



**Table I.** Yields, Melting Points, and Analytical Data for Complexes Obtained from Reaction of Thioureas and Thioamides with  $\text{Fe}_2(\text{CO})_9$ 

| Thio-<br>urea or<br>thio-<br>amide | Prod-<br>ucts    | Yield, %         | Mp, °C <sup>a</sup>      | C, %  |       | H, %  |       | N, %  |       | S, %  |       | Fe, % |       |
|------------------------------------|------------------|------------------|--------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|                                    |                  |                  |                          | Found | Calcd | Found | Calcd | Found | Calcd | Found | Calcd | Found | Calcd |
| 3a                                 | 4a <sup>b</sup>  | 6.2 <sup>c</sup> | 65 dec                   | 36.8  | 36.0  | 4.5   | 4.0   |       |       | 10.7  | 10.7  | 19.5  | 18.6  |
|                                    | 5a               | 2.6              | 65.0-66.0                | 31.3  | 32.1  | 2.8   | 2.9   | 6.7   | 6.8   | 7.9   | 7.8   | 27.9  | 27.7  |
|                                    | 6                | 0.1              | 113.0-114.0 <sup>d</sup> |       |       |       |       |       |       |       |       |       |       |
| 3b                                 | 4b               | 47.5             | 45 dec                   | 34.8  | 35.4  | 3.8   | 3.4   |       |       | 12.4  | 11.9  |       |       |
|                                    | 5b               | 4.3              | 85.5-86.0                | 31.1  | 31.4  | 2.6   | 2.4   | 3.5   | 3.7   |       |       |       |       |
|                                    | 6                | 0.3              |                          |       |       |       |       |       |       |       |       |       |       |
| 3c                                 | 4c               | <sup>e</sup>     |                          |       |       |       |       |       |       |       |       |       |       |
|                                    | 5c               | 9.1              |                          | 40.7  | 40.5  | 2.5   | 2.5   | 3.5   | 3.2   | 7.0   | 7.2   | 24.9  | 25.1  |
| 8a                                 | 9a               | <sup>e</sup>     |                          |       |       |       |       |       |       |       |       |       |       |
|                                    | 11a <sup>f</sup> | 11.1             | 64 dec                   | 42.7  | 43.2  | 3.3   | 3.4   | 7.0   | 7.2   | 8.2   | 8.2   | 21.7  | 21.5  |
| 8b                                 | 6                | Trace            |                          |       |       |       |       |       |       |       |       |       |       |
|                                    | 10b              | <sup>e</sup>     |                          |       |       |       |       |       |       |       |       |       |       |
|                                    | 11b              | 18.9             | 65 dec                   | 40.9  | 41.5  | 3.3   | 3.2   |       |       |       |       | 21.1  | 20.7  |
| 8c                                 | 6                | Trace            |                          |       |       |       |       |       |       |       |       |       |       |
|                                    | 9c               | <sup>e</sup>     |                          |       |       |       |       |       |       |       |       |       |       |
| 8d                                 | 9d               | <sup>e</sup>     |                          |       |       |       |       |       |       |       |       |       |       |
|                                    | 11d              | 16.6             | 80 dec                   | 42.5  | 41.9  | 2.6   | 2.3   | 6.6   | 7.0   | 7.7   | 8.0   | 20.7  | 20.9  |
| 8e                                 | 6                | 0.1              |                          |       |       |       |       |       |       |       |       |       |       |
|                                    | 10e              | <sup>e</sup>     |                          |       |       |       |       |       |       |       |       |       |       |
|                                    | 11e              | 5.2              | 70 dec                   | 50.2  | 50.5  | 3.2   | 3.4   | 5.7   | 6.2   | 6.9   | 7.1   | 18.6  | 18.6  |
| 8f                                 | 6                | 2.5              |                          |       |       |       |       |       |       |       |       |       |       |
|                                    | 9f               | <sup>e</sup>     |                          |       |       |       |       |       |       |       |       |       |       |
|                                    | 10f              | 33.7             | 85 dec                   | 30.7  | 31.5  | 4.1   | 3.5   |       |       | 19.5  | 18.6  |       |       |
| 8g                                 | 11f              | 0.4              |                          | 29.0  | 28.3  | 1.8   | 1.7   |       |       | 9.5   | 10.8  |       |       |
|                                    | 9g               | <sup>e</sup>     |                          |       |       |       |       |       |       |       |       |       |       |
|                                    | 10g              | 9.8              | 115 dec                  | 61.5  | 61.5  | 3.7   | 3.9   | 5.0   | 5.0   |       |       | 10.3  | 9.9   |
| 8h                                 | 11g <sup>g</sup> | 21.1             | 60 dec                   | 49.2  | 50.0  | 2.7   | 2.5   | 3.0   | 3.4   | 7.5   | 7.9   | 21.0  | 20.5  |
|                                    | 6                | Trace            |                          |       |       |       |       |       |       |       |       |       |       |
|                                    | 9h               | <sup>e</sup>     |                          |       |       |       |       |       |       |       |       |       |       |
| 8h                                 | 10h              | <sup>e</sup>     |                          |       |       |       |       |       |       |       |       |       |       |
|                                    | 11h              | 2.0              | 62 dec                   | 47.8  | 48.2  | 2.4   | 2.6   | 6.2   | 6.6   |       |       | 20.2  | 19.8  |
|                                    | 6                | Trace            |                          |       |       |       |       |       |       |       |       |       |       |

<sup>a</sup> In sealed capillary tubes. <sup>b</sup> Molecular weight by osmometry was 285 (calcd, 300). <sup>c</sup> The yield is a minimum one due to decomposition. <sup>d</sup> Lit. <sup>e</sup> mp 112.0-114.5°. <sup>e</sup> Not isolable. <sup>f</sup> Molecular weight by osmometry was 771, 785 (calcd, 778). <sup>g</sup> Molecular weight by osmometry was 761, 778 (calcd, 816).

the aromatic thioamide **3c**. The nitrogen atom, being a superior electron donor than the benzene ring, inhibits the ortho-metalation process. The melting points, yields, and analytical data for these complexes are listed in Table I.

The assignment of absorption bands in the infrared (ir) spectra of thioureas and thioamides has been a matter of considerable controversy, due to the occurrence of mixed vibrations.<sup>11,12</sup> Consequently, caution must be exercised in establishing the site of coordination of the thiourea or thioamide ligand to a metal solely on the basis of ir spectra. In Table II are listed pertinent ir data for the reactant thioureas and thioamides and for the complexes formed. The sulfur-donor ligand complexes **4** exhibit terminal metal carbonyl stretching bands in the 2100-1900-cm<sup>-1</sup> region, characteristic of an LFe(CO)<sub>4</sub> system.<sup>13</sup> As expected for **4**, the band assigned to  $\nu(\text{CN})$  [e.g., **4b**;  $\nu(\text{CN})$  1525 cm<sup>-1</sup>] occurs at higher frequency than in the free ligand [e.g., **3b**;  $\nu(\text{CN})$  1510 cm<sup>-1</sup>]. The thiocarbonyl stretching vibration (750-650 cm<sup>-1</sup>) undergoes a modest shift to lower wave number upon complexation. Vibrations in the 620-480-cm<sup>-1</sup> region are assigned to Fe-C-O deformations.<sup>8,14,15</sup>

The nuclear magnetic resonance (nmr) spectrum (Table II)

- (11) R. K. Ritchie, H. Spedding, and D. Steele, *Spectrochim. Acta, Part A*, **27**, 1597 (1971), and references cited therein.  
 (12) I. Suzuki, *Bull. Chem. Soc. Jap.*, **35**, 1449, 1456 (1962).  
 (13) F. Calderazzo, R. Ercoli, and G. Natta in "Organic Syntheses via Metal Carbonyls," I. Wender and P. Pino, Ed., Wiley-Interscience, New York, N. Y., 1968, p 1.  
 (14) D. C. Andrews and G. Davidson, *J. Organometal. Chem.*, **36**, 349 (1972).  
 (15) R. Cataliotti, A. Foffani, and L. Marchetti, *Inorg. Chem.*, **10**, 1594 (1971).

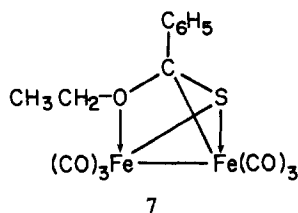
of tetramethylthioureairon tetracarbonyl (**4a**) shows only a singlet absorption for the four methyl groups. If bonding of the ligand to the metal occurred through nitrogen, rather than sulfur, then the methyl protons of the complexed dimethylamino group should have a different chemical shift than the methyl protons of the uncomplexed dimethylamino group. The mass spectra of the iron tetracarbonyl complexes show molecular ion peaks followed by successive loss of four carbonyls. A fragment also appeared which was assigned to the ligand.

In an attempt to form a more stable complex of type **4**, tetramethylthiourea was treated with triphenylphosphineiron tetracarbonyl in ether at room temperature. Starting materials were recovered under these reaction conditions as well as in refluxing ether or tetrahydrofuran. The organic ligand was liberated when **4a** was allowed to react with tri-*n*-butylphosphine. Also formed were (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>PFe(CO)<sub>4</sub> and *trans*-[(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>P]<sub>2</sub>Fe(CO)<sub>3</sub>. We did not detect any complex resulting from displacement of one of the carbonyls of **4a** by tri-*n*-butylphosphine.

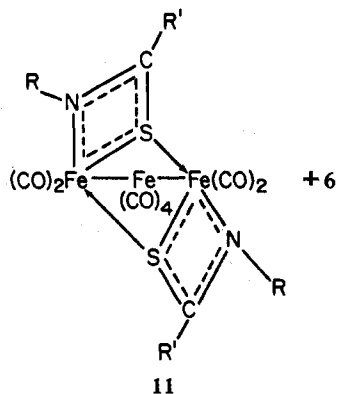
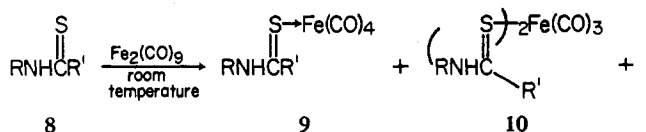
Four intense bands were observed in the 2100-1900-cm<sup>-1</sup> region of the ir spectra of **5** and are due to terminal metal carbonyl stretching. As expected for **5**, bands due to  $\nu(\text{C}=\text{S})$  disappeared and the carbon-nitrogen stretching vibration of **3** [e.g., **3c**;  $\nu(\text{CN})$  1515 cm<sup>-1</sup>] shifts to lower frequency on complexation [e.g., **5c**;  $\nu(\text{CN})$  1472 cm<sup>-1</sup>].

The nmr spectrum of **5a** (Table II) clearly indicated the nonequivalence of the protons of the two methyl groups of the complexed dimethylamino group. The mass spectra for **5a** and **5b** exhibit a molecular ion peak followed by suc-

cessive loss of six carbonyls. Other abundant fragments were assigned to  $[\text{Fe}_2]^+$  ( $m/e$  112) and  $[\text{Fe}]^+$  ( $m/e$  56). Complexes of type **5** are structurally similar to the major product **7** obtained from the reaction of *O*-ethyl thiobenzoate with  $\text{Fe}_2(\text{CO})_9$ .<sup>10</sup>



Treatment of  $\text{Fe}_2(\text{CO})_9$  with thioureas having a hydrogen atom attached to one of the nitrogens gives ligand-iron tetracarbonyl complexes **9** (analogous to **4**) and/or iron tricarbonyl complexes **10**, triiron octacarbonyl complexes of proposed structure **11**, and **6**. These complexes were obtained from a variety of di- and trisubstituted thioureas (**8a-c**, **8e**, **8f**, **8h**), thiobenzanilide (**8g**), and 5-methyl-3-phenyl-2-thiohydantoin (**8d**). Reaction solvents include ether, benzene, diglyme, and tetramethylurea. Complexes **9-11** are air-sensitive and, in most instances, the iron tetracarbonyl complexes **9** could only be characterized by ir spectroscopy. Complexes of type **5** were not detected in any of these reactions (**8a-h**).



- a,  $\text{R} = p\text{-CH}_3\text{C}_6\text{H}_4\text{-}$ ;  $\text{R}' = \text{N}(\text{CH}_3)_2$   
 b,  $\text{R} = p\text{-CH}_3\text{OC}_6\text{H}_4\text{-}$ ;  $\text{R}' = \text{N}(\text{CH}_3)_2$   
 c,  $\text{R} = \text{C}_6\text{H}_{11}\text{-}$ ;  $\text{R}' = \text{N}(\text{CH}_3)_2$   
 d,  $\text{R} = \text{C}_6\text{H}_5\text{-}$ ;  $\text{R}' = \text{NHCH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_3$   
 e,  $\text{R} = \text{CH}_3\text{-}$  (para)  $\text{C}_6\text{H}_4\text{-}$ ;  $\text{R}' = \text{NH}$  (para)  $\text{C}_6\text{H}_4\text{-CH}_3$   
 f,  $\text{R} = \text{-CH}_2\text{CH}_2\text{-}$ ;  $\text{R}' = \text{NH-}$   
 g,  $\text{R} = \text{R}' = \text{C}_6\text{H}_5$   
 h,  $\text{R} = \text{H}$ ;  $\text{R}' = \text{N}(\text{C}_6\text{H}_5)_2$

The ir carbonyl stretching bands for **9** were at very similar positions to those obtained for **4**. The bis(thiourea)iron tricarbonyls (**10**) exhibited two carbonyl stretching bands, 48–75  $\text{cm}^{-1}$  apart. Two carbonyl stretching bands, at somewhat lower frequency, were observed in the ir spectra of bis(tolyl isocyanide)iron tricarbonyls.<sup>16</sup> The higher frequency carbonyl band in **10** (presumably  $A_1'$ ,  $D_{3h}$  symmetry) is more

intense than the corresponding band for the bis(tolyl isocyanide)iron tricarbonyls and this may be due to the greater degree of nonlinearity of the thiourea ligand as compared to the isocyanide ligand. Molecular ion peaks were observed in the mass spectra of **10**, followed by successive loss of three carbonyls.

The structure for complex **11** was assigned on the basis of elemental analyses, molecular weight determinations by vapor-phase osmometry, and spectral data (repeated attempts to obtain electron impact or methane chemical ionization mass spectra were unsuccessful due to decomposition). The ir spectra of the triiron octacarbonyl complexes exhibited four medium to intense bands in the terminal metal carbonyl stretching region at 2080–2085, 2060–2061, 2038–2045, and 1992–1998  $\text{cm}^{-1}$  and a weaker absorption at 1945–1975  $\text{cm}^{-1}$  ( $\text{CCl}_4$ ). The NH stretching absorption in the ir of the trisubstituted thioureas, thiobenzanilide, and the thiohydantoin disappeared on forming **11**. It was, of course, still present, at a different wave number, in complexes derived from disubstituted thioureas. The absorption band due to a mixed  $\delta(\text{NH}) + \nu(\text{CN})$  vibration is generally shifted to lower frequency in conversion of **8** to **11** (1504–1526  $\text{cm}^{-1}$ ). Although increase in the double bond character of the carbon-nitrogen bond (that nitrogen previously attached to hydrogen) would result in a shift of  $\nu(\text{CN})$  to higher frequency, it is also clear that (except for complexes derived from disubstituted thioureas)  $\delta(\text{NH})$  is no longer possible and therefore cannot contribute to the mixed vibration. The latter factor, coupled with the anticipated decrease in the frequency of  $\nu(\text{CN})$  due to some  $n$  donation from nitrogen to iron, is responsible for the observation of  $\nu(\text{CN})$  in the 1504–1526- $\text{cm}^{-1}$  region. Since the double bond character of the thione group is less for **11** than for **8**,  $\nu(\text{CS})$  experiences a shift (28–83  $\text{cm}^{-1}$ ) to lower frequency upon complexation, *i.e.*,  $\nu(\text{CS})$  676–707  $\text{cm}^{-1}$  for **8** and  $\nu(\text{CS})$  613–667  $\text{cm}^{-1}$  for **11**.

Molecular models of the trinuclear complexes **11a** and **11b** indicate that, in each case, the two dimethylamino groups are in different environments. In nmr terms, one dimethylamino group is in the shielding cone of the  $\text{Fe}(\text{CO})_4$  group while the other dimethylamino group is remote from  $\text{Fe}(\text{CO})_4$ . Therefore, the nmr spectra of **11a** and **11b** each display two singlets for the dimethylamino groups, the signals occurring at higher field than for these protons in **8a** and **8b**, respectively. The nmr of complex **11d**, derived from 5-methyl-3-phenyl-2-thiohydantoin (**8d**), shows two sets of quartets and doublets for the methine and methyl protons, respectively, both types of protons existing in different environments in the two complexed thiohydantoin rings.

Vapor-phase osmotically determined molecular weights for **11a** and **11g** are in reasonable accord with the proposed structure. Complex **11** is similar, in some respects, to complex **2**. Other related structures for **11** are possible.

All previous studies<sup>2-7</sup> of metal carbonyl-thiourea reactions have paid scant attention to the effect of thiourea structure on the reaction pathway. This work has demonstrated the important influence of available hydrogen, *i.e.*, attached to nitrogen, on the course of the thiourea and thioamide- $\text{Fe}_2(\text{CO})_9$  reactions.

### Experimental Section

Melting points were measured in sealed capillary tubes using a Gallenkamp apparatus and are uncorrected. Microanalyses were performed by F. Pascher and E. Pascher, Bonn, West Germany; Par-Alexander Labs, South Daytona, Fla.; Meade Microanalytical Laboratory, Amherst, Mass.; and Hoffmann-La Roche Microanalytical Laboratory, Nutley, N. J. Infrared spectra were obtained using a Perkin-Elmer 457 grating spectrophotometer. A Perkin-Elmer 521 spectrome-

Table II. Pertinent Spectral Data for Thioamides, Thioamides, and Their Iron Carbonyl Complexes

| Compd | Ir, $\text{cm}^{-1}$  |                              |                             | Other bands (KBr)                                    | Nmr, $\delta$ , ppm (solvent)  | Mass spectrum, $m/e$  |
|-------|---|------------------------------|-----------------------------|--|--|---|
|       | $\nu(\text{CO})$  | $\delta(\text{FeCO})$ (KBr)  | $\delta(\text{FeCO})$ (KBr) |  |  |   |
| 3a    |   |                              |                             | 1490 s, 1465 s, 1360 vs, 1257 s, 661 m               | 3.08 [s, 12 H, $(\text{CH}_3)_2\text{N}$ ]<br>( $\text{CDCl}_3$ )  |   |
| 4a    | 2040 s, 1950 m, 1910 vs, (KBr); 2063 vw, 2042 vs, 1954 ms, 1939 s, 1916 s ( $\text{CCl}_4$ )  | 618 vs, 485 s                |                             | 1560 s, 1438 ms, 1377 s, 1257 ms, 637 m              | 3.23 [s, 12 H, $(\text{CH}_3)_2\text{N}$ ]<br>[( $\text{CD}_3$ ) <sub>2</sub> CO]  | 300 [M] <sup>+</sup> , 272 [M-CO] <sup>+</sup> , 244 [M-2CO] <sup>+</sup> , 216 [M-3CO] <sup>+</sup> , 188 [M-4CO] <sup>+</sup> , 132 [( $\text{CH}_3$ ) <sub>2</sub> N] <sub>2</sub> CS] <sup>+</sup> , 56 [Fe] <sup>+</sup>                     |
| 5a    | 2070 s, 2020 vs, 1985 vs, 1960 s (KBr); 2064 s, 2017 vs, 1988 ms, 1974 ms, 1966 vw, 1943 m ( $\text{CCl}_4$ )                           | 621 s, 608 s, 587 vs, 568 vs |                             | 1450 m, 1282 ms, 1204 m                              | 2.18 [s, 3 H, methyl of $\text{N}(\text{CH}_3)_2$ group complexed to Fe], 2.40 [s, 6 H, uncomplexed $\text{N}(\text{CH}_3)_2$ group], 2.56 [s, 3H, methyl of $\text{N}(\text{CH}_3)_2$ group complexed to Fe] ( $\text{CDCl}_3$ )  | 412 [M] <sup>+</sup> , 384 [M-CO] <sup>+</sup> , 356 [M-2CO] <sup>+</sup> , 328 (M-3CO) <sup>+</sup> , 300 [M-4CO] <sup>+</sup> , 272 [M-5CO] <sup>+</sup> , 244 [M-6CO] <sup>+</sup> , 112 [Fe] <sub>2</sub> <sup>+</sup> , 56 [Fe] <sup>+</sup> |
| 3b    |   |                              |                             | 1510 vs, 1420 s, 1350-1400 s (br), 1275 s, 655 ms    | 2.59 [s, 3 H, $\text{CH}_3\text{C}(\text{=S})$ -], 3.36 [s, 3 H, methyl of $\text{N}(\text{CH}_3)_2$ group], 3.44 [s, 3 H, methyl of $\text{N}(\text{CH}_3)_2$ group] [( $\text{CD}_3$ ) <sub>2</sub> CO]  |   |
| 4b    | 2045 m, 1920 vs (KBr); 2050 s, 1965 vs, 1930 vs ( $\text{CCl}_4$ )  | 615 vs, 480 ms               |                             | 1525 m, 1400 m, 1365 m, 1280 s, 647 m                | 2.83 [s, 3 H, $\text{CH}_3\text{C}(\text{=S})$ -], 3.57 [s, 6 H, $\text{N}(\text{CH}_3)_2$ ] [( $\text{CD}_3$ ) <sub>2</sub> CO]   | 271 [M] <sup>+</sup> , 243 [M-CO] <sup>+</sup> , 215 [M-2CO] <sup>+</sup> , 187 [M-3CO] <sup>+</sup> , 159 [M-4CO] <sup>+</sup> , 103 [CH <sub>3</sub> CSN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> , 56 [Fe] <sup>+</sup>                   |
| 5b    | 2070 ms, 2022 vs, 1992 ms, 1980 ms, 1970 vw (sh), 1944 m ( $\text{CCl}_4$ )   |                              |                             |  |  | 383 [M] <sup>+</sup> , 355 [M-CO] <sup>+</sup> , 327 [M-2CO] <sup>+</sup> , 299 [M-3CO] <sup>+</sup> , 271 [M-4CO] <sup>+</sup> , 243 [M-5CO] <sup>+</sup> , 215 [M-6CO] <sup>+</sup> , 112 [Fe] <sub>2</sub> <sup>+</sup> , 56 [Fe] <sup>+</sup> |
| 3c    |   |                              |                             | 1515 s, 1391 s, 1293 s, 1213 m, 679 m                | 3.10 [s, 3 H, methyl of $\text{N}(\text{CH}_3)_2$ group], 3.49 [s, 3H, methyl of $\text{N}(\text{CH}_3)_2$ group], 7.30 [s, 5 H, C <sub>6</sub> H <sub>5</sub> ] [( $\text{CD}_3$ ) <sub>2</sub> CO]   |   |
| 4c    | 2050 s, 1965 s, 1945 s, 1933 vs, ( $\text{CCl}_4$ )   |                              |                             |  |  |   |
| 5c    | 2072 s, 2030 vs, 1995 s, 1982 s, 1975 vvw, 1945 mw ( $\text{CCl}_4$ )   | 628 s, 612 s <sup>c</sup>    |                             | 1472 m, 1461 m, 1310 wm, 1238 m, 1214 m <sup>c</sup> | 2.47 [s, (br), 6 H, $\text{N}(\text{CH}_3)_2$ ], 7.30 [s, 5 H, C <sub>6</sub> H <sub>5</sub> ] [( $\text{CD}_3$ ) <sub>2</sub> CO]   |   |
| 8a    |   |                              |                             | 3282 m, 1537 s, 1445 m, 1327 s, 1255 m, 700 s        | 2.34 [s, 3 H, $p$ -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -], 3.30 [s, 6 H, $\text{N}(\text{CH}_3)_2$ ], 7.05 [s, 1 H, NH], 7.12 [s, 4 H, aromatic protons] ( $\text{CDCl}_3$ )  |   |
| 9a    | 2040 s, 1970 s, 1950 s, 1935 s, ( $\text{CCl}_4$ )  |                              |                             |  |  |   |
| 11a   | 2080 m, 2060 s, 2042 s, 2038 w (sh), 2000 vw (sh), 1998 ms, 1965 w (sh) ( $\text{CCl}_4$ ); 2082 ms, 2060 m, 2035 vs, 1985 s (br) (KBr) | 609 s, 601 s, 562 m, 540 m   |                             | 1513 ms, 1450 m, 1407 m, 633 m                       | 2.30 [s, 6 H, $p$ -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -], 2.65 [s, 6 H, $\text{N}(\text{CH}_3)_2$ shielded by Fe(CO) <sub>5</sub> ], 3.07 [s, 6 H, $\text{N}(\text{CH}_3)_2$ remote from Fe(CO) <sub>5</sub> ], 6.5-7.3 [m, 8 H, aromatic protons ( $\text{CDCl}_3$ )] |   |

Table II. (Continued)

| Compd | Ir, $\sigma$ cm $^{-1}$  |  | Nmr, $\delta$ , ppm (solvent)   | Mass spectrum, $m/e$   |
|-------|--|--|---|--|
|       | $\nu(\text{CO})$   | $\delta(\text{FeCO})$ (KBr)                                    |   |  |
| 8b    |  | 3273 m, 1540 s, 1455 m,<br>1330 s, 1240 s, 690 m               | 3.27 [s, 6 H, N(CH <sub>3</sub> ) <sub>2</sub> ], 3.79 [s, 3 H, OCH <sub>3</sub> ], 6.84 [d, 2 H, protons ortho to the thiourea group, $J = 9$ Hz], 7.10 [s, 1 H, NH], 7.14 [d, 2 H, protons ortho to the methoxy group] (CDCl <sub>3</sub> )                     |  |
| 10b   | 2038 ms, 1990 s<br>(CH <sub>2</sub> Cl <sub>2</sub> )  |  | 2.65 [s (br), 6 H, N(CH <sub>3</sub> ) <sub>2</sub> shielded by Fe(CO) <sub>4</sub> ], 3.04 [s, 6 H, N(CH <sub>3</sub> ) <sub>2</sub> remote from Fe(CO) <sub>4</sub> ], 3.76 [s, 6 H, OCH <sub>3</sub> ], 6.6-7.3 m, 8 H, aromatic protons] (CDCl <sub>3</sub> ) |  |
| 11b   | 2080 ms, 2050 m, 2020 s<br>1980 s (br) (KBr);<br>2080 ms, 2060 s, 2040 s<br>2007 w (sh), 1995 ms,<br>1960 m (sh) (CCl <sub>4</sub> ) | 612 s-vs, 587 ms,<br>572 ms, 540 m                             |   |  |
| 8c    |  | 3330 ms, 1528 s, 1452 ms,<br>1361 s, 1251 ms, 710 ms           |   |  |
| 9c    | 2050 m, 1970 vs, 1945 s<br>1930 s (CCl <sub>4</sub> )  |  |   |  |
| 8d    |  | 3192 s, 1755 s, 1528 s,<br>1444 ms, 1320 ms, 1270 vs,<br>713 s | 1.51 [d, 3 H, CH <sub>3</sub> ], 4.47 [q, 1 H, CHCH <sub>3</sub> ], 7.59 [s, 5 H, C <sub>6</sub> H <sub>5</sub> ] [(CD <sub>3</sub> ) <sub>2</sub> CO]  |  |
| 9d    | 2050 m, 1965 s, 1945 s,<br>1930 s (CCl <sub>4</sub> )  |  |   |  |
| 11d   | 2090 ms, 2066 s, 2040 vs,<br>1995 ms (br) (KBr); 2085 m,<br>2061 s, 2040 vs, 1998 m,<br>1975 w (sh) (CCl <sub>4</sub> )              | 610 s, 599 s,<br>583 ms, 560 ms                                | 1.48 [d, 3 H, CH <sub>3</sub> , $J = 7$ Hz], 1.72 [d, 3 H, CH <sub>3</sub> , $J = 7$ Hz], 3.93 [q, 1 H, CHCH <sub>3</sub> ], 4.41 [q, 1 H, CHCH <sub>3</sub> ], 7.42 [s (br), 5 H, C <sub>6</sub> H <sub>5</sub> ] [(CD <sub>3</sub> ) <sub>2</sub> CO]           |  |
| 8e    |  | 3240 m, 1545 s, 1470 s,<br>1343 mw (br), 1243 s, 700 s         | 2.35 [s, 6 H, <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -], 7.23 [s, 8 H, aromatic protons], 7.82 [s, 2 H, NH] (CDCl <sub>3</sub> )   |  |
| 10e   | 2043 s, 1982 ms (CCl <sub>4</sub> );<br>2035 s, 1965 s (KBr)   |  |   |  |
| 11e   | 2082 m, 2070 m, 2034 vs,<br>1995 ms (br), 1970 vw<br>(sh) (KBr); 2080 m,<br>2060 m, 2042 vs, 1995 ms<br>(CCl <sub>4</sub> )          | 613 s, 585 s,<br>563 s   | 2.27 [s, 6 H, <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -], 2.29 [s, 6 H, <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -], 7.0 [br, 8 H, aromatic protons] (CDCl <sub>3</sub> )  |  |
| 8f    |  | 3225 mw, 1485 s, 1460 s,<br>1360 ms, 1270 vs, 676 ms           | 3.50 [s, 4 H, -CH <sub>2</sub> -], 7.75 [s, 2 H, NH] [(CD <sub>3</sub> ) <sub>2</sub> CO]   |  |
| 9f    | 2050 s, 1962 s, 1930 s<br>(CCl <sub>4</sub> )  |  |   |  |
| 10f   | 2030 ms, 1958 s (KBr)  |  |   | 344 [M] <sup>+</sup> , 316 [M - CO] <sup>+</sup> , 288 [M - 2CO] <sup>+</sup> , 260 [M - 3CO] <sup>+</sup> , 102 [C <sub>3</sub> H <sub>6</sub> N <sub>2</sub> Si] <sup>+</sup> , 56 [Fe] <sup>+</sup> |
| 11f   | 2082 ms, 2060 s, 2038 vs,<br>2010 vs (sh), 1995 ms,<br>1969 w (sh) (CCl <sub>4</sub> )   | 608 s, 599 ms,<br>590 m, 561 s                                 |   |  |
| 8g    |  | 3155 ms, 1490 s, 1445 s,<br>1366 s, 1208 s, 688 ms             | 7.33 [m, 5 H, C <sub>6</sub> H <sub>5</sub> C(=S)-], 7.63 [m, 5 H, -NHC <sub>6</sub> H <sub>5</sub> ], 9.16 [s, 1 H, NH] (CDCl <sub>3</sub> )   |  |
| 9g    | 2056 vs, 1980 m, 1964 s,<br>1956 s (CCl <sub>4</sub> )   |  |   |  |

Table II. (Continued)

| Compd | $\nu(\text{CO})$   |                                  | $\delta(\text{FeCO})$ (KBr)   |  | $\text{Ir}^a \text{ cm}^{-1}$   |                   | Nmr, $\delta$ , ppm (solvent) | Mass spectrum, $m/e$ |
|-------|--|----------------------------------|---|--|---|-------------------|-------------------------------|----------------------|
|       | $\nu(\text{CO})$   | $\nu(\text{CO})$                 | $\delta(\text{FeCO})$ (KBr)   | $\delta(\text{FeCO})$ (KBr)  | Other bands (KBr)   | Other bands (KBr) |                               |                      |
| 10g   | 2042 s, 1986 s ( $\text{CCl}_4$ )<br>2030 ms, 1987 vs, 1940 w (sh) (KBr)   | 606 s, 568 ms,<br>540 ms         | 1538 s, 1487 m, 1446 m,<br>1256 ms, 652 m                                     | 7.10 [s (br), 10 H, $\text{C}_6\text{H}_5$ ] ( $\text{CDCl}_3$ )   | 566 [M] <sup>+</sup> , 538 [M - CO] <sup>+</sup> ,<br>510 [M - 2CO] <sup>+</sup> , 482 [M - 3CO] <sup>+</sup> ,<br>213 [ $\text{C}_6\text{H}_5\text{CSNHC}_6\text{H}_5$ ] <sup>+</sup> , 56 [Fe] <sup>+</sup> |                   |                               |                      |
| 11g   | 2082 ms, 2060 s, 2035 vs,<br>1985 s (br) (KBr); 2082 m,<br>2060 ms, 2042 vs, 1996 ms,<br>1945 vvw ( $\text{CCl}_4$ ) | 608 ms, 590 s,<br>577 ms, 588 ms | 1526 m, 1480 m, 1440 m, 1241 m,<br>613 ms                                     | 7.08 [br, 20 H, $\text{C}_6\text{H}_5$ ] ( $\text{CDCl}_3$ )   |   |                   |                               |                      |
| 8h    |  |                                  | 3454 s, 3270 s, 3140 m,<br>1590 s, 1490 s, 1438 s,<br>1352 s, 1258 ms, 707 s  | 2.72 [s, 2 H, $\text{NH}_2$ ], 7.58<br>[s, 10 H, $\text{C}_6\text{H}_5$ ] [ $(\text{CD}_3)_2\text{CO}$ ] |   |                   |                               |                      |
| 9h    | 2050 s, 1965 vs, 1948 vs,<br>1930 vs ( $\text{CCl}_4$ )  |                                  | 3453 s, 3273 m, 3140 m,<br>1623 m, 1517 m, 1433 ms,<br>1350 s, 1262 ms, 681 m |  | 596 [M] <sup>+</sup> , 568 [M - CO] <sup>+</sup> , 540<br>[M - 2CO] <sup>+</sup> , 512 [M - 3CO] <sup>+</sup> ,<br>228 [ $(\text{C}_6\text{H}_5)_2\text{NCSNH}_2$ ] <sup>+</sup> , 56 [Fe] <sup>+</sup>       |                   |                               |                      |
| 10h   | 2035 ms, 1960 s (KBr)  | 596 m, 568 m,<br>540 ms          | 3380 mw, 1510 m, 1450 m,<br>1414 w, 1307 ms, 624 m                            |  |   |                   |                               |                      |
| 11h   | 2080 m, 2050 w, 2034 vs,<br>1980 s (KBr); 2082 m,<br>2060 m, 2045 vs, 2010 vw<br>(sh), 1992 s ( $\text{CCl}_4$ )     | 607 ms, 595 s                    |   |  |   |                   |                               |                      |

<sup>a</sup> vs = very strong; s = strong; ms = medium strong; m = medium; mw = medium weak; w = weak; vw = very weak; vvw = very very weak; br = broad. <sup>b</sup> Tetramethylsilane was employed as the internal standard. s = singlet; d = doublet; q = quartet; m = multiplet. <sup>c</sup>  $\text{CCl}_4$  solution.

ter was used to locate more precisely ( $\pm 1.0 \text{ cm}^{-1}$ ) 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 and/or HA-100 spectrometers. Mass spectra were recorded on an Atlas CH-4 or Varian MS 902 spectrometer.

Diiron enneacarbonyl was purchased from Pressure Chemical Co. and used as received. Mr. R. A. Partis provided generous quantities of triphenylphosphineiron tetracarbonyl. We are grateful to Dr. B. E. Norcross for supplying us with *N,N*-dimethylthioacetamide. Solvents were dried and purified by standard techniques. All reactions were run and worked up under a dry nitrogen atmosphere.

**Reaction of  $\text{Fe}_2(\text{CO})_9$  with (i) Tetramethylthiourea (3a).** A mixture of tetramethylthiourea (Eastman Organic Chemicals, 1.00 g, 7.56 mmol) and  $\text{Fe}_2(\text{CO})_9$  (2.76 g, 7.56 mmol) in ether (55 ml) was stirred at room temperature for 24 hr. After evaporation of the solvent under nitrogen at room temperature, the residue was dissolved in 10% ether-petroleum ether (bp 38–50°) (v/v) and chromatographed on Florisil. Elution with petroleum ether gave 6. Elution with 20% ether-petroleum ether gave the magenta red complex 5a. Elution with 40% ether-petroleum ether or with ether yielded a viscous red liquid consisting of a mixture of 3a and 4a. Solidification occurred when the mixture was kept overnight at –30°. Tetramethylthiourea was removed by treating the solid with water several times and then filtering a brown solid. To the latter was added the minimum quantity of acetone necessary to dissolve most of the solid. The acetone solution was filtered, the filtrate dried over  $\text{Na}_2\text{SO}_4$ , and the solvent was evaporated under a stream of nitrogen depositing orange needles of 4a. See Table I for characterization data.

**(ii) *N,N*-Dimethylthioacetamide (3b).** Using essentially identical reaction conditions as described for i, the residue from solvent evaporation was dissolved in the minimum amount of ether, diluted with an equal volume of petroleum ether, and chromatographed on Florisil. Elution with petroleum ether gave 6. Elution with ether gave a mixture of 4b, 5b, and 6. The mixture was treated with petroleum ether-water (1:1) and filtered (fraction A) and the petroleum ether extract was separated from the filtrate. Yellow flakes of the iron tetracarbonyl complex 4b were obtained by slow evaporation of the petroleum ether extract under nitrogen. After filtering 4b, the binuclear complex 5b was separated from 6 by rechromatography of the filtrate on Florisil.

Fraction A was dissolved in 40% ether-petroleum ether (v/v) and chromatographed on Florisil. Elution with petroleum ether gave 6. Additional 5b was obtained by elution with 5–15% ether-petroleum ether. Elution with ether gave a mixture of 3b and 4b, which was worked up using essentially the procedure described for the isolation of 4a from a mixture of 3a and 4a.

**(iii) *N,N*-Dimethylthioacetamide (3c).** A mixture of 3c (0.847 g, 5.12 mmol) and  $\text{Fe}_2(\text{CO})_9$  (2.55 g, 7.00 mmol) in benzene (40 ml) was stirred at room temperature for 21 hr. The residue obtained after solvent evaporation was dissolved in 1:1 petroleum ether-ether and chromatographed on Florisil. Elution with petroleum ether gave a mixture of 5c and 6 (fraction A). Elution with petroleum ether-ether or with ether gave the iron tetracarbonyl complex 4c contaminated by reactant thioamide. The low stability of 4c (decomposes to 3c) prevented its isolation in analytically pure form. Fraction A was rechromatographed on Florisil using petroleum ether. Elution with petroleum ether gave 6. A 10% ether-petroleum ether (v/v) mixture was then used to move the binuclear complex 5c away from the top of the column (which also contained iron oxide). This red region (5c) was taken out and extracted with petroleum ether-ether to give analytically pure complex 5c.

**(iv) *N,N*-Dimethyl-*N'*-*p*-tolylthiourea (8a).** A mixture of *N,N*-dimethyl-*N'*-*p*-tolylthiourea (Maybridge Chemical Co., 1.12 g, 5.75 mmol) and  $\text{Fe}_2(\text{CO})_9$  (2.92 g, 8.00 mmol) in ether (140 ml)-benzene (40 ml) was stirred at room temperature for 36–48 hr. An ir spectrum of the residue obtained after removal of the solvents clearly showed the iron tetracarbonyl complex 9a as the predominant product, but all attempts at isolation (chromatography on Florisil, neutral or acidic alumina; crystallization and recrystallization) resulted in decomposition to starting material. The residue was dissolved in benzene and chromatographed on Florisil. Complex 6 was obtained using petroleum ether as the eluent. The triiron octacarbonyl complex 11a was obtained using the following procedure: elution with 20% ether-petroleum ether (v/v) resulted in movement of a red band (11a) partially down the column (leaving 8a, 9a, and iron oxide at top). Elution was stopped, the column divided into sections, and the red area extracted with ether to afford crude 11a. The crude complex was now chromatographed on acidic alumina (activity grade I) and elution with 5% ether-petroleum ether (v/v) gave 14 mg

of an unidentified purple-red material. The red band remaining on the column was treated as above to give pure 11a.

(v) *N,N*-Dimethyl-*N'*-*p*-methoxyphenylthiourea (8b). A mixture of the thiourea (Maybridge Chemical Co., 1.37 g, 6.50 mmol) and  $\text{Fe}_2(\text{CO})_9$  (4.57 g, 13.0 mmol) in diglyme (55 ml) was stirred at room temperature for 2 days, then poured into water, and extracted with ether. The ether extract was washed repeatedly with water to remove diglyme and then flash evaporated. The residue obtained from flash evaporation was dissolved in benzene and chromatographed on Florisil. Elution with benzene, benzene-ether, or with ether gave a red-brown solid containing 6, 8b, 10b, and 11b. Elution with acetone gave recovered starting material. The crude mixture was now dissolved in 50% ether-petroleum ether and rechromatographed on Florisil. Elution with petroleum ether gave a trace amount of 6. The portion above a dull red band was removed and extracted with acetone to give additional recovered starting material (from decomposition of 9b and 10b) and a trace quantity of unstable 10b. The dull red band was eluted off the column with ether and an ir spectrum indicated this fraction to be the trinuclear complex 11b. Purification of the latter was effected by chromatography on acidic alumina. Elution with 15% ether-petroleum ether (v/v) resulted in movement of a red band partially down the column. The chromatography was stopped, the column separated into several sections, and the section containing the red band was extracted with ether (the top section contained 8b) to afford 11b in reasonably pure form. Analytically pure 11b was obtained by repetition of the acidic alumina chromatographic process.

(vi) *N,N*-Dimethyl-*N'*-cyclohexylthiourea (8c). Using essentially identical conditions as described for i, the residue from solvent evaporation was chromatographed on Florisil with 50% ether-petroleum ether. Elution with 50% ether-petroleum ether gave 9c, contaminated by starting material. Starting material was eluted off the column with ether. All efforts (chromatography, recrystallization) to obtain analytically pure 9c proved fruitless, as the iron tetracarbonyl complex readily reverted to starting thiourea. The trinuclear complex 11c was not detected in this reaction.

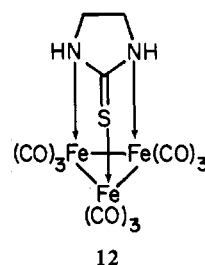
(vii) 5-Methyl-3-phenyl-2-thiohydantoin (8d). A mixture of  $\text{Fe}_2(\text{CO})_9$  (2.18 g, 6.00 mmol) and the thiohydantoin (Carbolabs, 1.00 g, 4.85 mmol) in tetramethylurea (20 ml) was stirred at room temperature for 14 hr. An ir spectrum ( $\text{CCl}_4$ ) of an aliquot clearly indicated the presence of the iron tetracarbonyl complex 9d, but all attempts to isolate 9d resulted in recovery of starting material. The trinuclear complex 11d was best worked up in the following manner. The reaction mixture was poured into benzene-water (1:1) and the benzene layer washed repeatedly with water to remove tetramethylurea. The benzene extract was dried and flash evaporated ( $50^\circ$ , ca. 11 mm) to remove  $\text{Fe}(\text{CO})_5$  and benzene, and the resulting viscous red residue was dissolved in the minimum amount of ether and chromatographed on Florisil. Elution with petroleum ether gave 6. Elution with 30% ether-petroleum ether (v/v) gave 11d. Analytically pure 11d was obtained by dissolving the crude material in benzene and rechromatographing on Florisil. Elution with petroleum ether resulted in motion of a red band part-way down the column. The chromatography was halted and the adsorbent above the red band was removed. Chromatography was then resumed, pure 11d being eluted off the column with ether.

(viii) *N,N'*-Di-*p*-tolylthiourea (8e). A diglyme (180 ml) solution of *N,N'*-di-*p*-tolylthiourea (Aldrich Chemical Co., 2.00 g, 7.80 mmol) and  $\text{Fe}_2(\text{CO})_9$  (7.75 g, 20.0 mmol) was stirred at room temperature for 36–48 hr. The pale red solution was poured into water and extracted with ether. The ether extract was washed repeatedly with water to remove diglyme and dried ( $\text{Na}_2\text{SO}_4$ ), and the ether was then concentrated to a small volume to give 10e and recovered starting material. The recovered thiourea, which is ether insoluble, arises from decomposition of 9e and 10e. The ether solution was chromatographed on Florisil. Elution with ether gave 6, followed by a mixture of 8e and 11e. This mixture was now dissolved in benzene and chromatographed on acidic alumina. Movement of an orange-red band partially down the column occurred on elution with 20% ether-petroleum ether (v/v). The chromatography was discontinued and the column divided into sections. The section containing the orange-red band was extracted with 30% ether-petroleum ether (v/v) to afford pure 11e. The upper section of the column contained starting material.

(ix) Ethylenethiourea (8f). A tetramethylurea (60 ml) solution of ethylenethiourea (Eastman Organic Chemicals, 2.00 g, 19.6 mmol) and  $\text{Fe}_2(\text{CO})_9$  (7.30 g, 20.0 mmol) was stirred at room temperature for 36 hr. The solution was added to benzene-water (1:1), the layers were separated, and the benzene extract was washed several times with water to remove tetramethylurea. The benzene extract was

dried, the solvent removed *in vacuo*, and the residue then treated with ether-petroleum ether to give a solid. The latter was filtered, the filtrate set aside (fraction A), and the solid washed with water and dried. Most of the solid was dissolved in acetone and filtered through Celite, and the filtrate was evaporated *in vacuo* to afford 10f.

Fraction A was chromatographed on Florisil. Elution with petroleum ether gave 6, followed closely by a mixture of 9f, 11f, and another complex. Elution with ether gave the unstable complex 9f, contaminated by 11f. The two mixtures were dissolved in carbon tetrachloride and exposed to air to effect decomposition of 9f to ethylenethiourea and thus permit isolation of pure 11f. The solution was filtered and the filtrate chromatographed on Florisil. Elution with petroleum ether gave small quantities of 6. The orange-red complex 11f was isolated by elution with 40% ether-petroleum ether. Elution with ether gave trace amounts of a purple-red solid having the following spectral properties: ir ( $\text{CCl}_4$ )  $\nu(\text{CO})$  2086 ms, 2080 ms, 2060 s, 2037 s, 2010 s, 1986 mw, and  $1967\text{ cm}^{-1}$  s (sh); mass spectrum (*m/e*) 522, 494, 466, 438, 410, 382, 354, 326, 298, 270, 112, 102, 56. These limited data suggest structure 12 for the complex.



(x) Thiobenzanilide (8g). A mixture of thiobenzanilide (Eastman Organic Chemicals, 1.00 g, 4.70 mmol) and  $\text{Fe}_2(\text{CO})_9$  (1.96 g, 5.37 mmol) in benzene (60 ml) was stirred for 48 hr at room temperature. After 1 hr, an ir spectrum of an aliquot indicated the presence of 9g, but all attempts to isolate the iron tetracarbonyl complex gave only recovered thiobenzanilide. An ir recorded after 48 hr showed no 9g. The reaction mixture was concentrated to a few milliliters and chromatographed on Florisil. Elution with petroleum ether gave traces of 6. Elution with 30% ether-petroleum ether gave a mixture of 10g and 11g (fraction A). Further elution with 30% ether-petroleum ether or with ether gave some 10g, but mainly 8g (fraction B).

Fraction A was dissolved in ether, diluted with an equal volume of petroleum ether, and evaporated under nitrogen to a small volume. Additional petroleum ether was then added, and the solution was filtered. Chromatography of the filtrate on Florisil gave the red, pure trinuclear complex 11g on elution with 10% ether-petroleum ether (v/v). The filtered solid (above) was dissolved in acetone and filtered through Celite, and the filtrate was evaporated under nitrogen to afford orange-red needles of 10g.

Fraction B, on treatment with 10% ether-petroleum ether (v/v), filtration, and subsequent evaporation of the filtrate, gave more of the mononuclear complex 10g.

(xi) *N,N*-Diphenylthiourea (8h). A tetramethylurea (60 ml) solution of *N,N*-diphenylthiourea (Eastman Organic Chemicals, 1.50 g, 6.56 mmol) and  $\text{Fe}_2(\text{CO})_9$  (2.89 g, 7.92 mmol) was stirred at room temperature. After 1 hr an ir spectrum of an aliquot indicated the presence of 9h, but all attempts to isolate the iron tetracarbonyl complex gave only recovered starting material. After 24 hr the reaction mixture was poured into an ether-water (1:1) solution, the layers were separated, and the ether extract was washed repeatedly with water and then dried. The residue obtained from *in vacuo* evaporation of ether was chromatographed on Florisil. Elution with ether gave a mixture of 8h, 10h, 11h, and 6. Acetone eluted 8h and 10h. The eluted fractions were treated with carbon tetrachloride and filtered from starting material, and the filtrate was evaporated. The new residue was dissolved in the minimum amount of methylene chloride. Addition of petroleum ether precipitated 10h (contaminated by 8h) which could not be further purified by recrystallization or chromatography (due to decomposition). The petroleum ether- $\text{CH}_2\text{Cl}_2$  solution was concentrated, and the residue was dissolved in ether and chromatographed on Florisil. Elution with petroleum ether gave a trace of 6. Elution with ether gave impure 11h. The pure trinuclear complex was isolated by rechromatography on Florisil. Elution with petroleum ether gave a minute quantity of 6. A 10% ether-petroleum ether (v/v) solution was used as eluent to move an orange-red band (11h) away from the origin of the col-

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<sup>17</sup> and *trans*-bis(tri-*n*-butylphosphine)iron tricarbonyl.<sup>17</sup>

**Acknowledgments.** We are grateful to the donors of the

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

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**Registry No.** Fe<sub>2</sub>(CO)<sub>9</sub>, 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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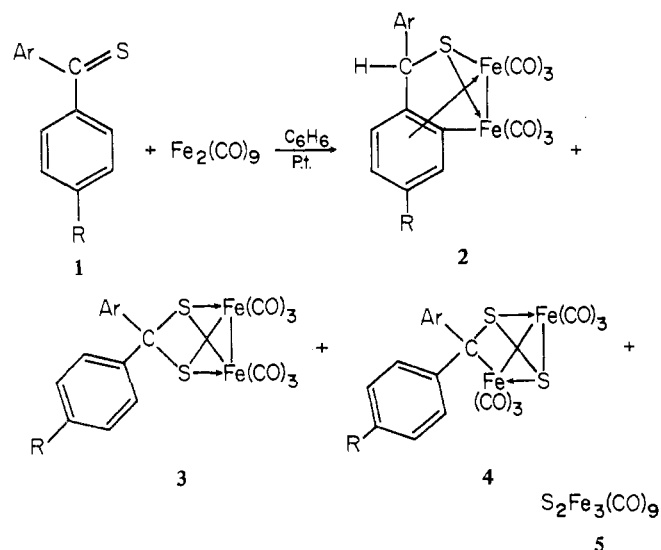
## Reactions of Nonaromatic Thioketones with Diiron Enneacarbonyl

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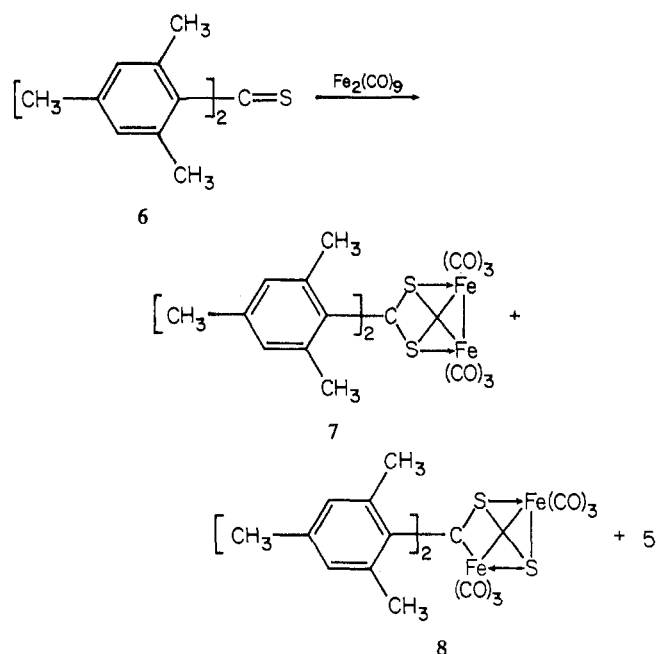
The major product (71.5% yield) obtained from reaction of adamantanethione and diiron enneacarbonyl was C<sub>16</sub>H<sub>14</sub>S<sub>2</sub>Fe<sub>2</sub>O<sub>6</sub>, which contains bridging and terminal carbonyl groups, as well as two sulfur atoms attached to the same carbon atom. By-products of the reaction were an isomeric complex lacking bridging carbonyls, but possessing a carbon-iron σ bond, and dimeric complexes of formula C<sub>26</sub>H<sub>28</sub>S<sub>2</sub>Fe<sub>2</sub>O<sub>6</sub>, 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<sub>2</sub>(CO)<sub>9</sub> gave complexes analogous to those obtained from adamantanethione (S<sub>2</sub>Fe<sub>3</sub>(CO)<sub>9</sub> 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<sub>2</sub>(CO)<sub>9</sub>) in benzene to give sulfur-donor ligand ortho-metalated complexes (2) in good



amounts of S<sub>2</sub>Fe<sub>3</sub>(CO)<sub>9</sub> (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<sub>2</sub>(CO)<sub>9</sub> results in the formation of 7 and 8, which are analogs

to excellent yields.<sup>1</sup> The diiron hexacarbonyl complexes 3 and/or 4 were by-products in certain instances and small



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