$(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)H$ (L = phosphine or phosphite) species show only small variations with changes in L.[32] The *cis*-styrene hydride formed at this point can have a different orientation of the styrene relative to the metal allowing transfer of the hydrogen to the terminal carbon resulting in $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^1\text{-}CH(CH_3)C_6H_5)$ that rapidly forms the corresponding η^3 18-valence-electron species. It should be noted that previous studies on $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2CD_3$ and the $-CD_2CH_3$ compound have shown that scrambling of α- and β-carbon can occur faster than formation of *trans*-alkene hydride. In that case the smaller olefin ethylene apparently can rotate faster than cis to trans isomerization occurs.

Acknowledgment. B.K. thanks the Swiss National Science Foundation for support as a Postdoctoral Fellow, 1980–1981. Support of the National Science Foundation by grant support is gratefully acknowledged. We thank the National Institutes of Health (Grant GM27551) for the Nicolet 7199 FTIR used in these studies.

Registry No. $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$, 12082-27-8; $HSiMe_2\text{–}(\eta^5\text{-}C_5H_4)W(CO)_3CH_3$, 82615-15-4; $C_6H_5CH_2\text{–}(\eta^5\text{-}C_5H_4)W(CO)_3CH_3$, 82615-16-5; $(\eta^5\text{-}C_5H_5)W(CO)_2CH_3$, 73715-35-2; $HSiMe_2\text{–}(\eta^5\text{-}C_5H_4)W(CO)_2CH_3$, 82615-17-6; $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)CH_3$, 12115-41-2; $HSiMe_2\text{–}(\eta^5\text{-}C_5H_4)W(CO)_2(PPh_3)CH_3$, 82615-18-7; $(\eta^5\text{-}C_5H_5)W(CO)_3C_2H_5$, 51232-59-8; $ASiMe_2\text{–}(\eta^5\text{-}C_5H_4)W(CO)_3C_2H_5$, 82615-19-8; $C_6H_5CH_2\text{–}(\eta^5\text{-}C_5H_4)W(CO)_3C_2H_5$, 82615-20-1; $(\eta^5\text{-}C_5H_5)W(CO)_2C_2H_5$, 82615-21-2; $ASiMe_2\text{–}(\eta^5\text{-}C_5H_4)W(CO)_2C_2H_5$, 82615-22-3; $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)C_2H_5$, 82615-23-4; $HSiMe_2\text{–}(\eta^5\text{-}C_5H_4)W(CO)_2(PPh_3)C_2H_5$, 82615-24-5; $(\eta^5\text{-}C_5H_5)W(CO)_2(H)(C_2H_4)$, 80376-16-5; $HSiMe_2\text{–}(\eta^5\text{-}C_5H_4)W(CO)_2(H)(C_2H_4)$, 82615-25-6; $(\eta^5\text{-}C_5H_5)W(CO)_3(\eta^1\text{-}CH_2C_6H_5)$, 38547-50-1; $(\eta^5\text{-}C_5H_5)W(CO)_3(\eta^3\text{-}CH_2C_6H_5)$, 82615-26-7; $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)(\eta^1\text{-}CH_2C_6H_5)$, 81371-86-0; $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2CH_2C_6H_5$, 82615-27-8; $(\eta^5\text{-}C_5H_5)W(CO)_2CH_2CH_2C_6H_5$, 82615-28-9; $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)CH_2CH_2C_6H_5$, 82615-29-0; $(\eta^5\text{-}C_5H_5)W(CO)_2(H)$(styrene), 82615-30-3; $(\eta^5\text{-}C_5H_5)W(CO)_3(\eta^1\text{-}CH(CH_3)C_6H_5)$, 82615-31-4; $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)(\eta^1\text{-}CH(CH_3)C_6H_5)$, 82615-32-5; $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}CH(CH_3)C_6H_5)$, 82615-33-6; $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$, 12128-24-4; $HSiMe_2\text{–}(\eta^5\text{-}C_5H_4)W(CO)_3Cl$, 82615-34-7; $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)Cl$, 12115-03-6; $HSiMe_2\text{-}(\eta^5\text{-}C_5H_4)W(CO)_2(PPh_3)Cl$, 82615-35-8.

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Chemistry of Octacarbonyl(μ-methylene)diiron and Its Derivatives

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The reaction of the $Fe_2(CO)_8^{2-}$ dianion with methylene iodide leads to the formation of the parent bridging methylene complex, octacarbonyl(μ-methylene)diiron, $Fe_2(CO)_8CH_2$. The reaction appears to be general and several derivatives have been prepared by using other geminal diiodides. The bridging methylene complexes react with unsaturated reactants such as olefins and acetylenes to produce new organometallic complexes in which the unsaturated molecule has inserted between the methylene ligand and an iron atom. With hydrogen, the complexes react to produce the dihydro form of the methylene ligand; nucleophilic reagents such as iodide ion, alcohols, and water appear to attack a CO ligand with subsequent rearrangement involving the bridging methylene group.

Introduction

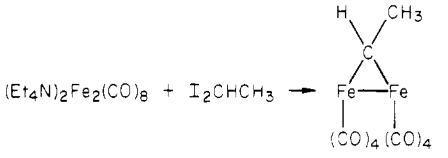
In addition to their interest from a structural point of view, organometallic complexes containing carbon ligands have been implicated as intermediates in several important chemical reactions, e.g., the disproportionation of olefins[1] and the Fischer–Tropsch reaction,[2] and the chemistry of such species has emerged as an important area of study. In this paper we discuss the preparation and chemical properties of octacarbonyl(μ-methylene)diiron and several of its derivatives.

Discussion

We recently reported the synthesis of the parent μ-methylene complex $Fe_2(CO)_8CH_2$[3] by the reaction of $(Et_4N)_2Fe_2(CO)_8$ with CH_2I_2 (eq 1). We have found the

$$(Et_4N)_2Fe_2(CO)_8 + CH_2I_2 \rightarrow Fe_2(CO)_8CH_2 \qquad (1)$$

reaction of geminal diiodoalkanes with $(Et_4N)_2Fe_2(CO)_8$ to be a general synthesis of diiron μ-alkylidene complexes. For example, treatment of $(Et_4N)_2Fe_2(CO)_8$ with 1,1-diiodoethane affords the μ-ethylidene complex **2** (eq 2).



(2)

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Similar results are obtained when 2,2-diiodopropane, 1,1-diiodo-2-methyl propane, α,α-diiodoethyl acetate, or diiodopropene[4] is substituted for CH_2I_2. The μ-alkylidene complexes obtained from these diiodides are listed in Table I along with their spectroscopic data. The use of the disodium salt of $[Fe_2(CO)_8]^{2-}$ in place of the tetraethyl-

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[§] Deceased December 10, 1981.

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(4) Used as a mixture of compounds prepared by the reaction of vinyldiazomethane with iodine.

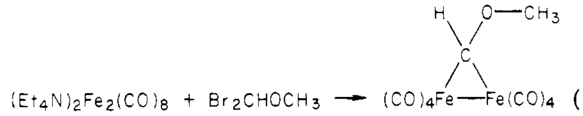
0276-7333/82/2301-1350$01.25/0

Table I

compd	color	mp, °C	IR ν(CO) (hexane), cm^{-1}	^{1}H NMR, δ	^{13}C NMR, ppm
$Fe_2(CO)_8(\mu\text{-}CH_2)$ (1)	yellow	135 dec	2118 (w), 2058 (vs), 2028 (vs), 2012 (s)	5.5 (s) (acetone-d_6)	
$Fe_2(CO)_8(\mu\text{-}C(H)CH_3)$ (2)	yellow	50 dec	2105, 2060, 2030, 2010, 1910–1840	2.7 (d, 3 H), 7.2 (g, 1 H) (acetone-d_6)	2111, 119, 39
$Fe_2(CO)_8(\mu\text{-}C(CH_3)_2)$ (3)	yellow	48 dec	2105, 2060, 2030, 2010 (sh), 1872, 1847	2.9 (s) (acetone-d_6)	
$Fe_2(CO)_8(\mu\text{-}CH[CH(CH_3)_2])$ (4)	yellow	75 dec	2105, 2050, 2020, 2005, 1985, 1940–1900	1.3 (d, 6 H), 2.6 (m, 1 H), 6.7 (d, 1 H) (acetone-d_6)	212, 140, 51, 31
$Fe_2(CO)_8(\mu\text{-}C(H)CHCH_2)$ (5)	yellow		2100, 2055, 2030, 2015, 1860 (br)	4.9 (d, 1 H), 5.2 (m, 1 H), 6.8 (dd, 2 H)	
$Fe_2(CO)_8(\mu\text{-}C(H)CO_2C_2H_5)$ (6)	orange	29	2114, 2066, 2033, 2016, 1973, 1688	5.8 (s, 1 H), 4.0 (qt, 2 H), 1.1 (t, 3 H) (C_6D_6)	208, 18 2, 101, 61, 15
$Fe_2(CO)_8(\mu\text{-}C(H)OCH_3)$ (7)	yellow	61	2110, 2055, 2030, 2019, 2003, 1980–1950, 1890, 1855	3.0 (s, 3 H), 8.2 (s, 1 H), (C_6D_6)	211, 174, 65
$Fe_2(CO)_7(\mu\text{-}C(H)OCOCH_3)$ (8)	red	84	2089, 2045, 2018, 2000, 1964, 1945, 1618	9.1 (s, 1 H), 1.0 (s, 2 H) (C_6D_6)	222, 184, 170, 19
$Fe_2(CO)_7(\mu\text{-}C(CH_3)OCOCH_3)$ (9)	red	62	2083, 2060, 2044, 2010, 1996, 1961, 1936, 1615	2.9 (s), 1.1 (s)	211–202, 197, 181, 42, 19
$Fe_2(CO)_7(\mu\text{-}C(H)N(H)COCH_3)$ (28)	red	108–112	2080, 2030, 1995 (br), 1980 (br), 1940–1860 (sh), 1561, 1540 (CH_2Cl_2)	2.0 (s, 3 H), 2.9 (br, 1 H), 8.3 (d, 1 H) (acetone-d_6)	
$Fe_2(CO)_8(\mu\text{-}C(H)OCOCH_3)$ (29)	yellow	46	2110, 2065, 2038, 2020, 1930–1900 (br), 1760	9.0 (s, 1 H), 2.1 (s, 3 H)	
$Fe_2(CO)_8(\mu\text{-}C(H)CO_2H\cdot H_2O)$ (33)	yellow	76–82 dec	2116, 2070, 2035, 2018, 1690, 1645 (CH_2Cl_2)		
$Fe_2(CO)_6(\mu\text{-}Cl)(\mu\text{-}C(H)CO)$ (34)	red	50–52	2105, 2062, 2052, 2015, 2005, 1972, 1952	0.7 (s) (C_6D_6)	208 (s), 162 (s), −4 (d) (off-resonance decoupd)
$Fe_2(CO)_7(\eta^{1,3}\text{-}CHCHCH_2)$ (15)	red		2099, 2039, 2015, 1984, 1975	3.0 (dd, 1 H), 2.3 (m, 1 H), 5.1 (m, 1 H), 8.0 (d, 1 H) (C_6D_6)	211, 209, 154, 97, 47
$Ph_3PFe_2(CO)_6(\eta^{1,3}\text{-}CHCHCH_2)$ (25)	red	108 dec	2060, 2015, 1980, 1965	8.1 (dm, 1 H), 7.5–7.2 (m, 6 H), 7.0 (m, 10 H), 5.4 (dd, 1 H), 2.5–2.2 (m, 2 H) (C_6D_6)	
$Fe_2(CO)_6(\eta^{2,4}\text{-}C(OH)CHCHCH)$ (16)	yellow	44–47	2080, 2040, 2020, 1980, 1965	6.1 (dd, 1 H), 5.0 (br, 1 H), 4.9 (dd, 1 H), 4.4 (dd, 1 H), (acetone-d_6)	
$Fe_2(CO)_8(\eta^{2,3}\text{-}CHCHCHCHCH)$ (17)	orange	33	2070, 2025, 1999, 1995, 1979	6.8 (dd, 1 H), 4.0–3.7 (m, 2 H), 3.5 (m, 1 H), 0.9 (dd, 1 H), 0.4 (dd, 1 H) (acetone-d_6)	
$Fe_2(CO)_6(\eta^{2,3}\text{-}CHCHCHC(CH_3)C(CH_3))$ (18)	orange	101–108	2070, 2025, 1995, 1991, 1973	4.0 (d, 1 H), 3.7 (n, 1 H), 2.3 (s, 3 H), 1.1 (s, 3 H), 0.9 (d, 1 H), 0.4 (d, 1 H), (acetone-d_6)	
$Fe_2(CO)_6(\eta^{2,3}\text{-}CH(CH_3)C(CH_3)CHC(CH_3)\text{-}C(CH_3))$ (20)	red	120–123	2060, 2018, 1989, 1980, 1968, 1939	3.8 (s, 1 H), 2.5 (s, 3 H), 1.8 (qt, 1 H), 1.7 (s, 3 H), 1.0 (d, 3 H) (C_6D_6)	
$Fe_2(CO)_6(\eta^{2,4}\text{-}C(OH)C(CH_3)C(CH_3)CH)$ (21)	yellow	109–120 dec	2040, 1988, 1959, 1940, 1920 (sh), 1640 (br) (THF)	7.1 (s, 1 H), 2.1 (s, 3 H), 1.4 (s, 3 H) (acetone-d_6)	
$Fe_2(CO)_7(\eta^{1,3}\text{-}CHCHC(H)Ph)$ (22)	red	66–68	2090, 2037, 2010, 1980, 1970	8.0 (d, 1 H), 7.1 (s, 5 H), 5.8 (dd, 1 H), 3.6 (d, 1 H) (C_6D_6)	

ammonium salt did not allow the isolation of μ-alkylidene complexes. This could be due to a side reaction involving NaI and the μ-alkylidene product, since NaI is much more soluble in acetone and THF than Et_4NI. The reaction of iodide ion with these μ-alkylidene complexes (vide infra) may explain the low yields (7–60%) produced by this reaction. Dinuclear methylene complexes of cobalt and palladium[5] have also been synthesized by using CH_2I_2 as the source of the methylene ligand.

Geminal chlorides fail to give μ-alkylidene complexes when reacted with $(Et_4N)_2Fe_2(CO)_8$, though certain dibromides react to give functionalized methylene complexes. For example, dibromomethyl methyl ether reacts with $(Et_4N)_2Fe_2(CO)_8$ to produce the methoxymethylene complex **7** (eq 3), while dichloromethyl methyl ether does not react with $(Et_4N)_2Fe_2(CO)_8$ to give **7**. The (carboethoxy)methylene complex **6** can also be prepared from α,α-dibromoethyl acetate in comparable yield.



(3)

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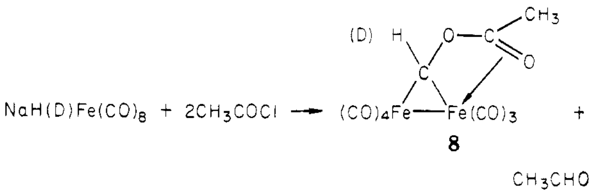
The IR spectra of bridging alkylidene complexes **2**, **3**, **4**, **5**, and **7** display bands between 1800 and 1900 cm^{-1}, indicative of bridging CO groups. This is in contrast to the parent complex **1** and the (carboethoxy)methylene complex **6** which have only terminal CO groups in solution; however, complex **1** has bridging CO groups in the solid state, as evidenced by strong absorptions at 1875 and 1836 cm^{-1} and confirmed by X-ray analysis. The ^{1}H NMR spectra of the bridging alkylidene complexes which have a hydrogen atom bound to the bridgehead carbon display downfield chemical shifts (δ 5.5–9.1) for the bridgehead hydrogens. The ^{13}C NMR spectra display absorptions ranging from 100 to 200 ppm, which is within the range expected for bridgehead carbons.[6] The structures of the parent complex **1** and the methoxymethylene complex **7**[7] have been confirmed by X-ray crystallographic analysis.

Diiron μ-alkylidenes have also been prepared by the acylation of diiron carbonyl anions. The addition of acetyl chloride to $NaHFe_2(CO)_8$ in THF gives among other products the acetoxymethylenediiron heptacarbonyl **8** and acetaldehyde (eq 4), while addition of 2 mol of acetyl bromide to the disodium salt of octacarbonyl ferrate gives acetoxyethylideneheptacarbonyldiiron **9** (eq 5). The infrared spectrum of **9** is virtually identical with that of **8**.



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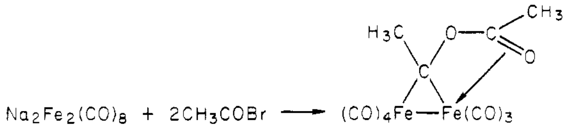
(4)

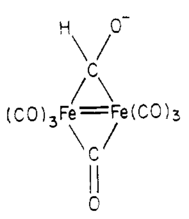


(5)

9

The structural assignment of **8** and **9** were made on the basis of their IR, ^{1}H NMR, and ^{13}C NMR spectra, as well as their chemical and physical properties. The infrared spectrum of **8** in hexane shows the expected absorptions of terminal bound metal carbonyls and a band at 1618 cm^{-1} assigned to the coordinated carbonyl of the acetoxy moiety. The ^{1}H NMR of **8** consists of two sharp singlets at δ 1.03 and 9.10, in ratio of 3:1. The ^{13}C NMR (δ 19, 170, 184, 222) is consistent with the structural assignment of **8** as an iron carbonyl containing a bridging rather than a terminally bound alkylidene ligand.[6] Mass spectral analysis exhibits the parent mass of **8** as well as peaks corresponding to stepwise loss of seven CO ligands. As in **8**, infrared analysis suggests that **9** contains an acetate group directly bound to iron through the oxygen atom of the organic carbonyl. The ^{1}H NMR spectrum of **9** displays two singlets in a ratio of 1:1 (δ 1.06 and 2.90). The ^{13}C NMR supports the assignment of **9** as that of a bridging alkylidenemetal carbonyl (δ 19, 42, 181, 197, 202–211). The mass spectrum exhibits the parent molecular ion of **9** and all fragments corresponding to loss of seven CO ligands.

The mechanism of the formation of the bridging alkylidene complex **8** is not clear. Conversion of $NaHFe_2(CO)_8$ to the bridging alkoxide[8] **10**, followed by acylation on oxygen, would lead to **8**. Alternatively, acylation of $NaHFe_2(CO)_8$ could precede hydrogen migration. If $NaDFe_2(CO)_8$ is acylated, **8** is found to contain deuterium at the bridgehead carbon (see Experimental Section). The acylation of carbon monoxide as in **11** has been discussed by Shriver et al.[9] and may provide a necessary driving force for the insertion of CO into a metal–hydride bond.[10]



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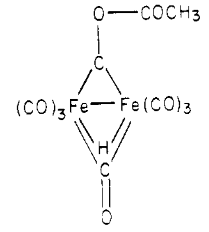
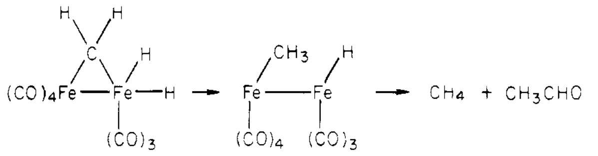


11

The Chemistry of Diiron μ-Methylenes. The parent complex **1** reacts with H_2 to give methane and acetaldehyde along with $Fe_3(CO)_{12}$. This behavior is consistent with the behavior postulated for methylene groups bound to a metal surface.[11] We speculate that the reaction proceeds through a dihydride such as **12** which undergoes intramolecular reductive elimination to give a methyl complex (eq 6). Insertion of CO into the metal methyl bond would give acetaldehyde upon reductive elimination. All of the methylene complexes studied appear to react similarly to liberate the dihydro form of the ligand which also serves as evidence for the structure of the complexes. The data are listed in Table II. It should be noted that reasonably vigorous conditions are required to achieve high



(6)

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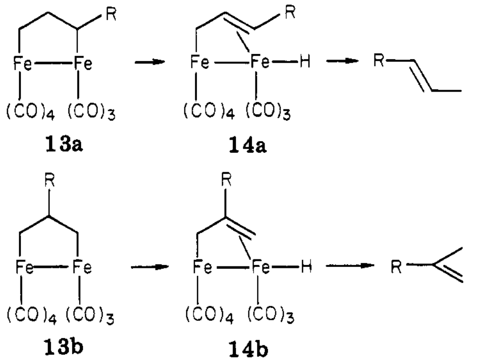
Table II. Hydrogenation of Alkylidenes

compd	temp, °C	$p(H_2)$, psi	time, h	solvent	product	yield, %
$Fe_2(CO)_8CH_2$	60	210	1	C_6H_6	CH_4	83
$Fe_2(CO)_8C(H)OCH_3$	120	250	1.3	C_7H_{16}	CH_3OCH_3	50
$Fe_2(CO)_7C(H)OAc$	100	250	1.5	C_6H_{14}	$CH_3CO_2CH_3$	67
$Fe_2(CO)_7C(H)NHCOCH_3$	90	850	1.3	C_6H_6	$CH_3CONHCH_3$	34
$Fe_2(CO)_8C(H)CO_2C_2H_5$	100	300	2	C_5H_{12}	$CH_3CO_2C_2H_5$	92
$Fe_2(CO)_8C(H)CO_2H$	100	200	1.5	glyme	CH_3CO_2H	66

yields of product which presumably reflects the need to thermally lose a CO ligand before hydrogen can react.

Olefins. Treatment of complex 1 with olefins results in a one-carbon homologation of the olefin. For example, ethylene reacts with 1 to give propylene. While the reaction of 1 with propylene gives mainly the branched isomer, isobutylene, along with *trans*-2-butene, *cis*-2-butene, and 1-butene, methyl acrylate reacts with 1 to give mainly the linear isomer, ethyl crotonate, along with small amounts of methyl methacrylate. The observed regiochemistry could be due to a cyclic intermediate such as a bimetallacyclopentane which is coordinatively unsaturated and would undergo a β-hydride elimination reaction to give an olefin π complex leading to the new olefin. When R is carbomethoxy (eq 7), metallacycle **13a** is favored and would lead to the linear isomer through the olefin π complex **14a**. When R is methyl, metallacycle **13b** is favored and, upon β-hydride elimination, would give the olefin π complex **14b** leading to the branched isomer.

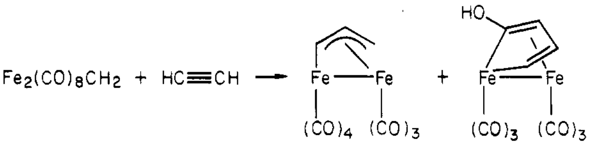


13a **14a** **13b** **14b**

(7)

No reaction is observed to occur when 1 is treated with isobutylene under conditions similar to those employed for reaction with ethylene or propylene. However, degenerate metathesis between 1 and isobutylene similar to that observed by Parshall[12] and co-workers for the Ti-C-H_2Al system does not occur. When $Fe_2(CO)_8CD_2$ is treated with isobutylene, there is no hydrogen incorporated into the recovered metal alkylidene.

Alkynes. Reaction of 1 with acetylene produces the σ,π-allyl complex **15** along with the ferrole **16** (eq 8). The

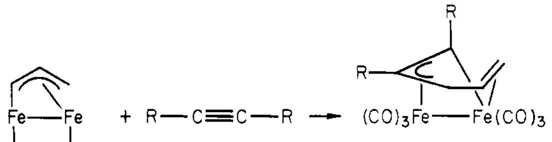


15 **16**

(8)

^1H NMR of **15** shows two high-field signals at δ 2.0 (1 H) and 2.3 (1 H) and a multiplet at δ 5.1 (1 H) as would be expected for a π-allyl ligand; however, there is also a signal at δ 8.0 (1 H), indicative of a bridgehead hydrogen atom. The ^{13}C NMR of **15** displays absorptions at δ 47, 97, and 154 for the allyl ligand with the signal at δ 154 being assigned to the bridgehead carbon atom. The metal carbonyl ligands resonate at δ 209 and 211. Complex **15** is also formed as a result of the decomposition of the vinylmethylene complex **5** (vide infra). The structure of the ferrol **16** was determined on the basis of IR, ^1H NMR, and chemical data. For example, **16** reacts with H_2 to give mainly 1-butanol, and treatment of **16** with acetyl chloride affords an acetate derivative.[13]

The σ,π-allyl complex **15** reacts with alkynes to give products resulting from the insertion of the alkyne into the Fe-allyl σ bond. For example, treatment of **15** with acetylene affords the diinsertion product **17** or with 2-butyne affords **18** (eq 9). Elemental analysis, IR, ^1H NMR, and mass spectral data are consistent with the formulation given above. The ^1H NMR spectrum of **17** exhibits two high-field pairs of doublets at δ 0.4 (1 H) and 0.9 (1 H) assigned to the terminal π-olefinic hydrogen atoms and a multiplet at δ 3.5 (1 H) assigned to the interior olefinic hydrogen atom. A multiplet at δ 3.7–4.0 (2 H) is assigned to the π-allylic hydrogens, and a pair of doublets at δ 6.8 (1 H) is assigned to the bridgehead hydrogen atom. The ^1H NMR spectrum of **18** exhibits two high-field doublets at δ 0.4 (1 H) and 0.9 (1 H) assigned to the terminal π-olefinic hydrogen atoms, a multiplet at δ 3.7 (1 H) assigned to the interior olefinic hydrogen, and a doublet at δ 4.0 (1 H) assigned to the allylic hydrogen. Singlets at δ 1.1 (3 H) and δ 2.3 (3 H) are assigned to the methyl groups with the latter one being assigned as the bridgehead methyl group. The diinsertion product **17** is also obtained when 1 is treated with excess acetylene. Compounds containing an organic ligand bonded similarly to that in **17**, **18**, and **20** have previously been prepared by the photolysis of $Fe(CO)_5$ in the presence of 2,7-dimethyloxepin[14] and by the addition of 2-butyne to a ditungsten μ-alkylidene complex.[15]

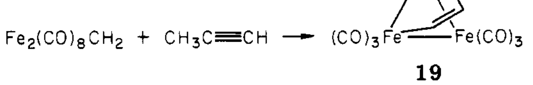


(9)

15

17, R = H
18, R = CH_3

Treatment of 1 with propyne results in the formation of a ferrole formulated as having structure **19** and a mixture of pentane-soluble compounds which were not readily separated (eq 10). On the basis of ^1H NMR data [δ (C_6D_6)



(10)

19

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[13] Sternberg, H. W.; Friedel, R. A.; Mackley, R.; Wender, I. *J. Am. Chem. Soc.* **1956**, *78*, 3621.

[14] Aumann, R.; Averbeck, H.; Kruger, C. *Chem. Ber.* **1975**, *108*, 3336.

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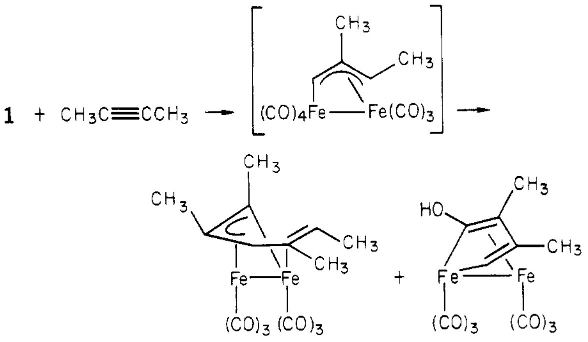
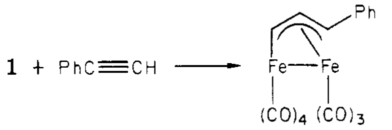
0.3 (d, 1.2 H), 0.8–1.1 (5 pk, 1.2 H), 1.7 (br, 4 H), 2.3 (s, 3 H), 2.4 (s, 0.3 H), 3.2 (s, 1 H), 3.8–4.0 (dd, 1.2 H), 6.4 (s, 0.3 H)], the pentane-soluble mixture is presumably a mixture of isomeric complexes arising from the insertion of **2** equiv of propyne.

Reaction of the μ-methylene complex **1** with 2-butyne results in the isolation of a red crystalline compound containing two 2-butyne units and a ferrole (eq 11), which are formulated as having structures **20** and **21**, respectively, on the basis of their elemental analysis, ^{1}H NMR, IR, and mass spectral data. The ^{1}H NMR spectrum of **20** displays a doublet at δ 1.0 (3 H) assigned to the terminal olefinic methyl group, a singlet at δ 1.2 (3 H) assigned to the interior olefinic methyl group, a singlet over a quartet at δ 1.7 (4 H) assigned to the allylic methyl group and the olefinic hydrogen atom respectively, a singlet at δ 2.5 (3 H) assigned to the bridgehead methyl group, and a singlet at δ 3.8 (1 H) assigned to the allylic hydrogen atom. Complex **20** is probably formed via a σ,π-allyl complex which rapidly reacts with 2-butyne under the reaction conditions. Interestingly, a hydrogen atom originally bound to the methylene ligand in **1** has migrated to the terminal olefinic carbon in **20**. This migration is also observed in the σ,π-allyl product **22**, isolated from the reaction of **1** with phenylacetylene (eq 12). The structure of **22** was determined on the basis of ^{1}H NMR, IR, and mass spectra and by hydrogenation to give *n*-propylbenzene. The ^{1}H NMR spectrum consists of a doublet at δ 3.6 (1 H) assigned to the hydrogen bound to the carbon bearing the phenyl group, a pair of doublets at δ 5.8 (1 H) assigned to the interior allylic hydrogen, a singlet at δ 7.1 (5 H) assigned to the aromatic hydrogens, and a doublet at δ 8.0 (1 H) assigned to the bridgehead hydrogen atom. The mechanism responsible for the migration of the methylenic hydrogen atom is not clear. Similar observations have been reported by Lewis et al.[16] for tetranuclear osmium clusters.



(11)

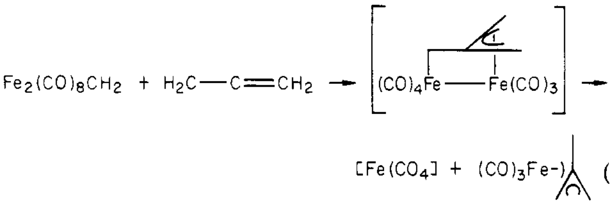
21



(12)

22

Allene. The addition of allene to complex **1** under conditions similar to those used for the reaction of **1** with acetylenes gives a complex mixture of metal carbonyls. The major product formed in 20% yield is (trimethylenemethane)iron tricarbonyl (**23**; eq 13). The expected diiron trimethylene heptcarbonyl was not isolated.



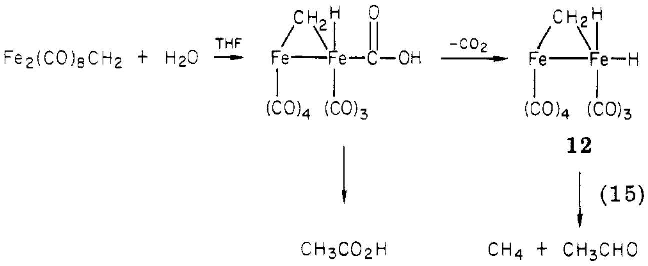
(13)

23

Nucleophiles. The reaction of **1** with nucleophiles leads to products containing an acetyl group (eq 14). For example, the reaction of **1** with NaI in the presence of water leads to the formation of mainly acetic acid. Treatment of the μ-methylene complex **1** with alcohols or amines produces acetates or acetamides, respectively. Thus, treatment of **1** with isoamyl alcohol in refluxing tetrahydrofuran (THF) produces isoamyl acetate. Similarly, treatment of **1** with aniline in benzene produces acetanilide. Consistent with these findings, the carboethoxy complex **6** reacts readily with ethanol to give good yields of diethyl malonate. The rate of the reaction of the μ-methylene complexes **1** and **6** with nucleophiles was qualitatively observed to be enhanced by the presence of iodide.

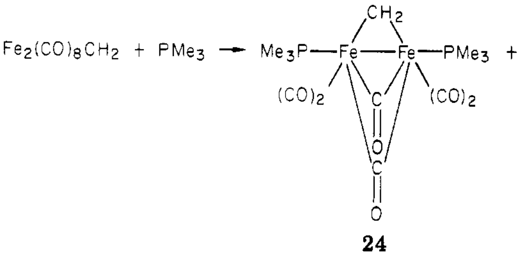
$$\mathrm{Fe(CO)_8CH_2 + R{-}Z{-}H \rightarrow CH_3C({=}O){-}Z{-}R} \qquad (14)$$
$$\mathrm{Z = O, NH}$$

When the μ-methylene complex **1** is treated with water at room temperature in acetone, acetic acid is produced as expected by analogy to the reaction of **1** with alcohols. However, methane and acetaldehyde, along with carbon dioxide, are also observed (eq 15). These results are consistent with the ability of a CO ligand to undergo nucleophilic attack to generate a metal hydride as in the water gas shift reaction.[17] Reaction of **1** with water to give the dihydride **12** would lead to the formation of methane and acetaldehyde. The fate of the iron carbonyl groups is as yet undetermined.



(15)

Trimethylphosphine. Reaction of the μ-methylene complex **1** with PMe$_3$ affords the bis(trimethylphosphine) complex **24** along with the mononuclear complexes (eq 16).



24

$$\mathrm{(CO)_4FePMe_3 + (CO)_3Fe(PMe_3)_2} \qquad (16)$$

Attempts to prepare the dinuclear monophosphine-sub-

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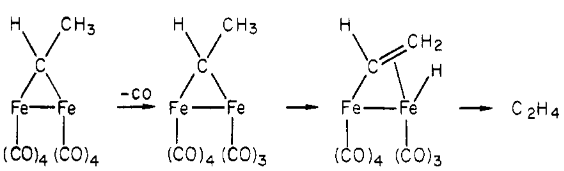
[16] Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Mann, A.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 547.

[17] Pearson, R. B.; Mauermann, H. *J. Am. Chem. Soc.* **1982**, *104*, 500–504. Pettit, R.; Cann, K.; Cole, T.; Mauldin, C. H.; Sleiger, W. *Anal. N.Y. Acad. Sci.* **1978**, *333*, 101. The products observed from the reaction of **1** with nucleophiles could also arise from a ketenyl-type intermediate formed by insertion of a CO ligand into a CH$_2$–Fe bond prior to nucleophilic attack. Roper, M.; Strutz, H.; Keim, W. *J. Organomet. Chem.* **1981**, *219*, C5.

stituted methylene complex by using only 1 equiv of PMe_3 were unsuccessful in that the same products were isolated as before, along with unreacted **1**. The structure of **24** was determined by X-ray analysis.[7]

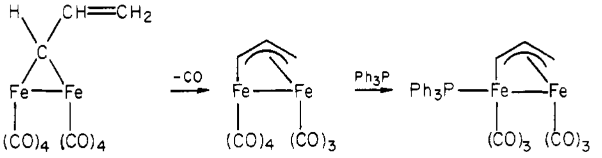
The diiron μ-alkylidene complexes which possess a β-hydrogen atom are unstable at room temperature in solution where they decompose to give the corresponding olefin and $Fe_3(CO)_{12}$. For example, the ethylidene complex **2** decomposes in pentane solution to give ethylene and $Fe_3(CO)_{12}$. Presumably, the decomposition involves prior loss of a CO ligand to give a coordinatively unsaturated complex which undergoes β-hydride elimination to give the π complex that would lead to ethylene (eq 17).



2

(17)

Complexes which do not possess a β-hydrogen atom, such as the parent complex **1**, the (carboethoxy)methylene complex **2**, and the methoxymethylene complex **7**, are stable in solution at room temperature. However, the vinylmethylene complex **5** readily looses a CO ligand to give the σ,π-allyl complex **15** (eq 18). Complex **15** is dark red oil at room temperature and reacts with 1 equiv of Ph_3P at ambient temperature to give a crystalline Ph_3P derivative which X-ray analysis[18] has determined to have structure **25**.

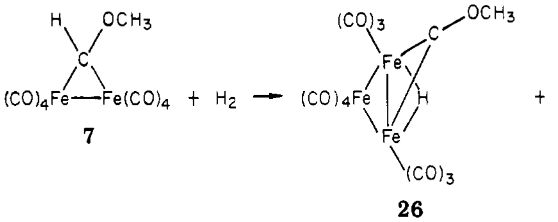


5 **15** **25**

(18)'

The Chemistry of $Fe_2(CO)_8CHOCH_3$. Oxygenated methylene ligands may play an important role in the catalytic conversion of carbon monoxide into small, oxygenated organic compounds such as methanol and ethylene glycol. Some chemistry of μ-alkoxymethylene ligands has recently been reported by Stone et al.[19]

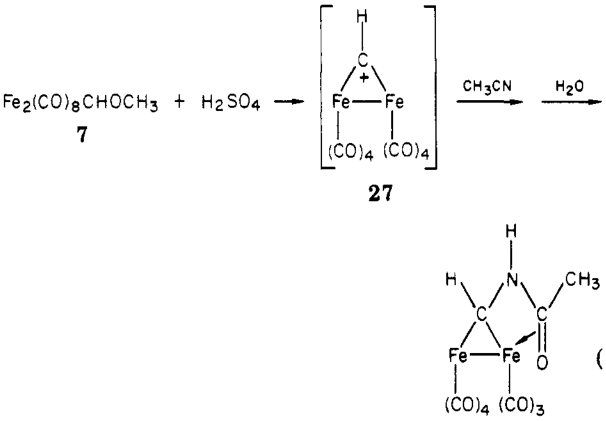
Treatment of the methoxymethylene complex **7** with H_2 at 125 °C in heptane produces dimethyl ether and a trinuclear hydride which has IR, ^1H NMR, and mass spectral data identical with the trinuclear cluster **26** prepared by Shriver et al.[19] (eq 19). The formation of **26** is presumably due to the reaction of coordinatively unsaturated iron carbonyl species with the methoxymethylene **7**. The hydride **26** was also obtained in good yield by treatment of **7** with $Fe_2(CO)_9$.



7 **26**

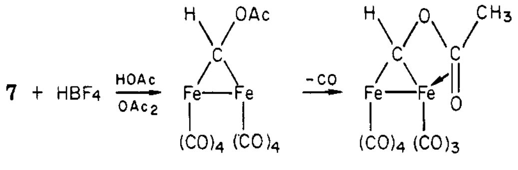
$CH_3—O—CH_3$ (19)

Reaction of the methoxymethylene complex **7** with strong acid leads to products that can be thought of as being derived from the bridging carbyne cation **27**. For example, treatment of **7** with H_2SO_4 in the presence of acetonitrile, followed by aqueous workup, results in the isolation of a red crystalline compound formulated as having structure **28** (eq 20) on the basis of its elemental analysis, IR, ^1H NMR, and mass spectra. Infrared stretching frequencies at 1561 and 1540 cm^{-1} are consistent with the acetanilide carbonyl group being coordinated to an iron atom. In an analogous reaction, treatment of **7** with HBF_4 in 95% acetic anhydride (5% acetic acid) results in the isolation of the octacarbonyl acetoxymethylene complex **29** as yellow crystals which, upon standing in solution at room temperature, rapidly lose a CO ligand to give the red, crystalline heptacarbonyl acetoxymethylene complex **9** (eq 21). The IR spectrum of **29** contains a band at 1760 cm^{-1} which is assigned to the acetoxy carbonyl group as well as bands corresponding to metal carbonyls. Upon warming, the band at 1760 cm^{-1} disappears and is replaced by a band at 1615 cm^{-1}, which is consistent with the acetoxy carbonyl group being coordinated to an iron atom.



7 **27** **28**

(20)



29 **9**

(21)

Similar reactivity has been observed for the dicyclopentadienyl-substituted methoxymethylene complex **30**.[20] Treatment of **30** with HBF_4 in CH_2Cl_2 at *low* temperature, followed by the addition of triphenylphosphine, results in the isolation of the phosphonium salt **32** which is presumably formed via the cation **31** (eq 22). If the methoxymethylene complex **7** is protonated in the absence of a trapping agent, the cation formed incorporates 1 equiv of CO to give carboxymethylene derivatives. For example, addition of **7** to cold, concentrated H_2SO_4, followed by addition of the H_2SO_4 solution to ethanol results in the isolation of the (carboethoxy)methylene complex **6** (eq 23).

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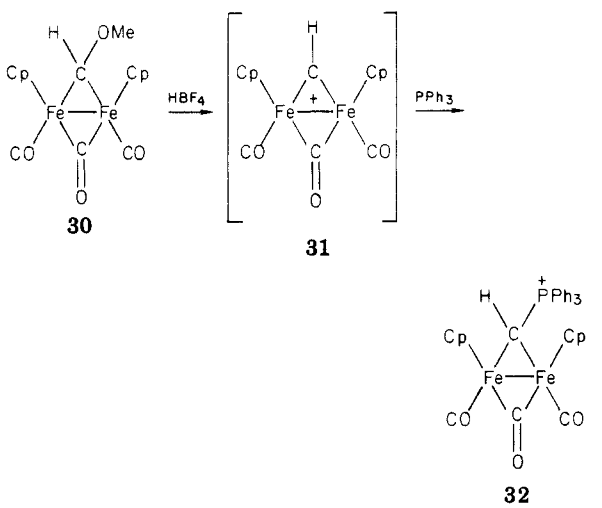
[18] Davis, R. E., The university of Texas at Austin, personal communication.

[19] Howard, J. A. K.; Jeffery, J. C.; Laguna, M.; Navano, R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1981**, 751. See also: Sternberg, H. W.; Shukys, J. G.; Donne, C. D.; Mackby, R.; Fuedel, R. A.; Wender *J. Am. Chem. Soc.* **1959**, *81*, 2339. Guthrie, D. J. S.; Khand, I. V.; Knox, G. R.; Kallmeier, J.; Pauson, P. L.; Watts, W. E. *J. Organomet. Chem.* **1975**, *90*, 93.

[20] Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. soc.* **1982**, *104*, 1134-1136. Kao, S. K.; Liu, P.; Pettit, R. *Organometallics* **1982**, *1* 811.

[21] Addition of ethanol or water to **34** gives the (carboethoxy)methylene complex **6** and the (carbohydroxy)methylene complex **32**, respectively.



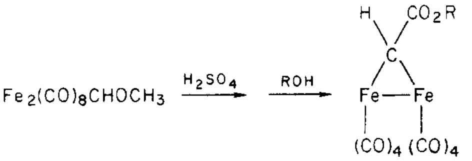
30

31

32

(22)

Cp = C_5H_5



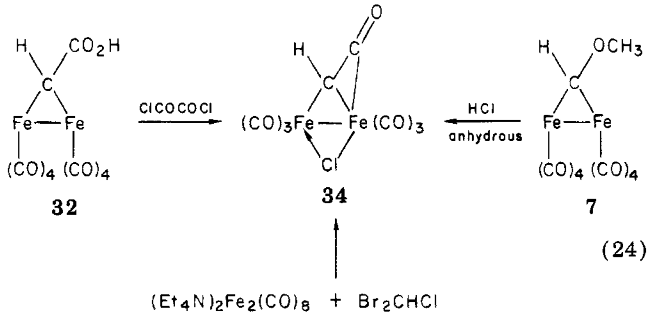
(23)

32, R = H
6, R = Et

If the H_2SO_4 solution is added to water, a compound identified as the (carbohydroxy)methylene complex **33** by comparison of its melting point (79 °C dec) and IR spectrum to a sample prepared by the hydrolysis of **6** (vide infra) is isolated.

The (carboethoxy)methylene complex $Fe_2(CO)_8C(H)CO_2Et$ (**6**) is observed to readily react with aqueous acids to give a yellow crystalline compound **33** which is only slightly soluble in organic solvents and dilute aqueous base solutions in which it slowly decomposes. The above hydrolysis is reversible, and facile esterification gives back the (carboethoxy)methylene **6** in 70% yield. Complex **33** is formulated as $Fe_2(CO)_8C(H)CO_2H$. The IR spectrum of solid **33** (C_5Cl_6 mull) displays absorptions at 3600–3200 (H_2O), 3100–2400 ($HCCO_2H$), 2120 (m), 2070 (s), 2035 (vs), 2020 (s), 1995 (s), and 1645 (m) cm^{-1}. The IR of **33** in solution (CH_2Cl_2) is very similar to $Fe_2(CO)_8CH_2$ except for a weak band at 1650 cm^{-1}. The elemental analysis of **33** is consistent with it being a hydrate. Hydrogenation of **33** gives acetic acid in 63% yield.

Reaction of **7** with anhydrous HCl produces a red, pentane-soluble solid which has also been prepared by treatment of the (carbohydroxy)methylene **33** with oxalyl chloride and by the reaction of $(Et_4N)_2Fe_2(CO)_8$ with chlorodibromomethane (eq 24). The structure of the red solid is tentatively assigned as the ketenyl diiron carbonyl **34** on the basis of its high-resolution mass spectrum, ^1H NMR [δ (C_6D_6) 0.75], ^{13}C NMR [δ (C_6D_6, off-resonance decoupled) 208 (s), 162 (s), −4 (d)], and reactivity.



32

34

7

(24)

The high-field chemical shifts for the hydrogen atom and the carbon bearing the hydrogen atom are consistent with the π complex as formulated in structure **34**. The infrared spectrum shows absorptions in the terminal carbonyl region at 2105 (m), 2062 (s), 2050 (s), 2005 (s), 1972 (w), and 1952 (w) cm^{-1} (hexane). If formulation **34** is indeed correct, then the ketenyl carbonyl stretch must be among the terminal CO absorptions.

Conclusion

The reaction of geminal diiodoalkanes and certain geminal dibromides with $(Et_4N)_2Fe_2(CO)_8$ to give diiron μ-alkylidene complexes appears to be a general reaction. The compounds formed by this reaction are reactive towards H_2, olefins, alkynes, nucleophiles, and phosphines. Complexes containing a functionalized methylene ligand such as methoxymethylene can undergo transformations involving the methylene ligand to give other functionalized μ-methylene complexes. The μ-alkylidine complexes which possess a β-hydrogen atom are unstable at room temperature in solution where they decompose to give an alkene and $Fe_3(CO)_{12}$. Briding methylene complexes are also produced by acylation of $Na_2Fe_2(CO)_8$ and $NaHFe_2(CO)_8$. In the case of $NaHFe_2(CO)_8$, the hydrogen atom originally bound to iron is incorporated into the methylene ligand.

Experimental Section

Preparation of $N(C_2H_5)_4Fe_2(CO)_8$. The synthesis of $[N(C_2H_5)_4]_2Fe_2(CO)_8$ was performed in a dry, 2-L, three-necked separatory type round-bottomed flask. The base of the reaction vessel was equipped with a 1.5-in. coarse glass frit, a No. 8 Pyrex stopcock, and a 24/40 male ground-glass joint. The reaction vessel was set atop a 3-L flask which could be evacuated. Clean sodium (9.33 g, 0.406 mol) and naphthalene (4.5 g, 0.035 mol) were added to the reaction flask under argon. The flask was fitted with a septum, and 400 mL of dry THF was added. The septum was replaced with a dry, pressure equalizing, dropping funnel containing $Fe(CO)_5$ (55 mL, 0.41 mol). Addition of $Fe(CO)_5$ to the mechanically stirred mixture was carried out at such a rate that the temperature of the reaction was maintained at about 30 °C when all of the $Fe(CO)_5$ had been added, the reaction was stirred for an additional 15 h; 5 mL of MeOH was added and the reaction mixture stirred an additional 0.5 h. Care should be taken to make sure all sodium has been consumed. Evacuation of the bottom flask allowed filtration of the reaction mixture by opening the No. 8 stopcock. When the level of the reaction solution was just even with the level of the solid mass of $Na_2Fe_2(CO)_8{\cdot}x$THF, filtration was stopped. Distilled water (200 mL) was added to the reaction vessel, and stirring was recommenced. Addition of $[N(C_2H_5)_4]Br$ (95 g, 0.45 mol) in distilled water (200 mL) afforded a brick-red precipitate. The mixture was filtered as before and then washed thoroughly with the following solvents: 400 mL of distilled H_2O, 2 × 400 mL of absolute EtOH, 2 × 400 mL of THF, and 2 × 400 mL of Et_2O. The solid thus obtained was dried under a vacuum to constant weight, giving 90 g of $(NEt_4)_2Fe_2(CO)_8$, yield 74%.

Preparation of $Fe_2(CO)_8CH_2$ (1). To a 1-L, three-necked, round-bottom flask equipped with a mechanical stirrer and dropping funnel were added $(Et_4N)_2Fe_2(CO)_8$ (41.5 g, 0.07 mol) and 250 mL of acetone. The mixture was cooled to 0 °C while being stirred. Methylene iodide (21.4 g, 0.08 mol), in 45 mL of acetone, was added over a 20-min period, and the reaction mixture was stirred at 0 °C a further 40 min under an argon atmosphere. The color of the solution changed from red to dark brown during the course of the reaction. The reaction mixture was filtered under a stream N_2, and the residue was washed with cold acetone until the washings were pale yellow. The residue, which consisted of $Fe_2(CO)_8CH_2$ and Et_4NI, was transferred to a 600-mL beaker and washed with 150 mL of distilled water, filtered, and washed again with 50 mL of cold acetone. The product was transferred to a 50-mL round-bottomed flask and dried under vacuum to constant weight: yield 14.5 g (60%); mp 135 °C dec; IR (CH_2Cl_2) 2112, 2061, 2031, 2016 (sh) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 5.5 (s); mass spectrum, *m/e* 350, 336, 322, 308. Anal. Calcd for $C_9H_2Fe_2O_8$: C, 30.90; H, 0.57. Found: C, 31.50; H, 0.90.

Preparation of $Fe_2(CO)_8C(CH_3)_2$ (3). To a 50-mL round-bottomed flask equipped with a magnetic stirring bar and rubber septum were added $(Et_4N)_2Fe_2(CO)_8$ (3.37 g, 5.7 mmol) and 25 mL of acetone. The mixture was stirred and cooled to 0 °C, and 2,2-diiodopropane (1.68 g, 5.7 mmol) in 5 mL of acetone was syringed into the reaction mixture. The reaction mixture was stirred at 0 °C for 1 h while the color changed from red to dark brown. The solvent was rapidly removed at 0 °C by high vacuum, leaving a black solid residue. The residue was extracted with 30-mL portions of pentane. The pentane was removed by vacuum at 0 °C, leaving 1.0 g of greenish yellow crystals, which were recrystallized from pentane at −78 °C: yield 1.0 g (49%); mp 47–48 °C dec; IR (hexane) 2105, 2060, 2030, 2010 (sh), 1872, 1847 cm^{-1}; ^{1}H NMR (acetone-d_6, 0 °C) δ 2.9 (s); ^{13}C NMR ($CDCl_3$, Me_4Si, −10 °C) δ 213, 148, 50; high-resolution mass spectrum, *m/e*(calcd) 377.8760, *m/e*(measd) 377.8751.

Preparation of $Fe_2(CO)_8CHCH_3$ (2). The procedure described for the preparation of $Fe_2(CO)_8C(CH_3)_2$ was followed, except that 1,1-diiodoethane was used. The product was obtained as yellow crystals: yield 16%; mp 50 °C dec; IR (hexane) 2105, 2060, 2030, 2010, 1910–1840 (br) cm^{-1}; ^{1}H NMR (acetone-d_6, −10 °C) δ 2.7 (d, 3 H, *J* = 8 Hz), 7.2 (q, 1 H, *J* = 8 Hz); ^{13}C NMR ($CDCl_3$, 0 °C) δ 211, 119, 39; high-resolution mass spectrum, *m/e*(calcd) 363.8604, *m/e*(measd) 363.8619.

The sample used for the ^{1}H NMR was let stand at ambient temperature for 30 min. The solution changed colors from yellow to dark green, indicating the formation of $Fe_3(CO)_{12}$.[22] The gasses over the solution were analyzed by gas chromatography and were found to contain approximately 75% ethylene.

Preparation of $Fe_2(CO)_8CHCH(CH_3)_2$ (4). The procedure described for the preparation of $Fe_2(CO)_8C(CH_3)_2$ was followed, except that 1,1-diiodo-2-methylpropane was used. The product was obtained as yellow crystals: yield 26%; mp 73–75 °C dec; IR (hexane) 2105, 2050, 2020, 2005, 1985 (sh), 1940–1900 (br) cm^{-1}; ^{1}H NMR (acetone-d_6, 0 °C) δ 1.3 (d, 6 H), 2.6 (m, 1 H), 6.7 (d, 1 H, *J* = 14 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si, −10 °C) δ 212, 140, 51, 31; high-resolution mass spectrum, *m/e*(calcd) 391.8917, *m/e*(measd) 391.8910.

The sample used for the ^{1}H NMR at 0 °C was let stand at room temperature for 30 min; then the spectrum was taken again. The signals at δ 1.3, 2.6, and 6.7 had disappeared and were replaced by signals at δ 1.6 (s, 1 H), and 4.5 (s, 1 H). The gasses over the solution were analyzed by gas chromatography and were found to contain isobutylene.

Preparation of $Fe_2(CO)_8CH(CH{=}CH_2)$ (5). To a 100-mL, round-bottomed flask equipped with a magnetic stirring bar were added $(Et_4N)_2Fe(CO)_8$ (3.95 g, 3.2 mmol) and 30 mL of acetone. The mixture was cooled to 0 °C with stirring; diiodopropene (1.93 g, 3.2 mmol) dissolved in 10 mL of acetone was syringed into the reaction mixture. The reaction mixture was stirred for three minutes at 0 °C while the color changed from red to dark brown. The solvent was rapidly removed by vacuum, leaving a black solid residue. The residue was extracted with pentane as described for the preparation of $Fe_2(CO)_8C(CH_3)_2$. the product was obtained as yellow crystals from the pentane at −78 °C: yield 13%; IR (hexane) 2100, 2055, 2030, 2015 (sh), 1860 (br) cm^{-1}; ^{1}H NMR ($CDCN_3$, −30 °C) δ 4.9 (d, 1 H), 5.2 (m, 1 H), 6.8 (two doublets, 2 H). Anal. Calcd for $C_{14}H_4Fe_2O_8$: C, 35.11; H, 0.80. Found: C, 34.22; H, 1.20.

The sample used for the ^{1}H NMR at −30° C was removed from the NMR probe and let stand at room temperature for 15 min while the color of the solution changed from yellow to dark red; then the spectrum was taken again. The signals at δ 4.5, 5.2, and 6.8 had disappeared and were replaced by signals at δ 2.2 (d of d, 1 H), 2.8 (m, 1 H), 5.7 (m, 1 H), and 8.5 (d of d, 1 H), indicating the formation of the σ,π-allyl complex **15**.

Preparation of $Fe_2(CO)_8C(H)CO_2Et$ (6; Dihalide Method). To a stirred suspension of $[N(C_2H_5)_4]Fe_2(CO)_8$ (5.14 g, 8.6 mmol) in 25% acetone–diethyl ether (v:v) held at 0 °C in an ice bath was added dropwise $I_2C(H)CO_2C_2H_5$ (2.94 g, 8.7 mmol) as a solution in 20% acetone–diethyl ether (v:v). The reaction mixture was stirred for 5 minutes and filtered. The volatile components were removed from the filtrate under vacuum, and the resulting tar was extracted with pentane. The extracts were combined, concentrated, and chromatographed on Florisil. Elution of an orange band with pentane–benzene (95:5, v:v) gave $Fe_2(CO)_8C(H)CO_2C_2H_5$ as an orange oil which solidified on standing at −10 °C: yield 0.26 g (7%); ~29 °C; IR (C_6H_{14}) 2114 (m), 2066 (s), 2033 (vs), 2016 (vs), 1973 (m), 1688 (m) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 5.8 (s, 1 H), 4.0 (q, 2 H, *J* = 8 Hz), 1.1 (t, 3 H, *J* = 9 Hz); ^{13}C NMR ($CDCl_3$, −10 °C) δ 208, 182, 101, 61, 15; mass spectrum, *m/e* 394, 366, 338, 210. Anal. Calcd for $C_{12}H_6Fe_2O_{10}$: C, 34.17; H, 1.43; Fe, 26.48. Found: C, 32.99; H, 1.40; Fe, 26.33.

Preparation of $Fe_2(CO)_8CHOCH_3$ (7). $(Et_4N)Fe_2(CO)_8$ (16.3 g, 27 mmol) was added over 35 min to a stirring solution of dibromomethyl methyl ether (5.4 g, 26 mmol) in 53 mL of CH_2Cl_2 at 0 °C. The resulting mixture was stirred 15 min and the solvent removed. The residue was extracted with pentane, and the extracts were filtered. Removal of the solvent gave 3.1 g of a brown crystalline material which was recrystallized from pentane: mp 60–61 °C; ^{1}H NMR (C_6D_6) δ 3.0 (s, 3 H), 8.2 (s, 1 H); IR (hexane) 2110, 2055, 2030 (sh), 2019, 2003, 1980–1950 (sh), 1890, 1855 cm^{-1}; ^{13}C NMR ($CDCl_3$, proton decoupled from Me_4Si) 65, 174, 211 ppm; mass spectrum, *m/e* 380, 352, 296. Anal. Calcd for $C_{10}H_3Fe_2O_8$: C, 31.62; H, 1.06; Fe, 29.41. Found: C, 31.81; H, 1.22; Fe, 30.38.

Reaction of $(Et_4N)_2Fe_2(CO)_8$ with $CHCl_2(OCH_3)$. To a 50-mL round-bottom flask equipped with a magnetic stirring bar and rubber septum were added $(Et_4N)_2Fe_2(CO)_8$ (2.72 g, 4.6 mmol) and 15 mL of degassed acetone. The mixture was cooled to 0 °C while being stirred vigorously. Neat dichloromethyl methyl ether (524 mg, 4.6 mmol) was added via syringe, and the reaction mixture was stirred for 3 h at 0 °C. After this time, the $(Et_4N)_2Fe_2(CO)_8$ was still observable (as an insoluble solid), and the reaction mixture contained no pentane-soluble products.

Reaction of $(NEt_4)_2Fe_2(CO)_8$ and Br_2CHCO_2K. To 4 mL of 50% aqueous acetone containing $(NEt_4)_2Fe_2(CO)_8$ (0.58 g, 0.97 mmol) was added Br_2CHCO_2K (0.25 g, 0.98 mmol) in 7 mL of 50% aqueous acetone. The reactants were shaken vigorously until no $(NEt_4)_2Fe_2(CO)_8$ remained. To this solution was then added 6 mL of 18% aqueous HCl, and the mixture was extracted with methylene chloride. The methylene chloride extract was separated from the aqueous layer and dried over $MgSO_4$. Removal of solvent gave a solid mass (0.13 g) containing green and yellow crystals. Purification was accomplished by dissolving the solid mixture in absolute ethanol (3 mL) to which was added 2 mL of concentrated H_2SO_4. The solution was shaken for several minutes. Extraction with pentane followed by chromatography over Florisil of the pentane extracts gave 28 mg of crystalline $Fe_2(CO)_8CH(CO_2C_2H_5)$ (6%).

Preparation of $Fe_2(CO)_8C(H)CO_2Et$ (6). Ethyl diazoacetate (0.50 g, 0.0044 mol) in 10 mL of hexane was added dropwise over a 10-min period to a stirring suspension of $Fe_2(CO)_9$ (0.70 g, 0.0018 mol) in 15 mL of hexane at 50–55 °C. When addition was complete, the reaction mixture was filtered and the volatile components were removed under vacuum. The remaining residue was extracted with pentane and chromatographed over Florisil. Development with 5% benzene–pentane (v:v) eluted $Fe_2(CO)_8C(H)CO_2C_2H_5$ as a yellow band (67 mg, 8%), the physical properties of which (IR, NMR, mass spectroscopy) were identical with those of authentic $Fe_2(CO)_8C(H)CO_2C_2H_5$.

Preparation of $Fe_2(CO)_8CHOCOCH_3$ (28). $Fe_2(CO)_8CHOCH_3$ (492 mg, 1.3 mol) was added as a solid (at 0 °C over a 10-min period) to a solution of $HBF_4{\cdot}Et_2O$ (626 mg, 3.9 mmol) in 4.5 mL of acetic anhydride containing 5% acetic acid. The reaction mixture was stirred until all the solid had dissolved (approximately 5 min) and poured slowly onto 9.1 g of ice. An immediate precipitation of small yellow crystals occurred. The ice water was extracted with pentane (3 × 5 mL), and the combined pentane layers were washed with 10 mL of ice water and dried over K_2CO_3 at 0 °C. The dried solution was filtered, concentrated, and chilled to −20 °C. Filtration yielded 250 mg of long yellow needles (yield 47%): mp 45–46 °C; IR (hexane) 2110, 2065, 2038, 2020, 1830–1900, 1760 cm^{-1}; ^{1}H NMR ($CDCl_3$, −10 °C) δ 2.1 (s, 4 H), 9.0 (s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si −10 °C) 208, 169, 154, 21 ppm.

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(22) Determined by high resolution mass spectrascopy.

(23) Blanchard, E. P.; Simmons, H. E. *J. Am. Chem. Soc.* **1964**, *86*, 1337.

A sample of the yellow crystalline material was dissolved in hexane and let stand at room temperature for 30 min. The color of the solution changed from yellow to red, and the IR spectrum of the solution showed it to contain $Fe_2(CO)_7CHOCOCH_3$. Removal of the solvent left red crystals of the heptacarbonyl complex, mp 83–84 °C.

Preparation of $Fe_2(CO)_7CHOCO(CH_3)$ (7). The procedure given for the preparation of $Fe_2(CO)_8CHOCO(CH_3)$ was followed; filtration and removal of the pentane solvent left a red oil which crystallized upon standing: yield 90%; mp 83–84 °C; IR (hexane) 2089, 2045, 2018, 2000, 1964, 1945, 1616 cm^{-1}; ${}^1H$ NMR (C_6D_6) δ 1.2 (s, 3 H), 9.1 (s, 1 H); ${}^{13}C$ (MR ($CDCl_3$, Me_4Si) 222, 184, 170, 19 ppm; mass spectrum, m/e 380, 352, 324, 296. Anal. Calcd for $C_{10}H_4Fe_2O_9$: C, 31.48; H, 1.05; Fe, 29.47. Found: C, 31.50; H, 1.03; Fe, 29.45.

Reaction of $(Et_4N)_2Fe_2(CO)_8$ with Dibromochloromethane. To a 100-mL, three-necked, round-bottomed flask equipped with a magnetic stirring bar and dropping funnel were added $(Et_4N)_2Fe_2(CO)_8$ (4.10 g, 6.9 mmol) and 20 mL of acetone. The mixture was cooled to −20 °C, and dibromochloromethane (1.45 g, 6.96 mmol) was added over a 15-min period. The reaction mixture was stirred an additional 10 min at −15 °C, and the color of the solution changed from red to black. The solvent was removed by high vacuum at −7 °C, leaving a black solid residue. The residue was extracted with 3 × 50-mL portions of pentane which were immediately filtered through a celite pad into a round-bottomed flask which was submerged in a dry ice–acetone bath. The pentane was evaporated under reduced pressure, leaving an orange crystalline residue which was chromatographed over Florisil.

Elution with hexane produced a dark red oil which was crystallized from pentane at −40 °C: yield 464 mg; mp 52–53 °C; IR (hexane) 2105, 2062, 2052, 2015, 2005, 1972, 1952 cm^{-1}; ${}^1H$ NMR (C_6D_6) δ 0.7 (s). Anal. Calcd for $C_9HClFe_2O_8$: C, 28.09; H, 0.26; Cl, 9.23; Fe, 29.13. Found: C, 25.53; H, 0.60; Cl, 11.54; Fe, 31.96.

Preparation of $Fe_2(CO)_6(PMe_3)_2CH_2$ (24). $Fe_2(CO)_8CH_2$ (1.94 g, 5.5 mmol) in 20 mL of hexane was warmed to 45 °C. $P(CH_3)_3$ (1.05 mL, approximately 11 mmol) dissolved in 20 mL of hexane was added dropwise over a 1.5-h period with stirring under an argon atmosphere. After the addition, the reaction mixture was stirred an additional 15 min, cooled, and filtered through a celite pad. Removal of the solvent left an orange residue which consisted of $Fe_2(CO)_6(PMe_3)_2CH_2$, $Fe(CO)_3(PMe_3)_2$, and $Fe(CO)_4PMe_3$. The two mononuclear by products were sublimed (0.22 torr at 65 °C) from the residue. The residue was recrystallized from hexane at −20 °C to give 339 mg (20%) of orange needles: mp 93–96 °C; ${}^1H$ NMR (C_6D_6) δ 4.1 (t, 2 H, J = 4 Hz), 0.9 (d, 18 H, J = 9 Hz); ${}^{13}C$ NMR (C_6D_6, Me_4Si) 17.0 (d, J = 29 Hz), 79.3 (t, J = 4 Hz), 226.5 (d, J = 3 Hz) ppm; ${}^{13}P$ NMR (C_6H_6, referenced to external H_3PO_4) 13.39 ppm (s); IR (hexane) 2025, 1995, 1963, 1940, 1825, 1850–1830 (br) cm^{-1}; mass spectrum, m/e 446, 418, 390, 362. Anal. Calcd for $C_{13}H_{20}Fe_2O_6P_2$: C, 34.98; H, 4.48; Fe, 25.11; P, 13.90. Found: C, 34.92; H, 4.63; Fe, 24.95; P, 6.67.

Acylation of $Na_2Fe_2(CO)_8$. Acetyl bromide (1.9 mL, 0.026 mol) was added dropwise to a mechanically stirred mixture of $Na_2Fe_2(CO)_8$ (4.8 g, 0.013 mol) and 40 mL of tetrahydrofuran at 0 °C. After 1 h, the solvent was removed while the temperature of the reaction vessel was maintained at 0 °C. The resulting residue was extracted with pentane; the pentane extracts were concentrated and chromatographed over Florisil. $Fe_2(CO)_7C(CH_3)OAc$ was eluted with pentane. Crystallization from pentane gave an orange-red solid: yield 0.55 g (11%); mp 59–62 °C; IR (C_6H_{14}) 2083 (m), 2060 (vw), 2044 (vs), 2010 (s), 1996 (vs), 1961 (m), 1936 (sh), 1615 (m) cm^{-1}; ${}^1H$ NMR (C_6D_6) δ 1.06 (s, 3 H), 2.90 (s, 3 H); ${}^{13}C$ NMR ($CDCl_3$) 211, 209, 197, 181, 42, 19 ppm; mass spectrum, m/e 394, 366, 338, 310. Anal. Calcd for $C_{11}H_6Fe_2O_9$: C, 33.54; H, 1.54; Fe, 28.36. Found: C, 33.77; H, 1.59; Fe, 30.95.

Acylation of $NaHFe_2(CO)_8$. $Na_2Fe_2(CO)_8$ (1.50 g, 3.93 mmol) was slurried in tetrahydrofuran (THF) (15 mL), protonated with acetic acid (0.23 mL, 4.0 mmol), and chilled immediately in an ice bath. The resulting mixture was filtered cold and the clear solution of $NaHFe_2(CO)_8$ allowed to react at 0 °C for 1.5 h with acetyl chloride (0.58 mL, 8.13 mmol). The solution was warmed to room temperature, and the volatile materials were removed and collected under vacuum. The remaining residue was extracted and chromatographed over Florisil. Elution with pentane gave $Fe_2(CO)_7C(H)OAc$ (0.29 g, 18%). The product obtained was found to be identical (IR, ${}^1H$ NMR, mixed melting point) with the complex produced from protonolysis of $Fe_2(CO)_8C(H)OCH_3$ in acetic acid. Analysis of the volatile materials showed the presence of acetaldehyde (20–25%).

Acylation of $NaDFe_2(CO)_8$. The above procedure was repeated except that deuterioacetic acid (99.5% 1-*d*) was used in place of acetic acid. Isolated **9** was found to contain 85% deuterium incorporation by ${}^1H$ NMR. ${}^{13}C$ NMR analysis of **9** confirmed deuteurium incorporation of the bridgehead carbon.

Acylation of the Ferrole 16. To a 10-mL, round-bottomed flask were added 300 mg of the ferrole [prepared from $Fe_2(CO)_8CH_2$ and acetylene], 3 mL of pyridine, and 3 mL of benzene. Acetyl chloride (1.1 g, 14 mmol) was added to the solution all at once. A precipitate was immediately formed. The reaction mixture was refluxed for 5 min, cooled, and poured into 2 mL of cold water. The benzene layer was washed with water, with dilute HCl, and again with water. Evaporation of the solvent left a yellow, oily residue which was chromatographed on Florisil. Elution with benzene–hexane (1:1) produced a yellow oil which was crystallized from hexane: yield 64 mg (19%); mp 63–64 °C; IR (hexane) 2080 (m); 2042 (2), 2000 (s), 1995 (sh), 1964 (m), 1771 (m) cm^{-1}; ${}^1H$ NMR (C_6D_6) δ 1.6 (s, 3 H), 5.0 (d of d, 1 H), 5.4 (d of d, 1 H), 5.9 (d of d, 1 H); mass spectrum, m/e 390, 362, 334, 306. Anal. Calcd for $C_{12}H_6Fe_2O_8$: C, 36.92; H, 1.54; Fe, 28.72. Found: C, 37.08; H, 1.47; Fe, 28.52.

Hydrogenation of Alkylidenes. Reaction between H_2 and the iron carbonyl alkylidenes listed in Table II gave good to excellent yields of the expected organic molecule. Hydrogenations were carried out in 60-mL stainless-steel autoclaves equipped with glass inserts. The reaction vessels were heated in an oil bath and stirred magnetically. The data are given in Table II of the text.

Reaction of $Fe_2(CO)_8CH_2$ with Ethylene. A 65-mL autoclave equipped with a magnetic stirring bar was charged with $Fe_2(CO)_8CH_2$ (1.179 g, 3.4 mmol), benzene (10 mL), and ethylene (400 psi) and heated at 55 °C for 2 h. After the mixture was cooled to 0 °C, the gas phase was vented into a 1-L water burette and analyzed for propylene (65%). The solution was purged with N_2 and this gas was analyzed. The solution was also analyzed for propylene (total yield was 96%). The IR of the solution exhibited bands at 2080, 1997, and 1980 cm^{-1} due to $C_2H_4Fe(CO)_4$.[24]

Reaction of $Fe_2(CO)_8CH_2$ with Propylene. The procedure described above was followed, except that propylene (approximately 50 psi) was used instead of ethylene. The C_4 hydrocarbons were analyzed on a Carbopak 0.19% picric acid column. The C_4 hydrocarbons fround were the following: isobutylene (78%), *trans*-2-butene (15%), *cis*-2-butene (5%), and 1-butene (1%). The IR of the solution showed bands at 2075, 2010 (sh), 1995, and 1968 cm^{-1}, probably due to $C_3H_6Fe(CO)_4$.

Reaction of $Fe_2(CO)_8CH_2$ with Isobutylene. $Fe_2(CO)_8CH_2$ (997 mg, 2.8 mmol) was added to 10 mL of degassed benzene in a 60-mL autoclave containing a magnetic stirring bar. The autoclave was sealed, and the solution was saturated with isobutylene. The autoclave was placed into an oil bath, heated to 60 °C and stirred for 1 h cooled to room temperature, and washed. Filtration of the reaction mixture left 800 mg (90%) of unreacted starting material (mp 135–140 °C dec).

Reaction of $Fe_2(CO)_8CD_2$ with Isobutylene. The procedure given above was followed except that $Fe_2(CO)_8CD_2$ (280 mg, 0.8 mmol) prepared by reaction of $(Et_4N)_2Fe_2(CO)_8$ and CD_2I_2[23] was used instead of $Fe_2(CO)_8CH_2$ and the reaction mixture was heated for 4 h. Filtration of the reaction mixture left 170 mg (60%) of unreacted starting material. The mass spectrum of the unreacted starting material showed only the presence of $Fe_2(CO)_8CD_2$.

Reaction of $Fe_2(CO)_8CH_2$ with Methyl Acrylate. To a 25-mL round-bottomed flask equipped with a magnetic stirring bar and reflux condensor were added $Fe_2(CO)_8CH_2$ (350 mg, 1.0 mmol), benzene (10 mL), and methyl acrylate (176 mg, 2.0 mmol). The reaction mixture was monitored by gas chromatography and was heated at 75 °C until the concentration of methyl crotonate remained constant (about 1 h). The solution was allowed to cool

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[24] Murdoch, H. D.; Weiss, E. *Helv. Chim. Acta* **1963**, *46*, 1588–1594.

and was analyzed by gas chromatography. The yield of methyl crotonate was 79%; the yields of methyl methacrylate and an unidentified product were approximately 2% and 3%, respectively.

Reaction of $Fe_2(CO)_8CH_2$ with Acetylene. To a 100-mL three-necked, round-bottomed flask equipped with a magnetic stirring bar, rubber septum, thermometer, and a gas inlet tube were added toluene (45 mL) and $Fe_2(CO)_8CH_2$ (2.00 g, 5.7 mmol). The solution [only a small amount of $Fe_2(CO)_8CH_2$ was dissolved] was heated to 65 °C. Acetylene (141 mL) was added to the reaction mixture over a 1.5-h period with occasional venting to release evolved CO, while the color changed from bright yellow to dark red. Stirring was continued an additional 25 min, and then the reaction mixture was cooled to 0 °C and filtered, which allowed the recovery of 287 mg (15%) of starting material. The filtrate was evaporated and the residue was taken up in pentane and chromatographed over Florisil. Elution with pentane produced 870 mg of the σ,π-allyl complex **15** as a dark red oil: yield 870 mg (51%); ^{1}H NMR (C_6D_6, σ,π-allyl) δ 3.0 (dd, 1 H, J_{ax} = 9 Hz, J_{bx} = 3 Hz), 2.3 (m, 1 H), 5.1 (m, 1 H), 8.0 (d, 1 H, J = 8 Hz); IR (hexane) 2099, 2039, 2015, 1984 (sh), 1975 cm^{-1}; ^{13}C NMR ($DCCl_3$, Me_4Si) δ 47, 97, 154, 209, 211. Anal. Calcd for $C_{10}H_4Fe_2O_7$: C, 34.48; H, 1.15. Found: C, 34.22; H, 1.20.

Elution with 10% ether–pentane produced 441 mg of the ferrole **16** which was crystallized from ether–hexane: yield 441 mg (26%); mp 44–47 °C; ^{1}H NMR (C_6D_6) δ 4.4 (dd, 1 H, J_{ax} = 3.0 Hz, J_{bx} = 2.7 Hz, α to hydroxyl group), 4.9 (dd, 1 H, J_{ax} = 5.4 Hz, J_{bx} = 3.0 Hz, β-hydrogen), 5.0 (br, 1 H, hydroxyl), 6.1 (dd, 1 H, J_{ax} = 5.4 Hz, J_{bx} = 2.7 Hz, α to Fe); IR (hexane) 2080, 2040, 2020, 1980, 1965 cm^{-1}. Anal. Calcd for $C_{10}H_4Fe_2O_7$: C, 34.48; H, 1.15; Fe, 32.18. Found: C, 35.08; H, 1.80; Fe, 30.85.

Reaction of the σ,π-Allyl Complex 15 with Ph_3P. The σ,π-allyl complex **15** dissolved in 7 mL of degassed hexane was added to a 25-mL round-bottom flask containing a magnetic stirring bar and Ph_3P (217 mg, 0.8 mmol). The reaction mixture was stirred at room temperature under argon for 3 h, during which time the product precipitated from the solution. Filtration of the reaction mixture yielded a dark red crystalline residue **25** which was washed twice with 5-mL portions of cold pentane: yield 300 mg (64%); mp 108 °C dec; IR (hexane) 2060, 2015, 1980, 1965 cm^{-1}; ^{1}H NMR (C_6D_6) δ 2.2–2.5 (m, 2 H), 5.4 (dd, 1 H), 7.0 (m, 10 H), 7.2–7.5 (m, 6 H), 8.1 (d of m, 1 H). Anal. Calcd for $C_{27}H_{19}Fe_2O_6P$: C, 52.76; H, 3.09; Fe, 18.24; P, 5.05. Found: C, 55.63; H, 3.35; Fe, 19.21; P, 5.10.

Reaction of $Fe_2(CO)_8CH_2$ with Propyne. To a 100-mL round-bottomed flask containing a magnetic stirring bar were added $Fe_2(CO)_8CH_2$ (1.58 g, 4.5 mmol) and 30 mL of benzene. This mixture was heated to 60 °C with stirring, and propyne (232 mL, 9.0 mmol) was bubbled into the solution over a 1-h period; the color of the reaction mixture changed from yellow to red. The reaction mixture was stirred another 0.5-h (until all solid had disappeared), cooled to 0 °C, and filtered, and the solvent was removed, leaving a red, oily residue. The residue was chromatographed on alumina. An orange, oily material (561 mg) was eluted with pentane–benzene (1:1). Crystallization from methanol produced red, oily crystals which the ^{1}H NMR showed to be impure: mp 78–85 °C; IR (hexane) 2081 (m), 2042 (s), 2002 (s), 1991 (m), 1981 (sh), 1963 (w) cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.3 (2 pk, 1.2 H), 0.9–1.1 (5 pk, 1.2 H), 1.7 (br, 4 H), 2.3 (s, 3 H), 3.2 (s, 1 H), 3.8–4.0 (dd, 1.2 H), 6.4 (s, 0.3 H); mass spectrum, *m/e* 388, 374, 346, 318.

The ferrole **19** (548 mg) was eluted from the column with methanol and was crystallized from toluene–ether (3:1): yield 34%; mp 80–88 °C; IR (THF) 2070 (w), 2040 (m), 2030 (sh), 1990 (s), 1959 (s), 1942 (s), 1920 (sh), 1712 (w) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.4 (d, 1 H, J = 5.4 Hz), 5.8 (d, 1 H, J = 5.4 Hz), 3.2 [s, 4.8 H (water)], 1.5 (s, 3 H). Attempts to obtain a mass spectrum were unsuccessful. Anal. Calcd for $C_{11}H_6Fe_2O_7 \cdot 3H_2O$: C, 31.73; H, 2.88; Fe, 26.92. Found: C, 30.55; H, 2.53; Fe, 25.68.

Reaction of $Fe_2(CO)_8CH_2$ with 2-Butyne. To a 50-mL round-bottom flask equipped with a magnetic stirring bar and rubber septum were added $Fe_2(CO)_8CH_2$ (1.05 g, 3.0 mmol), 20 mL of degassed benzene, and 2-butyne (197 mg, 3.6 mmol). The mixture was heated at 60 °C for 1.8 h while being stirred. The reaction mixture was chilled to 0 °C and filtered, which allowed the recovery of 100 mg of starting material. Removal of the solvent left a red, oily residue which was chromatographed on alumina. Elution with pentane produced 225 mg of a red oil which was crystallized from pentane and was identified as the diinsertion product **20**: yield 225 mg (21%); mp 120–123 °C; IR (hexane) 2060, 2018, 1989, 1980, 1968, 1939 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.0 (d, 3 H, J = 6 Hz), 1.2 (s, 3 H), 1.7 (s, 3 H), 1.8 (q, 1 H, J = 6 Hz), 2.5 (s, 3 H), 3.8 (s, 1 H); mass spectrum, *m/e* 402, 374, 346, 318. Anal. Calcd for $C_{12}H_{14}Fe_2O_6$: C, 44.78; H, 3.48. Found: C, 44.95; H, 3.68.

Elution with methanol produced 483 mg of a yellow solid which was recrystallized from toluene and identified as the ferrole **21**: yield 483 mg (40%); mp 109–120 °C dec; IR (THF) 2040, 1988, 1959, 1940, 1920 (sh), 1640 (br, w) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 1.4 (s, 3 H), 2.1 (s, 3 H), 3.15 (water, 4 H), 3.3 (methanol, 1.5 H), 7.1 (s, 1 H). Attempts to obtain a mass spectrum were unsuccessful. Anal. Calcd for $C_{12}H_8Fe_2O_7 \cdot 3H_2O$: C, 33.48; H, 3.26. Found: C, 33.40; H, 2.75.

Reaction of Allene and $Fe_2(CO)_8CH_2$. $Fe_2(CO)_8CH_2$ (2.04 g, 5.82 mmol) in benzene (35 mL) was stirred in a 100-mL flask fitted with a condensor and heated to 60 °C, and then allene was bubbled through the solution until no undissolved $Fe_2(CO)_8CH_2$ remained (approximately 20 min). The solution was cooled and the benzene distilled under reduced pressure; the remaining red oil was sublimed. The low melting yellow crystalline sublimate had spectroscopic properties (IR, NMR, mass spectroscopy) identical with those of authentic (trimethylenemethane)tricarbonyliron, 0.214 g (19%).

Reaction of $Fe_2(CO)_8CH_2$ with PhC≡CH. To a 100-mL three-necked, round-bottomed flask were added powdered $Fe_2(CO)_8CH_2$ (1.28 g, 3.7 mmol) and 15 mL of benzene. The mixture was stirred magnetically and heated to 50 °C, and then phenyl acetylene (377 mg, 3.7 mmol) dissolved in 10 mL of benzene was added dropwise over a 6-min period. The reaction mixture was stirred an additional 10 min, cooled to 0 °C, and filtered, and the solvent was removed, leaving a purple oil which was chromatographed over Florisil. Elution with hexane produced 440 mg (28%) of a dark red oil which was the σ,*p*-allyl complex **22**. Crystallization from hexane at −78 °C afforded dark red needles: mp 66–68 °C; IR (hexane) 2090 (m), 2037 (s), 2010 (s), 1980 (w), 1970 (w) cm^{-1}; ^{1}H NMR (C_6D_6) δ 3.6 (d, 1 H, J = 10 Hz), 5.75 (d of d, 1 H, J_{ab} = 10 Hz, J_{ax} = 7 Hz), 7.1 (s, 5 H), 8.0 (d, 1 H, J = 7 Hz); mass spectrum, *m/e* 424, 397, 368, 340. Anal. Calcd for $C_{16}H_8Fe_2O_7$: C, 45.28; H, 1.89. Found: C, 43.41; H, 2.27.

Elution with benzene produced 136 mg of a yellow, oily compound which was presumed to be a phenyl-substituted ferrole by analogy to the reactions of **1** with other alkynes: IR (THF) 2040 (m), 1990 (s), 1960 (s), 1940 (m), 1920 (sh) cm^{-1}; ^{1}H NMr (C_6D_6) δ 5.5 (m, 1 H), 5.1 (d, 1 H), 6.4 (br, 1 H), 6.9–7.4 (m, 10 H).

Reaction of the σ,π-Allyl Complex 15 with Acetylene. Acetylene (44 mL) was added to the σ,π-allyl complex (420 mg, 1.2 mmol) dissolved in 10 mL of hexane. The reaction mixture was stirred for 12 h at room temperature, concentrated, and chromatographed on Alumina (80–325 mesh). The orange zone, eluted with hexane, contained 162 mg of the hexacarbonyl complex **17**, which was recrystallized from hexane: yield 162 mg (40%); mp 32–33 °C; ^{1}H NMR (C_6D_6) δ 0.4 (dd, 1 H), J_{ax} = 12 Hz), 0.9 (dd, 1 H), J_{ax} = 8 Hz, J_{bx} = 1 Hz), 3.5 (m, 1 H), 3.7–4.0 (m, 2 H), 6.8 (dd, 1 H, J_{ax} = 5 Hz, J_{bx} = 3 Hz); ^{13}C NMR ($CDCl_3$) δ 42, 60, 83, 84, 149, 221; IR (hexane) 2070, 2025, 1999, 1995, 1979 cm^{-1}; mass spectrum, *m/e* 346, 318, 290, 262. Anal. Calcd for $C_{12}H_6Fe_2O_6$: C, 38.15; H, 1.73; Fe, 32.37. Found: C, 38.02; H, 1.80; Fe, 32.12.

Reaction of 15 with 2-Butyne. To the σ,π-allyl complex **15** (80 mg, 0.2 mmol) in 10 mL of hexane was added 2-butyne (15 mg, 0.3 mmol) in one portion. The reaction mixture was stirred at room temperature for 12 h. The solution was filtered through a celite pad and evaporated. The residue was crystallized from methanol at −78 °C, yielding orange cubes of **18**: yield 55 mg (74%); mp 101–108 °C; ^{1}H NMR (C_6D_6) δ 0.4 (d, 1 H, J = 12 Hz), 0.9 (d, 1 H, J = 7 Hz), 1.1 (s, 3 H), 2.3 (s, 3 H), 3.7 (m, 1 H), 4.0 (d, 1 H, J = 2 Hz); IR (hexane) 2070, 2025, 1995, 1991, 1973 cm^{-1}; mass spectrum, *m/e* 374, 346, 318, 290. Anal. Calcd for $C_{13}H_{10}Fe_2O_7$: C, 41.71; H, 2.67. Found: C, 41.78; H, 2.68.

Reaction of $Fe_2(CO)_8CH_2$ with Water. $Fe_2(CO)_8CH_2$ (757 mg, 2.2 mmol) was added to a 25-mL round-bottomed flask equipped with a magnetic stirring bar, a gas inlet tube, and a gas exit tube running to a solution of $Ba(OH)_2$ (0.13 M). Aqueous acetone (10%) was added, and the reaction mixture was stirred at room temperature for 5 h, during which time the color changed from yellow to dark red. Analysis of the solution by gas chromatography indicated the presence of acetaldehyde (5%) and acetic acid (33%); when the liquid phase was purged with argon, methane (10–30%) was detected in the gas phase together with small (5%) amounts of CO_2.

Reaction of $Fe_2(CO)_8CH_2$ with Aqueous NaI. $Fe_2(CO)_8CH_2$ (100 mg, 0.3 mmol) was added with stirring to 46 mg of NaI (0.31 mmol) in 1 mL of acetone. The solution immediately turned from yellow to dark red. Stirring was continued until all solid had dissolved (about 10 min), and then eight drops of 10% H_2SO_4 were added to the reaction mixture. The solution was analyzed by gas chroamtography and found to contain acetic acid (60%).

Reaction of $Fe_2(CO)_8CH_2$ with Aniline. A 65-mL autoclave was charged with $Fe_2(CO)_8CH_2$ (918 mg, 2.6 mmol), aniline (268 mg, 2.9 mmol), 10 mL of benzene, and CO (200 psi). The reaction mixture was heated at 85 °C for 2 h. After being cooled, the solution was filtered and evaporated. The brownish residue was recrystallized from benzene–ether, yielding 174 mg (50%) acetanilide as identified by its mass and IR (KBr) spectra and mixed melting point (111–113 °C).

Iodide-Catalyzed Reaction of $Fe_2(CO)_8CH_2$ with Aniline. Aniline (50 mg, 0.5 mmol) was added to a stirred acetone (2 mL) suspension of $Fe_2(CO)_8CH_2$ (100 mg, 0.3 mmol) at room temperature. A second reaction mixture identical with the one described was prepared, and 47 mg of NaI was added to it. The two reaction mixtures were stirred side-by-side. The mixture containing NaI turned red, and after stirring had continued for 45 min, most of the starting material had been consumed. Each reaction mixture was acidified with 2 mL of 10% H_2SO_4 and extracted with ether. Evaporation of the ether extract from the reaction without NaI left 5 mg of acetanilide. Evaporation of the ether extract from the reaction mixture that containing NaI left 25 mg (37%) of acetanilide.

Reaction of $Fe_2(CO)_8C(H)CO_2C_2H_5$ with C_2H_5OH. $Fe_2(CO)_8CH(CO_2C_2H_5)$ (41 mg, 0.10 mmol) and NaI (33 mg, 0.22 mmol) were stirred together in absolute ethanol (1 mL) at room temperature. After 3 h diethyl malonate was found to have been produced (56%). The same procedure was repeated as above, except no NaI was present. After 6 h, a 31% conversion of $Fe_2(CO)_8CH(CO_2Et)$ to diethyl malonate was found.

Reaction of $Fe_2(CO)_8CH_2$ with Isoamyl Alcohol. $Fe_2(CO)_8CH_2$ (1.10 g, 3.1 mmol) and isoamyl alcohol (1.09 g, 12.4 mmol) were refluxed in THF (11 mL) for 50 min. The solution was analyzed by gas chromatography and found to contain isoamyl acetate (1.0 mmol, 32%).

Reaction of $Fe_2(CO)_8CHOCH_3$ with $Fe_2(CO)_9$. To a 50-mL round-bottom flask equipped with a magnetic stirring bar, claisen head, and reflux condensor were added $Fe_2(CO)_8CHOCH_3$ (266 mg, 0.7 mmol) and 10 mL of degassed hexane. The solution was brought to a gentle reflux, and $Fe_2(CO)_9$ (764 mg, 2.1 mmol) was added as a solid to the solution over a 10-min period. The color of the reaction mixture changed from orange to purple during the course of the reaction. The reaction mixture was refluxed for 15 min after the addition of $Fe_2(CO)_9$ was complete and then filtered through a celite pad. Evaporation of the solvent left 170 mg of a very dark red crystalline solid which was recrystallized from hexane and determined to be $Fe_3(CO)_{10}H(COCH_3)$ (**26**) by comparison of its IR, ^1H NMR, and mass spectral data to those of an anthentic sample: mp 170 °C dec (lit. mp 135 °C dec); yield 170 mg (50%).

Reaction of $Fe_2(CO)_8CHOCH_3$ with H_2SO_4. $Fe_2(CO)_8CHOCH_3$ (300 mg, 0.8 mmol) was added as a solid to 15 mL of ice-cold H_2SO_4. The solution immediately turned blood red. When all starting material had dissolved, the reaction mixture was slowly poured into a stirred beaker of ice water. A yellow solid immediately precipitated. The solid was extracted from the reaction mixture with ether, washed with water, and dried over $MgSO_4$. Filtration and removal of the solvent left 170 mg of yellow crystals which were identified as $Fe_2(CO)_8CHCO_2H$ (**33**) by comparison of the melting point and IR spectrum to those of an authentic sample prepared by the hydrolysis of $Fe_2(CO)_8CH(CO_2C_2H_5)$: yield 170 mg (55%); mp 76–84 °C; IR (CH_2Cl_2) 2110, 2062, 2030, 2015, 1690 cm^{-1}.

Reaction of $Fe_2(CO)_8CHOCH_3$ with H_2SO_4 in Acetonitrile. To $Fe_2(CO)_8CHOCH_3$ (278 mg, 0.76 mmol) dissolved in 3.0 mL of acetonitrile at 0 °C was added 0.3 mL of H_2SO_4. The solution was stirred at 0 °C for 30 min while the color changed from yellow to red. The reaction mixture was poured onto ice (1 g) and extracted with ether (10 mL). The ether layer was dried over K_2CO_3 and filtered. Removal of the ether left a crystalline residue which was a mixture of starting material and $Fe_2(CO)_7CHNHCOCH_3$. The residue was washed with hexane which removed the starting material (46 mg) and left 87 mg $Fe_2(CO)_7CHNHCO(CH_3)$ (**28**) as red crystals: yield 87 mg (38%); mp 108–112 °C; IR (CH_2Cl_2) 3382, 2080, 2030, 1995 (br), 1980 (br), 1940–1860 (sh), 1561, 1540 cm^{-1}; ^1H NMR (acetone-d_6) δ 2.0 (s, 3 H), 2.9 (br, 1 H), 8.3 (d, 1 H, $J = 2.7$ Hz; mass spectrum, m/e 378, 350, 322, 294. Anal. Calcd for $C_{10}H_5Fe_2NO_8$: C, 31.66; H, 1.32; Fe, 29.55; N, 3.69. Found: C, 31.30; H, 1.37; Fe, 29.29; N, 3.69.

Reaction of $Fe_2(CO)_8CHOCH_3$ with Anhydrous HCl. $Fe_2(CO)_8CHOCH_3$ (218 mg, 0.6 mmol) was dissolved in 10 mL of pentane and cooled to 0 °C. Anhydrous HCl was bubbled through the solution until no starting material could be detected by IR (about 1 h). The color of the solution changed from yellow to dark red during the course of the reaction. The reaction mixture was flushed with argon, filtered through a celite pad, and let stand over K_2CO_3. The solution was filtered, concentrated to 2 mL, and slowly cooled to −40 °C. An 127-mg sample of dark red crystals separated: yield 127 mg (59%); mp 50–52 °C; IR (hexane) 2105, 2062, 2052, 2015, 2005, 1972, 1952 cm^{-1}; ^1H NMR (C_6D_6) δ 0.7 (s); ^{13}C NMR (C_6D_6, Me_4Si, off-resonance decoupled) 208 (s), 162 (s), −4 (d) ppm; high-resolution mass spectrum, m/e(calcd) 355.8108, m/e(measd) 355.8112. Anal. Calcd for $C_8HClFe_2O_7$: C, 26.97; H, 0.28; Cl, 9.97; Fe, 31.46. Found: C, 24.31; H, 1.52; Cl, 10.41; Fe, 31.17.

Hydrolysis of $(Fe_2(CO)_8C(H)CO_2C_2H_5$. An acetone solution (5 mL) of $Fe_2(CO)_8C(H)CO_2C_2H_5$ (0.10 g, 0.24 mmol) was treated with concentrated HCl (5 mL). The solution was stirred for 10–15 min at room temperature during which time a yellow precipitate of $Fe_2(CO)_8C(H)CO_2H{\cdot}H_2O$ was formed. The contents of the flask were transferred to a separatory funnel and diluted with 10 mL of water. The mixture was extracted with 2 × 20-mL portions of CH_2Cl_2. The CH_2Cl extracts were combined and dried over NaCl. The solvent was removed, and the solid obtained was washed with a minimal amount of cold pentane. Crystallization from CH_2Cl_2 gave $Fe_2(CO)_8C(H)CO_2H{\cdot}H_2O$: mp 76–82 °C dec; IR ($CH_2Cl_2$) 2116 (m), 2070 (vs), 2035 (vs), 2018 (s), 1690 (vw), 1645 (m) cm^{-1}. Anal. Calcd for $C_{10}H_4Fe_2O_{11}$: C, 29.16; H, 0.98; Fe, 27.17. Found: C, 28.84; H, 0.85; Fe, 27.88.

Esterification of $Fe_2(CO)_8C(H)CO_2H$. $Fe_2(CO)_8C(H)CO_2H$ (47 mg, 0.12 mmol) was dissolved in a solution of absolute ethanol (3 mL) and concentrated sulfuric acid (0.5 mL). The solution was stirred for 10 min at room temperature and then poured into 25 mL of water. The aqueous solution was extracted with pentane. The pentane extracts were washed with water, dried over NaCl, and filtered. Removal of solvent left partially crystalline orange material whose properties (IR, NMR) were identical with those of authentic $Fe_2(CO)_8C(H)CO_2C_2H_5$, yield 35 mg (70%).

Registry No. **1**, 73448-09-6; **2**, 82665-68-7; **3**, 82665-69-8; **4**, 82665-70-1; **5**, 82665-71-2; **6**, 82665-72-3; **7**, 82665-73-4; **8**, 82665-74-5; **9**, 82665-75-6; **15**, 82665-76-7; **16**, 74381-48-9; **16**-Ac, 82665-87-0; **17**, 82665-77-8; **18**, 82678-90-8; **19**, 82665-78-9; **20**, 82665-79-0; **21**, 82678-91-9; **22**, 82678-92-0; **23**, 12078-33-0; **24**, 82665-80-3; **25**, 82665-81-4; **26**, 82665-89-2; **28**, 82665-82-5; **29**, 82665-83-6; **33**, 82665-84-7; **34**, 82665-85-8; $[N(C_2H_5)_4]_2Fe_2(CO)_8$, 26024-88-4; $Fe(CO)_5$, 13463-40-6; $[N(C_2H_5)_4]Br$, 71-91-0; $I_2C(H)CO_2C_2H_5$, 82665-91-6; Br_2CHCO_2K, 67060-06-4; $Fe_2(CO)_9$, 15321-51-4; $P(CH_3)_3$, 594-09-2; $NaHFe_2(CO)_8$, 60308-01-2; PPh_3, 603-35-0; $PhC{\equiv}CH$, 536-74-3; NaI, 7681-82-5; C_2H_5OH, 64-17-5; H_2SO_4, 7664-93-9; HCl, 7647-01-0; methylene iodide, 75-11-6; 2,2-diiodopropane, 630-13-7; 1,1-diiodoethane, 594-02-5; 1,1-diiodo-2-methylpropane, 10250-55-2; 1,1-diiodopropene, 82665-90-5; dibromomethyl methyl ether, 3492-44-2; dichloromethyl methyl ether, 4885-02-3; ethyl diazoacetate, 623-73-4; dibromochloromethane, 124-48-1; dark red oil, 82665-86-9; acetyl bromide, 506-96-7; acetyl chloride, 75-36-5; ethylene, 74-85-1; propylene, 115-07-1; isobutylene, 115-11-7; methyl acrylate, 96-33-3; acetylene, 74-86-2; propyne, 74-99-7; (*Z*)-butyne, 503-17-3; allene, 463-49-0; phenyl-substituted ferrole, 82665-88-1; water, 7732-18-5; aniline, 62-53-3; isoamyl alcohol, 123-51-3.