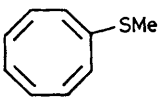
Organosulphur–Transition-metal Chemistry. Part 6.[1] Reactions of Cyclo-octatetraenyl and Cycloheptatrienyl Thioethers with Metal Carbonyls

By **Susan C. Carleton, Fiona G. Kennedy,** and **Selby A. R. Knox,** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The compound C_8H_7SMe has been prepared by treating cyclo-octatetraenyl-lithium with MeSCl. Reaction with $[Fe_2(CO)_9]$ provides tricarbonyliron complexes $[Fe(CO)_3(C_8H_7SMe)]$ and *trans*-$[Fe_2(CO)_6(C_8H_7SMe)]$; the former appears to undergo the characteristic oscillatory fluxional motion of such monosubstituted cyclo-octatetraene complexes, but the latter is non-fluxional. Sulphur–C_8H_7 bond cleavage is also evident, in the formation of $[Fe_2(CO)_6(\mu\text{-}SMe)_2]$ and $[Fe_4(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}SMe)_2]$, and of bicyclo-octatetraenyl when C_8H_7SMe and $[Ru_3(CO)_{12}]$ react. Similarly S–C_7H_7 bond cleavage is predominant in reactions of known C_7H_7SR-7 (R = Me or Ph) and new $C_7H_7SBu^t$-7 (from $[C_7H_7][BF_4]$ and $Na[SBu^t]$) with a variety of metal carbonyls. Only $[Fe_2(CO)_6(\mu\text{-}SR)_2]$ is obtained with $[Fe_2(CO)_9]$, and $[Mo_2(CO)_2(\mu\text{-}SBu^t)_2(\eta\text{-}C_5H_5)_2]$ with $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$, but from $[Ru_3(CO)_{12}]$ complexes, $[Ru_3(CO)_6(\mu_3\text{-}SBu^t)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ and $[Ru_2(CO)_4(\mu\text{-}SR)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$ (R = Me or Bu^t) are isolated, containing the components of C_7H_7SR as separate ligands. Fluxional rotation of the C_7H_7 ring in the diruthenium complexes is slowed at −100 °C, shown by n.m.r. spectra which also reveal restricted rotation about the S–Bu^t bond.

THE transition-metal chemistry of cyclo-octatetraene and its derivatives has attracted interest because of the variety of modes of co-ordination, the altered reactivity, and the rearrangements observed for the hydrocarbons, and also because of the fluxional behaviour which is frequently encountered.[2] Although a large number of monosubstituted derivatives of cyclo-octatetraene is known,[3] no thioether (or thiolato-derivative) such as C_8H_7SMe (1) has been described. In order to investigate the influence of the SR group on the co-ordination chemistry of cyclo-octatetraene this derivative has been prepared, and some reactions with metal carbonyls studied. The reactions of known [4,5] and new cycloheptatrienyl thioethers C_7H_7SR-7 are also described.



(1)

RESULTS AND DISCUSSION

Cyclo-octatetraenyl Thioethers.—Attempts to prepare cyclo-octatetraenyl thioethers by treating cyclo-octatetraenyl bromide with Na[SR] (R = Me, Ph, or Bu^t) or with RSH in the presence of triethylamine were unsuccessful. However, C_8H_7SMe (1) was obtained in 40% yield as a yellow oil when methanesulphenyl chloride (MeSCl) was added to a tetrahydrofuran (thf) solution of cyclo-octatetraenyl-lithium at −78 °C. Identification was achieved through elemental analyses, the mass spectrum, which showed the appropriate molecular ion, and the ^1H n.m.r. spectrum. The latter has a singlet signal due to the SMe group at τ 7.80 and multiplet olefinic proton resonance at τ 4.28, in the expected 3 : 7 intensity ratio.

Purification of (1) was by column chromatography, and provides the product contaminated with *ca.* 10% of an aromatic compound or compounds, revealed in the ^1H n.m.r. spectrum. It has not proved possible to remove the impurity; distillation (100 °C at 10^{-1} mmHg †) increases the contamination to *ca.* 30%. On standing in a nitrogen atmosphere a freshly prepared sample of (1) acquires a green-brown colouration within 12 h and the proportion of aromatic impurity rises to *ca.* 20%, but over another week no significant additional increase occurs. It is possible that some (1) is converted into PhCH=CH(SMe) through C_8 ring closure, by analogy with the thermal rearrangement of cyclo-octatetraenyl bromide to *trans*-β-bromostyrene.[6]

Care must be taken in the preparation of (1) because if the temperature rises substantially above −78 °C bicyclo-octatetraenyl [7,8] is formed readily. Moreover, use of less than pure MeSCl or C_8H_7Li gives exclusively aromatic products. Attempts to synthesise C_8H_7SPh by the same route from PhSCl and C_8H_7Li were unsuccessful, only bicyclo-octatetraenyl being formed.

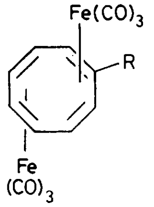
It had been anticipated that (1) might react with a metal carbonyl to act as an unusual chelating ligand, bonded to the metal through both the C_8 ring and sulphur. In the event it did not. In reactions with $[Fe_2(CO)_9]$ the thioether either gave typical carbonyliron complexes of the olefinic ring or underwent S–C bond cleavage. Room-temperature reaction with $[Fe_2(CO)_9]$ in thf provided $[Fe_2(CO)_6(C_8H_7SMe)]$ (2) as the major product, together with a very small amount of $[Fe(CO)_3(C_8H_7SMe)]$ (3). Insoluble, yellow crystalline (2) is assigned the *trans* arrangement of $Fe(CO)_3$ groups indicated on the basis of i.r., ^1H, and ^{13}C n.m.r. spectra. The i.r. spectrum is characteristic of two independent $Fe(CO)_3$ groups rather than of the alternative *cis* arrangement, when an iron–iron bond is present, as in *cis*-$[Fe_2(CO)_6(C_8H_8)]$.[9] The three carbonyl-stretching bands observed are in pattern and frequencies similar to those of unsubstituted *trans*-$[Fe_2(CO)_6(C_8H_8)]$ (4) [9-11] and its

---

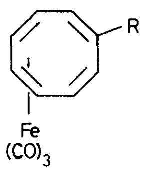
† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

derivatives *trans*-[$Fe_2(CO)_6(C_8H_7SiMe_3)$] (5) and *trans*-[$Fe_2(CO)_6(C_8H_7SnMe_3)$] (6).[12]

Like each of these complexes (2) is non-fluxional. The ^1H n.m.r. spectrum displays a singlet at τ 7.5 (3 H) due to the SMe substituent, and ring-proton signals at τ 4.4 (m, 3 H), 6.4 (d, 1 H), and 6.9 (m, 3 H). It is characteristic of $Fe(CO)_3$ η^4-co-ordinated to a 1,3-diene system for the ' inner ' diene protons to resonate at lower field than the ' outer ' diene protons, and on this basis the SMe group is clearly attached to an inner diene carbon. There are consequently three inner diene protons, those observed as a low-field multiplet, with the four outer diene protons providing the signals in the τ 6—7 region. The doublet signal at τ 6.4 is assigned to the inner proton adjacent to the SMe group, being brought to slightly lower field than the others by the inductive effect of that substituent. In accord with the structure (2) the ^{13}C n.m.r. spectrum has four signals in the region 49—60 p.p.m., three in the range 88—94 p.p.m., and one at 116 p.p.m. for the ring carbons; the latter may safely be attributed to the carbon bearing the electron-withdrawing SMe group.



(2; R = SMe)
(4; R = H)
(5; R = SiMe$_3$)
(6; R = SnMe$_3$)



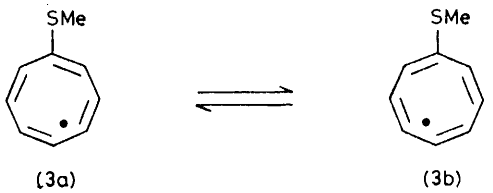
(3; R = SMe)
(7; R = H)

The other product obtained from [$Fe_2(CO)_9$] was identified readily as the η^4-C_8H_7SMe complex (3). It was not possible to determine the position of SMe substitution because the ring protons resonate in the narrow range τ 3.3—4.9 as a series of overlapping multiplets, but a large number of [$Fe(CO)_3(C_8H_7R)$] complexes is known and it is invariably the case that electron-withdrawing groups such as CN, Ph, CO_2R, *etc.* are found attached to an inner diene carbon on the unco-ordinated portion of the C_8 ring.[13,14] It seems likely, therefore, that a similar position of substitution will be adopted in (3) with $Fe(CO)_3$ co-ordinated to the electron-rich diene unit.

The complex [$Fe(CO)_3(C_8H_8)$] (7) is a classic fluxional molecule, and a progressive 1,2-shift of the $Fe(CO)_3$ group about the cyclo-octatetraene ring has been firmly established.[15] When a substituent is introduced into the ring the fluxionality becomes localised and oscillatory in nature as the metal undergoes a reversible 1,2-shift to avoid a particular diene portion of the hydrocarbon, determined by the nature of the substituent.[16] This oscillation is rapid even at low temperature, and for (3) will be of the form represented as (3a) $\rightleftharpoons$ (3b). It can be seen that this should manifest itself in the n.m.r. spectrum by generating time-averaged mirror symmetry. The overlap of the ring-proton signals of (3) does not allow this to be clearly detected, but the very narrowness of the range implies fluxionality. Were (3) stereochemically rigid, resonances for inner and outer diene protons would be observed at very different shifts, and averaging of proton environments is therefore indicated.

Prolonging the reaction of [$Fe_2(CO)_9$] with C_8H_7SMe reduced the yields of both (2) and (3) and provided complexes resulting from S–C_8H_7 bond cleavage. Thus, after 60 h the major product is [$Fe_4(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}SMe)_2$] (8),[17] in association with [$Fe_2(CO)_6(\mu\text{-}SMe)_2$] (9),[18] each a known complex. The formation of (8) requires cleavage of both organic groups from (1).

Reactions of [$Ru_3(CO)_{12}$] with C_8H_7SMe under a variety of thermal and photochemical conditions led to the isolation only of bicyclo-octatetraenyl, but presumably methylthio-derivatives of ruthenium carbonyl were also formed.



(3a) (3b)

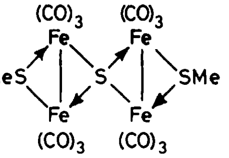
• = $Fe(CO)_3$

Cycloheptatrienyl Thioethers.—Both 7-methylthiocycloheptatriene (10) [4] and 7-phenylthiocycloheptatriene (11) [5] were prepared in good yield by a new method, namely treatment of tropylium tetrafluoroborate with the appropriate sodium thiolate in thf. Previously unreported 7-t-butylthiocycloheptatriene (12) may be obtained in *ca.* 80% yield in the same manner. The latter, a colourless oil which turns yellow on exposure to air, was identified by the usual methods (see Experimental section).

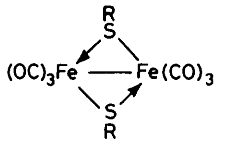
The reactions of the thioethers (10)—(12) with a variety of metal carbonyls were investigated, but no complex was isolated in which the S–C_7H_7 bond was retained. Products contained either only the SR group or both the SR and C_7H_7 fragments as separate ligands. Thus, with [$Fe_2(CO)_9$] in thf the bridging thiolato-complexes [$Fe_2(CO)_6(\mu\text{-}SR)_2$] (9), (13), and (14) [18-20] were formed, and the C_7H_7 ring appeared as bitropyl. Likewise, heating $C_7H_7SBu^t$ with [$Mo_2(CO)_6(\eta\text{-}C_5H_5)_2$] in boiling toluene led only to [$Mo_2(CO)_2(\mu\text{-}SBu^t)_2(\mu\text{-}C_5H_5)_2$] (15) [21] as a metal-containing product, a species much better prepared directly from Bu^tSH. Reactions with [$Mn_2(CO)_{10}$], [$Fe_2(CO)_4(\eta\text{-}C_5H_5)_2$], [$Cr(CO)_6$], and [$Mo(CO)_6$] gave no adequately characterised products. Nor did that with [$Cr(CNMe)_3(CO)_3$], in spite of the fact that [$Cr(CO)_3(C_7H_7SH)$] is known.[22]

Much the most interesting reactions of C_7H_7SR were achieved with [$Ru_3(CO)_{12}$] in boiling heptane. Here the C_7H_7 and SR components of the thioether appear together in the products, which were identified as

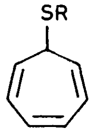
$[Ru_2(CO)_4(\mu\text{-}SR)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$, (16) and (17), and $[Ru_3(CO)_6(\mu_3\text{-}SBu^t)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ (18). Both (17) and (18) are also formed in the reaction of cycloheptatriene with the sulphur–ruthenium cluster $[Ru_3H(CO)_9(\mu_3\text{-}SBu^t)]$, which is described in the preceding paper.[1] All the spectroscopic properties of (16) and (17) suggest that their structures are analogous to that of the halide-bridged complexes $[Ru_2(CO)_4(\mu\text{-}X)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$ (19).[23,24]



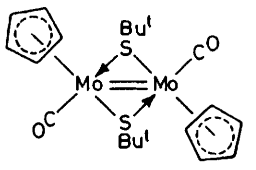
(8)



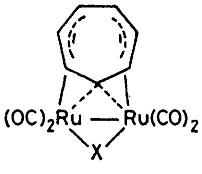
(9; R = Me)
(13; R = Ph)
(14; R = Bu^t)



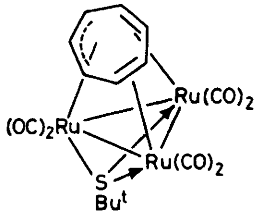
(10; R = Me)
(11; R = Ph)
(12; R = Bu^t)



(15)



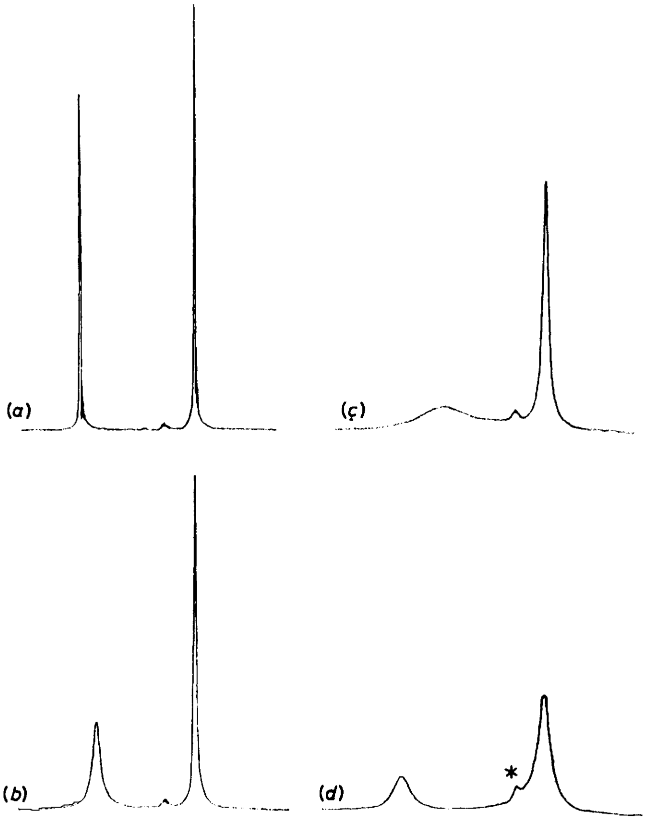
(16; X = SMe)
(17; X = SBu^t)
(19; X = Cl, Br or I)



(18)

The μ_3-(η^7-C_7H_7) ligand in (18) and the μ-(η^7-C_7H_7) ligands in (19) are fluxional, each undergoing rapid rotation even at −100 °C.[1,23,24] Both (16) and (17) also contain a μ-(η^7-C_7H_7) ring which is fluxional, as shown by the single ^1H and ^{13}C n.m.r. signals observed at room temperature. However, the C_7H_7 ring in (16) and (17) appears to experience a greater energy barrier to rotation than that in (18) or (19). This is concluded from the fact that the n.m.r. spectra of (16) and (17) recorded at low temperature show substantial changes, consistent with slowed rotation. Although this is probably a safe conclusion, it is of course just possible that chemical-shift variations for the C_7H_7 nuclei in (18) and (19) are small enough that an equally slowed rotation is not manifested in the n.m.r. spectra of these complexes.

The ^1H n.m.r. spectrum of (17) at various temperatures is displayed in the Figure. It can be seen that the C_7H_7 ring signal broadens considerably on cooling to −70 °C and below that temperature is replaced by two signals, one of intensity 4 H at *ca.* τ 6.5 and another of intensity 3 H which is coincident with the Bu^t group signal, together giving a signal of total intensity 12 H. Over this temperature range the Bu^t group signal also broadens. We attribute these changes to two effects, the slowing of cycloheptatrienyl ring rotation previously mentioned and of rotation about the S–CMe_3 bond. There can be little doubt of the former, but clearly lower temperatures would have to be attained before a limiting spectrum is achieved since at −90 °C the seven ring protons are grouped into two sets of four and three protons, whereas four signals of relative intensity 2 : 2 : 2 : 1 are expected for the truly static molecule. Slowing of the fluxional rotation of a μ-(η^7-C_7H_7) ring has been observed previously for $[Mo(CO)_2(\eta\text{-}C_5H_5)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}\{Fe(CO)_3\}]$[25] which has the metal atoms co-ordinated on opposite sides of the ring and is static below −50 °C. On the other hand the complexes $[Fe(CO)_3\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}\{M(CO)_n\}]$ (M = Mn or Re, $n = 3$; M = Rh, $n = 2$)[26] and $[Ru_2(SiMe_3)(CO)_5\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$,[27] in which the metal atoms are bonded to the same face of the ring, are undergoing fluxional rotation rapidly even below −100 °C.



Proton n.m.r. spectrum of $[Ru_2(CO)_4(\mu\text{-}SBu^t)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$(17) in $C_6D_5CD_3$ at various temperatures: 30 (*a*); −50 (*b*); −70 (*c*); −90 °C (*d*). The asterisk indicates resonance due to $C_6D_5CD_2H$

Evidence for restricted rotation about the S–CMe$_3$ bond comes from the ^{13}C n.m.r. spectrum of (17). At −90 °C the C$_7$H$_7$ signal has collapsed completely as a result of slowed ring rotation and only two resonances have reappeared (at 66.5 and 15.8 p.p.m.), but the methyl signal of the Bu^t group has broadened considerably while the *C*Me$_3$ resonance remains sharp. If the broadening of the methyl resonance were due to the slowing of a pyramidal sulphur-inversion process then broadening of the tertiary carbon resonance would also be expected, since the Bu^t group is then exploring two different spatial orientations. Further support for restricted rotation is provided by the ^{1}H n.m.r. spectrum of [Ru$_3$(CO)$_6$(μ_3-SBu^t){μ_3-(η^7-C$_7$H$_7$)}] [1] (18); in this molecule no inversion is possible for quaternary sulphur, yet broadening of the SBu^t proton resonance also occurs on cooling, and is surely due to such restriction. Moreover, although the ^{1}H n.m.r. spectrum of (16), the methyl analogue of (17), undergoes almost identical changes in the C$_7$H$_7$ resonance with temperature, the methyl signal is still sharp at −90 °C. No restriction on S–CH$_3$ bond rotation would be expected.

In conclusion, it is apparent that the cyclo-octatetraenyl thioether (1) can generate complexes in which the S–C$_8$H$_7$ bond remains intact and the compound acts as a substituted cyclo-octatetraene, but that cycloheptatrienyl thioethers (10)—(12) invariably undergo S–C$_7$H$_7$ bond fission. This may be attributed to the very stable co-ordination achieved separately by thiolato- and cycloheptatrienyl ligands with transition metals. Desulphurisation of (1) releases C$_8$H$_7$, which does not have the same co-ordination ability as C$_7$H$_7$ and appears as a product in the form of bicyclo-octatetraenyl.

EXPERIMENTAL

Experimental techniques and instrumentation were as described in Part 5 of this series.[1] Photochemical reactions were performed using silica glass flasks and a 250-W mercury-vapour lamp source. Methanesulphenyl chloride was prepared by the literature method [28] and distilled at 60 °C prior to use.

Preparations of Thioethers.—(*a*) C$_8$H$_7$SMe (1). Cyclo-octatetraenyl-lithium was prepared by adding n-butyl-lithium (15 cm^3 of a 2 mol dm^{-3} solution in hexane) over 2 min to a diethyl ether (15 cm^3) solution of cyclo-octatetraenyl bromide (5 g, 27.3 mmol) held at −78 °C.[29] After stirring at this temperature for 1.5 h, MeSCl (2.3 g, 28 mmol) was added and the orange-brown solution allowed to warm to room temperature. After another hour at this temperature the solution was filtered to remove precipitated LiCl, and then evaporated at water-pump vacuum. Chromatography of the residual brown oil on an alumina column, eluting with hexane, gave C$_8$H$_7$SMe as a yellow oil (1.6 g, 39%) [^{1}H n.m.r. (CDCl$_3$) τ 4.28 (m, 7 H) and 7.80 (s, 3 H); Found: C, 72.4; H, 5.3; S, 22.5%. *M*, 150. C$_9$H$_{10}$S requires C, 72.0; H, 6.7; S, 21.3%. *M*, 150].

(*b*) C$_7$H$_7$SMe (10). A thf (50 cm^3) solution of Na[SMe] was prepared by treating Me$_2$S$_2$ (1.08 g, 11.5 mmol) with sodium amalgam (2 g Na, 40 cm^3 Hg) for 1 h. The solution was then separated and [C$_7$H$_7$][BF$_4$] (4 g, 22.5 mmol) in thf (50 cm^3) added. After stirring for 2 h the solution was filtered and then evaporated at reduced pressure to leave a yellow oil which was distilled (100 °C, 0.1 mmHg) to afford 2.5 g (72%) of C$_7$H$_7$SMe [4] as a colourless oil (Found: C, 68.6; H, 7.0; S, 23.4. C$_8$H$_{10}$S requires C, 69.6; H, 7.3; S, 23.2%). The mass spectrum had heaviest ions corresponding to (C$_7$H$_7$)$_2^+$ and C$_7$H$_6$SMe$^+$.

(*c*) C$_7$H$_7$SPh (11). In a manner identical to that described in (*b*), Ph$_2$S$_2$ (1.21 g, 5.55 mmol) was treated with sodium amalgam to produce a solution of Na[SPh], to which was then added [C$_7$H$_7$][BF$_4$] (2 g, 11.2 mmol). After filtration to remove Na[BF$_4$], chromatography on an alumina column, eluting with hexane–dichloromethane (4 : 1), gave 0.9 g (40%) of yellow liquid C$_7$H$_7$SPh [5] (Found: C, 77.3; H, 6.1; S, 16.1. C$_{13}$H$_{12}$S requires C, 78.0; H, 6.0; S, 16.0%). The heaviest ion in the mass spectrum corresponded to Ph$_2$S$_2^+$.

(*d*) C$_7$H$_7$SBu^t (12). A thf (50 cm^3) solution of Na[SBu^t] was prepared from Bu^{t}SH (2 g, 22.2 mmol) and NaH (0.5 g, 20.8 mmol), and stirred for 3 h. To this was added [C$_7$H$_7$][BF$_4$] (2.7 g, 15.2 mmol) in thf (30 cm^3). After additional stirring for 1 h, filtration, and chromatography on an alumina column, eluting with hexane, provided 2.2 g (82%) of yellow liquid C$_7$H$_7$SBu^t [Found: C, 71.6; H, 9.6%. *M*, 180. C$_{11}$H$_{16}$S requires C, 73.3; H, 8.9%. *M*, 180. ^{1}H n.m.r. (CDCl$_3$) τ 3.3 (m, 2 H), 3.9 (m, 2 H), 4.5 (dd, 2 H), 6.8 (t, 1 H), and 8.7 (s, 9 H)]. Further purification by distillation at 120 °C (0.1 mmHg) produces (12) as a colourless liquid which rapidly becomes yellow on exposure to air.

Reactions of C$_8$H$_7$SMe (1).—(*a*) *With* [Fe$_2$(CO)$_9$]. (*i*) A thf (50 cm^3) solution of (1) (0.5 g, 3.33 mmol) and [Fe$_2$(CO)$_9$] (12.1 g, 33.3 mmol) was stirred for 12 h at room temperature, during which time a colour change from orange to brown occurred. The reaction mixture was evaporated to dryness and the residue chromatographed on an alumina column. Elution with hexane developed yellow and orange bands. The former yielded 0.33 g (23%) of yellow crystalline [Fe$_2$(CO)$_6$(C$_8$H$_7$SMe)] (2) [m.p. 165 °C (decomp.); ν(CO) (hexane) 2 046s, 1 992s, and 1 984s cm^{-1}; ^{1}H n.m.r. (CDCl$_3$) τ 4.4 (m, 3 H), 6.4 (d, 1 H), 6.9 (m, 3 H), and 7.5 (s, 3 H); ^{13}C n.m.r. (CDCl$_3$) δ(p.p.m.) 15.3, 49.9, 55.8, 57.7, 59.2, 88.3, 92.9, 93.1, 115.9, and 209.8; Found: C, 42.0; H, 2.6; S, 7.7%. *M*, 430. C$_{15}$H$_{10}$Fe$_2$O$_6$S requires C, 41.9; H, 2.3; S, 7.4%. *M*, 430] and the latter a few mg of red crystalline [Fe(CO)$_3$(C$_8$H$_7$SMe)] (3) [m.p. 62—63 °C; ν(CO) (hexane) 2 048s, 1 992vs, and 1 976s cm^{-1}; ^{1}H n.m.r. (CDCl$_3$) τ 3.3—4.9 (m, 7 H) and 7.65 (s, 3 H); Found: C, 50.3; H, 3.6%. *M*, 290. C$_{14}$H$_{10}$FeO$_3$S requires C, 50.0; H, 3.5%. *M*, 290].

(*ii*) The reaction was performed in an identical manner to (*i*), over 60 h, using C$_8$H$_7$SMe (1 g, 6.67 mmol) and [Fe$_2$(CO)$_9$] (4.84 g, 13.3 mmol) in an attempt to produce (3) in greater yield. Chromatography as in (*i*) gave 90 mg (7%) of known [18] orange crystalline [Fe$_2$(CO)$_6$(μ-SMe)$_2$] (9), identified by i.r. and mass spectra, and 150 mg (13%) of known red crystalline [Fe$_4$(CO)$_{12}$(μ_4-S)(μ-SMe)$_2$] (8) (Found: C, 24.1; H, 1.4%. *M*, 686. C$_{14}$H$_6$Fe$_4$O$_{12}$S$_3$ requires C, 24.5; H, 0.9%. *M*, 686), further identified by comparison of its i.r. and ^{1}H n.m.r. spectra with literature data.[17]

(*b*) *With* [Ru$_3$(CO)$_{12}$]. Reactions of (1) with [Ru$_3$(CO)$_{12}$] in toluene under u.v. radiation and in hexane at reflux gave no identifiable products. Heating [Ru$_3$(CO)$_{12}$] (0.5 g, 0.78 mmol) in heptane at reflux with (1) (1 g, 6.67 mmol) for 17 h resulted in much decomposition. Chromatography on alumina separated only yellow crystals of bicyclo-octatetraenyl [7,8] (*ca.* 50 mg, 7%), identified by ^{1}H n.m.r. and mass spectra.

Reactions of C_7H_7SMe (10).—(*a*) *With* $[Fe_2(CO)_9]$. A mixture of (10) (0.5 g, 3.62 mmol) and $[Fe_2(CO)_9]$ (0.65 g, 1.78 mmol) was stirred in thf (50 cm^3) at room temperature for 12 h. Evaporation to dryness and subsequent chromatography on alumina of the residue, eluting with hexane, yielded 105 mg (15%) of known orange crystalline $[Fe_2(CO)_6(\mu\text{-}SMe)_2]$, identified by its i.r. spectrum.[18]

(*b*) *With* $[Ru_3(CO)_{12}]$. A heptane (50 cm^3) solution of (10) (0.5 g, 3.6 mmol) and $[Ru_3(CO)_{12}]$ (0.77 g, 1.21 mmol) was heated at reflux for 12 h, then evaporated and the residue chromatographed as in (*b*). Elution with hexane developed a yellow band from which 120 mg (15%) of yellow crystalline $[Ru_2(CO)_4(\mu\text{-}SMe)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$ (16) were obtained [m.p. 148 °C (decomp.); ν(CO) (hexane) 2 027m, 2 005s, 1 965s, and 1 956m cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) τ 6.14 (s, 7 H) and 6.85 (s, 3 H); Found: C, 32.2; H, 2.3%. *M*, 453; $C_{12}H_{10}O_4Ru_2S$ requires C, 31.9; H, 2.2%. *M*, 453].

Reactions of C_7H_7SPh (11).—(*a*) *With* $[Fe_2(CO)_9]$. A thf (50 cm^3) solution of (11) (0.2 g, 1.0 mmol) and $[Fe_2(CO)_9]$ (0.5 g, 1.37 mmol) was stirred at room temperature for 12 h. Chromatography as above then afforded 90 mg (14%) of known [19] red crystalline $[Fe_2(CO)_6(\mu\text{-}SPh)_2]$, characterised by its i.r. spectrum and m.p. of 117—118 °C.

(*b*) *With* $[Ru_3(CO)_{12}]$. After heating a heptane (50 cm^3) solution of (11) (0.5 g, 2.5 mmol) and $[Ru_3(CO)_{12}]$ (0.5 g, 0.78 mmol) at reflux for 12 h, the solution was evaporated and the residue chromatographed as above. Elution with hexane–dichloromethane mixtures developed a yellow, two orange, and one red band. These provided only small amounts of unidentified material. The first orange band provided an orange solid with ν(CO) in the i.r. at 2 009s and 1 965m cm^{-1}, and ^{1}H n.m.r. signals at τ 2—3 and 6.2 (s) suggesting the presence of SPh and fluxional η^7-C_7H_7 groups.

Reactions of $C_7H_7SBu^t$ (12).—(*a*) *With* $[Fe_2(CO)_9]$. A mixture of (12) (0.5 g, 2.78 mmol) and $[Fe_2(CO)_9]$ (0.5 g, 1.37 mmol) was stirred in thf (50 cm^3) at room temperature for 12 h. Chromatography then afforded 120 mg (20%) of known [20] red crystalline $[Fe_2(CO)_6(\mu\text{-}SBu^t)_2]$, identified by i.r. and ^{1}H n.m.r. spectra, and a trace of bitropyl (m.p. 55—58 °C; lit.,[30] 61 °C), further identified by its ^{1}H n.m.r. spectrum [τ 3.2 (m, 4 H), 3.6 (m, 4 H), 4.6 (m, 4 H), and 8.0 (m, 2 H)].

(*b*) *With* $[Ru_3(CO)_{12}]$. After heptane (50 cm^3) reflux of (12) (0.5 g, 2.78 mmol) and $[Ru_3(CO)_{12}]$ (0.6 g, 0.94 mmol) for 12 h, the solution was evaporated and chromatographed on silica gel. Elution with hexane–dichloromethane (4 : 1) gave a yellow band which provided 118 mg (17%) of yellow crystalline $[Ru_2(CO)_4(\mu\text{-}SEu^t)\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}]$ (17), identified by its i.r. and ^{1}H n.m.r. spectra.[1] Further elution with hexane–dichloromethane (1 : 1) removed a yellow band from which 31 mg (5%) of yellow crystalline $[Ru_3(CO)_6(\mu_3\text{-}SBu^t)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$ (18) were obtained, also identified by i.r. and ^{1}H n.m.r. spectra.

(*c*) *With* $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$. Similar treatment of (12) (0.5 g, 2.78 mmol) with $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.7 g, 1.43 mmol) in heptane (50 cm^3) at reflux for 24 h gave 80 mg (9%) of dark green crystals of the known $[Mo_2(CO)_2(\mu\text{-}SBu^t)_2(\eta\text{-}C_5H_5)_2]$ (15) [21] after chromatography. Identification was by i.r., ^{1}H n.m.r., and mass spectra.

We are grateful to the S.R.C. for the award of a Research Studentship (to F. G. K.) and to Johnson Matthey Chemicals Ltd. for a loan of ruthenium trichloride.

[1/341 *Received, 27th February,* 1981]

REFERENCES

[1] Part 5, T. A. Cresswell, J. A. K. Howard, F. G. Kennedy, S. A. R. Knox, and H. Wadepohl, preceding paper.

[2] See, A. P. Humphries and S. A. R. Knox, *J. Chem. Soc., Dalton Trans.*, 1978, 1523 and refs. therein.

[3] G. I. Fray and R. G. Saxton, 'The Chemistry of Cyclo-octatetraene and its Derivatives,' Cambridge University Press, 1978.

[4] K. Okamoto, K. Komatsu, and O. Sakaguchi, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 2431.

[5] P. Bladon, P. L. Pauson, G. R. Proctor, and W. J. Rodger, *J. Chem. Soc. C*, 1966, 926.

[6] R. Huisgen and W. Konz, *J. Am. Chem. Soc.*, 1970, **92**, 4102.

[7] A. C. Cope and D. J. Marshall, *J. Am. Chem. Soc.*, 1953, **75**, 3208.

[8] J. D. Edwards, J. A. K. Howard, S. A. R. Knox, V. Riera, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1976, 75.

[9] C. E. Keller, G. F. Emerson, and R. Pettit, *J. Am. Chem. Soc.*, 1965, **87**, 1388; see also F. A. Cotton and W. T. Edwards, *J. Am. Chem. Soc.*, 1968, **90**, 5412.

[10] T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, 1960, **82**, 336.

[11] B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **37**, 2084.

[12] M. Cooke, C. R. Russ, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1975, 256.

[13] C. E. Keller, Ph.D. Thesis, University of Texas, Austin, 1966.

[14] L. A. Bock, Ph.D. Thesis, University of California, Los Angeles, 1969.

[15] F. A. Cotton and D. L. Hunter, *J. Am. Chem. Soc.*, 1976, **98**, 1413.

[16] F. A. L. Anet, *J. Am. Chem. Soc.*, 1967, **89**, 2491.

[17] J. M. Coleman, A. Wojcicki, P. J. Pollick, and L. F. Dahl, *Inorg. Chem.*, 1967, **6**, 1236.

[18] L. Manesca, F. Greggio, S. Sbrigiadello, and G. Bor, *Inorg. Chim. Acta*, 1971, **5**, 667 and refs. therein.

[19] P. C. Ellgen and J. N. Gerlach, *Inorg. Chem.*, 1973, **12**, 2526.

[20] G. Natile, L. Maresca, and G. Bor, *Inorg. Chim. Acta*, 1977, **23**, 37.

[21] I. B. Benson, S. D. Killops, S. A. R. Knox, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1980, 1137.

[22] J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 1961, 3475.

[23] J. C. Burt, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1975, 731.

[24] J. A. K. Howard and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1977, 366.

[25] F. A. Cotton and C. R. Reich, *J. Am. Chem. Soc.*, 1969, **91**, 847.

[26] M. J. Bennett, J. L. Pratt, K. A. Simpson, L. K. K. Li Shing Man, and J. Takats, *J. Am. Chem. Soc.*, 1976, **98**, 4810.

[27] A. Brookes, S. A. R. Knox, V. Riera, B. A. Sosinsky, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1975, 1641.

[28] W. H. Mueller and P. E. Buller, *J. Am. Chem. Soc.*, 1968, **90**, 2075.

[29] A. C. Cope, M. Burg, and W. Fenton, *J. Am. Chem. Soc.*, 1952, **74**, 173.

[30] W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, 1957, **79**, 352.