

Chemistry of the Metal Carbonyls. Part LXX.¹ Trimethylsilyl, Trimethylgermyl, and Trimethylstannyl Derivatives of Cyclo-octatetraene and their Complexes with the Tricarbonyliron Group

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Reactions of the compounds Me_3MCl ($\text{M} = \text{Si}$ or Sn) and Me_3GeBr with diethyl ether solutions obtained by treating bromocyclo-octatetraene with *n*-butyl-lithium at -80°C afford the monosubstituted cyclo-octatetraene compounds $\text{C}_8\text{H}_7\text{MMe}_3$. The complex $[\text{Fe}(\text{CO})_2(\text{C}_8\text{H}_7)(\eta\text{-C}_5\text{H}_5)]$ has been similarly prepared from $[\text{FeCl}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$. These cyclo-octatetraene derivatives react with enneacarbonyliron to yield complexes of the tricarbonyliron group: the silicon and tin derivatives also form binuclear iron complexes $[\text{Fe}_2(\text{CO})_8(\text{C}_8\text{H}_7\text{MMe}_3)]$. The complexes $[\text{Fe}(\text{CO})_3(\text{C}_8\text{H}_7\text{MMe}_3)]$ ($\text{M} = \text{Si}$ or Ge) react with Ph_3CBF_4 to yield tetrafluoroborate salts which on hydrolysis give complexes $[\text{Fe}(\text{CO})_3\{\text{C}_8\text{H}_6(\text{MMe}_3)(\text{CPh}_3)\}]$ containing disubstituted cyclo-octatetraene ligands.

It has long been known² that bromocyclo-octatetraene and *n*-butyl-lithium react at low temperatures in diethyl ether to give *n*-butyl bromide and cyclo-octatetraenyl-lithium. The latter proved to be a useful intermediate in the synthesis of some monosubstituted derivatives of cyclo-octatetraene. For example, with carbon dioxide $\text{C}_8\text{H}_7\text{CO}_2\text{H}$ is obtained. Cyclo-octatetraene itself reacts with aryl- or alkyl-lithium compounds to give monosubstituted aryl- or alkyl-cyclo-octatetraenes.^{3,4} In contrast, cyclo-octatetraene derivatives are not readily obtainable from electrophilic reagents, although recent work has shown that co-ordination of a tricarbonyliron group to cyclo-octatetraene allows certain electrophilic addition and substitution reactions to occur.⁵⁻⁷ In this way many complexes in which a functional organic group has been substituted on to the cyclo-octatetraene ring of tricarbonyl(η -cyclo-octatetraene)iron have been prepared.

Work involving new ligands^{8,9} in this laboratory required the synthesis of cyclo-octa-tetraene and -triene derivatives containing trimethylsilyl and trimethylgermyl substituent groups. Herein we report the preparation of the monocyclo-octatetraene compounds $\text{C}_8\text{H}_7\text{R}$ [$\text{R} = \text{SiMe}_3$, $\text{SiMe}_2(\text{CH}_2\text{CH}:\text{CH}_2)$, GeMe_3 , and SnMe_3], as well as that of the iron complex $[\text{Fe}(\text{C}_8\text{H}_7)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$. The latter is believed to be the first example of a transition-metal complex with a σ -bonded cyclo-octatetraene ligand. Some preliminary studies on reactions of the new compounds are also described.

RESULTS AND DISCUSSION

Bromocyclo-octatetraene in diethyl ether at -80°C with *n*-butyl-lithium afforded an orange solution which

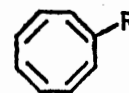
¹ Part LXIX, D. H. Bowen, M. Green, D. M. Grove, J. R. Moss, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 1189.

² A. C. Cope, M. Burg, and W. Fenton, *J. Amer. Chem. Soc.*, 1952, **74**, 173.

³ A. C. Cope and M. R. Kinter, *J. Amer. Chem. Soc.*, 1950, **70**, 630; 1951, **73**, 3424.

⁴ A. C. Cope and H. O. van Orden, *J. Amer. Chem. Soc.*, 1952, **74**, 175.

on warming to room temperature readily reacted with the compounds Me_3MCl ($\text{M} = \text{Si}$ or Sn), Me_3GeBr , $\text{Me}_2(\text{CH}_2\text{CH}:\text{CH}_2)\text{SiCl}$, and $[\text{FeCl}(\text{CO})_2(\text{C}_5\text{H}_5)]$ to afford compounds (I)–(IV) as yellow oils, and complex (V) as



- (I) $\text{R} = \text{SiMe}_3$
 (II) $\text{R} = \text{SiMe}_2(\text{CH}_2\text{CH}:\text{CH}_2)$
 (III) $\text{R} = \text{GeMe}_3$
 (IV) $\text{R} = \text{SnMe}_3$
 (V) $\text{R} = \text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)$

crystals melting at *ca.* 30°C . The ^1H n.m.r. spectra of (I), (III), and (IV) showed signals attributable to the MMe_3 groups (9H) but the ring C–H protons appeared as a broad resonance near τ 4.3 (7H). The influence of the MMe_3 group on the signals of the various ring protons is thus similar to that of Me and Ph groups on the shifts of the corresponding signals in methyl- and phenyl-cyclo-octatetraene.⁵ The ^1H n.m.r. spectrum of (II) was complicated by coincidence of the chemical shift of one of the protons of the allyl group with the seven protons on the cyclo-octatetraene ring. By contrast the σ -bonded $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)$ group had a pronounced effect on the shifts of the ring C–H protons of the cyclo-octatetraene group and a complex multiplet (7H) was observed from τ 3.75 to 4.75. The i.r. spectrum of (V) showed a shoulder on each of the two strong carbonyl bands (2021 and 1970 cm^{-1}) perhaps indicating the presence in solution of two conformations, possibly due

⁵ C. E. Keller, Ph.D. Thesis, University of Texas (Austin), 1966.

⁶ B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *J. Chem. Soc., (A)*, 1971, 422.

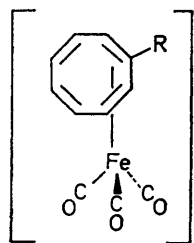
⁷ M. Green, S. Heathcock, and D. C. Wood, *J.C.S. Dalton*, 1973, 1564.

⁸ J. A. K. Howard, S. A. R. Knox, A. C. Szary, F. G. A. Stone, and P. Woodward, *J.C.S. Chem. Comm.*, 1974, 788.

⁹ A. C. Szary, Ph.D. Thesis, Bristol University, 1974.

to the known C_8 -ring inversion.¹⁰ Complex (V) is surprisingly robust, being recovered unchanged after heating under reflux in methylcyclohexane (2 h). No evidence was obtained for loss of CO with concomitant co-ordination to iron of one of the double bonds of the cyclo-octatetraene ring.

Compounds (I)—(V) readily react with enneacarbonyldi-iron to give complexes (VI)—(X), of which all except (IX), a red oil, are air-stable red crystalline solids. Each complex had an i.r. spectrum showing three carbonyl-stretching bands, compatible with the presence of an $Fe(CO)_3$ group, with the exception of (X) which



- (VI) R = $SiMe_3$
 (VII) R = $GeMe_3$
 (VIII) R = $SnMe_3$
 (IX) R = $SiMe_2(CH_2CH:CH_2)$
 (X) R = $Fe(CO)_2(C_5H_8)$

was more complex due to the superimposition of a dicarbonyl spectrum. The mass spectra of (VI)—(X) all showed peaks due to their molecular ions. In the 1H n.m.r. spectra of (VI)—(X) the C_8 ring protons had the same general pattern down to $-100^\circ C$: a low-field multiplet (3H); an apparent triplet (2H) showing evidence of fine structure; and an apparent doublet (2H) at higher field. This pattern is similar⁵ to that found in the spectra of the complexes $[Fe(CO)_3(C_8H_7R)]$ (R = Me or Et), which are known to undergo very low-energy degenerate rearrangement.¹¹ This behaviour is the reverse of that shown^{5,12} by $[Fe(CO)_3(C_8H_7R)]$ (R = CO_2R , CN, COMe, or CHO) where the doublet is observed as the signal at lowest field with the multiplet at higher field. On this basis we assign (VI)—(X) structures in which the $Fe(CO)_3$ group is co-ordinated to the diene system carrying the substituent group R.^{5,11,12} An oscillatory fluxional process¹¹ would account for the observed high-field doublet in the spectra of (VI)—(X), as well as the overall simplicity of the spectra which would average the environments of the proton pairs H^2, H^8 ; H^3, H^7 ; and H^4, H^6 (Scheme). In contrast, tricarbonyl(phenyl-cyclo-octatetraene)iron is believed¹² to undergo the fluxional process shown (Scheme) which averages the same proton pairs but produces a different order of chemical shifts with the doublet (H^2 and H^8) at low field.

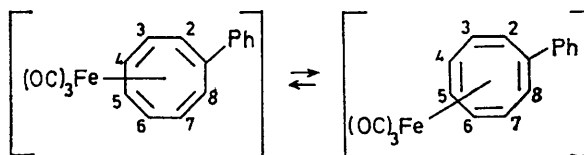
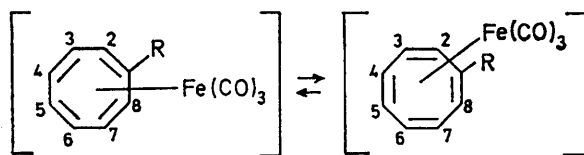
Careful chromatography of the products of reactions of enneacarbonyldi-iron with (I) or (IV) led to isolation of binuclear iron complexes $[Fe_2(CO)_6(C_8H_7MMe_3)]$ [(XI) M = Si, (XII) M = Sn]. Only mass-spectral

¹⁰ F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *J. Amer. Chem. Soc.*, 1964, **86**, 3576.

¹¹ F. A. L. Anet, *J. Amer. Chem. Soc.*, 1967, **89**, 2491.

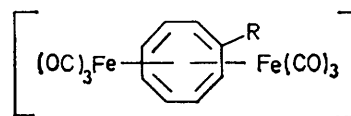
¹² L. A. Bock, Ph.D. Thesis, University of California (Los Angeles), 1969.

evidence was obtained (parent ion at m/e 502, followed by loss of six CO groups) for the existence of the germanium analogue. In compounds (XI) and (XII)



SCHEME

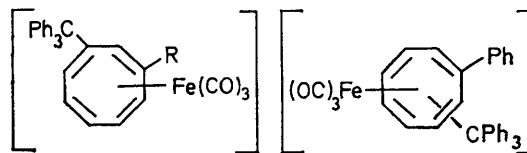
the two iron atoms could be on the same or on opposite sides of the C_8 ring. The latter is favoured on the basis of the i.r. spectra in the carbonyl-stretching region which did not resemble those observed in the spectra of related compounds known to contain an $Fe_2(CO)_6$ group with a metal-metal bond.^{13,14} Moreover, the 1H n.m.r. spectrum of (XI) showed signals



- (XI) R = $SiMe_3$
 (XII) R = $SnMe_3$

[τ 4.45 (2H), 4.72 (H), and 6.88 (4H)] with shifts similar to those observed in the spectrum of $[(OC)_3FeC_8H_8Fe(CO)_3]$ [τ 4.2 (4H) and 6.7 (4H)], whereas the shifts observed for the isomers with two $Fe(CO)_3$ groups on the same side of the cyclo-octatetraene ring are different.¹³

Complexes (VI), (VII), and $[Fe(CO)_3(C_8H_7Ph)]$ react with trityl tetrafluoroborate in nitromethane to give salts but their low solubility precluded n.m.r. studies. Hydrolysis of these yellow powders, followed by extraction with diethyl ether and chromatography, afforded complexes (XIII)—(XV) as air-stable red crystalline complexes, moderately soluble in hydrocarbons and ether. Mass spectra of the complexes show



- (XIII) R = $SiMe_3$
 (XIV) R = $GeMe_3$

(XV)

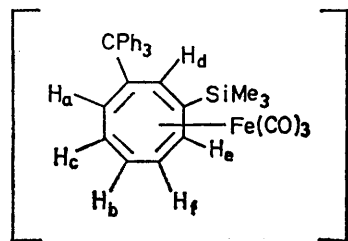
parent ions and ions at m/e 418, 464, and 422 corresponding to $[C_8H_8(SiMe_3)(CPh_3)]^+$, $[C_8H_8(GeMe_3)(CPh_3)]^+$, and $[C_8H_8(Ph)(CPh_3)]^+$, respectively.

The 1H n.m.r. spectra of (XIII) and (XIV) did not

¹³ C. E. Keller, G. F. Emerson, and R. Pettit, *J. Amer. Chem. Soc.*, 1965, **87**, 1388.

¹⁴ F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, 1971, **93**, 5069.

vary with temperature and allow a structural assignment to be made. They were of similar pattern, that of (XIII) (in CDCl_3) showing signals at τ 2.7 (m, 16H, C_6H_5), 3.57 (d, H_a , J 9.5), 4.06 (dd, H_b , J 8.5 and 10.5), 4.43 (dd, H_c , J 10.5 and 9.5), 5.32 (s, H_d), 5.42 (d, H_e , J 9.0), 5.57 (dd, H_f , J 8.5 and 9.0 Hz), and 9.85 (s, 9H, SiMe_3). Double irradiation indicated the sequence $\text{H}_a\text{-H}_c\text{-H}_b\text{-H}_f\text{-H}_e$ to be present, and that the singlet (τ 5.32) is slightly broadened (ca. 0.5 Hz) by a small



coupling to H_a . Since H_a and H_e display only one major coupling constant they must be located on carbon atoms adjacent to those carrying the CPh_3 and SiMe_3 substituents, which dictates that the singlet is due to a proton (H_d) on a carbon atom located between these groups. The position of the $\text{Fe}(\text{CO})_3$ moiety is assigned on the basis of the relatively high-field shifts of the signals assigned to H_d , H_e , and H_f , in accord with the trend for protons of a metal π -complexed diene system to occur at higher field. The proposed structure for (XIII) is supported by the results of an X-ray crystallographic study¹⁵ on a complex obtained by heating (XIII), which revealed that the CPh_3 and SiMe_3 groups were bonded to carbon atoms which were themselves separated by a single carbon atom. The ^1H n.m.r. spectrum of (XV) was complex and no firm assignment of structure can be made. Moreover, there was no signal obviously assignable to a single proton located on a carbon atom between the Ph and CPh_3 substituents, and thus (XV) may well have a different structure from (XIII) or (XIV).

Protonation of tricarbonyl(methylcyclo-octatetraene)-iron at low temperature yields two monocyclic isomeric complexes (66 and 33%) the structures of which show that electrophilic attack takes place at the internal carbon atoms of the uncomplexed diene moiety.¹⁶ This result contrasts with electrophilic attack of $[\text{Ph}_3\text{C}]^+$ on (VI) and (VII) to yield (XIII) and (XIV), respectively, where attack has occurred at an outer carbon atom of the 'free' diene part of the ligand to give a 1,3-disubstituted derivative. The absence in our systems of products in which 1,4-disubstitution has taken place indicates a preference for substitution at one end of the free diene group.

EXPERIMENTAL

^1H N.m.r. spectra were recorded on Varian HA100 and T60 spectrometers, and mass spectra with an A.E.I. MS902 instrument operating at 70 eV.* I.r. spectra were measured

* $1 \text{ eV} \approx 1.60 \times 10^{-19} \text{ J}$; $1 \text{ m} = 1 \text{ mol dm}^{-3}$.

¹⁵ M. Cooke, J. A. K. Howard, C. R. Russ, F. G. A. Stone, and P. Woodward, *J. Organometallic Chem.*, 1974, **78**, C43.

on a Perkin-Elmer 257 spectrophotometer. Solvents were dried and distilled under nitrogen, and all operations were conducted in an atmosphere of dry oxygen-free nitrogen.

Synthesis of Monosubstituted Cyclo-octatetraene Compounds, $\text{C}_8\text{H}_7\text{R}$.—In a typical preparation, bromocyclo-octatetraene (5 g, 27.3 mmol) and diethyl ether (15 cm^3) were stirred at -80°C , and n-butyl-lithium (15 cm^3 , 2.0M in hexane) was added over 2 min. Stirring was continued (1.5 h, -80°C), and chlorotrimethylsilane (10 g, 92.5 mmol) was then added to the orange-brown solution. After 30 min at room temperature, hydrolysis of the yellow reaction mixture with saturated ammonium chloride solution and fractional distillation of the dried ether layer afforded trimethylsilylcyclo-octatetraene, $\text{C}_8\text{H}_7\text{SiMe}_3$ (I), as a yellow oil, b.p. 50°C (0.1 mmHg), 3.9 g (80%) [Found: C, 75.2; H, 9.2%; M , 176 (mass spec.). $\text{C}_{11}\text{H}_{16}\text{Si}$ requires C, 75.0; H, 9.1%; M , 176]. ^1H N.m.r. spectrum (CCl_4): τ 4.27 (s, br, 7H) and 9.9 (s, 9H, Si-CH_3).

In a similar manner the following compounds were obtained. (a) $[(\sigma\text{-Allyl})\text{dimethylsilyl}]$ cyclo-octatetraene, $\text{C}_8\text{H}_7\{\text{SiMe}_2(\text{CH}_2\text{CH}(\text{CH}_2))\}$ (II), yellow oil, b.p. 58°C (0.1 mmHg), 6.0 g (50%) from $\text{Me}_2\text{Si}(\text{CH}_2\text{CH}(\text{CH}_2))\text{Cl}$ (8 g) [Found: C, 77.0; H, 9.1%; M , 202 (mass spec.). $\text{C}_{13}\text{H}_{18}\text{Si}$ requires C, 77.2; H, 8.9%; M , 202]. ^1H N.m.r. spectrum (CS_2): τ 4.4 (m, 8H); 5.32 (d, 2H, J 13 Hz, $\text{CH}(\text{CH}_2)$); 8.55 (d, 2H, J 8 Hz, SiCH_2); and 10.05 (s, 6H, Si-CH_3). (b) Trimethylgermylcyclo-octatetraene, $\text{C}_8\text{H}_7\text{GeMe}_3$ (III), yellow oil, b.p. 58°C (0.1 mmHg), 3.9 g (55%) from Me_3GeBr (6 g) [Found: C, 59.8; H, 7.0%; M , 222 (mass spec.). $\text{C}_{11}\text{H}_{16}^{74}\text{Ge}$ requires C, 59.8; H, 7.3%; M , 222]. ^1H N.m.r. spectrum (CCl_4): τ 4.3 (s, br, 7H) and 9.8 (s, 9H, Ge-CH_3). (c) Trimethylstannylcyclo-octatetraene, $\text{C}_8\text{H}_7\text{SnMe}_3$ (IV), yellow oil, b.p. 80°C (0.1 mmHg), 4.0 g (55%) from Me_3SnCl (5.2 g) [Found: C, 49.9; H, 6.2%; M , 268 (mass spec.). $\text{C}_{11}\text{H}_{16}^{120}\text{Sn}$ requires C, 49.6; H, 6.0%; M , 268]. ^1H N.m.r. spectrum (CCl_4): τ 4.28 (s, br, 7H) and 9.85 (s, 9H, Sn-CH_3). (d) Dicarboxyl(cyclo-octatetraenyl)(η -cyclopentadienyl)iron, $[\text{Fe}(\text{C}_8\text{H}_7)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (V), low melting (ca. 30°C) yellow crystals, 0.7 g (10%) from $[\text{FeCl}(\text{CO})_2(\text{C}_5\text{H}_5)]$ (6.0 g), and isolated by chromatography in hexane on alumina [Found: C, 64.2; H, 4.2%; M , 280 (mass spec.). $\text{C}_{15}\text{H}_{11}\text{FeO}_2$ requires C, 64.4; H, 4.3%; M , 280], $\nu(\text{CO})$ (max) in hexane at 2 024 (sh), 2 021s, 1 976 (sh), and 1 970s cm^{-1} . ^1H N.m.r. spectrum (C_6D_6): τ 3.77 (d, 1H, J 11); 3.9–4.4 (m, 5H); 4.67 (d, 1H, J 10 Hz); and 5.84 (s, 5H, C_5H_5).

Preparation of Tricarbonyliron Complexes.—Compound (I) (0.35 g, 2.0 mmol) and $\text{Fe}_2(\text{CO})_9$ (1.0 g, 2.75 mmol) were stirred in heptane (25 cm^3) for 12 h. Removal of solvent and chromatography of the product in hexane on alumina afforded deep red crystals of tricarbonyl(η -trimethylsilylcyclo-octatetraene)iron, (VI) (0.25 g, 40%), m.p. 49°C [Found: C, 53.5; H, 5.3%; M , 316 (mass spec.). $\text{C}_{14}\text{H}_{16}\text{FeO}_3\text{Si}$ requires C, 53.2; H, 5.1%; M , 316], $\nu(\text{CO})$ (max) in hexane at 2 053s, 2 001s, and 1 977s cm^{-1} . ^1H N.m.r. spectrum (CS_2): τ 4.19 (m, 3H); 4.65 (m, 2H); 5.57 (d, 2H); and 9.83 (s, 9H).

Similarly, from compound (III) (2.2 g, 10 mmol) and $\text{Fe}_2(\text{CO})_9$ (4 g, 11 mmol) were obtained red crystals of tricarbonyl(η -trimethylgermylcyclo-octatetraene)iron, (VII) (2.2 g, 60%), m.p. $62\text{--}64^\circ\text{C}$ [Found: C, 46.3; H, 4.5%; M , 362 (mass spec.). $\text{C}_{14}\text{H}_{16}\text{Fe}^{74}\text{GeO}_3$ requires C, 46.6; H, 4.5%; M , 362], $\nu(\text{CO})$ (max) in hexane at 2 044s,

¹⁶ M. Brookhart, E. R. Davis, and D. L. Harris, *J. Amer. Chem. Soc.*, 1972, **94**, 7853.

1 984s, and 1 974s cm^{-1} . ^1H N.m.r. spectrum (CS_2): τ 4.25 (m, 3H); 4.71 (m, 2H); 5.61 (d, 2H); and 9.7 (s, 9H).

Reaction between compound (IV) (0.5 g, 1.88 mmol) and $\text{Fe}_2(\text{CO})_9$ (1 g, 2.75 mmol) gave red *crystals* of tricarbonyl-(η -trimethylstannylcyclo-octatetraene)iron, (VIII) (79 mg, 10%), m.p. 91 $^\circ\text{C}$ [Found: C, 41.1; H, 3.9; *M*, 408 (mass spec.). $\text{C}_{14}\text{H}_{16}\text{FeO}_3^{120}\text{Sn}$ requires C, 41.3; H, 3.9%; *M*, 408], $\nu(\text{CO})$ (max) in hexane at 2 050s, 1 991s, and 1 971s cm^{-1} . ^1H N.m.r. spectrum (CS_2): τ 4.1 (m, 3H); 4.7 (m, 2H); 5.77 (d, 2H); and 9.75 (s, 9H).

{ η -[(σ -Allyl)dimethylsilyl]cyclo-octatetraene}tricarbonyliron, (IX), was obtained (1.28 g, 60%) as a red *oil* from (II) (1.25 g, 6.2 mmol) and $\text{Fe}_2(\text{CO})_9$ (3 g, 8.25 mmol) [Found: C, 56.6; H, 5.5%; *M*, 342 (mass spec.). $\text{C}_{16}\text{H}_{18}\text{FeO}_3\text{Si}$ requires C, 56.1; H, 5.3%; *M*, 342], $\nu(\text{CO})$ (max) in hexane at 2 052s, 1 988s, and 1 968s cm^{-1} . ^1H N.m.r. spectrum (CS_2): τ 4.3 (m, 4H); 4.8 (t, 2H); 5.15 (s, 1H); 5.25 (m, 1H); 5.64 (d, 2H); 8.45 (d, 2H); and 9.75 (s, 6H).

Using (V) (0.5 g, 1.79 mmol) and $\text{Fe}_2(\text{CO})_9$ (1 g, 2.75 mmol), red-orange *crystals* of tricarbonyl{ η -[dicarbonyl(η -cyclopentadienyl)ferrio]cyclo-octatetraene}iron, (X) (55 mg, 7%), m.p. 109 $^\circ\text{C}$ [Found: C, 51.4; H, 2.9%; *M*, 420 (mass spec.). $\text{C}_{18}\text{H}_{12}\text{Fe}_2\text{O}_5$ requires C, 51.5; H, 2.9%; *M*, 420] were obtained, $\nu(\text{CO})$ (max) in hexane at 2 048s, 2 021m, and 1 983vs cm^{-1} . ^1H N.m.r. spectrum (CS_2): τ 4.13 (m, 3H); 5.09 (m, 2H); 5.2 (s, 5H, C_5H_5); and 5.85 (d, 2H).

Isolation of Complexes [$\text{Fe}_2(\text{CO})_6(\text{C}_8\text{H}_7\text{SiMe}_3)$], (XI), and [$\text{Fe}_2(\text{CO})_6(\text{C}_6\text{H}_7\text{SnMe}_3)$], (XII).—Chromatography of the products from the reactions of (I) and (IV) with $\text{Fe}_2(\text{CO})_9$ gave in low yield (ca. 2%) yellow *needles* of μ -(1—4- η :5—8- η -trimethylsilyl- and μ -(1—4- η :5—8- η -trimethylstannylcyclo-octatetraene)-bis(tricarbonyliron) (XI) (m.p. 160 $^\circ\text{C}$) and (XII) (m.p. 133 $^\circ\text{C}$ decomp.), respectively. For (XI) [Found: C, 44.8; H, 3.6%; *M*, 456 (mass spec.). $\text{C}_{17}\text{H}_{16}\text{Fe}_2\text{O}_6\text{Si}$ requires C, 44.8; H, 3.5%; *M*, 456], $\nu(\text{CO})$ (max) in hexane occurred at 2 044s, 1 987vs, 1 982vs, and 1 978 (sh) cm^{-1} . ^1H N.m.r. spectrum (CDCl_3): τ 4.45 (m, 2H); 4.72 (d, 1H); 6.88 (m, 4H); and 9.75 (s, 9H). For (XII) [Found: C, 37.6; H, 3.1%; *M*, 548 (mass spec.). $\text{C}_{17}\text{H}_{16}\text{Fe}_2\text{O}_6^{120}\text{Sn}$ requires C, 37.2; H, 2.9%; *M*, 548],

$\nu(\text{CO})$ (max) in hexane occurred at 2 042s, 1 986vs, 1 981 (sh), and 1 974m cm^{-1} .

Reactions with Trityl Tetrafluoroborate.—In a representative experiment, Ph_3CBF_4 (0.31 g, 0.94 mmol) and (VI) (0.23 g, 0.73 mmol) were stirred in nitromethane (8 cm^3) for 15 min. The resulting solution was added to diethyl ether to afford a brownish yellow precipitate which was filtered off and hydrolysed with water (20 cm^3) for 4 h. Extraction with diethyl ether (3 \times 50 cm^3) gave a red solution which was dried (MgSO_4) and, after removal of ether, chromatographed in hexane on alumina to give red *crystals* of tricarbonyl(η -1-trimethylsilyl-3-tritylcyclo-octatetraene)iron [$\text{Fe}(\text{CO})_3\{\text{C}_6\text{H}_6(\text{SiMe}_3)(\text{CPh}_3)\}$], (XIII) (80 mg, 15%), m.p. 162—165 $^\circ\text{C}$ [Found: C, 71.8; H, 5.9%; *M*, 558 (mass spec.). $\text{C}_{33}\text{H}_{30}\text{FeO}_3\text{Si}$ requires C, 71.8; H, 5.4%; *M*, 558], $\nu(\text{CO})$ (max) in hexane at 2 047s, 1 990s, and 1 974s cm^{-1} . ^1H N.m.r. spectrum (CDCl_3): τ 2.7 [m, 15H, $\text{C}(\text{C}_6\text{H}_5)_3$]; 3.57 [d, H_a , $J(\text{H}_a-\text{H}_c)$ 9.5]; 4.06 [dd, H_b , $J(\text{H}_b-\text{H}_c)$ 10.5, $J(\text{H}_b-\text{H}_f)$ 8.5]; 4.43 (dd, H_c); 5.32 [s, H_d , $J(\text{H}_a-\text{H}_d) < 1$]; 5.42 [d, H_e , $J(\text{H}_e-\text{H}_f)$ 9.0 Hz]; 5.57 (dd, H_f); and 9.85 (s, 9H, SiMe_3).

Tricarbonyl(η -1-trimethylgermyl-3-tritylcyclo-octatetraene)iron, [$\text{Fe}(\text{CO})_3\{\text{C}_8\text{H}_8(\text{GeMe}_3)(\text{CPh}_3)\}$] (XIV), m.p. 161—163 $^\circ\text{C}$ (70 mg, 12%), red *crystals*, was prepared in a similar way from Ph_3CBF_4 (0.33 g, 1 mmol) and (VII) (0.36 g, 1 mmol) [Found: C, 66.0; H, 5.1%; *M*, 604 (mass spec.). $\text{C}_{33}\text{H}_{30}\text{Fe}^{74}\text{GeO}_3$ requires C, 65.7; H, 5.0%; *M*, 604], $\nu(\text{CO})$ (max) in hexane at 2 041s, 1 982s, and 1 973s cm^{-1} . ^1H N.m.r. spectrum (CS_2): τ 3.64 (d, 1H); 4.1 (dd, 1H); 4.53 (dd, 1H); 5.69 (m, 3H); and 9.9 (s, 9H) (CHCl_3 reference); and 2.75 (m, 15H) (Me_3Si reference).

Red crystalline [$\text{Fe}(\text{CO})_3\{\text{C}_8\text{H}_8(\text{Ph})(\text{CPh}_3)\}$], (XVI) (60 mg, 11%), m.p. 160—162 $^\circ\text{C}$ was prepared by the same method [Found: C, 77.3; H, 5.3%; *M*, 562 (mass spec.). $\text{C}_{36}\text{H}_{26}\text{FeO}_3$ requires C, 76.9; H, 4.7%; *M*, 562], $\nu(\text{CO})$ (max) in hexane at 2 042s, 1 985s, and 1 975s cm^{-1} . ^1H N.m.r. spectrum (CDCl_3): τ 2.8 (m, 20H); 4.1 (m, 2H); and 4.8—5.5 (m, 4H).

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