the $^{11}B-^{11}B$ couplings in this molecule. Interpretation of this pattern would best be reserved until more of the parameters can be established. It is possible that a combination study involving proton decoupling and line narrowing could at least furnish information concerning the $^{11}B-^{11}B$ coupling constants. It is hoped that such a study can be undertaken in the near future.

n-B_9H_{15}, n-Nonaborane(15). The structure and ^{11}B nmr of n-B_9H_{15} are shown in Figure 15. The complexity of the spectrum can be attributed to accidental overlap of B(5,6,7,8) and B(3) resonances. The line-narrowed spectrum of this region yields little interpretable data due to its complexity. The PRFT method[1] does, however, separate the B(3) triplet resonance from the rest of the overlapped resonances and, in this case, seems superior to the line-narrowing technique. But the B(4,9) resonance, which does not overlap with other resonances, does show a doublet fine structure ($J_{^{11}B-^{1}H_\mu}$) in the line-narrowed spectrum. Thus even in the large cage molecules like n-B_9H_{15}, there is still information to be gained through the use of this new technique.

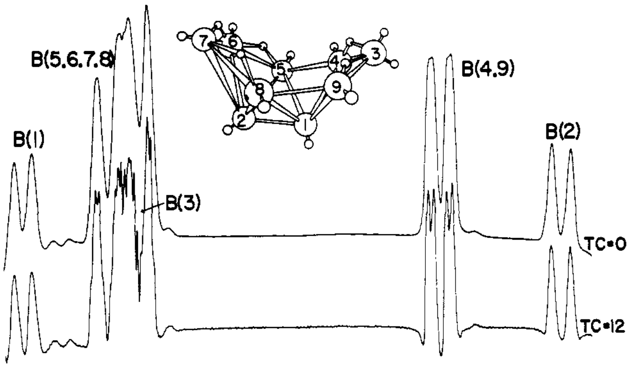

Figure 15. Normal and line-narrowed FT ^{11}B nmr spectra of n-B_9H_{15}.

The line-narrowing technique has been presented here for ^{11}B nmr only; however, the technique is not restricted to this one nucleus. It is thus felt that research in many other areas can benefit from the use of this line-narrowing technique, and it is hoped that there will be more applications in the near future.

Acknowledgments. This research was supported by Grant GP-24266X from the National Science Foundation. We thank Professor Adam Allerhand for his suggestion of this approach and for supplying the initial instrumentation used for line narrowing, supported by Grants GP-7922 and GP-17966 from the National Science Foundation.

Stabilization of 1,3-Dipoles by π-Complex Formation. Iron Carbonyl Derivatives of Thio- and Selenoketocarbenes

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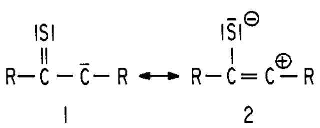
Received November 1, 1972

Abstract: *Trihapto*-1,2-diphenylthioketocarbenehexacarbonyldiiron, the first transition metal derivative of a 1,3-dipolar species, was obtained by the reaction of 1,4-dimethylnickel(II) bis(*cis*-stilbenedithiolate) or of diphenyl-1,2,3-thiadiazole with iron carbonyls on heating and light irradiation. The corresponding selenoketocarbene complex was prepared analogously from diphenyl-1,2,3-selenodiazole. The same method was used to synthesize the hexacarbonyldiiron complex of unsubstituted thioketocarbene. The complexed 1,3-dipoles form σ and π bonds with the iron carbonyl moieties and exhibit low residual reactivity, undergoing cycloaddition reactions with alkynes only on thermolysis. Ketocarbenes could not be stabilized analogously.

Although a large body of information on the reactivity and selectivity of "1,3-dipoles" is available,[2] the evidence for their existence is frequently indirect. Recently[3] we have reported on the synthesis and structure of *trihapto*-1,2-diphenylthioketocarbenehexacarbonyldiiron, the first transition metal complex of a thioketocarbene. Thioketocarbenes, whose ground state is described by the limiting valence-bond structures **1**



$$R-\overset{\overset{|S|}{\|}}{C}-\bar{C}-R \longleftrightarrow R-\overset{\overset{|\bar{S}|^{\ominus}}{|}}{C}=\overset{\oplus}{C}-R$$

1 **2**

and **2**, were first shown to be intermediates in the decomposition of 1,2,3-thiadiazoles[4] and have also been postulated to occur in certain reactions of chelates of 1,2-*cis*-ethylenedithiolates.[3] In the present paper we report the results of more extensive studies on complexes of thioketocarbenes, the synthesis of analogous

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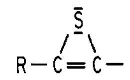
(1) On leave of absence from Max Planck Institut für Kohlenforschung, Division of Radiation Chemistry, Mülheim/Ruhr, Germany.

(2) R. Huisgen, *Angew. Chem.*, 75, 604, 741 (1963), and references cited therein.

(3) G. N. Schrauzer, H. N. Rabinowitz, J. K. Frank, and I. C. Paul, *J. Amer. Chem. Soc.*, 92, 212 (1970).

(4) W. Kirmse and L. Horner, *Justus Liebigs Ann. Chem.*, 614, 4 (1958).

derivatives of selenoketocarbenes, and the attempted stabilization of other 1,3-dipolar species. Since thioketocarbenes could in principle isomerize to thiirenes, **3**, attention was given to the possible synthesis of complexes thereof. CNDO/2 calculations on the hypothetical unsubstituted thioketocarbene and thiirene, respectively, do indeed indicate a greater stability of the thiirene **3** relative to the ring-opened isomer.[5]



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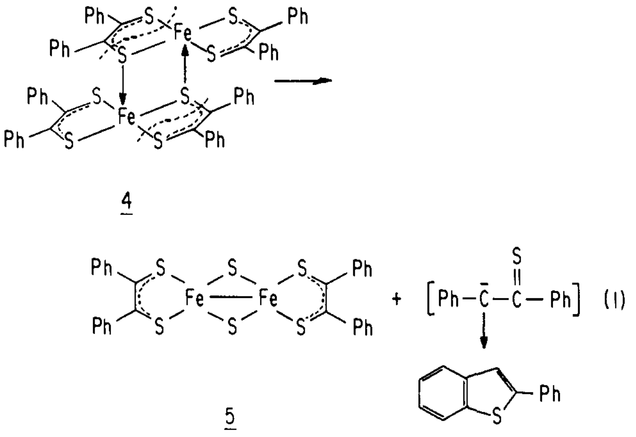
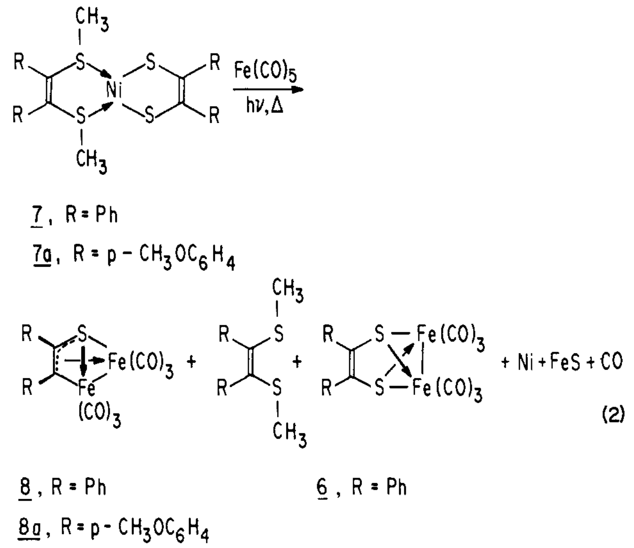
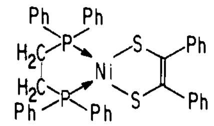
Results

Synthesis of *Trihapto*-1,2-diarylthioketocarbenehexacarbonyldiiron from Complexes of *cis*-1,2-Stilbenedithiol. Metal dithienes,[6] also known as metal dithiolenes,[7] were initially selected as starting materials for the generation of thioketocarbenes. The dimeric iron chelate **4**, for example, on heating decomposes to yield **5** and 2-phenylthionaphthene.[8a] The latter was assumed to result from the rearrangement of diphenylthioketocarbene or the corresponding thiirene as indicated (eq 1).[8b,c] When reaction 1 was conducted in the presence of iron carbonyls, only the formation of μ,μ'-(*cis*-stilbene-α,β-dithiolato)-bis(tricarbonyliron) (**6**) was observed. Complex **6** was also obtained by allowing other neutral phenyl-substituted metal dithienes to react with iron carbonyls.[8] However, the corresponding reaction with 1,4-dialkyl derivatives of planar nickel bis(*cis*-stilbenedithiolate) (**7**) afforded a product shown to be a complex of diphenylthioketocarbene (**8**), together with traces of **6** (eq 2).





Complex **8** was also obtained, although in lower yields and together with **6** as the main product, from **9** and **10**[9] in place of complex **7**.



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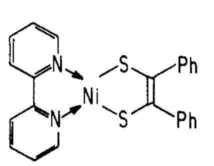

10

Mechanism of Formation of 1,2-Diphenylthioketocarbenehexacarbonyldiiron (8). The reaction of **7** with iron pentacarbonyl was initially observed to produce **8** and $Ni(CO)_4$, the latter decomposing into Ni and CO under the reaction conditions.[3] In the search for possible intermediates in the formation of **8**, the above reaction was studied under milder conditions, *i.e.*, by treating **7** with $Fe_2(CO)_9$ in benzene at room temperature. In this case **8** is not obtained. Instead, $Ni(CO)_4$ (detected by ir analysis) and an iron-containing complex, **11**, of composition $C_{30}H_{26}S_4Fe_2(CO)_6$ are formed. Various reactions of **11** are summarized in Scheme I and will be described in the following.

The brown-red complex **11** on heating and irradiating with excess $Fe(CO)_5$ produces **8** in quantitative yield. In absence of $Fe(CO)_5$, refluxing of **11** in toluene yields Fe, Co, and hygroscopic olive crystals of **12**. The latter complex was also isolated as a dihydrate on recrystallization from water containing CH_3OH–CH_2Cl_2 mixtures. The thermolysis of the dihydrate above 248° produces H_2O, FeS, 2-phenylthionaphthene, and a mixture of *cis*- and *trans*-bismethylthiostilbene. The ^1H nmr and optical absorption spectra of **12** and its dihydrate closely resemble those of **7** and are in agreement with the assumed structures. The irradiation of warm solutions of **12** in the presence of excess $Fe(CO)_5$ first yields complex **11** and on further reaction **8**, as evidenced by ir analysis of samples of the reacting solution. Complex **11** is rather labile and already decomposes on recrystallization from CH_2Cl_2–*n*-pentane to yield a new complex, **13**, of composition $C_{30}H_{26}S_4$-$Fe(CO)_2$. The ir spectrum of **13** exhibits two CO absorptions at 2030 and 1990 cm^{-1}, suggesting the pres-

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(5) F. Mark, F. Olbrich, and O. E. Polansky (Mülheim, Germany), private communication of results to the authors at whose request the calculations were performed.

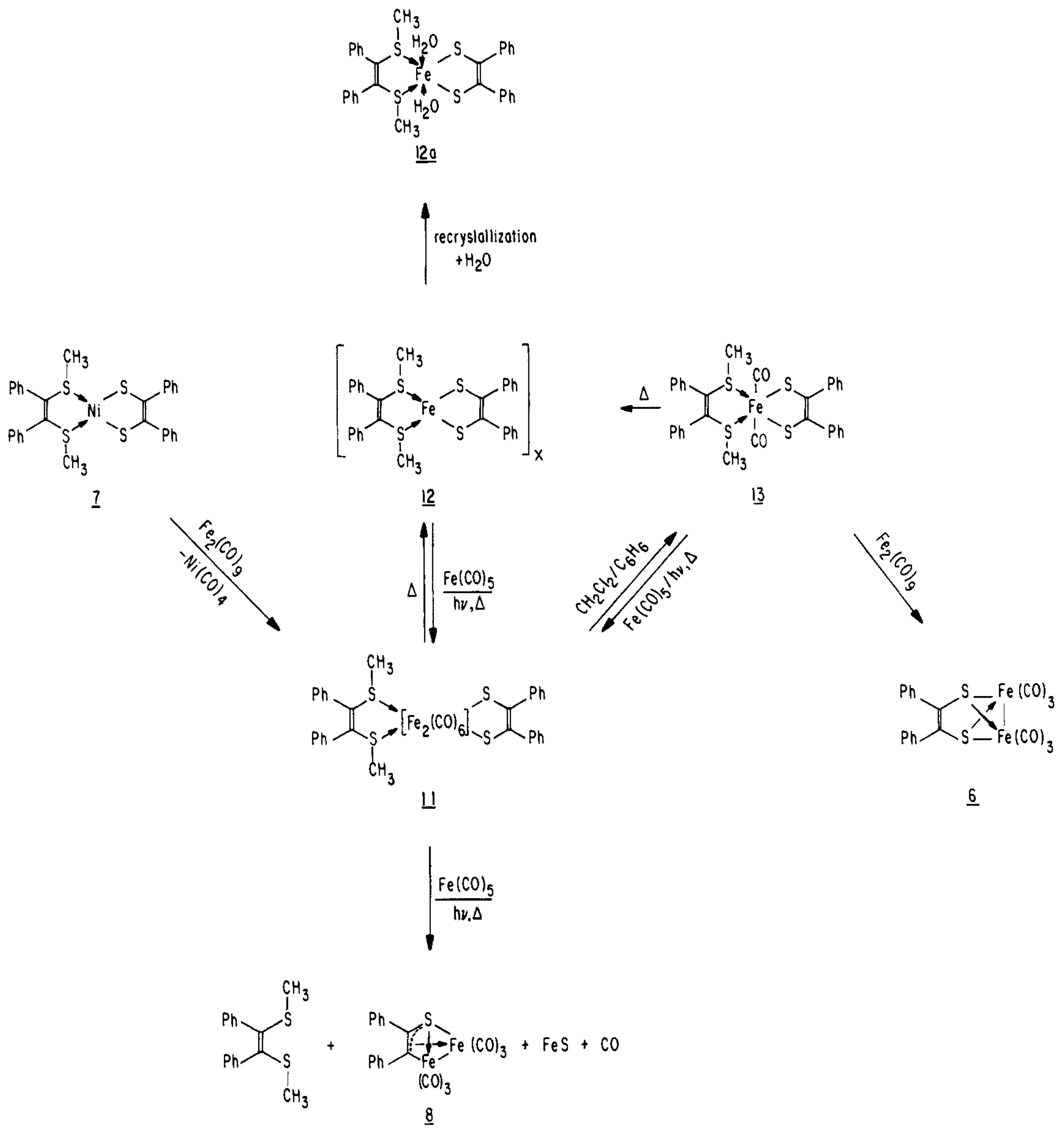
(6) (a) G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 72 (1969); (b) *Advan. Chem. Ser.*, No. 110, 73 (1972); (c) *Transition Metal Chem.*, 4, 299 (1968).

(7) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

(8) (a) G. N. Schrauzer, V. P. Mayweg, W. H. Finck, and W. Heinrich, *J. Amer. Chem. Soc.*, **88**, 4604 (1966). (b) Complex **5** in eq 1 is written as a monomer. Recent work[8c] suggests that it could be dimeric in the solid state. Molecular weight determinations in CH_3CHCl_2 appear consistent with the monomeric formulation, but monomer–dimer equilibria are not excluded. Anionic derivatives of **5** are presumably dimeric both in solution and in the solid state. (c) I. Bernal, B. R. Davis, M. L. Good, and S. Chandra, *J. Coord. Chem.*, **2**, 61 (1972).

(9) G. N. Schrauzer and H. N. Rabinowitz, *J. Amer. Chem. Soc.*, **90**, 4297 (1968).

Scheme I



ence of a *cis*-Fe(CO)$_2$ moiety and the structure proposed in Scheme I. On refluxing and irradiating with excess Fe(CO)$_5$, **13** affords the thioketocarbene complex **8** *via* **11**, while the dithiolato complex **6** is produced on stirring with Fe$_2$(CO)$_9$ at room temperature.

The structure of **11** is as yet unknown; ^{1}H nmr analysis demonstrates the presence of nearly equivalent aromatic and aliphatic protons with relative intensities in accordance with the analytical data. The ir spectrum indicates four resolved absorptions of terminal metal CO groups; bands corresponding to bridged CO groups are absent.

All observations indicate that **11** is an intermediate in the formation of the thioketocarbene complex **8** from Fe(CO)$_5$ and **7** according eq 2. The intermediate appearance of **11** in this reaction was unambiguously demonstrated by ir analysis of the reacting solution. Thus, **11** appears to be the first detectable intermediate. The conversion of the latter to **8** requires a C–S bond cleavage and occurs only at elevated temperatures and in the presence of iron carbonyl fragments as acceptors for the leaving sulfur. Minor changes in the reaction conditions, *i.e.*, lower temperatures, prevent C–S bond scission and give rise to the formation of the dithiolato complex **6** instead of **8**.

Synthesis of Related Complexes. The *p*-methoxy derivative of **8** was synthesized in analogy with eq 2. The generality of this reaction appears to be limited to aryl-substituted derivatives of thioketocarbene. An alternative method of preparing some compounds analogous to **8** is described below.

1,2,3-Thiadiazoles release nitrogen on thermal or photochemical decomposition and are convenient starting materials for the generation of thioketocarbenes or thiirenes, respectively.[10] Complex **8** and several other substituted derivatives have been obtained by decomposing the thiadiazoles in the presence of iron carbonyls (eq 3). Although the yields are low, the synthesis was used to prepare the selenium derivative of **8** from 4,5-diphenyl-1,2,3-selenodiazole and Fe$_2$(CO)$_9$. The complex of *unsubstituted thioketocarbene* (**15**) was also obtained in this fashion. However, the corresponding complex of selenoketocarbene could not be synthesized by this method. Although selenodiazole

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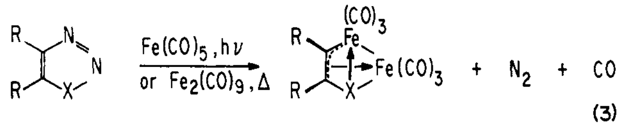
(10) O. P. Strausz, J. Font, E. L. Dedio, P. Kebarle, and H. E. Gunning, *J. Amer. Chem. Soc.*, **89**, 4805 (1967).

Table I. Physical Properties of Isolated Complexes

Complex	Infrared CO stretching frequencies, cm^{-1} [a]	^{1}H nmr signals, ppm[b]	Optical absorptions,[a] nm (log ϵ)
8	2070 (s), 2050 (sh), 2040 (vs), 2010 (s), 1990 (m) 2070 (vs), 2040 (vs), 2020 (vs), 2000 (m), 1980 (s), 1970 (vs)[c]	7.23 (s), 7.33 (s)	460 (3.3), 326 (sh) (3.94), 280 (sh) (4.05)
8a	2070 (s), 2050 (vs), 2000 (s), 1990 (sh)	6.6–7.2 (m), 3.83 (s), 3.8 (s)	460 (3.4), 325 (sh), (4.23), 290 (sh), (4.36)
11	2030 (w), 1990 (w), 1970 (vs), 1920 (vs)	7.0 (s), 2.3 (s)	440 (3.76), 337 (sh) (4.54)
12	None	7.2 (s), 2.43 (s)	700 (3.00), 450 (sh) (3.70), 375 (sh) (4.23), 344 (4.42)
13	2030 (vs), 1990 (m)	7.2 (s), 2.40 (s)	450 (3.15), 335 (sh) (4.18)
15	2060 (s), 2040 (s), 2020 (vs), 1990 (vs)[c]	7.07 (d), 6.2 (d), (J = 3 Hz)	450 (3.46), 335 (sh) (4.43)
16	2060 (vs), 2040 (m), 2020 (vs), 1990 (vs), 1985 (sh)	7.5 (s), 7.2–7.5 (m)	460 (3.34), 330 (sh) (3.93), 280 (sh) (4.09)
17	2040 (vs), 1990 (vs), 1980 (vs), 1975 (sh), 1910 (w)	7.57–7.07 (m), 7.46 (s)	470 (3.45), 320 (sh) (4.04)
18	1990 (vs), 1980 (w), 1950 (s), 1930 (s), 1900 (w)	7.2–6.7 (m), 7.08 (s)	420 (3.68), 328 (sh) (4.13)

[a] $CHCl_3$ solution. [b] $CDCl_3$ solution; TMS as internal standard; s = singlet, d = doublet, m = multiplet. [c] KBr pellet.



(3)

14a R = Ph } X = S
14b R = H }
14c R = Ph } X = Se
14d R = H }

8 R = Ph } X = S
15 R = H }
16 R = Ph, X = Se

reacts with $Fe_2(CO)_9$, the only product isolated was the known diselenononacarbonyltriiron.[11]

Spectroscopic Data. Infrared Spectra. The infrared spectra of the complexes **8**, **8a**, **15**, and **16** in KBr show a similar pattern of absorptions in the frequency region of terminal metal carbonyls. (Signals in the bridged carbonyl region are absent.) The observed multiplicity is consistent with the established asymmetric bonding of the thioketocarbene moiety to the $Fe_2(CO)_6$ unit. The spectrum of **8** in $CHCl_3$ shows only four carbonyl bands (as opposed to six in KBr) and is hardly distinguishable from the spectrum of **6**. No bands are observable which could be assigned to the C–S group with any degree of certainty. Complex **15** exhibits CH absorptions consistent with its structure.

Electronic Spectra. The electronic spectra of complexes **8**, **8a**, **15**, and **16** are virtually identical, exhibiting one resolved band at 460 nm and shoulders at about 325 and 280 nm. The two low-energy absorptions are presumably due to excitation mainly involving the coordinated $Fe_2(CO)_6$ groups, since complex **6** exhibits similar bands at 440 and 340 nm. Complex **19** also shows three bands of similar energy and intensity. A detailed assignment of these transitions is deferred.

^{1}H Nmr Spectra. The ^{1}H nmr spectrum of **15** shows two doublets (J = 3 Hz) and is in accordance with the unsymmetrical structure of the thioketocarbene complex. Analogously, the protons of the diphenylthioketocarbene ligand in complexes **8**, **8a**, **15**, and **16** appear at different chemical shifts. The spectra of **11**–**13** contain only two sharp signals corresponding to the methyl and phenyl protons, indicating the absence of the diphenylthioketocarbene moiety in these complexes. Table I gives the physical properties of all compounds.

Attempted Stabilization of Diphenylketocarbene. In attempts to stabilize diphenylketocarbene by complex formation, benzoylphenyldiazomethane was irradiated in the presence of $Fe(CO)_5$. However, only saltlike, metal–carbonyl-free iron salts were obtained, whose acid hydrolysis yielded diphenylacetic acid as the main product. The rearrangement of the diphenylketocarbene to diphenylketene is obviously the preferred reaction even in the presence of iron carbonyls.

Reactions of 1,2-Diphenylthioketocarbenehexacarbonyldiiron (8). Reactions of the diphenylthioketocarbene complex (**8**) are summarized in Scheme II. The complex is remarkably stable against concentrated acids including concentrated H_2SO_4. Pyrolysis at 180° yielded CO, Fe, some FeS, and, as the main product, tetraphenylthiophene together with small amounts of diphenylacetylene. Attention was given to possible verification of 1,3-cycloadditions of the coordinated thioketocarbene. No reaction occurred on refluxing of **8** in benzene solutions containing diphenylacetylene, diethyl maleate, or maleic anhydride. Reaction with diphenylacetylene takes place in the melt at temperatures above the decomposition point of **8**, affording tetraphenylthiophene and the products listed in Scheme II. With triphenylphosphine, the purple mono and bis adducts of **17** and **18** were isolated. Reaction of **17** and **18** with diphenylacetylene afforded tetraphenylthiophene and hexaphenylbenzene, the latter from a secondary catalytic reaction induced by phosphine–iron carbonyl fragments which are known to be catalysts of alkyne trimerization.[12] Reaction of the bis-*p*-methoxy derivative (**8a**) with diphenylacetylene produced 2,3-bis-*p*-methoxyphenyl-4,5-diphenylthiophene. This demonstrates that the thiophenes are formed by addition of the alkyne to the thioketocarbene moiety. The remaining reactions outlined in Scheme II are straightforward, *i.e.*, the decomposition by alcoholic NaOH and the reduction with $HI-CH_3COOH$, both of which yield bibenzyl as the product of reduction and desulfurization of the diphenylthioketocarbene.

Reactions of Complex 15. The unsubstituted thioketocarbene complex **15** was thermally decomposed and the volatile products were analyzed mass spectrographically. Fragments identified include thiophene, acetylene, as well as the ion $C_2H_2S^+$, presumably derived from thiirene or thioketene. An ion of mass 44, pre-

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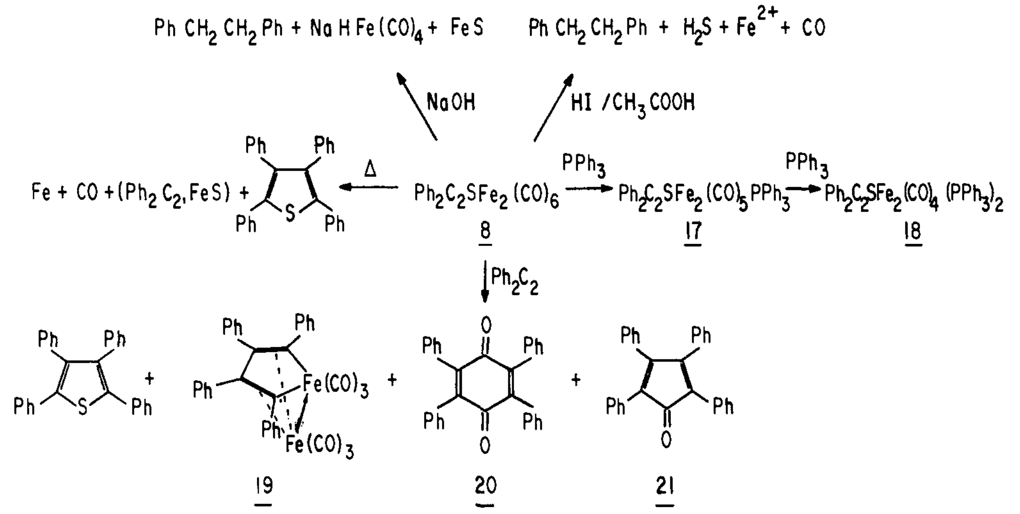
(11) W. Hieber and J. Gruber, *Z. Anorg. Allg. Chem.*, **296**, 91 (1958).

(12) C. Hoogzand and W. Hübel in "Organic Synthesis via Metal Carbonyls," Vol. I, Interscience, New York, N. Y., 1968, p 343.

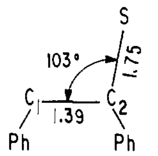
Scheme II



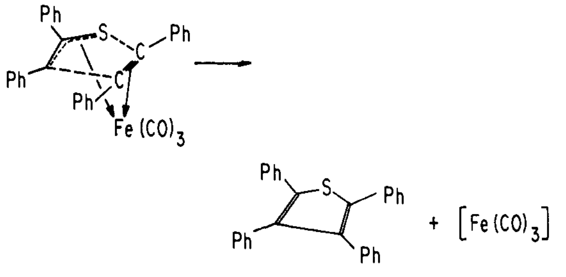
sumably CS$^+$, is also formed. The formation of CS$^+$ could be rationalized by assuming a rearrangement of the initially formed thioketocarbene to thioketene; the latter is known to lose CS on electron impact.[13] When the decomposition of **15** is conducted in an atmosphere of hexafluorobutyne-2, mass spectrographical analysis shows the presence of a peak with the mass 220, corresponding to the formation of 2,3-bis(trifluoromethyl)thiophene *via* 1,3-dipolar addition of thioketocarbene to the butyne.

Discussion

The results of the X-ray structural investigation[3] of **8** indicate bond lengths of the coordinated C–C–S moiety consistent with an approximately equal weight of the canonical forms **1** and **2**. The relatively steep C–C–S angle of 103° may be either due to strain imposed on the ligand or a C_1–S interaction. The two $Fe(CO)_3$ groups are bound asymmetrically; one essentially by a σ bond to C_1, the other *via* π bonds to the C–C–S system. Since the two nonbonding electron pairs on sulfur are bonded symmetrically to both iron atoms, the complexed C–C–S system is coordinatively saturated. The virtual absence of residual chemical reactivity of the thioketocarbene moiety in **8**, and related complexes, thus is consistent with the structural evidence. In all reactions of the complexes, the $Fe(CO)_3$ moieties are removed or modified first. The inertness of the coordinated thioketocarbene toward 1,3-dipolarophiles thus is also not surprising; reaction with diphenylacetylene occurs only above the decomposition temperature of **8**, conceivably according to eq 4.



Whether or not the tetraphenylthiophene is formed by the reaction with the free diphenylthioketocarbene or thiirene or a complexed form of the former appears to depend on the reaction conditions; both reactions seem possible. At a reaction temperature of 130–150° it seems unlikely that the diphenylthioketocarbene is entirely free. Conceivably, tetraphenylthiophene is formed by reaction of a complex of diphenylthioketocarbene and diphenylacetylene with an iron carbonyl fragment, as suggested in eq 4. The iron carbonyl fragments released in the reaction evidently have sufficient stability to undergo secondary reactions with diphenylacetylene, giving rise to complex **19**, small amounts of tetraphenyl-*p*-benzoquinone (**20**), and traces of tetraphenylcyclopentadienone (**21**). Complex **19** as well as complexes of **21** are the main products in the reaction of diphenylacetylene with iron carbonyls.[14,15] The virtual absence of complexes of **21**, as well as the formation of **21** itself, is of interest as it indicates that the nature of products formed is dependent on the composition of the iron carbonyl fragments. The reaction of diphenylacetylene with iron carbonyls normally does not yield **20** directly.[15]



(4)

The formation of tetraphenylthiophene in the thermolysis of **8** suggests that a free or complexed Ph_2C_2S fragment dimerizes to tetraphenyldithiadiene (1,4), which loses sulfur under the reaction conditions to yield tetraphenylthiophene. It is of interest that only traces of diphenylacetylene are formed on thermolysis of **8**, in contrast to the behavior of **6**, which decomposes quantitatively into FeS, CO, and diphenylacetylene.[8] This suggests that the Ph_2C_2S fragment is actually a rather stable species which is not readily desulfurized even in the presence of iron.

The reactions of complex **15** on heating suggest that a free thioketocarbene or thiirine is formed, which undergoes secondary reactions. Judging from the large amount of CS$^+$ in the mass spectrum of **15**, the fragment C_2H_2S appears to rearrange mainly to thioketene, which subsequently loses CS. Desulfurization of C_2H_2S also occurs, as evidenced by the presence of acetylene in the mass spectrum. Thiophene is also

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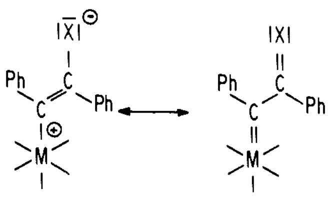
[13] K. P. Zeller, H. Meier, and E. Müller, *Tetrahedron*, **28**, 1353 (1972).

[14] W. Hübel, ref 12, p 286.

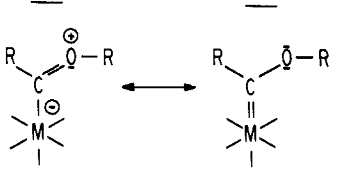
[15] G. N. Schrauzer, *J. Amer. Chem. Soc.*, **81**, 5307 (1959).

formed on thermolysis. As in the thermolysis of **8**, thiophene could result from 1,4-dithiadiene followed by extrusion of sulfur or addition of acetylene to either one of the former. Thiophene has previously been shown to be formed as a product in the reactions of $^1D_2$ sulfur atoms with acetylene, or in the photolysis of 1,2,3-thiadiazoles in the presence of acetylene.[10] The decomposition of **15** in the presence of hexafluorobutyne-2 accordingly afforded detectable amounts of 2,3-bis(trifluoromethyl)thiophene on the basis of mass spectrographic analysis. Mente and Rees have recently shown that a symmetrical intermediate is formed in the thermolysis of 1,2,3-thiadiazole in the presence of $Fe_2(CO)_9$.[16] This intermediate, believed[16] to be a thiirine–iron tricarbonyl complex, has not been isolated since further reaction with the metal carbonyl yields the thioketocarbene complex.

The stabilization of 1,3-dipoles by complex formation with transition metals is presently still restricted to thio- and selenoketocarbenes and to iron carbonyl moieties as the coordinating groups. No stable complex was obtained in our attempts to prepare an iron carbonyl derivative of 1,2-diphenylketocarbene. The ketocarbene moiety is expected to yield a more labile $Fe_2(CO)_6$ complex, if only because of the diminished coordinating power of oxygen relative to sulfur or selenium, and the higher polarity of the carbon–oxygen bond, in comparison to carbon–sulfur and carbon–selenium bonds, respectively. One condition for the existence of stable complexes of reactive 1,3-dipolar species appears to be their ability to form essentially nonpolar σ and π bonds with iron(0). Other metals may share this ability with iron, but could bind thioketocarbenes differently. Group VI metal carbonyls, for example, could in principle form complexes such as **22**, which would formally resemble Fischer's complexes of alkoxycarbenes (**23**). However, the metal–carbon bond in **23** is undoubtedly stabilized by a significant contribution of canonical form **23a**. Contribution of canonical form **22a** induces the opposite polarization, and thus should destabilize the metal–carbon bond. As a consequence, complexes of type **22** are expected to be unstable.

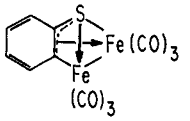


22a 22b



23a 23b

The theoretical possibilities of stabilization of other 1,3-dipolar species may be assessed by considering their degree of electronic unsaturation and estimating their ability to form nonpolar σ and π bonds with metals. The thermodynamic stability of the underlying three-atom skeleton is another important factor which must be taken into account. Disregarding more obvious extensions of our stabilization concept to complexes such as **24**, for example, which are expected to be capable of existence, the outlook for successful complexation of other reactive dipoles,[17] particularly of those which are not octet stabilized, does not appear promising at present, at least not with first-row transition metal derivatives as stabilizing groups. The prospects for synthesis of complexes of 1,3-dipoles with octet stabilization would seem more favorable, although the possibility of side reactions must always be considered. For example, diazoalkanes have previously been shown to react with nickel and iron carbonyls, but in this case the reaction takes a different course, proceeding with extrusion of N_2 and the formation of intermediate complexes of carbenes.[18] Nickel(0) complexes of diazoalkanes of composition $R_2CN_2NiL_2$, where R is phenyl and L is t-C_4H_9NC, have been reported recently.[19] Although no structural proposals have been made, the authors of ref 19 suggest side-on coordination of the $>C{=}N{=}N$ system to the nickel atom. The complexes decompose with regeneration of the diazoalkanes on reaction with oxygen or triphenylphosphine.[19] Conceivably, these compounds fall into the class of complexes of 1,3-dipoles.



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Experimental Section

Ir spectra were recorded on a Beckman IR-33 and uv spectra on a Beckman DK-2 spectrophotometer, respectively. ^1H nmr spectra were obtained on a Varian T-60 instrument, using TMS as internal standard. Mass spectra were measured with a LKB 9000 spectrometer.

Molecular weight determinations and microanalyses were performed by Mikroanalytisches Laboratorium Dornis & Kolbe, Mülheim/Ruhr, Germany. A nitrogen atmosphere was routinely provided for all reactions carried out with metal carbonyl derivatives.

Preparation of 1,2-Diphenylthioketocarbenehexacarbonyldiiron (8). A mixture of 20 g (3.5 mmol) of complex **7**, 160 g (82 mmol) of iron pentacarbonyl, and 200 ml of benzene was refluxed and irradiated with a 150-W tungsten lamp overnight. The filtered red solution was evaporated under reduced pressure; crystallization of the remaining oil from CH_2Cl_2–CH_3OH afforded 13.5 g (80%) of crystalline **8**, mp 125–126°.

Anal. Calcd for $C_{20}H_{10}Fe_2O_6S$: C, 49.04; H, 2.06; Fe, 22.8; O, 19.6; S, 6.56; mol wt, 490. Found: C, 49.24; H, 2.10; Fe, 22.35; O, 19.50; S, 6.60; mol wt, 495 (osmometrically in CH_3-$CHCl_2$).

When the above reaction was conducted with **9** or **10** instead of **7**, **8** was formed in 5–10% yield together with **6** as the main product; the reaction conditions were not optimized in this case.

Reactions of 8. Thermolysis. Complex **8** (0.3 g) was decomposed at 180° (0.01 Torr) in a sublimation apparatus. The sublimate was dissolved in 3 ml of CH_2Cl_2; addition of 3 ml of CH_3OH and subsequent evaporation of CH_2Cl_2 afforded 30 mg of tetraphenylthiophene, mp 184° (mixture melting point with authentic material unchanged), and trace amounts of diphenylacetylene.

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(16) P. G. Mente and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 418 (1972).

(17) For a recent compilation and discussion of various 1,3-dipolar species, see T. L. Gilchrist and R. C. Storr, "Organic Reactions and Orbital Symmetry," Cambridge University Press, London, 1972, Chapter 5.3.

(18) C. Rüchardt and G. N. Schrauzer, *Chem. Ber.*, **93**, 1840 (1960).

(19) S. Otsuka, A. Nakamura, T. Koyama, and Y. Tatsuno, *J. Chem. Soc., Chem. Commun.*, 1105 (1972).

The nonvolatile ferromagnetic black products consist of Fe and FeS. (FeS was ascertained by dissolving the residues in dilute HCl and detection of H_2S.)

Alkaline Decomposition. Complex **8** (1 g) was heated to 100° in 20 ml of 50% NaOH for 45 min. After cooling, the reaction mixture was carefully acidified with dilute HCl, and the organic products were extracted with CH_2Cl_2. The solvent was evaporated and the remaining solid sublimed, producing 100 mg of bibenzyl, mp 50°, identified by comparison of the ir spectrum with that of an authentic sample.

Reduction with Hydrogen Iodide–Glacial Acetic Acid. Complex **8** (1 g) was heated with a mixture of 2 ml of 70% hydrogen iodide and 5 ml of glacial acetic acid in a closed vial to 110°. When no more gas was evolved, water was added and the reaction was worked up as described above, yielding 120 mg of bibenzyl (mp 50°, mixture melting point with authentic bibenzyl unchanged).

Reaction with Triphenylphosphine (PPh_3). Complex **8** (4 g, 8.16 mmol) and 2.2 g (8.16 mmol) of PPh_3 were heated without solvent in a closed vial for 3 hr at 160°. After cooling the reaction mixture was dissolved in 50 ml of CH_2Cl_2 and filtered. Subsequent addition of 200 ml of petroleum ether afforded 1 g of **18** and 3.2 g (54%) of **17**, which was recrystallized from CH_2Cl_2–petroleum ether; mp 185–187°.

Anal. Calcd for $C_{37}H_{25}Fe_2O_5PS$: C, 61.32; H, 3.45; Fe, 15.47; P, 4.28; S, 4.42; mol wt, 724. Found: C, 61.4; H, 3.8; Fe, 15.7; P, 4.6; S, 4.79; mol wt, 664 (osmometrically in benzene).

When the reaction was performed with a fivefold excess of PPh_3, **18** was obtained as the main product (70%), mp 225–226°.

Anal. Calcd for $C_{54}H_{40}Fe_2O_4P_2S$: C, 67.64; H, 4.17; Fe, 11.69; P, 6.47; S, 3.34; mol wt, 958. Found: C, 67.03; H, 4.04; Fe, 12.7; P, 7.0; S, 3.7; mol wt, 855 (osmometrically in benzene).

Reaction with Diphenylacetylene. Complex **8** (2.3 g, 4.7 mmol) and 8.4 g (47 mmol) of diphenylacetylene were heated in a closed vial for 1 hr at 150°. The cooled reaction mixture was dissolved in 80 ml of CH_2Cl_2 and filtered from small amounts of FeS. Addition of 25 ml of CH_3OH followed by partial removal of CH_2Cl_2 afforded 1.5 g (83%) tetraphenylthiophene, identified by its ir spectrum. Partial evaporation of solvent from the filtrate yielded 1.3 g (43%) of orange crystals, mp 173–175° dec, shown to be complex **19** by comparison of ir and uv spectra with the reported spectra,[15] and 100 mg of pale yellow crystals of **20** (tetraphenyl-*p*-benzoquinone, mp 318–320°, lit. mp 321°, ir spectrum was identical with authentic sample). From the filtrates was finally obtained 130 mg of violet crystals, mp 220–222° (CH_2Cl_2–CH_3OH), consisting of **21** (tetraphenylcyclopentadienone). When the above reaction was performed with **8a** instead of **8**, it afforded 2,3-bis(*p*-methoxyphenyl)-4,5-diphenylthiophene, mp 168–170°, ^1H nmr ($CDCl_3$) (ppm) 3.8 (s, 6) and 6.8–7.5 (multiplet, 18). When the above reaction was performed with **17** or **18** instead of **8**, the only products obtained are tetraphenylthiophene and hexaphenylbenzene (mp 450°, mixture melting point with authentic sample unchanged).

Preparation of 1,2-Bis(*p*-methoxyphenyl)thioketocarbenehexacarbonyldiiron (8a). The complex was prepared analogously to **8** in 90% yield, mp 131–132°.

Anal. Calcd for $C_{22}H_{14}Fe_2O_8S$: C, 48.0; H, 2.55; Fe, 20.4; S, 5.82; mol wt, 550. Found: C, 48.5; H, 2.8; Fe, 20.1; S, 5.70; mol wt, 557 (osmometrically in benzene).

Preparation of 11. Complex **7** (20 g, 35 mmol) and 26 g (70 mmol) of $Fe_2(CO)_9$ were stirred overnight in 150 ml of benzene. The red solution was filtered and evaporated at 25° (0.01 Torr). The oily residue was crystallized twice from ether–*n*-pentane, affording 11 g (40%) of **11**, mp 158–160° dec.

Anal. Calcd for $C_{36}H_{26}Fe_2O_6S_4$: C, 54.5; H, 3.28; Fe, 14.10; S, 16.15; mol wt, 794. Found: C, 54.35; H, 3.45; Fe, 13.93; S, 16.22; mol wt, 783 (osmometrically in benzene).

Reactions of 11. Complex **11** (0.3 g, 0.378 mmol) and 10 g (51 mmol) of iron pentacarbonyl were refluxed and irradiated with a tungsten 150-W lamp overnight in 50 ml of benzene. Work-up as described in the preparation of **8** afforded 180 mg (97%) of crystalline **8**, mp 125–126°.

Complex **11** (3 g, 3.78 mmol) was refluxed in 150 ml of toluene for 15 hr; the solution was filtered and addition of 100 ml of methanol produced 2 g (90%) of crude **12**. Recrystallization from CH_2Cl_2–CH_3OH to which a drop of aqueous HCl was added afforded olive crystals of a dihydrate of **12**, mp 248° dec (**12a**).

Anal. Calcd for $C_{30}H_{26}FeS_4 \cdot 2H_2O$: C, 59.3; H, 4.95; Fe, 9.23; S, 21.2; mol wt, 606. Found: C, 59.3; H, 4.2 Fe, 9.6; S, 19.2; mol wt, 616 (osmometrically in benzene).

The presence of H_2O was ascertained by ir analysis of the sample in CH_2Cl_2 solution and by direct detection among the products of thermolysis above 248°. The recrystallization of crude **12** from *anhydrous* CH_2Cl_2–CH_3OH mixtures afforded a nearly anhydrous product (hygroscopic, olive crystals, mp 275° dec). *Anal.* Calcd for $C_{30}H_{26}FeS_4$: C, 63.2; H, 4.6; Fe, 9.8. Found: C, 62.4; H, 4.6; Fe, 10.3.

Attempts to recrystallize **11** from CH_2Cl_2–C_6H_6 by addition of *n*-pentane led to formation of a new product; the latter was extracted with benzene. Evaporation of this solution produced a red oil which crystallized from *n*-pentane, affording **13**, mp 125–126°.

Anal. Calcd for $C_{32}H_{26}FeS_4O_2$: C, 61.30; H, 4.15; Fe, 8.93; S, 20.45; O, 5.12; mol wt, 626. Found; C, 61.38; H, 4.05; Fe, 9.0; S, 20.42; O, 5.20; mol wt, 622 (osmometrically in benzene).

Reaction of 12 and 13 with Iron Pentacarbonyls. Complex **12** (in the form of the dihydrate) or **13** (0.3 g, 0.526 mmol) and 4 g (20 mmol) of iron pentacarbonyl were refluxed and irradiated in 50 ml of benzene with a tungsten 150-W lamp for 5 hr. Work-up as described in the preparation of **8** afforded 0.1 g (40%) of complex **8**.

When the above reaction was conducted with $Fe_2(CO)_9$ at room temperature instead of iron pentacarbonyl, there was produced complex **6** instead of **8**.

Ir Spectroscopic Experiments. In the preparation of **8** from **7** or **12** and iron pentacarbonyl, as described above, aliquots of 0.2 ml of the reaction mixture were withdrawn at various intervals. The solvent and excessive $Fe(CO)_5$ were removed under reduced pressure and the ir spectrum was recorded in the range between 2200 and 1800 cm^{-1} in chloroform. At short reaction times the spectrum shows bands corresponding to **8** (2070, 2040, and 2010 cm^{-1}) and to **11** (1970 and 1920 cm^{-1}); the absorptions of the latter disappear gradually at longer reaction times concomitant with a steady increase of the bands of complex **8**.

Preparation of Thioketocarbenehexacarbonyldiiron (15). 1,2,3-Thiadiazole[20] (4 g, 46.5 mmol) and 100 g (0.5 mol) of $Fe(CO)_5$ were refluxed and irradiated in 100 ml of benzene with a tungsten 150-W lamp for 6 hr. The solution was filtered and evaporated at 20° (0.01 Torr), and the residue dissolved in 50 ml of CH_2Cl_2. Addition of CH_3OH afforded a red oil. Water was added and the complex was extracted into petroleum ether. Drying over $MgSO_4$ and removing the solvent at 0° (0.01 Torr) yielded 2.4 g (15%) of **15**, mp <20°, 90–95° dec.

Anal. Calcd for $C_8H_2Fe_2O_6S$: C, 28.4; H, 0.5. Found: C, 29.12; H, 0.62.

Thermolysis of 15. Complex **15** (10 mg) was heated 5 min to 150° and the volatile products were analyzed mass spectrographically. The spectrum exhibits intense peaks at the mass numbers 84 (thiophene), 58 (C_2H_2S), 44 (CS), and 26 (C_2H_2).

Reaction of 15 with Hexafluorobutyne-2. Complex **15** (6.2 mg) was heated in an atmosphere of hexafluorobutyne-2 for 1 hr at 150°. The mass spectrum of the gas phase contained, *inter alia*, an intense peak at 220, corresponding to 2,3-bis(trifluoromethyl)thiophene.

Preparation of 1,2-Diphenylselenoketocarbenehexacarbonyldiiron (16). 4,5-Diphenylselenodiazole[21] (1.5 g, 5.3 mmol) and 5 g (13.7 mmol) of $Fe_2(CO)_9$ were refluxed in 80 ml of benzene for 12 hr. The reaction was worked up as described in the preparation of **8**, affording 0.6 g (21%) of red crystalline **16**, mp 126–129°.

Anal. Calcd for $C_{20}H_{10}Fe_2O_6Se$: C, 44.7; H, 1.86; Fe, 20.86; Se, 14.7; mol wt, 537. Found: C, 44.0; H, 1.90; Fe, 21.2; Se, 15.2; mol wt, 522 (osmometrically in benzene).

8 was prepared analogously from 4,5-diphenyl-1,2,3-thiadiazole and $Fe_2(CO)_9$. Attempts to prepare selenoketocarbenehexacarbonyldiiron by the reaction of 1,2,3-selenodiazole and $Fe_2(CO)_9$ at room temperature have been unsuccessful. Although the reaction occurred, the only product formed was the known diselenononacarbonyltriiron.[11]

Acknowledgments. This work was supported by Grant GP 28485 X of the National Science Foundation. One of us (H. K.) is indebted to the Max Kade Foundation for a postdoctoral fellowship. We also thank Dr. Paul Doemeny for the mass spectrographic analyses. Credit to NSF Grant GT 18245 for use of the mass spectrograph is also given.

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