umn. The chromatography was halted, and the area above the orange-red band was removed. The chromatography was resumed and **11h** isolated by elution with ether–petroleum ether.

Reaction of Tetramethylthiourea with Triphenylphosphineiron Tetracarbonyl. An ether solution (200 ml) of the thiourea (1.00 g, 7.56 mmol) and triphenylphosphineiron tetracarbonyl (3.26 g, 7.56 mmol) was stirred at room temperature for 24 hr. Work-up led to complete recovery of the reactants. Starting materials were also obtained after refluxing in ether or tetrahydrofuran for 24 hr.

Reaction of Tetramethylthioureairon Tetracarbonyl (4a) with Tri-*n*-butylphosphine. Complex **4a** (0.070 g, 0.233 mmol) and tri-*n*-butylphosphine were dissolved in acetone and stirred at room temperature for 20 hr. Work-up by chromatography on Florisil gave tetramethylthiourea, tri-*n*-butylphosphineiron tetracarbonyl[17] and *trans*-bis(tri-*n*-butylphosphine)iron tricarbonyl.[17]

Acknowledgments. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Foundation of the State University of New York for support of this research. We are indebted to Hoffmann-La Roche, Inc., for carrying out some of the elemental analyses. Professor Hunt of the University of Virginia was kind enough to run some methane chemical ionization mass spectra on several of the trinuclear complexes.

Registry No. $Fe_2(CO)_9$, 15321-51-4; **3a**, 2782-91-4; **4a**, 41777-45-1; **5a**, 41913-70-6; **3b**, 631-67-4; **4b**, 41828-34-6; **5b**, 41812-87-7; **3c**, 15482-60-7; **4c**, 41768-29-0; **5c**, 41913-71-7; **8a**, 2741-13-1; **9a**, 41768-30-3; **11a**, 41768-31-4; **8b**, 31124-88-6; **10b**, 41875-31-4; **11b**, 41768-32-5; **8c**, 24070-58-4; **9c**, 41768-33-6; **8d**, 4333-19-1; **9d**, 41768-34-7; **11d**, 41768-35-8; **8e**, 621-01-2; **10e**, 41768-36-9; **11e**, 41768-37-0; **8f**, 96-45-7; **9f**, 41768-38-1; **10f**, 41875-32-5; **11f**, 41768-39-2; **8g**, 636-04-4; **9g**, 41768-40-5; **10g**, 41875-33-6; **11g**, 41768-41-6; **8h**, 3898-08-6; **9h**, 41768-42-7; **10h**, 41944-81-4; **11h**, 41875-34-7; **12**, 41875-35-8.

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[17] W. Strohmeier and F. J. Muller, *Chem. Ber.*, **100**, 2812 (1967).

Contribution from the Department of Chemistry, State University
of New York at Binghamton, Binghamton, New York 13901

Reactions of Nonaromatic Thioketones with Diiron Enneacarbonyl

HOWARD ALPER* and ALBERT S. K. CHAN

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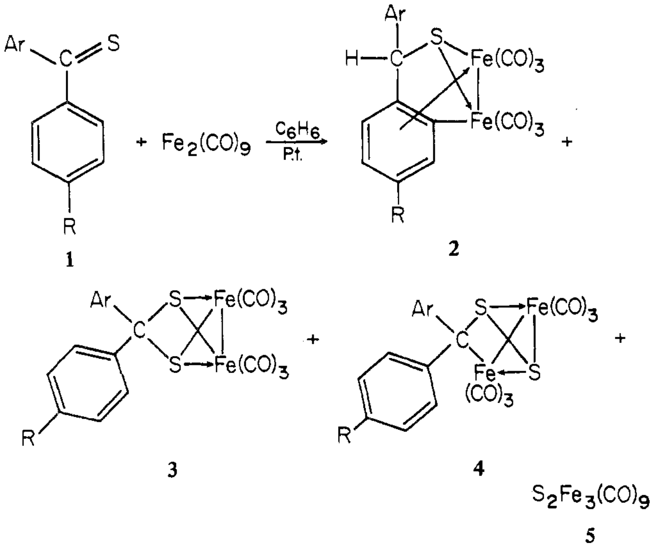
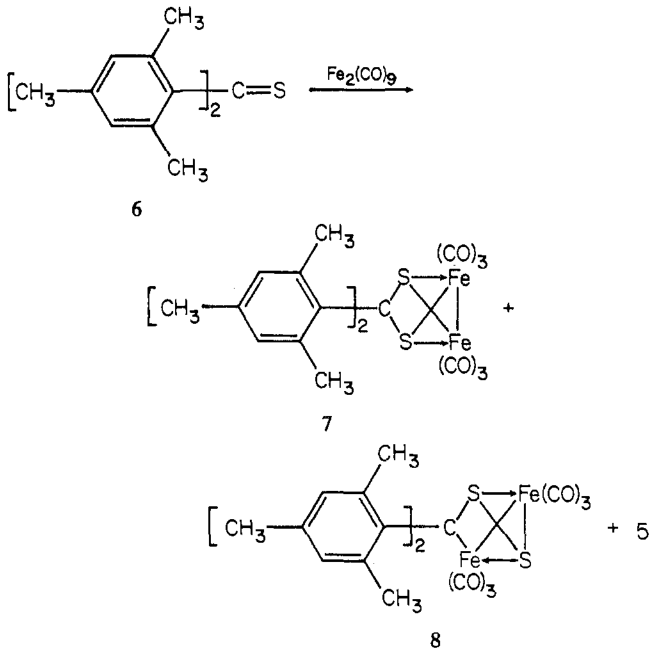
The major product (71.5% yield) obtained from reaction of adamantanethione and diiron enneacarbonyl was $C_{16}H_{14}S_2Fe_2O_6$, which contains bridging and terminal carbonyl groups, as well as two sulfur atoms attached to the same carbon atom. By-products of the reaction were an isomeric complex lacking bridging carbonyls, but possessing a carbon–iron σ bond, and dimeric complexes of formula $C_{26}H_{28}S_2Fe_2O_6$, differing by the presence or absence of bridging carbonyls. The major product was easily converted to an isomeric, nonbridging carbonyl complex still having a sulfur–carbon–sulfur linkage. Reductive cleavage of these complexes afforded adamantanone or a disulfide, subject to the nature of the complex. While treatment of thiocamphenilone with $Fe_2(CO)_9$ gave complexes analogous to those obtained from adamantanethione ($S_2Fe_3(CO)_9$ was also formed), only sulfur–iron carbonyls were produced using thiofenchone as the reactant thioketone.

Thiobenzophenones (**1**) possessing ortho hydrogens react with diiron enneacarbonyl ($Fe_2(CO)_9$) in benzene to give sulfur-donor ligand ortho-metalated complexes (**2**) in good to excellent yields.[1] The diiron hexacarbonyl complexes **3** and/or **4** were by-products in certain instances and small amounts of $S_2Fe_3(CO)_9$ (**5**) were usually isolated from these reactions. 2,2′,4,4′,6,6′-Hexamethylthiobenzophenone (**6**) contains no ortho hydrogens, and treatment of **6** with $Fe_2(CO)_9$ results in the formation of **7** and **8**, which are analogs





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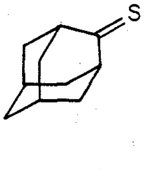
[1] H. Alper and A. S. K. Chan, *J. Amer. Chem. Soc.*, **95**, 4905 (1973).

of **3** and **4**, respectively. This paper describes the first transition metal carbonyl complexes of nonaromatic thioketones. Although ortho metalation is impossible, it was conceivable that exposure of nonaromatic thiones to $Fe_2(CO)_9$ might lead to complexes of the same skeletal structure as **3**, **4**, **7**, or **8**. Alternatively, new and interesting complexes could result from this work.

Results and Discussion

The reactions of $Fe_2(CO)_9$ with three nonaromatic thioketones, adamantanethione (**9**), thiocamphenilone (**10**), and thiofenchone (**11**), were investigated. These thioketones were chosen for this study because of their ease of synthesis (see Experimental Section) and because they are nonenolizable in contrast to most straight-chain and monocyclic thiones which exist partly or completely as the enethiol tautomer.[2] The structures of the products of the investigated reactions were characterized on the basis of microanalytical and spectral data and by reductive cleavage experiments.



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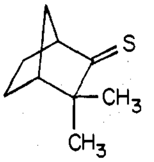

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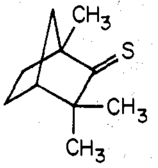
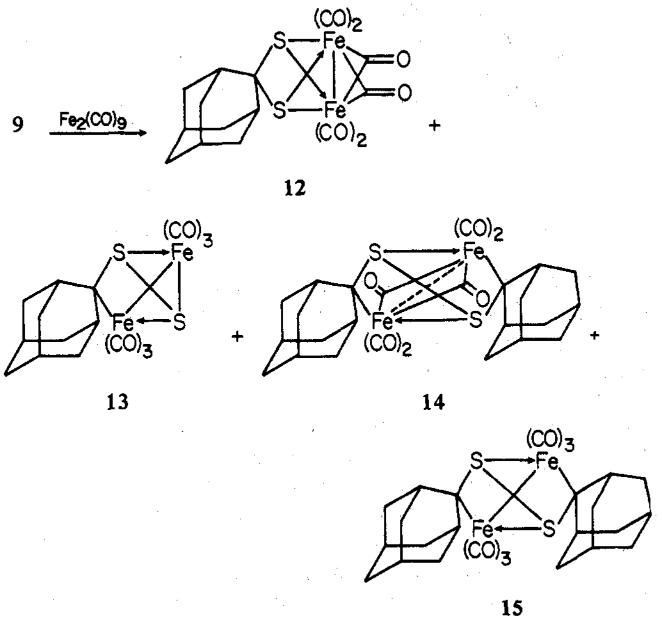


11

Adamantanethione (**9**) reacts with $Fe_2(CO)_9$ in benzene at room temperature to give a mixture of four complexes (**12**–**15**) which, after considerable experimentation, were separated and isolated in analytically pure form. The major product (71.5%) of the reaction was the air-sensitive complex **12**,[3] which is structurally different from any of the complexes encountered in the thiobenzophenone-$Fe_2(CO)_9$ reactions in that **12** contains both bridging and terminal carbonyl groups. Evidence for the presence of bridging carbonyls comes from the observation of an absorption band in the infrared (ir) region at 1850 cm^{-1} [CCl_4, 1845 cm^{-1} (neat)]. Terminal metal carbonyl stretching bands appeared at 2081 s, 2038 s, 2010 m, 2004 s (br), and 1978 ms cm^{-1} (CCl_4). The thiocarbonyl stretching absorption of **9** (1150 cm^{-1}, CCl_4)[4] was absent in the ir of the complex. Electron impact mass spectrometry of **12** gave a molecular ion peak at *m/e* 478, followed by successive loss of six carbonyls. Other important fragments were observed at *m/e* 198 $(C_{10}H_{14}S_2)^+$, 176 $(Fe_2S_2)^+$, 166 $(\mathbf{9})^+$, 144 $(Fe_2S)^+$, 112 $(Fe_2)^+$, and 56 $(Fe)^+$. The signal occurring at lowest field (δ 2.58) in the nuclear magnetic resonance (nmr) spectrum (C_6D_6) of **12** is assigned to the two protons α to the sulfur bearing carbon atom. The remaining 12 protons (integral ratio of 12.1 to 2.0 α protons) absorbed in the region of δ 1.35–1.71 with the highest field absorption (δ 1.35) being due to the four γ and δ protons.[4]



12

13

14

15

A low-yield (1.3%) by-product of the adamantanethione reaction was **13**, isomeric with **12**, the differences between the two structures being the lack of bridging carbonyls and the presence of a carbon–iron σ bond in **13**. The positions of the ir terminal metal carbonyl stretching bands for **13** are very similar to those observed for the analogous complexes, **4** and **8**.[1] The mass spectrum displayed a molecular ion peak at *m/e* 478, followed by successive loss of six carbonyls (also fragments at *m/e* 112 $(Fe_2)^+$ and 56 $(Fe)^+$). No thioketone fragment was observed (*m/e* 166) in agreement with the mass spectral results for **4** and **8**. It should be noted that complexes having a sulfur–carbon–sulfur linkage (*e.g.*, **3**, **7**, and **12**) give a thioketone fragment in the mass spectrum. The nmr spectrum of **13** (C_6D_6) is more complex (δ 1.27–2.70 (m)) than that of **12**, due to the change in configuration of the $S_2Fe_2(CO)_6$ unit. Molecular models of **13** indicate that, as a consequence of the arrangement of the carbonyl groups, the axial β protons exist in different environments, and hence 3–4 distinct signals are expected for these protons. Complexes **12** and **13** contain two sulfur atoms per adamantane unit raising the question as to the fate of the other adamantane skeleton. Repeated attempts made to isolate simple monomeric, dimeric, or trimeric organic byproducts from reactions of **9**–**11** with $Fe_2(CO)_9$ were unsuccessful.

The remaining two complexes obtained from the adamantanethione-$Fe_2(CO)_9$ reaction contained one sulfur and one iron atom per adamantane unit and were assigned structures **14** (14.5% yield) and **15** (4.6%). Complexes **14** and **15**, which differ from each other with respect to the types of carbonyl groups, were never isolated or detected in reactions of aromatic thioketones with $Fe_2(CO)_9$. The ir spectra of **14** and **15** were quite similar, except for the presence of a bridging carbonyl absorption at 1835 cm^{-1} (CCl_4) in the spectrum of **14**. Attempts to obtain electron impact or chemical ionization mass spectra of **14** or **15** resulted in decomposition. The nmr spectrum of **15** was not informative while **14** was insufficiently soluble in C_6D_6 for nmr purposes.

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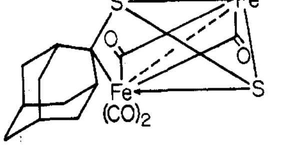
(2) D. Paquer and J. Vialle, *Bull. Soc. Chim. Fr.*, 3595 (1969); 4407 (1971).

(3) H. Alper and A. S. K. Chan, *Chem. Commun.*, 1203 (1971). A brief preliminary communication on this subject gave i as the tentative structure for **12**. However, reductive cleavage experiments revealed the presence of an S–C–S rather than an S–C–Fe linkage. In addition, mass spectral analysis of **12** gave a fragment at *m/e* 198 $(C_{10}H_{14}S_2)^+$.

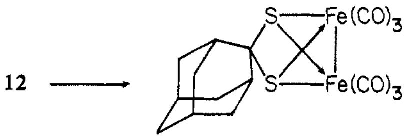


i

(4) J. W. Greidanus, *Can. J. Chem.*, **48**, 3530 (1970).

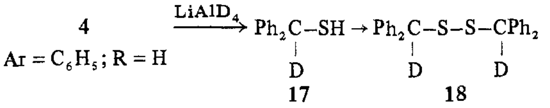
Elemental analyses of **14** and **15** indicated the empirical formula $C_{13}H_{14}SFeO_3$, but vapor phase osmometry showed them to be dimeric.

The least stable of the four complexes was **12**. When a petroleum ether solution of **12** was exposed to air in the dark, gradual conversion occurred to a new, quite stable, isomeric complex **16** (and a trace of adamantanone). Complex **16** does not have any bridging carbonyls and therefore is considerably less strained than **12**. The structure assigned to **16** is similar to the structures of complexes **3** and **7**, and the ir (ν_{CO}) and mass spectra show the same characteristics for the three complexes. The nmr spectrum of **16** is related to that of **12** (*e.g.*, lowest field signal at δ2.57 is due to the two α protons). It is worthwhile noting that a similar isomerization of **14** to **15** took place when a carbon tetrachloride solution of the dimeric bridging carbonyl complex was allowed to stand at room temperature. In addition, complexes containing a sulfur-carbon-sulfur linkage (**3**, **7**, **16**, and **23**) slowly collapse to ketone (*e.g.*, adamantanone) on exposure to air, while carbonyl formation did not result from those complexes bearing a sulfur-carbon-iron linkage.



16

Reductive cleavage experiments provided further evidence for the structures of the complexes. In principle, lithium aluminum hydride ($LiAlH_4$) reduction of complexes containing an S-C-S linkage (*e.g.*, **12**) should result in cleavage of the sulfur-metal bond and, on work-up, afford the *gem*-dithiol. Collapse of the latter to a carbonyl compound is expected when work-up is effected under aqueous conditions. In contrast, reductive fission of a complex containing a carbon atom σ bonded to both iron and sulfur atoms would lead to a mercaptan which may be isolable as such, or the mercaptan may oxidize to disulfide. For example, **4** ($Ar = C_6H_5$; $R = H$) gave **18** (*via* **17**) when treated with $LiAlD_4$ in tetrahydrofuran.

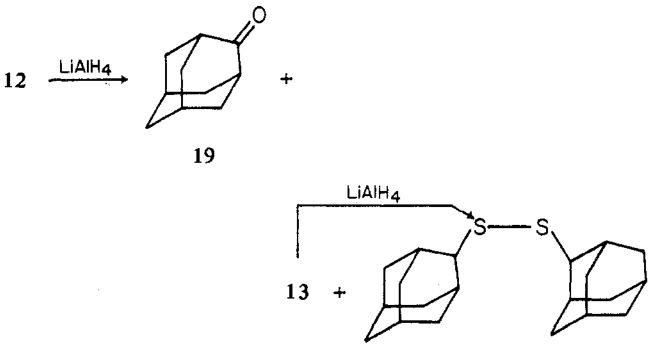


$$4 \xrightarrow{LiAlD_4} Ph_2\underset{D}{C}-SH \rightarrow Ph_2\underset{D}{C}-S-S-\underset{D}{C}Ph_2$$

$Ar = C_6H_5; R = H$

17 18

Treatment of **12** with $LiAlH_4$ (2.25:1.00 mol ratio of hydride-**12**) in tetrahydrofuran gave adamantanone as the major product, along with smaller amounts of complex **13** and the known di(2-adamantyl) disulfide (**20**).[5] That the disulfide arises from **13** was demonstrated by reduction of **12**, using a greater excess of hydride (6.1:1.0 mol ratio of $LiAlH_4$-**12**) to give approximately the same yield of **19** (**19** is not reduced to 2-adamantanol by using more $LiAlH_4$ since **19** is only obtained on work-up of the hydride reaction), an increased amount of **20**, but only a trace of **13** (**13** separately gives **20** on reductive cleavage). What has been observed here, to some extent, is a remarkable rearrangement of **12** to **13** under nucleophilic conditions. This rearrangement was unanticipated as one usually expects a carbon-metal σ bond in a complex such as **13** to undergo facile nucleophilic cleavage. Only adamantanone, but not **13** or **20**, was formed when **16** was subjected to cleavage by $LiAlH_4$ or $LiAlD_4$. Treatment of **14** with $LiAlH_4$ gave **20** in 94.4% yield.



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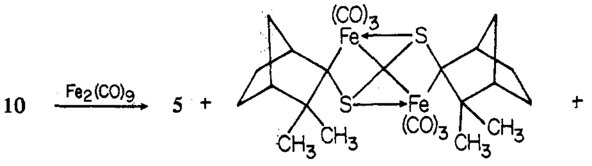
20

Reaction of thiocamphenilone (**10**) with $Fe_2(CO)_9$ at room temperature resulted in the formation of the bridging carbonyl complex **21**, the dimeric complex **22**, and a small amount of **5**. The bridging carbonyl complex **21** was considerably less stable than the adamantane analog **12** and on attempted work-up quickly collapsed to the reasonably stable, isomeric nonbridging carbonyl complex **23**. However, we were able to record an ir spectrum of **21** which proved to be virtually identical, in the carbonyl stretching region, with that of **12**. Infrared terminal metal carbonyl stretching bands for **16** and **23** were in good agreement. The signal for the methine proton on the carbon atom α to the sulfur bearing carbon was observed in the nmr at δ 2.82. Singlets were observed for the methyl groups at δ 0.92 and 1.05, the nonequivalence being due to the different environments in which these groups exist in **23**. A molecular model of **23** indicates that the endo methyl group should be closer to one of the carbonyl groups than the exo methyl group. The ir spectra for **22** and **15** were very similar in the carbonyl stretching region. Elemental analyses and a vapor phase osmometric determination are in good accord with the dimeric nature of **22**. Note that the thiocamphenilone analog of **14**, containing bridging carbonyls, was not detected, and the failure to detect such a complex, as well as the very low stability of **21**, is likely a consequence of methyl-carbonyl repulsion in both cases.



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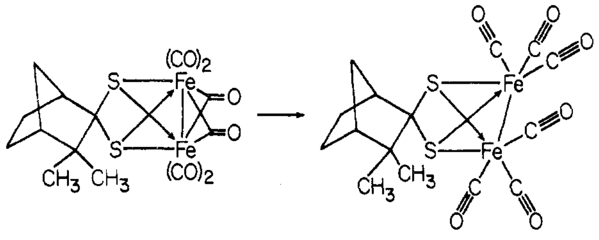

21 **23**

The importance of steric effects is indicated by the failure to obtain any thiofenchone complexes from reaction of **11** with $Fe_2(CO)_9$ for 36-96 hr at room temperature. Except for recovered starting material, only the mixed sulfur-iron carbonyls **5** and **24** were isolated from this reaction. Mo-

$$11 \xrightarrow{Fe_2(CO)_9} 5 + S_2Fe_2(CO)_6$$

24

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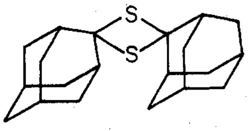
[5] J. W. Greidanus, *Can. J. Chem.*, **48**, 3593 (1970).

lecular models of thiofenchone complexes analogous to **12**-**15** clearly indicate that bridgehead methyl-carbonyl repulsion would be very significant and may account for the lack of formation of complexes of type **12-15** from **11**.

A possible pathway for formation of complexes **3**, **4**, and their analogs (*i.e.*, **7**, **8**, **13**, **16**, and **23**), might involve initial dimerization of the thioketone to a 1,3-dithietane derivative followed by complexation and subsequent ring opening of the complex. However, the dimer[4] of **9**, dispiro [1,3-dithietan-2,2′:4,2″-adamantane] (**25**), failed to react with $Fe_2(CO)_9$



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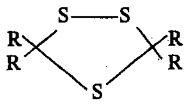
under identical reaction conditions to those used for the reaction of **9** with the metal carbonyl. In addition, no reaction occurred between **9** and $S_2Fe_3(CO)_9$.

Another conceivable reaction intermediate is a trithiolane (**26**). We previously showed[1] that treatment of **26** (R =



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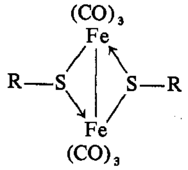
C_6H_5) with $Fe_2(CO)_9$ under the usual conditions did afford **3** (Ar = C_6H_5; R = H), **4**(Ar = C_6H_5; R = H), and **5** in the same ratio as was obtained from reaction of **1** (Ar = C_6H_5; R = H) with $Fe_2(CO)_9$. The ortho-metalated complex **2** (Ar = C_6H_5; R = H) was formed in much lower yield using **26** (R = C_6H_5) instead of **1** (R = H; Ar = C_6H_5) as the reactant (complexes of type **2** are formed *via* a different mechanism). These results indicate the possible involvement of **26**, or a similar species, in the reactions of nonaromatic thioketones with $Fe_2(CO)_9$. Trithiolanes contain a disulfide linkage and it is known[6] that disulfides react with iron carbonyls to form binuclear complexes having the general structure, **27**. Application of this reaction process to **26**



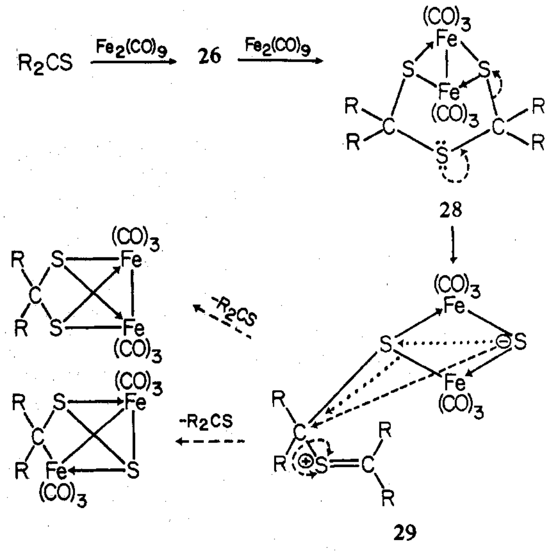
27

would generate **28** which, being a quite strained polycycle, may cleave to the dipolar species **29**. Attack by S^- at carbon or sulfur would give the S-C-S and S-C-Fe complexes, respectively. Note that thioketone would be regenerated on forming these complexes.

In summary, nonaromatic thioketones react with $Fe_2(CO)_9$ to give a number of interesting monomeric and dimeric complexes, the formation of such complexes subject, at least in part, to the steric environment of the thione group. An investigation of the reactions of these and other thioketones with a variety of metal carbonyls is currently in progress.

Experimental Section

Melting points were measured in sealed capillary tubes using a Gallenkamp apparatus and are corrected. Microanalyses were performed by: A. Bernhardt, Elbach uber Engelskirchen, West Germany; and F. Pascher and E. Pascher, Bonn, West Germany. Infrared spectra were obtained on a Perkin-Elmer 457 grating spectrophotometer. A Perkin-Elmer 521 spectrophotometer was used to more precisely locate (±1.0 cm^{-1}) the positions of the bands associated with the iron carbonyl groups. All ir determinations were calibrated using polystyrene film. Nuclear magnetic resonance spectra were determined on Varian A-60 (TMS as internal standard) and/or HA-100 spectrometers. Mass spectra were recorded on Atlas CH-4 or Varian MS-902 spectrometers.



Diiron enneacarbonyl was purchased from Pressure Chemical Co. and used as received. Solvents were dried and purified by standard techniques. All reactions were run and worked up under an atmosphere of dry nitrogen.

Reaction of 2-Adamantanethione (9) with $Fe_2(CO)_9$. A mixture of 2-adamantanethione[4] (2.12 g, 12.8 mmol) and $Fe_2(CO)_9$ (6.70 g, 18.4 mmol) in anhydrous benzene (100 ml) was stirred at room temperature for 36 hr. The solution was filtered and the filtrate was evaporated under nitrogen at room temperature. The residue was treated with petroleum ether (bp 37-40°), and filtered, and the filtrate was chromatographed on Florisil. Elution with petroleum ether gave 2.18 g (71.5%) of the viscous green complex **12**: ir (CCl_4) ν_{CO} 2081 s, 2038 s, 2010 m, 2004 s (br), 1978 s, 1850 mw cm^{-1}; ir (neat) ν_{CO} 2075 vs, 2050-1955 s (br), 1845 s cm^{-1}; nmr (C_6D_6) δ 1.35-1.70 (m, 12 H, highest field absorption assigned to the four γ and δ protons), 2.58 (s, 2 H, protons α to the sulfur bearing carbon atom); mass spectrum *m/e* 478 $(M)^+$, 450 $(M - CO)^+$, 422 $(M - 2CO)^+$, 394 $(M - 3CO)^+$, 366 $(M - 4CO)^+$, 338 $(M - 5CO)^+$, 310 $(M - 6CO)^+$, 268 $(C_9H_{14}C{=}CC_9H_{14})^+$, 198 $(C_{10}H_{14}S_2)^+$, 176 $(Fe_2S_2)^+$, 166 $(9)^+$, 144 $(Fe_2S)^+$, 112 $(Fe_2)^+$, 56 $(Fe)^+$.

Anal. Calcd for $C_{16}H_{14}S_2Fe_2O_6$: C, 40.19; H, 2.95; S, 13.41; Fe, 23.36. Found: C, 40.70; H, 3.29; S, 13.47; Fe, 23.12.

Elution with ether-petroleum ether afforded a mixture of complexes **13**, **14**, and **15**. The latter mixture was combined with the petroleum ether insoluble solid (above). This new mixture was repeatedly extracted with petroleum ether to give two fractions: fraction A (petroleum ether soluble) and fraction B (petroleum ether insoluble). Fraction A was chromatographed on Florisil and elution with petroleum ether eventually gave 40 mg (1.3%) of the orange complex **13**: mp 120° dec; ir (CCl_4) ν_{CO} 2080 m, 2065 wm, 2040 s, 2010 m, and 1985 s cm^{-1}; ir (KBr) ν_{FeCO} 615 mw, 585 (sh), 566 mw, 500 m cm^{-1}; nmr (C_6D_6) 1.27-2.70 m; mass spectrum *m/e* 478 $(M)^+$, 450 $(M - CO)^+$, 422 $(M - 2CO)^+$, 394 $(M - 3CO)^+$, 366 $(M - 4CO)^+$, 338 $(M - 5CO)^+$, 310 $(M - 6CO)^+$, 112 $(Fe_2)^+$, 56 $(Fe)^+$.

Anal. Calcd for $C_{16}H_{14}S_2Fe_2O_6$: C, 40.19; H, 2.95; S, 13.41. Found: C, 39.67; H, 2.74; S, 13.89.

Elution with petroleum ether containing a few per cent ether afforded 181 mg (4.6%) of the deep red complex **15**: mp 64-70° (decomposes above 110°); ir (CCl_4) ν_{CO} 2055 s, 2034 vw, 1992 s, 1978 s, and 1945 w cm^{-1}; δ_{FeCO} 615 mw, 565 mw cm^{-1}; nmr (C_6D_6) δ 1.30-2.80 (m).

Anal. Calcd for $C_{26}H_{28}S_2Fe_2O_6$: C, 51.00; H, 4.61; S, 10.47. Found: C, 51.11; H, 5.27; S, 10.80.

Fraction B was dissolved in the minimum amount of acetone and filtered through Celite. Evaporation of the filtrate gave 0.57 g (14.5%) of the dull green complex **14**: mp 100° dec; ir (CCl_4) ν_{CO} 2098 vvw, 2058 s, 2033 vw, 1992 vs, 1978 m (sh), 1948 ms, 1835

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(6) J. Cooke, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 170 (1968), and references cited therein.

mw cm^{-1}; ir (KBr) ν_{CO} 2060 s, 2005 s, 1989 s, 1949 s (br), 1916 (sh), 1819 s cm^{-1}; δ_{FeCO} 620 m, 595 mw, 560 m, 525 w, and 460 w cm^{-1}.

Anal. Calcd for $C_{26}H_{28}S_2Fe_2O_6$: C, 51.00; H, 4.61; S, 10.47; mol wt, 612. Found: C, 50.49; H, 4.88; S, 10.31; mol wt (osmometry), 581.

Conversion of 12 to 16. A petroleum ether solution of **12** (92 mg) was exposed to air, in the dark, for 50 hr. After filtering the solution to remove iron oxide, the concentrated filtrate was chromatographed on acidic alumina. Elution with petroleum ether gave 46.9 mg (51% yield) of the orange-red complex **16**: mp 148° dec; ir (CCl_4) ν_{CO} 2075 s, 2033 s, 2003 s, 1998 ms, and 1977 (sh) cm^{-1}; ir (KBr) δ_{FeCO} 618 m, 580 (sh), 560 m, 520 vw, 510 vw, and 490 w cm^{-1}; nmr (C_6D_6) δ 1.35–1.85 (m, 12 H, highest field signal (δ 1.35) assigned to the four γ and δ protons), 2.57 (s, 2 H, protons α to the sulfur bearing carbon); mass spectrum *m/e* 478 $(M)^+$, 450 $(M - CO)^+$, 422 $(M - 2CO)^+$, 394 $(M - 3CO)^+$, 366 $(M - 4CO)^+$, 338 $(M - 5CO)^+$, 310 $(M - 6CO)^+$, 176 $(S_2Fe_2)^+$, 166 $(9)^+$, 144 $(SFe_2)^+$, 112 $(Fe_2)^+$, 56 $(Fe)^+$. Further elution with petroleum ether gave a trace amount of adamantanone.

Cleavage of 12 by $LiAlH_4$. Complex **12** (0.892 g, 1.87 mmol) in tetrahydrofuran (THF, 35 ml) was added dropwise to a stirred ice-cold THF solution of $LiAlH_4$ (0.16 g, 4.00 mmol). After stirring for 1–2 hr, ethyl acetate (40 ml) was added, the solution was filtered, and the filtrate was evaporated at *ca.* 11 mm. The residue was dissolved in petroleum ether and chromatographed on Florisil. Elution with petroleum ether gave 0.130 g (14.5%) of **13**. Further elution with petroleum ether resulted in the formation of di(2-adamantyl) disulfide (0.037 g, 11.8%): mp 250–252 (lit.[5] mp 275°); nmr (C_6D_6) δ 1.41 (d, 4 H, equatorial β protons syn to each of the 2-adamantyl SS groups), 2.21 (s, 4 H, protons on carbons adjacent to the sulfur bearing carbon atoms), 2.35 (d, 4 H, axial β protons syn to each of the 2-adamantyl SS groups), and 3.27 (s, 2 H, C*H*S); mass spectrum *m/e* 334 $(M)^+$, 135 $(C_{10}H_{15})^+$.

Elution with petroleum ether–ether or with more polar solvents gave 0.105 g (37.5%) of 2-adamantanone (**19**). Repetition of the experiment using a 6.1:1.0 mol ratio of $LiAlH_4$–**12** gave 2-adamantanone (34.5%), **13** (2.0%), and the disulfide **20** (27.0%). Note that **13** gave **20** on treatment with $LiAlH_4$.

Cleavage of 14 by $LiAlH_4$. A THF solution (10 ml) of the bridging carbonyl complex **14** (0.200 g, 0.326 mmol) was added, drop by drop, to a THF solution (10 ml) of $LiAlH_4$ (0.320 g, 8.00 mmol). After stirring for 1 hr, ethyl acetate was first added, followed by benzene, and finally by water. The mixture was filtered, and the filtrate was evaporated *in vacuo* (at 50°, 11 mm). The residue was then chromatographed on a neutral alumina column (ether). Elution with ether gave 0.103 g (94.4%) of the disulfide (**20**), having identical spectral properties with the disulfide obtained above, and admixture of the two did not cause a depression of the melting point.

Cleavage of 16 by $LiAlH_4$ and by $LiAlD_4$. Only 2-adamantanone was formed when **16** was treated with $LiAlH_4$ (or $LiAlD_4$) using the procedure described for **14** (ratio of metal hydride–**16** was 6.0:1.0).

Reaction of Thiocamphenilone (10) with $Fe_2(CO)_9$. A benzene (40 ml) solution of thiocamphenilone[7] (1.00 g, 6.50 mmol) and $Fe_2(CO)_9$ (3.10 g, 8.50 mmol) was stirred at room temperature for 48 hr. Benzene was removed at room temperature under a stream of nitrogen, and the residue was then dissolved in petroleum ether and chromatographed on Florisil. Elution with petroleum ether gave **21**: ir (CCl_4) ν_{CO} 2082 ms, 2037 vs, 2015 m, 2002 s (br), 1975 ms, 1850 mw cm^{-1}. Decomposition of **21** to the nonbridging carbonyl complex **23** occurred very rapidly, thus preventing isolation of the bridging carbonyl complex. In fact, the chromatography has to be carried out as expeditiously as possible; otherwise, **21** will be converted, on the column, to **23** and some camphenilone. The following constitutes the best technique for effecting separation of **22**, **23**, and **5**; the reaction mixture was chromatographed on acidic alumina (activity grade I) with petroleum ether. Elution with petroleum gave a mixture of **23**, **5**, and a slight trace of camphenilone (fraction A). Elution with 5% ether–petroleum ether (v/v) gave **5**, **21**, **22**, **23**, and camphenilone (fraction B). Fraction A was now chromatographed on neutral alumina. Elution with 3–5% ether–petroleum ether (v/v) was continued until an orange-red band (**23**) moved about one-third the way down the column, at which time petroleum ether was employed as the eluent, affording 81.6 mg [5.40%; a *minimum* yield] of the orange-red complex **23**: mp 114.5–115.5° (decomposes above 145°); ir (CCl_4) ν_{CO} 2076 s, 2034.5 vs, 2004 vs, 1990 s, 1978 (sh) cm^{-1}; nmr (C_6D_6) δ 0.92 (s, 3 H, exo methyl group), 1.05 (s, 3 H, endo methyl group), 2.82 (s, 1 H, methine proton on carbon adjacent to the sulfur bearing carbon), 1.00–1.90 (m, 7 H, remainder of the protons).

Anal. Calcd for $C_{15}H_{14}S_2Fe_2O_6$: C, 38.65; H, 3.03; S, 13.76; Fe, 23.97. Found: C, 38.59; H, 3.17; S, 13.82; Fe, 23.70.

Elution with ether gave 30.4 mg (1.9%) of $S_2Fe_3(CO)_9$.[1]

Fraction B was chromatographed on Florisil. Elution with petroleum ether gave 98 mg of a mixture of **5** and **21** (separation of **21**, as **23**, from **5** could be achieved repeating the acidic alumina chromatographic procedure described below). Further elution with petroleum ether gave 0.39 g of a mixture of **22**, **23**, and camphenilone (from decomposition of **21** and/or **23**). The ketone was removed by vacuum pumping at 54° (0.02 mm). The mixture of **22** and **23** was now chromatographed on acidic alumina. Elution with petroleum ether (bp, 38–50°) gave **23**. The chromatography was discontinued when a red band had moved partway down the column. The column was broken into sections, and the red band was treated with ether to afford 30 mg (minimum yield) of the red, analytically pure complex **22**: mp 130° dec; ir (CCl_4) ν_{CO} 2050 vw, 2043.5 s, 1986.5 vs, 1963.5 ms, 1934 m cm^{-1}; nmr (C_6D_6) δ 1.00–2.80 (m).

Anal. Calcd for $C_{24}H_{28}S_2Fe_2O_6$: C, 48.99; H, 4.79; S, 10.90; Fe, 18.98; mol wt 588. Found: C, 48.26; H, 5.04; S, 10.20; Fe, 18.25; mol wt (osmometry) 550.

Reaction of Thiofenchone (11) with $Fe_2(CO)_9$. A solution of thiofenchone[7] (1.50 g, 8.92 mmol) and $Fe_2(CO)_9$ (5.31 g, 14.6 mmol) in benzene (60 ml) was stirred at room temperature for 36 hr. The solvent (and some unreacted **11**) was flash evaporated (45°, 11 mm) and the residue was then treated with petroleum ether and filtered to remove 3.9 mg of $Fe_3(CO)_{12}$, and the filtrate was evaporated *in vacuo* to remove solvent and **11**. The new residue was chromatographed on neutral alumina. Elution with petroleum ether gave **11** (not previously removed by flash evaporation). Further elution with petroleum ether and then with ether–methylene chloride gave **5** and **24**. The latter complexes were separated by chromatography on acidic alumina, $S_2Fe_2(CO)_6$[8] (70 mg, 4.57%) being eluted ahead of $S_2Fe_3(CO)_9$[1,8] (250 mg, 15.7%) using petroleum ether as the eluent.

Repetition of the experiment using hexane as the solvent and a 96 hr reaction time gave the same results.

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