fe(3)-Fe(1)	77.8 (2)
C(44)-Fe(1)-Fe(3)	89.2 (2)	C(1)-Fe(3)-Fe(2)	46.8 (2)
C(44)-Fe(1)-Fe(2)	51.2 (2)	C(1)-Fe(3)-Fe(1)	45.8 (2)
C(13)-Fe(1)-C(12)	91.7 (3)	Fe(2)-Fe(3)-Fe(1)	58.6 (1)
C(13)-Fe(1)-C(11)	92.1 (4)	C(2)-C(1)-Fe(3)	79.4 (4)
C(12)-Fe(1)-C(11)	102.6 (3)	C(2)-C(1)-Fe(2)	134.5 (5)
C(1)-Fe(1)-Fe(3)	48.7 (2)	C(2)-C(1)-Fe(1)	135.1 (5)
C(1)-Fe(1)-Fe(2)	48.0 (2)	Fe(3)-C(1)-Fe(2)	84.3 (2)
Fe(3)-Fe(1)-Fe(2)	60.4 (1)	Fe(3)-C(1)-Fe(1)	85.5 (2)
C(44)-Fe(2)-C(1)	97.7 (3)	Fe(2)-C(1)-Fe(1)	84.8 (2)
C(44)-Fe(2)-Fe(3)	89.3 (2)	C(1)-C(2)-Fe(3)	61.8 (3)
C(44)-Fe(2)-Fe(1)	50.6 (2)	O(11)-C(11)-Fe(1)	178.3 (6)
C(23)-Fe(2)-C(22)	94.9 (4)	O(12)-C(12)-Fe(1)	177.3 (7)
C(23)-Fe(2)-C(21)	104.8 (3)	O(13)-C(13)-Fe(1)	176.0 (9)
C(22)-Fe(2)-C(21)	91.8 (4)	O(21)-C(21)-Fe(2)	175 (1)
C(1)-Fe(2)-Fe(3)	48.9 (2)	O(22)-C(22)-Fe(2)	179.7 (8)
C(1)-Fe(2)-Fe(1)	47.2 (2)	O(23)-C(23)-Fe(2)	176.9 (7)
Fe(3)-Fe(2)-Fe(1)	61.0 (1)	O(31)-C(31)-Fe(3)	176.0 (7)
C(33)-Fe(3)-C(32)	95.4 (3)	O(32)-C(32)-Fe(3)	177.1 (8)
C(33)-Fe(3)-C(31)	95.5 (3)	O(33)-C(33)-Fe(3)	178.6 (6)
C(32)-Fe(3)-C(31)	98.3 (4)	O(44)-C(44)-Fe(2)	140.1 (6)
C(2)-Fe(3)-C(1)	38.8 (3)	O(44)-C(44)-Fe(1)	141.6 (6)
C(2)-Fe(3)-Fe(2)	78.6 (2)	Fe(2)-C(44)-Fe(1)	78.3 (2)

The former pathway would explain why PhLi, although not possessing an active β-hydrogen atom, nevertheless reduces $Fe_3(CO)_{12}$. However, the latter mechanism, which has been extensively investigated by G. Wilke et al.[11] in the reduction of Ni(II) salts by alkylaluminum reagents, could play a fundamental role here, especially in the cases of n-BuLi and t-BuLi.

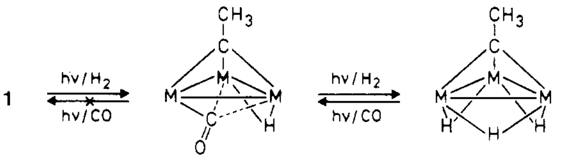
Compound 1 was first obtained by Grevels et al.,[12] but, lacking ^{13}C NMR data, it was erroneously formulated as containing a coordinated acetylene ligand. While the current paper with the complete characterization of this compound was in preparation, a report appeared by Lourdichi and Mathieu[13] in which they proposed, based primarily on the proton-coupled ^{13}C NMR spectrum, an $Fe_3(\mu_3\text{-}C{=}CH_2)(CO)_{10}$ structure.

Our spectroscopic data and X-ray crystal structure analysis of 1 (Figure 2, Table II) confirm the proposition as correct. Three iron atoms, two of which are chemically equivalent, build a triangle [Fe(1)-Fe(2) = 2.547 (1), Fe(1)-Fe(3) = 2.611 (1), Fe(2)-Fe(3) = 2.595 (1) Å] with a carbonyl bridge across the shorter edge. The triangle is capped by a vinylidene moiety [C(1)-C(2) = 1.399 (9) Å], which is σ-bound to Fe(1) and Fe(2) [C(1)-Fe(1) = 1.877 (6), C(1)-Fe(2) = 1.901 (6) Å] and η^2-coordinated to Fe(3) [C(1)-Fe(3) = 1.966 (6), C(2)-Fe(3) = 2.194 (6) Å]. Thus, with two metal-metal bonds, three CO ligands, and the η^2-vinylidene group, Fe(3) achieves the rare-gas configuration as do Fe(1) and Fe(2) with three CO ligands, two metal-metal bonds, the bridging CO, and the vinylidene group.

The hydrocarbon unit in 1 appears to originate wholly from the reductive dimerization of two CO ligands on the cluster compound (Scheme II). This is evidenced by our successful synthesis of 1 from 3 in a 19.5% yield by addition of $LiHB(Et)_3$ followed by protonation. A similar example of this reaction can be found in osmium carbonyl chemistry where a C-O bond is cleaved followed by formation of a C-H bond.[14] Ligand-induced dimerization of two μ_3-CH groups on an Os_3 cluster has recently been demonstrated,[15] and rearrangement of an acetylene ligand to a vinylidene group bonded on an Fe_3 unit is now a well-known reaction.[16]

Compound 1 is thermally stable under 10 bar of H_2 in n-hexane solution at 50 °C for 0.5 h and at ambient temperatures for up to 3 days. Photochemically, however, it is very reactive. IR-monitored broad-band irradiation (solidex glass, $\lambda > 280$ nm) of a 1.6 mM solution in hexane under 1 bar of H_2 leads to initial formation of $HFe_3(\mu_3\text{-}CCH_3)(CO)_{10}$ (4)[17] which remains at a steady low concentration while the amount of a second product, $H_3Fe_3(\mu_3\text{-}CCH_3)(CO)_9$[2d] (5), increases rapidly. Compound 4 begins to decrease after 1 has been consumed, and at the same time a brown precipitate appears in the dark orange solution. According to the IR spectral data this insoluble material apparently does not contain carbonyl complexes. From the solution one can isolate compounds 4 and 5 in 14% and 57% yields, respectively. On the other hand, when a 0.53 mM solution of 1 is photolyzed with hydrogen bubbling through it, the reaction is completed within 10 min to give a clear orange-yellow solution of pure 5.

When isolated chromatographically and irradiated under H_2, 4 converts to 5 cleanly and quantitatively. Conversely, irradiation of 5 under a stream of CO quickly leads to a mixture of 4 and 5 with the latter being the major component. Concomitantly the above-mentioned insoluble brown material is formed. Careful IR monitoring of the reaction progress shows 1 to be totally absent, indicating that the reaction is photochemically irreversible up to that stage (eq 2).[18]



4 5 (2)

[M = Fe(CO)3]

Photolysis of 1 with (E)-cyclooctene results in nearly quantitative formation of a new, green compound 6. The mass spectrum of 6 indicates that one CO group has been

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(11) Fischer, K.; Jonas, K.; Misbach, P.; Stabba, R.; Wilke, G. *Angew. Chem.* **1973**, *85*, 1002.

(12) Grevels, F.-W.; Schulz, D.; Koerner von Gustorf, E.; Bunbury, D. St. P. *J. Organomet. Chem.* **1975**, *91*, 341.

(13) Lourdichi, M.; Mathieu, R. *Organometallics* **1986**, *5*, 2067.

(14) Shaply, J. R.; Cree-Uchiyama, M. E.; St. George, G. M.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 140.

(15) (a) Vollhardt, K. P. C.; Wolfgruber, M. *Angew. Chem.* **1986**, *98*, 919. (b) For a related example where two CO groups are reduced to carbenes which subsequently dimerize, see: Masters, C.; van der Woude, C.; van Doorn, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1633.

(16) Lourdichi, M.; Mathieu, R. *Nouv. J. Chim.* **1982**, *6*, 231.

(17) This compound is known. See, for example: Vites, J.; Fehlner, T. P. *Organometallics* **1984**, *3*, 491. We identified it by MS, NMR, and IR spectroscopy.

(18) The analogous nonphotochemical reaction has been studied qualitatively (see ref 17).

substituted by (*E*)-cyclooctene. The infrared spectrum shows, in addition to bands in the terminal CO region, a broad absorption at 1867 cm^{-1}, characteristic for a bridging CO group; i.e., the CO bridge of 1 is maintained. Thus, complex 6 is tentatively assigned the structural formula $Fe_3(\mu_2\text{-}CO)(\mu_3\text{-}C{=}CH_2)(CO)_8(\eta^2\text{-}(E)\text{-cyclooctene})$.

Experimental Section

General Remarks. Procedures. All preparations and reactions were conducted under a purified argon atmosphere. Appropriate techniques were used in the handling and transfer of air- and moisture-sensitive compounds and reagents.[19]

Solvents. Absolute diethyl ether and *n*-hexane (Merck, analytical grade) were stirred for 24 h over $LiAlH_4$ and then distilled. Dichloromethane was distilled under argon from P_2O_5. The water used was distilled and then argon-saturated by passing the gas from below through a frit.

Reagents. $Fe_3(CO)_{12}$, with methanol as a stabilizer, was purchased from Strem Chemicals and dried under high vacuum for 6 h before use. $Fe_2(CO)_9$[20] and (*E*)-cyclooctene[21] were synthesized according to published procedures. PhLi (1.6 M solution in benzene), *n*-BuLi (2.32 M), and *t*-BuLi (1.6 M) were purchased from Aldrich, and Me_3OBF_4 was obtained from Fluka.

Column Chromatography. Solvents used were deoxygenated by argon saturation as described above. Silica gel 60 (0.040–0.063 mm, 230–400 mesh, Merck) was degassed under vacuum for 6 h and then made into a hexane slurry. The eluent used was *n*-hexane and the standard column size 30 cm × 2.5 cm.

Instrumentation. IR spectra in the ν(CO) region were recorded in a CaF_2 cell on a Perkin-Elmer 580 spectrometer and calibrated by using the DCl bands at 2101.62 and 2080.28 cm^{-1}. *n*-Hexane was the solvent used. NMR spectra were taken on Bruker WH 270 and AM 400 spectrometers. ^{1}H and ^{13}C{^{1}H} chemical shifts are reported as δ values with the respective solvent signal as the internal standard. Mass spectra data were collected on a Finnigan-MHT 311 A instrument, and the elemental analyses were carried out by Mikroanalytisches Laboratorium Dornis und Kolbe, D-4330 Mülheim a.d. Ruhr, West Germany. The photolysis experiments were performed in a water-cooled immersion-well vessel (Solidex glass), with a Philips HPK 125-W mercury lamp.

Reaction of $Fe_3(CO)_{12}$ with Alkyllithium Reagents. In all procedures, unless otherwise stated, reaction workup consisted of (1) solvent removal in vacuo, (2) addition of ca. 100 mL of argon-saturated water and then the same amount of *n*-hexane, (3) portionwise treatment of the vigorously stirred biphasic mixture with more than 2 equiv of Me_3OBF_4 (a large excess of this reagent did not decrease the yields), (4) separation by siphonation of the organic layer followed by two extractions of the aqueous layer with 50-mL portions of *n*-hexane and drying the red organic solution for 1 h over Na_2SO_4, and (5) chromatography of the vacuum-concentrated product solution.

(a) *n*-BuLi. $Fe_3(CO)_{12}$ (2.90 g, 5.70 mmol) and 150 mL of Et_2O were transferred into a Schlenk tube and cooled to −20 °C. To the stirred green suspension was added, over a period of 1 h, 6 mL (ca. 1.2 mmol) of 2.32 M *n*-BuLi, whereupon the solution turned red-brown. Stirring was continued for 3 h as the temperature was allowed to rise gradually to 5 °C. The cooling bath was removed, the solvent stripped-off by vacuum, and to the red-brown residual 50 mL water was added followed by 200 mL of *n*-hexane. Then, while the mixture was vigorously stirred, 3.5 g (24 mmol) of Me_3OBF_4 was added in small portions over a period of 1 h. The red organic layer was dried over degassed Na_2SO_4, concentrated, and chromatographed. First eluted $Fe(CO)_5$ (confirmed by the ν(CO) stretching bands at 2023 and 2000 cm^{-1}), followed by $Fe_3(\mu_3\text{-}C{=}CH_2)(CO)_{10}$ (1) (0.06 g, 2%), $HFe_3(\mu_2\text{-}COMe)(CO)_{10}$ (2) (0.95 g, 34%), and $Fe_3(\mu_3\text{-}COMe)_2(CO)_9$ (3) (0.42 g, 15%). A number of dark bands remained on the column and were not investigated further.

Compound 1: MS, *m/e* 474, successive loss of 10 CO. NMR: ^{1}H (400 MHz, CD_2Cl_2, 297 K) 5.23 (s) ppm; ^{13}C{^{1}H} (100 MHz, CD_2Cl_2, 293 K) 75.12 (=CH_2), 212.0 (CO), 250.12 (μ_3-C) ppm. IR: 2094.5 (vw), 2053.8 (st), 2035.5 (vst), 2027.5 (m), 2011.8 (w), 2009.5 (w), 1984.4 (w), 1877.5 (w, br) cm^{-1}. UV [*n*-hexane, λ/nm (ϵ/L mol^{-1} cm^{-1})]: 645 (979), 490 (1245), 380 (3184), 330 (6250), 280 (13 726).

Compound 3: MS, *m/e* 506, successive loss of 9 CO. NMR: ^{1}H (400 MHz, methyl cyclohexane-d_{14}, 273 K) 4.58 (s) ppm; ^{13}C{^{1}H} (100 MHz, CD_2Cl_2, 173 K) 71.71 (Me), 209.66 (CO), 345.99 (μ_3-C) ppm. IR: 2085.3 (vw), 2042.8 (vst), 2037.3 (vst), 2016.3 (m, br), 1992.3 (w, br) cm^{-1}. UV [*n*-hexane, λ/nm (ϵ/L mol^{-1} cm^{-1})] 575 (471), 462 (1529), 373 (2392). Anal. Calcd (Found): C, 30.90 (31.13); H, 1.20 (1.36); Fe, 33.10 (33.17).

(b) *t*-BuLi. To 3.65 g (7.20 mmol) of $Fe_3(CO)_{12}$ in 150 mL of Et_2O at −60 °C was added over a period of 10 min 12 mL (ca. 19.20 mmol) of 1.6 M *t*-BuLi. The mixture was stirred for 3 h, during which time the temperature was allowed to rise to −30 °C, then the cooling bath was removed, and the greenish red solution was stirred for another 2 h. Workup of the resultant red-brown solution (3.50 g (23.7 mmol) of Me_3OBF_4 used) and subsequent chromatography yielded, in addition to $Fe(CO)_5$, the green compound 1 (0.05 g, 1.5%), the red compound 2 (1.20 g, 34%), the brown compound 3 (0.63 g, 17%), and a trace of the known green compound $HFe_4(CO)_{12}COMe$[4] (MS, *m/e* 604, successive loss of 12 CO; IR 2090 (w), 2050 (vst), 2038 (st), 2026 (st), 2010 (m), 2002 (m), 1998 (sh), 1987 (w), 1974 (w), 1968 (w) cm^{-1}). The mother liquor of 1, on concentration and cooling to −78 °C, yielded a trace of a new yellow compound, $Fe_2[\mu_2\text{-}C(OMe)t\text{-}C_4H_9)(\mu_2\text{-}CO)_2(CO)_6]$ (7).

Compound 7: MS, *m/e* 436, successive loss of 8 CO. NMR: ^{1}H (C_6D_6, 297 K) 1.24 (s, 9 H), 2.65 (s, 3 H) ppm; ^{13}C{^{1}H} (C_6D_6, 297 K) 209.63 (CO), 51.64 (OMe), 36.45 (3 Me), the tertiary carbon atom was not located. IR: 2075.6 (m), 2032.9 (vst), 1999.9 (st), 1985.6 (st), 1973.1 (w), 1947.0 (vw), 1895.0 (w, br), 1880.0 (w, br) cm^{-1}.

(c) PhLi. A suspension of 2.3 g (4.6 mmol) of $Fe_3(CO)_{12}$ in 60 mL of Et_2O was cooled to −20 °C, and to this was added 5.7 mL (9.1 mmol) of 1.6 M PhLi over a period of 45 min. The dark brown solution was stirred for another 1.5 h at ambient temperature and then worked-up (2.04 g (13.8 mmol) of Me_3OBF_4 used) and the organic phase chromatographed to separate $Fe_3(\mu_3\text{-}C{=}CH_2)(CO)_{10}$ (1) (0.10 g, 5%), $HFe_3(\mu_2\text{-}COMe)(CO)_{10}$ (2) (0.56 g, 25%), $Fe_3(\mu_3\text{-}COMe)_2(CO)_9$ (3) (0.18 g, 8%), and a trace of the green compound $HFe_4(COMe)(CO)_{12}$.

(d) $LiAlH_4$. $Fe_3(CO)_{12}$ (3.3 g, 6.5 mmol) suspended in 100 mL of Et_2O was cooled to −78 °C, then 0.5 g (13 mmol) of $LiAlH_4$ added, and the reaction mixture vigorously stirred for 4 h while the temperature was allowed to rise to −10 °C. The cooling bath was removed and the red-brown reaction mixture stirred for a further 3 h, before it was cooled back to −60 °C and excess CF_3CO_2H (1.5 mL), was added. Stirring was continued at room temperature for 1 h, then the volatile components were stripped off by vacuum, and the usual workup of the residue was performed (3.1 g (21.0 mmol) of Me_3OBF_4 used). Chromatography led to the separation of three main bands: $(\mu\text{-}H)_3Fe_3(\mu_3\text{-}CCH_3)(CO)_9$[2d] (5) (0.11 g, 4%), 2 (0.44 g, 14%), and $HFe_4(COMe)(CO)_{12}$ (0.2 g, 5%).

Reaction of $Fe_2(CO)_9$ with PhLi. $Fe_2(CO)_9$ (3.13 g, 8.6 mmol), suspended in 50 mL of Et_2O and cooled to −5 °C, was treated dropwise over a period of 1 h with 9.4 mL (8.6 mmol) of 0.92 M PhLi diluted in 20 mL of Et_2O. The vigorously stirred mixture turned brown-red after a 2-h reaction period, at which stage the $Fe_2(CO)_9$ had disappeared. The volatile components stripped off in vacuo contained large amounts of $Fe(CO)_5$ (IR 2023, 2000 cm^{-1}). The usual workup of the residue (1.35 g (9.1 mmol) of Me_3OBF_4 used) yielded $Fe(CO)_5$ (identified by IR), 1 (0.2 g, 5%), 2 (0.8 g, 19%), 3 (0.2 g, 5%), and the dark green compound $HFe_4(COMe)(CO)_{12}$ in a trace amount.

Reaction of $HFe_3(\mu_2\text{-}COMe)(CO)_{10}$ (2). (a) With *n*-BuLi. A solution of 0.3 g (0.61 mmol) of 2 in 30 mL of Et_2O was cooled to −196 °C (liquid nitrogen). This frozen solution was carefully layered with 10 mL of Et_2O and then treated with 0.4 mL (1.04 mmol) of 2.6 M *n*-BuLi which was slowly added via a syringe, such that it froze on the wall of the reaction flask. The cooling bath was removed and the reaction mixture stirred as it thawed. After

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[19] Eisch, J. J. *Organometallic Syntheses*; Eisch, J. J., King, R. B., Eds.; Academic: New York, London, 1981; Vol. 2, Part 1.

[20] King, R. B. *Organometallic Syntheses*; Eisch, J. J., King, R. B., Eds.; Academic: New York, 1965; Vol. 1, p 93.

[21] A modified, scaled up version of: Vedejs, E.; Snoble, K. A. J.; Fuchs, P. L. *J. Org. Chem.* **1973**, *38*, 1178.

Table III. X-ray Diffraction Data for 1 and 3

	1	3
formula	$C_{12}H_2O_{10}Fe_3$	$C_{13}H_6O_{11}Fe_3$
cryst size (mm)	0.25 × 0.50 × 0.54	0.32 × 0.32 × 0.40
cryst system	orthorhombic	monoclinic
space group	$Pna2_1$[a]	$P2_1/n$
a (Å)	21.129 (2)	8.606 (1)
b (Å)	9.079 (1)	13.955 (2)
c (Å)	8.599 (1)	14.899 (1)
β (deg)		92.117 (9)
V (Å^3)	1649.6	1788.1
Z	4	4
d_{calcd} (g cm^{-3})	1.91	1.88
μ(Mo Kα) (cm^{-1})	26.57	24.55
abs correctn	empirical min 0.831 max 1.262	
diffractometer	Enraf-Nonius CAD-4	
Mo radiatn	graphite-monochromated, λ = 0.71069 Å	
scan mode	$\omega-2\theta$	$\omega-2\theta$
T (°C)	20	20
$(\sin\theta)/\lambda_{max}$	0.701	0.700
measd reflctns	5152	5583
unique reflctns	2526	5140
obsd reflctns ($I > 2\sigma(I)$)	2048	3834
no. of variables	226	244
R	0.037	0.032
R_w ($w = 1/\sigma^2(F_o)$)	0.046	0.039
goodness of fit	2.54	1.90
residual electron density (e Å^{-3})	0.99 (around Fe)	0.45
structure solution	direct method[b]	heavy-atom method[b]

[a] Space group *Pnma* ruled out by intensity statistics, structure solution, and refinement tests. [b] Hydrogen atom positions were calculated and kept fixed in the final refinement stage.

1.5 h the solvent was vacuum removed, the red solid residue cooled to −70 °C, dissolved in 30 mL of CH_2Cl_2, and then 0.36 g (2.4 mmol) of Me_3OBF_4 was added. The cooling bath was removed, stirring continued for 1 h, and then the usual workup procedure performed. On chromatography, compounds **1** (trace), **3** (0.11 g, 34%), and a third, green complex with the proposed formula $Fe_4(\mu_3\text{-}CHCH_3)(\mu_2\text{-}CO)_2(CO)_9$ (**8**) (0.04 g, 12%) was isolated.

Compound 8: MS, *m/e* 560, successive loss of 11 CO; IR 2092.8 (w), 2054.3 (st), 2029.8 (vst), 2019.3 (m), 2005.3 (w), 1978.3 (w, sh), 1972.8 (w), 1883.3 (w, br) cm^{-1}. NMR: ^1H (CD_2Cl_2, 203 K) 7.90 (br, 1 H), 3.84 (br, 3 H), no hydride located; $^{13}C\{^1H\}$ (CD_2Cl_2, 203 K) 249.04 (μ-CO), 204.82 (terminal CO), 128.87 (CH, DEPT confirmed), 60.21 (CH_3, DEPT confirmed) ppm. (NMR spectra were recorded while the sample tube was stationary.)

(b) With *t*-BuLi. The experimental and workup procedures were as in the preceding example. Materials used: compound **2**, 0.5 g (1.0 mmol); *t*-BuLi, 2 mL (3.2 mmol), 1.6 M; and Me_3OBF_4, 1 g (7 mmol). Yields: recovered **2** (0.28 g, 56%) and compound **3** (0.11 g, 22%). Compound **8** was also present (identified by its R_f value) but was not eluted from the column.

Reaction of $Fe_3(\mu_3\text{-}COMe)_2(CO)_9$ (3) with $LiHB(Et)_3$. A solution of **3** (0.33 g, 0.65 mmol) in 15 mL of THF was cooled to −20 °C and treated dropwise over a period of 5 min with 2 mL (2 mmol) of 1 M $LiHB(Et)_3$. The solution was stirred for 0.5 h at this temperature and then the cooling bath removed. After a further 1 h of stirring the volatile components were stripped off by vacuum, the brown solid residue cooled to −78 °C, and 20 mL of dichloromethane added. Then 0.15 mL (1.96 mmol) of argon-saturated CF_3CO_2H was introduced via syringe. The reaction mixture was stirred for 15 min at this temperature and then another 15 min at room temperature. Solvent removal by vacuum, followed by addition of 50 mL of *n*-hexane and 5 mL of argon-saturated water, led to a red-green organic layer after a 0.5-h extraction period. Two further extractions of the aqueous layer with 20-mL portions of *n*-hexane and drying of the organic solution over Na_2SO_4 followed by chromatography separated the following five compounds: **5** (trace), **4** (trace), **1** (0.06 g, 19%), $Fe_3(CO)_{12}$ (0.07 g, 21%), and finally, eluting with 10/1 hexane/dichloromethane, **8** (0.065 g, 18%).

Photoreactions of $Fe_3(\mu_3\text{-}C{=}CH_2(CO)_{10}$ (1). (a) Under 1 bar of H_2. **1** (0.07 g, 0.15 mmol) in 90 mL of *n*-hexane was loaded into a 100-mL photolysis vessel and briefly pumped to a partial vacuum. H_2 gas was introduced by bubbling until normal pressure was attained. Irradiation resulted in a gradual color change to dark orange. Simultaneously, IR spectral changes were observed. After a reaction time of 30 min the lamp was turned off and the solution concentrated to ca. 30 mL. At this point, a brown solid deposited, but due to insolubility it was not investigated further, apart from an IR spectrum in KBr. The IR spectrum of the solution showed compounds **4** (ca. 20%) and **5** (ca. 70%) to be present. Separation by column chromatography, followed by fractional recrystallization, gave **4** (0.01 g, 14%) and **5** (0.04 g, 57%).

When photolysis was conducted as above, but in a flowing stream of H_2, 90 mL of a 0.53 mM solution of **1** turned from green to orange in 10 min without precipitate formation. IR spectrum of the concentrated solution showed only pure **5**, indicating a quantitative conversion.

(b) With (*E*)-Cyclooctene. A solution of **1** (0.03 g, 0.065 mmol) and (*E*)-cyclooctene (7 mg, 0.065 mmol) in *n*-hexane (50 mL) was irradiated, and the reaction progress IR-monitored at 5-min intervals. As indicated by the IR spectral changes, the reaction was complete after 15 min and there was no precipitate, thus ruling out any decomposition. Concentration of the dark green solution, followed by cooling to −30 °C, yielded crystals of a new complex tentatively assigned as $Fe_3(\mu_2\text{-}CO)(\mu_3\text{-}C{=}CH_2)(CO)_8((E)\text{-cyclooctene})$ (**6**).

Compound 6: MS, *m/e* 556, sequential loss of 9 CO; IR 2075 (m), 2034 (vst), 2016 (st), 2010.5 (st), 1989 (w), 1974 (w), 1867 (w, br) cm^{-1}; UV-vis [*n*-hexane, λ/nm (ϵ/L mol^{-1} cm^{-1})] 226 (sh, 11786), 285 (sh, 5178), 395 (sh, 4642), 520 (1535), 673 (1714).

Photoreaction of $HFe_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}CO)(CO)_9$ (4) with H_2. A 0.5 mM solution of **4** (90 mL) was irradiated while purged with hydrogen. After 10 min, the red color of the solution had turned to orange, with no precipitate formation. The IR spectrum showed a quantitative conversion to $H_3Fe_3(\mu_3\text{-}CCH_3)(CO)_9$ (**5**).

Photoreaction of 5 with CO. A 0.2 M solution of **5** (40 mL), saturated with CO, was irradiated as above. The color changed from orange to red with concomitant deposition of an insoluble brown material. IR monitoring of the solution showed a gradual disappearance of **5** while **4** appeared and then remained at a steady low level. After 0.5-h reaction time, large amounts of the brown material had accumulated at the expense of the starting material, indicating significant decomposition. Pure **4** was isolated in a trace amount by chromatography and identified by its IR spectrum.

X-ray Analyses of 1 and 3. Suitable crystals of **1** and **3** were obtained by slow cooling of the respective *n*-hexane solutions. In addition to several locally written programs, the following programs were used in the analyses: TRACER by Lawton and Jacobson for cell reduction; DATAP by Coppens, Leiserowitz, and Rabinovich for data reduction, DIFABS by Walker and Stuart for empirical absorption correction, Sheldrick's SHELX84 for Fourier calculations and initial least squares refinement; GFMLS, a highly modified version of ORFLS, by Hirshfield, Coppens, Leiserowitz, and Rabinovich for subsequent full-matrix least-squares refinement; Davis' DAESD for bond distance and angle calculations, Roberts and Sheldrick's XANADU for best plane and torsion angle calculations; Johnson's ORTEP for the molecular drawings.[22] The data are summarized in Table III.

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Registry No. **1**, 103751-58-2; **2**, 55992-19-3; **3**, 112220-73-2; **4**, 88610-52-0; **5**, 69440-00-2; **7**, 112220-74-3; **8**, 112220-75-4; $Fe_3(CO)_{12}$, 17685-52-8; *n*-BuLi, 109-72-8; *t*-BuLi, 594-19-4; $HFe_4(CO)_{12}COMe$, 75983-14-1; PhLi, 591-51-5; $LiAlH_4$, 16853-85-3;

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[22] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

$Fe_2(CO)_9$, 15321-51-4; $Fe(CO)_5$, 13463-40-6; $LiHB(Et)_3$, 22560-16-3; (*E*)-cyclooctene, 931-89-5.

Supplementary Material Available: Detailed information on the crystal structure determination of 1 and 3 including tables of final atomic positional parameters, final anisotropic thermal parameters, interatomic distances, and bond angles (10 pages); lists of observed and calculated structure factors for 1 and 3 (24 pages). Ordering information is given on any current masthead page.

Activation of Benzene Carbon-Hydrogen Bonds via Photolysis or Thermolysis of $(\eta^5\text{-}C_5Me_5)_2Zr(alkyl)H$. Isolation of $(\eta^5\text{-}C_5Me_5)_2Zr(C_6H_5)H$ and Its Conversion to a Complex Containing a Tetramethylfulvene Ligand

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A new high-yield synthesis of $Cp^*_2ZrH_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) is described, and olefin insertion into its Zr-H bond is used to prepare several new $Cp^*_2Zr(alkyl)H$ complexes. Photolysis or thermolysis of $Cp^*_2Zr(alkyl)H$ in benzene yields the respective alkane by intramolecular reductive elimination of the cis alkyl and hydride ligands, as well as the benzene C-H bond activation product $Cp^*_2Zr(C_6H_5)H$. Photochemically induced reductive elimination is also observed for $Cp^*_2Zr(C_6H_5)H$ and $Cp^*_2ZrH_2$. Deuterium-labeling experiments show that hydrogen exchange between the hydride and Cp* methyl groups occurs in both $Cp^*_2Zr(H)CH_2CH(CH_3)_2$ and $Cp^*_2Zr(C_6H_5)H$. An additional exchange process in $Cp^*_2Zr(C_6H_5)H$ involves the hydride ligand and an ortho phenyl hydrogen atom. Thermolysis of $Cp^*_2Zr(C_6H_5)H$ in benzene causes quantitative evolution of dihydrogen and reversibly forms the tetramethylfulvene complex $Cp^*(\eta^6\text{-}C_5Me_4CH_2)Zr(C_6H_5)$. Reaction of this compound with iodine produces the Cp* ring substituted phenyl iodide $Cp^*(\eta^5\text{-}C_5Me_4CH_2I)Zr(C_6H_5)I$. Several of the transformations involving $Cp^*_2Zr(C_6H_5)H$ are believed to proceed via β-hydrogen elimination from the phenyl group to yield a benzyne dihydride intermediate.

Introduction

In recent years, the activation of carbon-hydrogen bonds has attracted considerable interest.[2] Early work in this area, notably Green's studies with tungstenocene complexes,[3] demonstrated the utility of transition-metal compounds in the activation of aromatic C-H bonds. Bergman's preparation[4] of iridium alkyl hydride complexes via intermolecular oxidative addition of aliphatic carbon-hydrogen bonds was an important discovery since this is a crucial step in the functionalization of saturated hydrocarbons. Further work by Bergman,[4,5] Jones,[6] and Graham[7] has broadened the scope of this oxidative addition reaction to include other metals such as rhodium and rhenium.

In addition to these intermolecular hydrocarbon reactions, transition metals are also known to insert into the C-H bonds of coordinated ligands; phosphines are notably prone to such behavior.[8] Even the usually inert cyclopentadienyl group is susceptible to attack, especially in its early-transition-metal complexes.[9] However, use of the pentamethylcyclopentadienyl ligand ($\eta^5\text{-}C_5Me_5$, usually called Cp*) can often circumvent this problem[10] although a few reports of metal-ligand reactions have appeared. The most common pathway for these reactions involves intramolecular insertion of the transition metal into a methyl C-H bond on the Cp* ring, which results in conversion of $\eta^5\text{-}C_5Me_5$ into $\eta^6\text{-}C_5Me_4CH_2$. (In this paper we will refer to this ligand as "tetramethylfulvene" although this is not meant to imply a particular resonance form or bonding mode for the $\eta^6\text{-}C_5Me_4CH_2$ moiety.) Such reversible transformations have been proposed to explain the reactions of some early-transition-metal compounds[11,12] and

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