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α,β-Unsaturated Thioamide and Thioester Iron Tricarbonyls: Synthesis, Characterization, and Novel Cycloaddition Reactions with Alkynes

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α,β-Unsaturated thioamides and thioesters react with iron pentacarbonyl or diiron enneacarbonyl to form iron tricarbonyl complexes, characterized on the basis of analytical and spectral data, as well as X-ray structure determinations in two cases. These complexes undergo ligand substitution reactions with triphenylphosphine and a novel cyclization reaction with alkynes affording iron tricarbonyl complexes of cyclopentenone thioamides. An X-ray analysis of one such complex reveals that the two functionalities, bonded to the $Fe(CO)_3$ moiety, are not conjugated to each other.

α,β-Unsaturated heterodienes have been utilized as ligands in complexation to a number of transition metals. The most thoroughly investigated group of complexes are those of α,β-unsaturated ketones, with the focus being on iron tricarbonyl complexes of these ligands.[1] The ligand in such complexes is readily displaced by dienes, thus allowing exchange to occur under mild conditions. In this manner, benzylideneacetone iron tricarbonyl has been used for the preparation of polyolefin–iron tricarbonyl and other reactive or thermally sensitive complexes.[2-4] Nucleophilic addition can produce 1,4-diketones,[5] while electrophilic addition occurs at the heteroatom.[6] Although tetracarbonyl complexes of α,β-unsaturated esters and amides are known,[7,8] their $Fe(CO)_3$ analogues, to our knowledge, have not been described in the literature.

α,β-Unsaturated imines also react with iron carbonyls to form azadiene–iron tricarbonyl complexes.[8] The latter can be used to synthesize pyrroles amongst other compounds.[9]

Ring opening of thietes by diiron enneacarbonyl results in the formation of α,β-unsaturated thioaldehyde and thioketone complexes.[10] Cobalt complexes of these ligands have also been prepared, and both types of complexes are reactive toward electrophiles including trialkyloxonium tetrafluoroborates.[11-13]

To our knowledge, only one complex of an α,β-unsaturated thioamide has been prepared by treatment of lithium tetrachloropalladate with thioamides.[14] We have been interested, for some time, in the organometallic chemistry of the thiocarbonyl group. For example, dithioesters and thioketones react with complexes containing a metal–metal triple bond to give novel compounds having a symmetrically bridging thioacyl function and a bridging thioalkyl group.[15,16] Also, *N,N*-dimethylthioacetamide and *N,N*-dimethylthiobenzamide react with diiron enneacarbonyl to mainly give complexes of the type $LFe(CO)_4$ and $L_2Fe_2(CO)_6$ (L = thioamide), the latter coordinated to iron by both nitrogen and sulfur atoms.[17] This paper describes the synthesis and characterization of $Fe(CO)_3$ complexes of α,β-unsaturated thioamides and several thioesters. In addition, the thioamide complexes undergo a novel cyclization reaction with alkynes.

Results and Discussion

(a) Ligands. A series of thioamides (1′–9′) containing alkyl or aryl substituents attached to one or both unsaturated carbon atoms or to the nitrogen atom were prepared by treatment of the corresponding amides with Lawesson's reagent [2,4-bis(*p*-methoxyphenyl)-1,3-dithiaphosphetane 2,4-disulfide].[18] The amides were, in turn, synthesized from the acid chlorides,[19] and if the acid halide was not commercially available, it was obtained from the acid by using thionyl chloride. Several thioesters (10′, 11′), which were used in this study, were obtained by reaction of the appropriate ester with Lawesson's reagent.

The properties of the ligands were consistent with literature data for identical or analogous compounds. For instance, the parent ion was observed as an intense signal in the mass spectra of all the ligands. In addition, the proton nuclear magnetic resonance (NMR) spectra for all thioamides displayed nonequivalence, geometrically and magnetically, of the nitrogen substituents.[20] Assignment of signals in the ^{13}C NMR spectra of these compounds was

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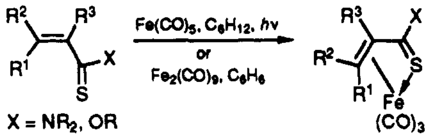
Table I. Pertinent Carbon and Proton NMR Data for 1–11 and 1′–11′[a]

	δ_C, ppm				δ_H, ppm		
compd	C=O	C=S	β-C	γ-C	$C_\beta H$	$C_\gamma H$	$^3J_{HH}$, Hz
1 (1′)	210.50	161.69 (193.65)	63.96 (124.85)	52.42 (143.82)	5.04 (7.07)	3.47 (7.85)	7.7 (15.3)
2 (2′)	210.00	141.20 (197.62)	(123.59)	66.18 (141.07)		5.17 (6.72)	
3 (3′)	209.43	155.85 (194.79)	63.30 (126.52)	60.16 (144.03)	5.11 (6.72)	3.63 (7.91)	8.2 (15.0)
4 (4′)	210.39	159.69 (193.37)	59.85 (128.40)	58.78 (141.97)	4.10 (6.38)	2.53 (6.92)	7.3 (14.6)
5 (5′)	211.40	143.01 (200.76)	92.52 (137.00)	46.22 (126.49)		1.13 (5.01)	
6 (6′)		(195.73)	49.55 (125.01)	54.45 (134.66)	2.63 (5.79)		
7 (7′)	209.98	152.95 (195.58)	67.59 (129.86)	60.85 (143.34)	4.41 (5.85)	2.28 (7.10)	7.8 (15.0)
8 (8′)	208.20	148.96 (190.82)	92.85 (145.94)	51.45 (115.00)		1.62, 1.93 (4.78, 4.82)	
9 (9′)	210.77	148.07 (201.45)	67.30 (146.79)	54.07 (111.09)		2.21, 2.28 (4.81, 4.86)	
10 (10′)	207.87	155.00 (209.87)	71.53 (113.80)	63.30 (140.09)	6.18 (7.02)	2.70 (7.69)	8.8 (15.7)
11 (11′)	209.00	155.52 (210.68)	77.79 (133.63)	59.84 (140.46)	5.16 (6.38)	1.45 (6.96)	8.3 (15.6)

[a] ^1H, ^{13}C assignments made with the aid of DEPT and HETCOR techniques.

made on the basis of distortionless enhancement by polarization transfer (DEPT).

(b) Synthesis and Spectral Properties of Iron Tricarbonyl Complexes of 1′–11′. All of the iron tricarbonyl complexes were prepared by reaction of the ligand with diiron enneacarbonyl in benzene at 25–40 °C or by irradiation of a cyclohexane solution of the mixture of ligand and iron pentacarbonyl. The photolysis procedure often gave higher yields (e.g., 5, 6), and product isolation was more facile. On a qualitative basis, the stability of the complexes in solution decreased in the order aliphatic hydrocarbons > aromatic hydrocarbons > halocarbons. Complexes 5, 6, and 11 have limited thermal stability above 0 °C and gave unacceptable elemental analyses (spectral data were consistent with the assigned structures) while satisfactory analytical data were obtained for all of the other complexes (see Experimental Section).

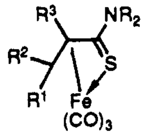


1–11

1: $R^1 = R^3 = H, R^2 = Ph, X = NEt_2$
2: $R^1 = H, R^2 = R^3 = Ph, X = NEt_2$
3: $R^1 = R^3 = H, R^2 = Ph, X = N(Ph)CH_2CH{=}CH_2$
4: $R^1 = R^3 = H, R^2 = Me, X = NEt_2$
5: $R^1 = H, R^2 = Et, R^3 = Me, X = NEt_2$
6: $R^1 = R^2 = CH_3, R^3 = H, X = NEt_2$
7: $R^1 = R^3 = H, R^2 = Me, X = N(Ph)Me$
8: $R^1 = R^2 = H, R^3 = CH_3, X = N(Ph)Me$
9: $R^1 = R^2 = H, R^3 = CH_3, X = NEt_2$
10: $R^1 = R^3 = H, R^2 = Ph, X = OEt$
11: $R^1 = R^3 = H, R^2 = CH_3, X = OEt$

The infrared spectra ($CHCl_3$ solution) for most of the complexes gave two intense terminal metal carbonyl bands, a sharp A′(1) absorption in the region 2020–2060 cm^{-1} and a broad overlapping A′(2) and A″ band in the 1950–1995-cm^{-1} region. The latter could be distinguished by obtaining the spectrum in cyclohexane.

The ^1H NMR spectra of the thioamide complexes containing diethylamino units displayed ABX_3 patterns for each of the *N*-ethyl groups, as was the case for ligands 2′ and 5′. The latter, unlike the other thioamides, have a β-methyl or β-phenyl substituent. In the complexes, π-olefin coordination can also be depicted as in structure 12.



12

This structure may also be said to have β-substitution if one considers the Fe–C bond. Coordination of the iron disrupts the planarity of the ligand thereby creating a different environment for each of the methylene protons. This effect was also observed for the thioester complexes 10 and 11, which gave an ABX_3 pattern for the ethyl protons in contrast to ligands 10′ and 11′ where the ethyl protons appeared as A_2X_3.

As anticipated, a significant upfield shift of the olefin protons of the ligands occurred on complexation (Table I). The γ-CH proton experiences the largest chemical change in that the signal moves upfield by as much as 5.51 ppm (11) on complexation, with a relatively minor change observed in the case of the β-olefin proton. It is conceivable that the large change observed for the γ-olefin CH proton is due to its orientation with respect to the metal center, which shields this proton more effectively than the β-olefin CH proton. Thus one can propose that an *E* geometry about the double bond of the organic ligand is maintained on complexation to minimize steric interactions. The upfield shift of the γ-olefin CH proton on complexation for 2 was appreciably less than that for the other complexes, and an X-ray crystal structure determination (see below) was made to confirm that the structure of 2 was analogous to those of the other complexes (e.g., 1) described herein.

Coupling between β- and γ-unsaturated protons of the ligands also changes upon complex formation. In the free ligand, the coupling constant is usually 14–15 Hz, while it is 7–8 Hz for the $Fe(CO)_3$ complexes, and is probably due to the decrease in π-character on the carbon–carbon double bond on coordination to the metal. The β- and γ-olefin carbons approach sp^3 character, resulting in coupling constants that are typical of a three-bond coupling value to neighboring protons on sp^3 carbons.[21]

The olefin carbons of 1′–11′ experienced significant upfield shifts (as high as 84 ppm) on complexation to $Fe(CO)_3$, with the magnitude of the shift usually being greater for the γ than for the β-olefin carbon. A less pronounced change occurred for the thiocarbonyl carbon on complexation. The metal carbonyl carbons usually give a single broad absorption in the region 208–213 ppm. A temperature-dependent ^{13}C NMR study of 4 (Figure 1) indicates that the coalescence temperature is approximately −13 °C. At −60 °C, three distinct signals appeared at δ 206.2, 213.1, and 213.7 ppm. Rewarming the solution to −40 °C gave broadening, but no movement of the signals was observed. At −18 °C some shift occurred, and at −10 °C a single broad absorption was found. Note that the carbons of the two ethyl groups of 4 gave distinct signals at −60 °C, while coalescence of the methyl carbons occurred

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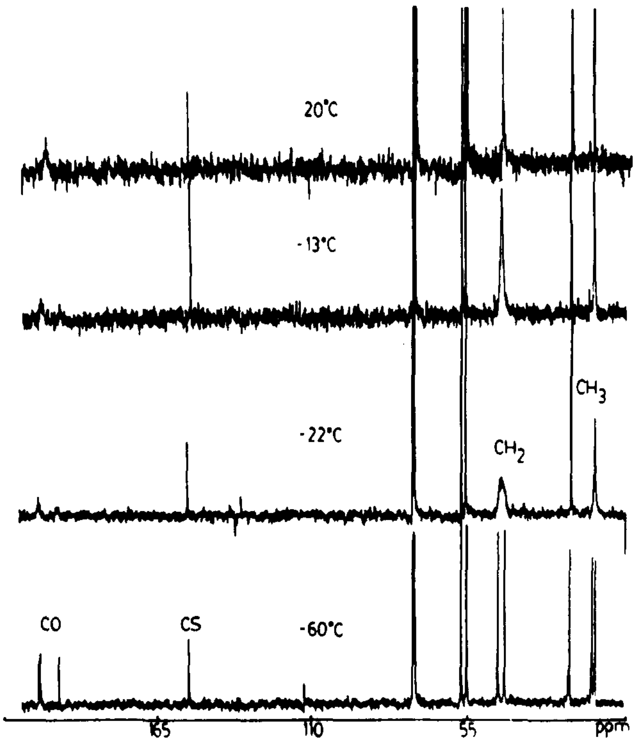

Figure 1. ^{13}C NMR temperature profile of 4.

at −22 °C and a single broad signal appeared for the methylene carbons.

(c) Crystal Structure Determinations. X-ray analyses of several α,β-unsaturated carbonyl[22,23] and iminoiron[22] carbonyl complexes indicate that the four atoms of the π-system lie in the same plane and that the lone pair of the heteroatom does not participate in bonding to the metal. In addition, the structure of (triphenylphosphine)(thioacrolein)iron dicarbonyl suggests planarity of the π-system. However, if one assumes that the metal donates two electrons to the sulfur atom, HMO calculations on dinegative thioacrolein predict bond orders (C_1–S, 1.09; C_1–C_2, 1.72; C_2–C_3, 1.68) that are qualitatively in accord with approximate bond orders derived from the bond distances (C_1–S_1, 1.1; C_1–C_2, 2.0; C_2–C_3, 1.7). This essentially predicts a full negative charge on sulfur and a second negative charge distributed by resonance between the α- and γ-carbons.[10]

A crystal structure of 1 was obtained in order to determine the nature of bonding of the organic ligand to iron. As noted above, an X-ray analysis of 2 was necessitated as a consequence of the unusual NMR spectrum observed for this complex.

In contrast to $Fe(CO)_3$ complexes of α,β-unsaturated ketones where the ligand is planar, the structures of 1 and 2 (Figures 2 and 3) reveal significant distortion of the sulfur atom from the plane formed by the three carbons, and there appears to be direct sulfur–iron bonding (pertinent crystal data information, bond distances and angles, and atomic parameters for 1 and 2 are given in Tables II–VI). There is a plane passing through C(1), C(2), and C(3) of both complexes, and the location of the sulfur atom deviates from the plane by 26.3 and 44.4° in 1 and 2, respectively. The perpendicular distance from the plane to the iron atom is 1.972 Å in 1 and 1.912 Å in 2. The bond lengths for C(1)–C(2) and C(2)–C(3) in both 1 and 2 are similar and suggest little localization of single and double C–C bonds in either complex.

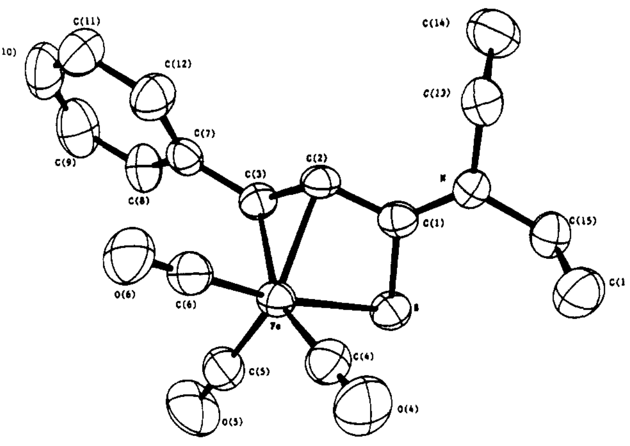

Figure 2. View of 1 showing the atom-numbering scheme.

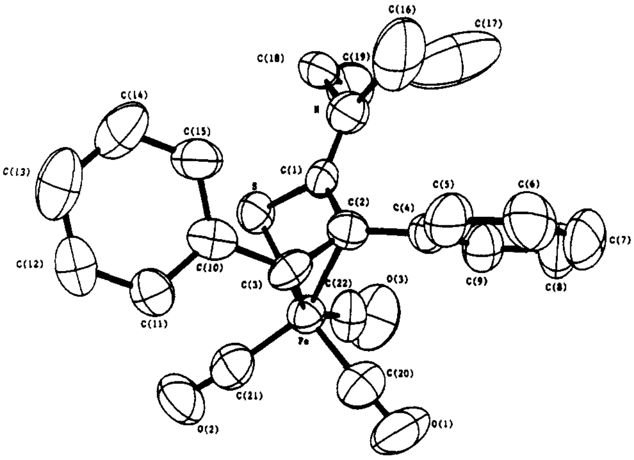

Figure 3. View of 2 showing the atom-numbering scheme.

The distance from C(3) to the ipso carbon of the phenyl substituent [C(3)–C(7)] of 1 is 1.416 Å, which is slightly less than that of a normal C–C bond length and is the same value as that found for the corresponding bond in (triphenylphosphine)(η^4-cinnamaldehyde)iron dicarbonyl.[23] The value of the endocyclic C(8)–C(7)–C(12) angle of 116.7° in 1 is smaller than the anticipated value of 120°. Such deviations of bond angle and distance from the norm indicates a certain degree of conjugation between the π-system of the heterodiene and the phenyl group. The same characteristics were found for 2.

The carbon–nitrogen bond distance, C(1)—N, is shorter than the uncomplexed C–N bond length (1.47 Å),[24] and the nitrogen deviates from the plane formed by C(1)—C(2)—C(3) (1, 19.8°; 2, 53.8°). The carbon–sulfur bond lengths C(1)—S in 1 and 2 are 1.732 and 1.705 Å, respectively, and are certainly longer than the typical C=S bond lengths of 1.61–1.62 Å.[25] Bond lengthening would be expected for π-coordination of the carbon–sulfur double bond to iron, and although there is significant deviation of sulfur from the plane formed by C(1)—C(2)—C(3), favoring lone pair donation from the heteroatom, the possibility of π-coordination cannot be ruled out. The iron–sulfur bond lengths in 1 and 2 are 2.353 and 2.316 Å, respectively. In contrast, the iron–olefin carbon bond lengths in 2 are longer than those of 1, implying stronger Fe—S interaction and less π-back-bonding to the olefin in 2 than in 1. This is, perhaps, surprising, since a shorter

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Table II. Crystal Data Collection and Refinement Information for 1, 2, and 14[a]

	1	2	14
formula	$FeC_{16}H_{17}NO_3S$	$FeC_{22}H_{21}NO_3S$	$FeC_{21}H_{19}NO_8S$
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$P2_12_12_1$	$P2_1/n$
a, Å	13.620 (3)	8.913 (11)	12.991 (4)
b, Å	7.660 (16)	12.260 (16)	12.921 (14)
c, Å	15.979 (4)	19.601 (17)	14.636 (3)
β, deg	96.296 (2)	90	111.401 (8)
V, Å^3	1657.0	2141.7	2287.4
fw	359.22	435.32	501.29
d(calcd), g cm^3	1.440	1.350	1.456
cryst size, mm	0.20 × 0.30 × 0.40	0.44 × 0.14 × 0.14	0.30 × 0.20 × 0.20
total no. of reflns	5157	6131	3292
no. of unique reflns	2140	2775	2967
no. of obsd reflns[b]	1580	1930	1714
no. of variables	267	253	340
final R_F[c]	0.028[d]	0.048[d]	0.045[d]
final R_{wF}[e]	0.029[d]	0.051[d]	0.024[d]
final GOF[f]	0.29[d]	0.35[d]	1.68[d]

[a] Features common to all X-ray structure determinations include use of an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation (graphite monochromator); λ of radiation = 0.7093 Å; scan mode ω–2θ (coupled); ω scan speed of 4°/min; 2θ range of 0–45°; $Z = 4$. [b] Reflections with $I > 2.5[(\sigma(I)]$. [c] $R_F = \sum||F_o| - |F_c||/F_o|$. [d] Observed reflections only. [e] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum F_o^2]^{1/2}$. [f] $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(\text{no. of obs} - \text{no. of vars})]^{1/2}$.

Table III. Atomic Parameters *x*, *y*, *z* and B_{iso} for the Non-Hydrogen Atoms of 1[a]

	x	*y*	*z*	B_{iso}, Å^2
Fe	0.44565 (4)	0.28861 (8)	0.18205 (3)	3.071 (24)
S	0.29487 (8)	0.32433 (15)	0.23922 (6)	3.74 (5)
N	0.20813 (22)	0.4349 (4)	0.08915 (19)	3.35 (14)
C(1)	0.2883 (3)	0.4367 (5)	0.14473 (23)	3.08 (17)
C(2)	0.3806 (3)	0.5134 (5)	0.1301 (3)	3.10 (18)
C(3)	0.4520 (3)	0.5592 (5)	0.19845 (24)	3.19 (19)
C(4)	0.3998 (3)	0.0871 (6)	0.1347 (3)	4.28 (22)
O(4)	0.3722 (3)	−0.0414 (5)	0.10522 (24)	6.39 (20)
C(5)	0.5125 (3)	0.2331 (6)	0.2812 (3)	4.54 (21)
O(5)	0.5530 (3)	0.2024 (6)	0.34566 (21)	7.42 (21)
C(6)	0.5477 (3)	0.2798 (6)	0.1232 (3)	3.99 (19)
O(6)	0.61397 (23)	0.2724 (4)	0.08481 (21)	5.68 (17)
C(7)	0.5400 (3)	0.6638 (5)	0.18843 (24)	3.28 (17)
C(8)	0.5929 (3)	0.7370 (7)	0.2588 (3)	4.75 (23)
C(9)	0.6751 (4)	0.8391 (8)	0.2522 (4)	6.2 (3)
C(10)	0.7071 (4)	0.8733 (7)	0.1757 (4)	6.0 (3)
C(11)	0.6556 (4)	0.8022 (7)	0.1049 (4)	5.4 (3)
C(12)	0.5738 (3)	0.6992 (6)	0.1106 (3)	4.34 (21)
C(13)	0.2036 (3)	0.5279 (6)	0.0081 (3)	3.89 (20)
C(14)	0.1713 (4)	0.7118 (7)	0.0153 (4)	5.4 (3)
C(15)	0.1177 (3)	0.3414 (6)	0.1048 (3)	4.20 (22)
C(16)	0.1144 (4)	0.1592 (7)	0.0695 (4)	4.9 (3)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) of 1

Bond Distances			
Fe–S	2.3534 (2)	C(9)–C(10)	1.369 (10)
Fe–C(2)	2.068 (4)	C(9)–H(9)	0.94 (5)
Fe–C(3)	2.090 (4)	C(10)–C(11)	1.376 (9)
Fe–C(4)	1.800 (5)	C(10)–H(10)	1.00 (5)
Fe–C(5)	1.789 (5)	C(11)–C(12)	1.376 (7)
Fe–C(6)	1.762 (4)	C(11)–H(11)	0.92 (5)
S–C(1)	1.732 (4)	C(12)–H(12)	0.93 (4)
N–C(1)	1.330 (5)	C(13)–C(14)	1.484 (7)
N–C(13)	1.473 (5)	C(13)–H(13A)	0.93 (4)
N–C(15)	1.469 (5)	C(13)–H(13B)	1.01 (4)
C(1)–C(2)	1.430 (5)	C(14)–H(14A)	1.01 (5)
C(2)–C(3)	1.425 (6)	C(14)–H(14B)	0.99 (6)
C(2)–H(2)	0.87 (3)	C(14)–H(14C)	0.98 (5)
C(3)–C(7)	1.464 (5)	C(15)–C(16)	1.505 (7)
C(3)–H(3)	0.93 (4)	C(15)–H(15A)	0.92 (4)
C(4)–O(4)	1.138 (6)	C(15)–H(15B)	1.01 (4)
C(5)–O(5)	1.139 (6)	C(16)–H(16A)	0.96 (5)
C(6)–O(6)	1.148 (5)	C(16)–H(16B)	0.97 (5)
C(7)–C(8)	1.385 (6)	C(16)–H(16C)	1.02 (5)
C(7)–C(12)	1.399 (6)	H(14A)–H(14B)	1.53 (7)
C(8)–C(9)	1.379 (7)	H(16A)–H(16B)	1.53 (7)
C(8)–H(8)	1.01 (4)		
Bond Angles			
S–Fe–C(2)	72.87 (12)	C(9)–C(8)–H(8)	123.2 (25)
S–Fe–C(3)	82.07 (11)	C(8)–C(9)–C(10)	121.1 (5)
S–Fe–C(4)	89.16 (14)	C(8)–C(9)–H(9)	119 (3)
S–Fe–C(5)	93.72 (14)	C(10)–C(9)–H(9)	119 (3)
S–Fe–C(6)	169.81 (14)	C(9)–C(10)–C(11)	118.4 (5)
C(2)–Fe–C(3)	40.07 (15)	C(9)–C(10)–H(10)	124 (3)
C(2)–Fe–C(4)	115.56 (18)	C(11)–C(10)–H(10)	117 (3)
C(2)–Fe–C(5)	135.00 (19)	C(10)–C(11)–C(12)	121.0 (5)
C(2)–Fe–C(6)	98.39 (18)	C(10)–C(11)–H(11)	119 (3)
C(3)–Fe–C(4)	155.61 (18)	C(12)–C(11)–H(11)	119 (3)
C(3)–Fe–C(5)	96.58 (19)	C(7)–C(12)–C(11)	121.2 (5)
C(3)–Fe–C(6)	94.62 (18)	C(7)–C(12)–H(12)	117.9 (21)
C(4)–Fe–C(5)	106.71 (21)	C(11)–C(12)–H(12)	120.7 (22)
C(4)–Fe–C(6)	90.04 (20)	N–C(13)–C(14)	112.0 (4)
C(5)–Fe–C(6)	96.23 (19)	N–C(13)–H(13A)	107.0 (23)
Fe–S–C(1)	71.53 (12)	N–C(13)–H(13B)	107.5 (22)
C(1)–N–C(13)	122.3 (3)	C(14)–C(13)–H(13A)	112.3 (24)
C(1)–N–C(15)	122.2 (3)	C(14)–C(13)–H(13B)	108.2 (22)
C(13)–N–C(15)	115.4 (3)	H(13A)–C(13)–H(13B)	109 (3)
S–C(1)–N	122.5 (3)	C(13)–C(14)–H(14A)	111 (3)
S–C(1)–C(2)	112.6 (3)	C(13)–C(14)–H(14B)	113 (3)
N–C(1)–C(2)	124.5 (3)	C(13)–C(14)–H(14C)	112 (3)
Fe–C(2)–C(1)	86.43 (24)	H(14A)–C(14)–H(14B)	100 (4)
Fe–C(2)–C(3)	70.79 (23)	H(14A)–C(14)–H(14C)	109 (4)
Fe–C(2)–H(2)	124.8 (20)	H(14B)–C(14)–H(14C)	108 (4)
C(1)–C(2)–C(3)	120.9 (4)	N–C(15)–C(16)	112.3 (4)
C(1)–C(2)–H(2)	116.8 (20)	N–C(15)–H(15A)	108.7 (24)
C(3)–C(2)–H(2)	121.0 (20)	N–C(15)–H(15B)	105.7 (21)
Fe–C(3)–C(2)	69.14 (22)	C(16)–C(15)–H(15A)	109 (3)
Fe–C(3)–C(7)	123.5 (3)	C(16)–C(15)–H(15B)	112.2 (21)
Fe–C(3)–H(3)	100.4 (23)	H(15A)–C(15)–H(15B)	107 (3)
C(2)–C(3)–C(7)	123.3 (4)	C(15)–C(16)–H(16A)	113 (3)
C(2)–C(3)–H(3)	115.9 (22)	C(15)–C(16)–H(16B)	112 (3)
C(7)–C(3)–H(3)	114.8 (22)	C(15)–C(16)–H(16C)	110 (3)
Fe–C(4)–O(4)	178.9 (4)	H(16A)–C(16)–H(16B)	104 (4)
Fe–C(5)–O(5)	177.4 (4)	H(16A)–C(16)–H(16C)	106 (4)
Fe–C(6)–O(6)	179.4 (4)	H(16B)–C(16)–H(16C)	107 (4)
C(3)–C(7)–C(8)	119.5 (4)	C(14)–H(14A)–H(14B)	39 (3)
C(3)–C(7)–C(12)	123.8 (4)	C(14)–H(14B)–H(14A)	40 (3)
C(8)–C(7)–C(12)	116.7 (4)	C(16)–H(16A)–H(16B)	37.8 (24)
C(7)–C(8)–C(9)	121.5 (5)	C(16)–H(16B)–H(16A)	37.3 (25)
C(7)–C(8)–H(8)	115.2 (25)		

Fe—S bond points toward enhanced electron density on the iron, which would be compensated for by back-bonding into the π-olefin and carbonyl ligands, thus decreasing the olefin carbon–iron bond lengths. It is possible that, through resonance stabilization, the two phenyl groups of 2 markedly influence the degree of iron–olefin bonding. This rationalization leads one to expect that shorter Fe—C and longer C—O bonds of the carbonyl ligands would result for 2 than for 1. Comparison of Fe—C(20) (1.761 Å), Fe—C(21) (1.763 Å), and Fe—C(22) (1.760 Å) of 2 with Fe—C(4) (1.800 Å), Fe—C(5) (1.789 Å), and Fe—C(6) (1.762 Å) of 1, and the carbon–oxygen bonds of 2 [C(20)—O (1.146 Å), C(21)—O(2) (1.174 Å), and C(22)—O(3) (1.150 Å)] with those of 1 [C(4)—O(4) (1.138 Å), C(5)—O(5) (1.139 Å), and C(6)—O(6) (1.148 Å)] shows that this is indeed the case, confirming greater back-bonding from the metal to the carbonyls in 2 than in 1. ν_{CO} values of 2 occur at lower wavelengths than those of 1, consistent with greater back-bonding for 2.

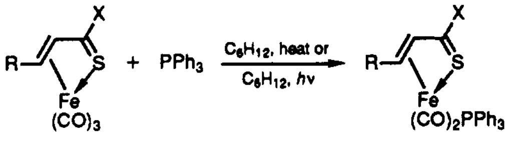
(d) Ligand Substitution Reactions. Thermal or photolytic reaction of 1, 7, or 10 with an equimolar amount of triphenylphosphine afforded 13 in 26–85% yields. The

Table V. Atomic Parameters x, y, z and B_{iso} for the Non-Hydrogen Atoms of 2[a]

	x	y	z	B_{iso}, Å^2
Fe	0.45851 (20	0.20334 (15)	0.18707 (9)	4.38 (8)
S	0.4184 (4)	0.2678 (3)	0.07753 (15)	4.82 (14)
O(1)	0.4579 (16)	0.1523 (10)	0.3319 (5)	9.5 (7)
O(2)	0.7155 (12)	0.0653 (10)	0.1512 (6)	8.3 (6)
O(3)	0.5721 (16)	0.4198 (10)	0.2201 (6)	10.9 (8)
N	0.1425 (14)	0.3462 (10)	0.0886 (5)	5.7 (6)
C(1)	0.2451 (13)	0.2787 (10)	0.1136 (5)	4.1 (6)
C(2)	0.2284 (12)	0.2082 (11)	0.1725 (5)	4.4 (6)
C(3)	0.2848 (13)	0.0976 (10)	0.1651 (5)	4.0 (5)
C(4)	0.1272 (13)	0.2337 (10)	0.2320 (6)	4.4 (6)
C(5)	0.1468 (16)	0.3254 (11)	0.2723 (7)	5.5 (7)
C(6)	0.0509 (20)	0.3433 (12)	0.3268 (7)	6.9 (8)
C(7)	−0.0612 (20)	0.2746 (14)	0.3409 (7)	7.4 (9)
C(8)	−0.0840 (16)	0.1853 (14)	0.2997 (8)	7.2 (8)
C(9)	0.0103 (17)	0.1627 (12)	0.2466 (7)	6.3 (7)
C(10)	0.2854 (13)	0.0300 (10)	0.1009 (6)	4.3 (6)
C(11)	0.3829 (14)	−0.0599 (10)	0.0975 (6)	4.8 (6)
C(12)	0.3787 (16)	−0.1296 (11)	0.0414 (8)	5.9 (7)
C(13)	0.2781 (22)	−0.1122 (13)	−0.0109 (8)	7.3 (9)
C(14)	0.1826 (21)	−0.0236 (14)	−0.0069 (7)	7.0 (9)
C(15)	0.1847 (16)	0.0450 (11)	0.0485 (7)	5.4 (7)
C(16)	−0.052 (4)	0.3243 (17)	0.1036 (9)	12.4 (18)
C(17)	−0.057 (3)	0.4123 (24)	0.1348 (11)	14.6 (20)
C(18)	0.1719 (15)	0.4146 (11)	0.0279 (6)	5.2 (7)
C(19)	0.2416 (20)	0.5232 (13)	0.0455 (8)	7.3 (9)
C(20)	0.4608 (17)	0.1710 (11)	0.2746 (7)	5.8 (7)
C(22)	0.5264 (20)	0.3346 (13)	0.2071 (7)	7.2 (8)
C(21)	0.6161 (17)	0.1232 (13)	0.1665 (7)	6.3 (8)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

spectral data were consistent with the structure assigned for 13. In the ^{13}C NMR spectrum, two carbonyl carbon



13

R = Me, Ph; X = Et$_2$, NPhMe, OEt

signals were present at room temperature in contrast to the Fe(CO)$_3$ analogues where a broad single peak occurred at the same temperature. Coupling of the phosphorus atom to the carbonyl carbons was observed for 13 (R = Ph, X = NEt$_2$). The largest coupling, 12 Hz, was found for the carbonyl furthest downfield, suggesting that the degree of s character between PPh$_3$ and CO in an axial position to PPh$_3$ is greater than that between PPh$_3$ and equatorial CO, which has a coupling constant of 5.6 Hz. This may be due to the orientation of axial CO also being trans to sulfur, with increased s character in the Fe–CO bond. These coupling constants are lower than those found for Ph$_3$PFe(CO)$_4$ and (Ph$_3$P)$_2$Fe(CO)$_3$.[26] The ^{31}P chemical shifts of 13 ranged from 54.33 to 61.99 and, as expected, were downfield from free triphenylphosphine (δ = 5.02 ppm).

(e) Ligand Recovery from Complexes. Recovery of dienes from the corresponding Fe(CO)$_3$ complexes is generally realized by using trimethylamine *N*-oxide. When 1, 4, or 10 was treated with Me$_3$NO in chloroform–tetrahydrofuran, decomplexation occurred but oxidation of thioamide to amide also took place. The best of a number of other reagents used for decomplexation was ceric ammonium nitrate. Exposure of 1, 4, or 10 to ceric ion in aqueous acetone at 0 °C or less afforded the ligand in 94–98% yields. Above 0 °C, mixtures of thioamide and amide (or thioester and ester) were isolated.

Table VI. Selected Interatomic Distances (Å) and Angles (deg) of 2

	Bond Distances		
Fe–S	2.316 (3)	C(8)–C(9)	1.367 (20)
Fe–C(2)	2.072 (11)	C(8)–H(8)	1.103 (15)
Fe–C(3)	2.065 (12)	C(9)–H(9)	1.126 (15)
Fe–C(20)	1.761 (13)	C(10)–C(11)	1.405 (18)
Fe–C(22)	1.763 (16)	C(10)–C(15)	1.377 (18)
Fe–C(21)	1.760 (17)	C(11)–C(12)	1.393 (19)
S–C(1)	1.705 (11)	C(11)–H(11)	1.111 (12)
O(1)–C(20)	1.146 (16)	C(12)–C(13)	1.38 (3)
O(2)–C(21)	1.174 (20)	C(12)–H(12)	1.089 (13)
O(3)–C(22)	1.150 (20)	C(13)–C(14)	1.38 (3)
N–C(1)	1.327 (17)	C(13)–H(13)	1.082 (14)
N–C(16)	1.78 (4)	C(14)–C(15)	1.373 (21)
N–C(18)	1.478 (17)	C(14)–H(14)	1.111 (16)
C(1)–C(2)	1.450 (16)	C(15)–H(15)	1.121 (14)
C(2)–C(3)	1.454 (19)	C(16)–C(17)	1.24 (4)
C(2)–C(4)	1.506 (16)	C(16)–H(17A)	1.074 (22)
C(3)–C(10)	1.506 (18)	C(16)–H(17B)	1.06 (3)
C(3)–H(3)	1.106 (11)	C(17)–H(16A)	1.099 (23)
C(4)–C(5)	1.385 (19)	C(17)–H(16B)	1.135 (24)
C(4)–C(9)	1.388 (19)	C(17)–H(16C)	1.13 (3)
C(5)–C(6)	1.385 (19)	C(18)–C(19)	1.509 (23)
C(5)–H(5)	1.106 (13)	C(18)–H(18A)	1.091 (13)
C(6)–C(7)	1.34 (3)	C(18)–H(18B)	1.083 (13)
C(6)–H(6)	1.150 (14)	C(19)–H(19A)	1.128 (17)
C(7)–C(8)	1.38 (3)	C(19)–H(19B)	1.109 (17)
C(7)–H(7)	1.097 (13)	C(19)–H(19C)	1.044 (15)
	Bond Angles		
S–Fe–C(2)	73.1 (3)	C(4)–C(9)–C(8)	119.4 (14)
S–Fe–C(3)	84.5 (3)	C(4)–C(9)–H(9)	120.6 (12)
S–Fe–C(20)	169.1 (5)	C(8)–C(9)–H(9)	120.0 (14)
S–Fe–C(22)	87.0 (5)	C(3)–C(10)–C(11)	118.3 (11)
S–Fe–C(21)	95.8 (5)	C(3)–C(10)–C(15)	123.2 (12)
C(2)–Fe–C(3)	41.2 (5)	C(11)–C(10)–C(15)	118.2 (12)
C(2)–Fe–C(20)	98.7 (6)	C(10)–C(11)–C(12)	120.2 (12)
C(2)–Fe–C(22)	110.1 (7)	C(10)–C(11)–H(11)	120.5 (11)
C(2)–Fe–C(21)	140.7 (6)	C(12)–C(11)–H(11)	119.3 (12)
C(3)–Fe–C(20)	94.1 (5)	C(11)–C(12)–C(13)	120.6 (13)
C(3)–Fe–C(22)	151.3 (7)	C(11)–C(12)–H(12)	122.1 (14)
C(3)–Fe–C(21)	101.5 (6)	C(13)–C(12)–H(12)	117.3 (13)
C(20)–Fe–C(22)	89.1 (6)	C(12)–C(13)–C(14)	118.8 (13)
C(20)–Fe–C(21)	95.1 (7)	C(12)–C(13)–H(13)	123.2 (17)
C(22)–Fe–C(21)	106.6 (7)	C(14)–C(13)–H(13)	118.0 (17)
Fe–S–C(1)	77.4 (4)	C(13)–C(14)–C(15)	121.2 (14)
C(1)–N–C(16)	121.1 (11)	C(13)–C(14)–H(14)	118.3 (14)
C(1)–N–C(18)	121.9 (11)	C(15)–C(14)–H(14)	120.5 (16)
C(16)–N–C(18)	113.0 (11)	C(10)–C(15)–C(14)	121.1 (14)
S–C(1)–N	121.3 (9)	C(10)–C(15)–H(15)	121.8 (13)
S–C(1)–C(2)	112.1 (8)	C(14)–C(15)–H(15)	117.0 (13)
N–C(1)–C(2)	126.5 (10)	N–C(16)–C(17)	89.3 (24)
Fe–C(2)–C(1)	91.4 (7)	N–C(16)–H(17A)	114.0 (21)
Fe–C(2)–C(3)	69.2 (6)	N–C(16)–H(17B)	114.1 (18)
Fe–C(2)–C(4)	119.5 (8)	C(17)–C(16)–H(17A)	111.8 (19)
C(1)–C(2)–C(3)	116.1 (10)	C(17)–C(16)–H(17B)	114.6 (22)
C(1)–C(2)–C(4)	123.6 (11)	H(17A)–C(16)–H(17B)	111 (3)
C(3)–C(2)–C(4)	118.6 (10)	C(16)–C(17)–H(16A)	116 (3)
Fe–C(3)–C(2)	69.7 (6)	C(16)–C(17)–H(16B)	113.7 (23)
Fe–C(3)–C(10)	121.2 (8)	C(16)–C(17)–H(16C)	113 (3)
Fe–C(3)–H(3)	106.2 (7)	H(16A)–C(17)–H(16B)	104.3 (21)
C(2)–C(3)–C(10)	126.8 (10)	H(16A)–C(17)–H(16C)	104.5 (22)
C(2)–C(3)–H(3)	112.6 (10)	H(16B)–C(17)–H(16C)	102.2 (24)
C(10)–C(3)–H(3)	112.5 (10)	N–C(18)–C(19)	112.9 (11)
C(2)–C(4)–C(5)	122.3 (11)	N–C(18)–H(18A)	112.1 (12)
C(2)–C(4)–C(9)	118.6 (11)	N–C(18)–H(18B)	110.8 (11)
C(5)–C(4)–C(9)	119.1 (11)	C(19)–C(18)–H(18A)	106.2 (11)
C(4)–C(5)–C(6)	119.4 (13)	C(19)–C(18)–H(18B)	105.9 (12)
C(4)–C(5)–H(5)	118.4 (12)	H(18A)–C(18)–H(18B)	108.4 (11)
C(6)–C(5)–H(5)	122.2 (13)	C(18)–C(19)–H(19A)	108.7 (14)
C(5)–C(6)–C(7)	121.4 (13)	C(18)–C(19)–H(19B)	109.5 (12)
C(5)–C(6)–H(6)	117.7 (15)	C(18)–C(19)–H(19C)	115.6 (14)
C(7)–C(6)–H(6)	120.9 (13)	H(19A)–C(19)–H(19B)	104.0 (14)
C(6)–C(7)–C(8)	119.4 (12)	H(19A)–C(19)–H(19C)	108.5 (14)
C(6)–C(7)–H(7)	118.4 (16)	H(19B)–C(19)–H(19C)	109.9 (15)
C(8)–C(7)–H(7)	122.2 (16)	Fe–C(20)–O(1)	177.5 (14)
C(7)–C(8)–C(9)	121.2 (14)	Fe–C(22)–O(3)	179.3 (15)
C(7)–C(8)–H(8)	118.6 (14)	Fe–C(21)–O(2)	176.1 (12)
C(9)–C(8)–H(8)	120.1 (16)		

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(26) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1.

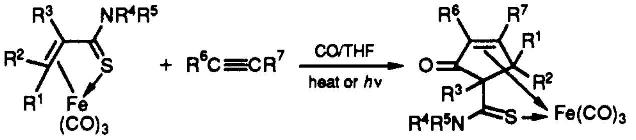
Table VII. Cycloaddition of 1, 4, and 7 with Alkynes in Refluxing THF

complex	alkyne	reaction time, h	product, %
7	MeOOC—C≡C—COOMe	2	14, 69
	HC≡C—COOC$_4$H$_9$	2	15, 11
	HC≡C—COOMe	15	16, 78
4	MeOOC—C≡C—COOMe	6	17, 81
1	MeOOC—C≡C—COOMe	3[a]	18, 22

[a] Photolysis instead of thermal reaction.

(f) Reaction with Alkynes and Carbon Monoxide. A novel reaction occurred when α,β-unsaturated thioamide iron tricarbonyls were treated with dimethylacetylene dicarboxylate, or with methyl or *n*-butyl propynoate in refluxing THF, or by irradiation in cyclohexane. Complexed cyclopentenones were formed with a thioamide side chain. Coordination of the double bond and the thiocarbonyl sulfur to iron took place *without* conjugation of the two functionalities. This is an unusual example of coordination without isomerization to a conjugated heterodiene complex. Yields ranged from 11 to 81%, depending on the nature of the reactant complex and the alkyne (Table VII). The structures of these complexes were determined on the basis of analytical and spectral data, as well as an X-ray determination in one case.

The infrared spectra of 14–18 showed three intense terminal metal carbonyl stretching bands. A curious feature of the proton NMR spectrum was the absence of coupling between the proton (R^3 = H) attached to the carbon adjacent to C═S and the proton on the neighboring carbon atom [i.e. C*H*(CH$_3$)]. The dihedral angle between these protons in 14 (see X-ray structure below) is 100.2°, and on the basis of the Karplus relation, one would expect to find small coupling between the noted protons. In the ^{13}C NMR spectrum, there are five signals in the region δ 200–215 ppm, which can be assigned to the metal carbonyls, ketone, and thiocarbonyl groups. Thus, the thiocarbonyl carbon of 14–18 occurs downfield in comparison with the chemical shift of the same carbon in 1–9.



14: R^1 = R^3 = H, R^2 = R^4 = Me, R^5 = Ph, R^6 = R^7 = COOMe
15: R^1 = R^3 = R^6 = R^4 = H, R^2 = R^4 = Me, R^5 = Ph, R^7 = COOC$_4$H$_9$
16: R^1 = R^3 = R^6 = H, R^2 = R^4 = Me, R^5 = Ph, R^7 = COOMe
17: R^1 = R^3 = H, R^2 = Me, R^4 = R^5 = Et, R^6 = R^7 = COOCH$_3$
18: R^1 = R^3 = H, R^2 = Ph, R^4 = R^5 = Et, R^6 = COOMe

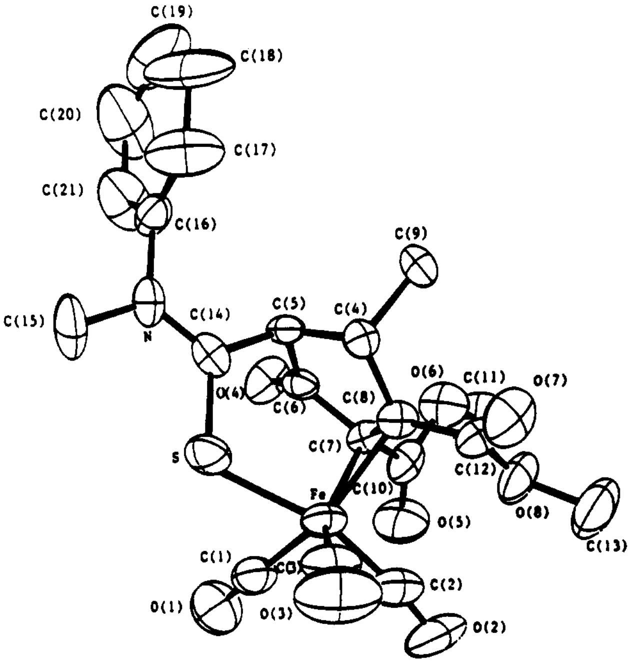


Figure 4. View of 14 showing the atom-numbering scheme.

Table VIII. Atomic Parameters *x*, *y*, *z* and B_{iso} for the Non-Hydrogen Atoms of 14[a]

	x	*y*	*z*	B_{iso}, Å^2
Fe	0.23474 (9)	0.63971 (10)	0.00983 (8)	3.81 (6)
S	0.26697 (17)	0.46857 (16)	0.06976 (15)	4.57 (12)
O(1)	0.0342 (5)	0.6249 (6)	0.0588 (4)	7.7 (4)
O(2)	0.1365 (5)	0.8254 (5)	−0.0989 (4)	8.2 (4)
O(3)	0.1945 (6)	0.5462 (6)	−0.1832 (4)	9.3 (5)
O(4)	0.3515 (4)	0.6595 (4)	0.2834 (3)	4.6 (3)
O(5)	0.2333 (5)	0.8692 (5)	0.1223 (4)	6.7 (4)
O(6)	0.4160 (5)	0.8758 (4)	0.2017 (4)	5.3 (3)
O(7)	0.4768 (5)	0.7139 (4)	−0.0618 (4)	5.7 (4)
O(8)	0.3806 (4)	0.8422 (4)	0.0193 (3)	5.2 (3)
N	0.4194 (5)	0.3813 (5)	0.2254 (4)	3.5 (4)
C(1)	0.1092 (7)	0.6293 (7)	0.0408 (5)	4.7 (5)
C(2)	0.1810 (7)	0.7567 (7)	−0.0538 (6)	5.6 (6)
C(3)	0.2113 (7)	0.5803 (7)	−0.1073 (6)	5.5 (5)
C(4)	0.4855 (6)	0.5991 (5)	0.1110 (5)	2.8 (4)
C(5)	0.4504 (6)	0.5628 (6)	0.1959 (5)	2.8 (4)
C(6)	0.3763 (5)	0.6504 (6)	0.2121 (5)	2.8 (4)
C(7)	0.3469 (6)	0.7190 (5)	0.1248 (5)	3.1 (4)
C(8)	0.4011 (6)	0.6839 (6)	0.0596 (5)	3.1 (4)
C(9)	0.6021 (6)	0.6428 (7)	0.1521 (6)	4.3 (5)
C(10)	0.3223 (8)	0.8292 (7)	0.1466 (6)	4.0 (5)
C(11)	0.4058 (10)	0.9805 (9)	0.2327 (9)	8.1 (9)
C(12)	0.4267 (7)	0.7445 (7)	−0.0132 (6)	4.0 (5)
C(13)	0.3975 (10)	0.9018 (8)	−0.0985 (8)	7.9 (8)
C(14)	0.3852 (6)	0.4650 (6)	0.1710 (5)	3.3 (4)
C(15)	0.3566 (10)	0.2837 (8)	0.1983 (6)	5.6 (7)
C(16)	0.5236 (7)	0.3781 (6)	0.3102 (5)	3.5 (5)
C(17)	0.6181 (8)	0.3586 (8)	0.2943 (6)	6.7 (6)
C(18)	0.7164 (9)	0.3550 (9)	0.3727 (10)	9.6 (8)
C(19)	0.7117 (11)	0.3689 (10)	0.4656 (8)	10.2 (8)
C(20)	0.6129 (10)	0.3857 (11)	0.4799 (8)	10.4 (10)
C(21)	0.5188 (8)	0.3925 (8)	0.4007 (7)	6.7 (7)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

An ORTEP drawing of 14 is illustrated in Figure 4. Pertinent crystal data, including all bond angles and distances, are given in Tables II, VIII, and IX. The structure can be described as a distorted octahedron with respect to iron, in which the metal is π-bonded to the olefin carbons of the cyclopentenone fragment, with sulfur complexed to iron via its lone pair. The three metal carbonyls are staggered relative to the other three iron ligand bonds, and one of the carbonyls lies in a plane normal to the midpoint of the cyclopentenone double bond. This carbonyl has a small Fe–C(2)–O(2) angle of 172.6° compared with the other two Fe–C–O angles. The iron carbonyl carbon bond lengths in 14 are slightly longer than in complexes of structural type 1, and this is reflected in the observation that ν_{CO} bands for 14 occur at higher frequency than those in 1. The shortest C–Fe bond length is for the carbonyl trans to sulfur. The Fe–S bond distance of 14 is similar to that of 1. The bond length (1.450 Å) between the olefin carbons of the cyclopentenone ring is intermediate between that of a normal double and single bond and is of the same magnitude as that of 2.

In summary, a series of new sulfur–iron complexes have been synthesized and characterized and react in an interesting manner with alkynes.

Table IX. Selected Interatomic Distances (Å) and Angles (deg) of 14

	Bond Distances		
Fe–S	2.3592 (25)	C(6)–C(7)	1.486 (10)
Fe–C(1)	1.849 (8)	C(7)–C(8)	1.450 (10)
Fe–C(2)	1.779 (9)	C(7)–C(10)	1.518 (11)
Fe–C(3)	1.801 (9)	C(8)–C(12)	1.455 (11)
Fe–C(7)	2.053 (7)	C(9)–H(9A)	0.99 (6)
Fe–C(8)	2.093 (7)	C(9)–H(9B)	1.16 (7)
S–C(14)	1.702 (7)	C(9)–H(9C)	1.01 (6)
O(1)–C(1)	1.100 (10)	C(11)–H(11A)	0.82 (8)
O(2)–C(2)	1.131 (11)	C(11)–H(11B)	0.94 (7)
O(3)–C(3)	1.139 (10)	C(11)–H(11C)	1.57 (7)
O(4)–C(6)	1.206 (9)	C(13)–H(13A)	1.04 (6)
O(5)–C(10)	1.197 (10)	C(13)–H(13B)	0.98 (7)
O(6)–C(10)	1.333 (11)	C(13)–H(13C)	0.91 (7)
O(6)–C(11)	1.449 (12)	C(15)–H(15A)	1.38 (7)
O(7)–C(12)	1.193 (11)	C(15)–H(15B)	0.91 (6)
O(8)–C(12)	1.347 (11)	C(15)–H(15C)	0.73 (7)
O(8)–C(13)	1.431 (12)	C(16)–C(17)	1.354 (13)
N–C(14)	1.320 (10)	C(16)–C(21)	1.362 (12)
N–C(15)	1.476 (12)	C(17)–C(18)	1.371 (14)
N–C(16)	1.465 (9)	C(17)–H(17)	1.02 (6)
C(4)–C(5)	1.544 (10)	C(18)–C(19)	1.395 (19)
C(4)–C(5)	1.538 (10)	C(18)–C(18)	1.01 (7)
C(4)–C(9)	1.520 (11)	C(19)–C(20)	1.391 (20)
C(4)–H(4)	1.08 (5)	C(19)–H(19)	1.010 (10)
C(5)–C(6)	1.559 (10)	C(20)–C(21)	1.346 (15)
C(5)–C(14)	1.490 (11)	C(20)–H(20)	0.944 (10)
C(5)–H(5)	0.94 (6)	C(21)–H(21)	0.98 (7)
	Bond Angles		
S–Fe–C(1)	83.9 (3)	C(4)–C(9)–H(9A)	119 (4)
S–Fe–C(2)	166.8 (3)	C(4)–C(9)–H(9B)	115 (3)
S–Fe–C(3)	84.2 (3)	C(4)–C(9)–H(9C)	116 (4)
S–Fe–C(7)	100.75 (20)	H(9A)–C(9)–H(9B)	86 (5)
S–Fe–C(8)	96.07 (21)	H(9A)–C(9)–H(9C)	107 (5)
C(1)–Fe–C(2)	88.7 (4)	H(9B)–C(9)–H(9C)	106 (5)
C(1)–Fe–C(3)	110.1 (4)	O(5)–C(10)–O(6)	123.7 (8)
C(1)–Fe–C(7)	105.1 (3)	O(5)–C(10)–C(7)	126.7 (8)
C(1)–Fe–C(8)	145.7 (3)	O(6)–C(10)–C(7)	109.6 (7)
C(2)–Fe–C(3)	88.0 (4)	O(6)–C(11)–H(11A)	108 (6)
C(2)–Fe–C(7)	91.8 (3)	O(6)–C(11)–H(11B)	109 (5)
C(2)–Fe–C(8)	96.2 (4)	O(6)–C(11)–H(11C)	110.2 (25)
C(3)–Fe–C(7)	144.7 (4)	H(11A)–C(11)–H(11B)	127 (9)
C(3)–Fe–C(8)	104.0 (3)	H(11A)–C(11)–H(11C)	66 (7)
C(7)–Fe–C(8)	40.9 (3)	H(11B)–C(11)–H(11C)	65 (6)
Fe–S–C(14)	109.3 (3)	O(7)–C(12)–O(8)	122.5 (8)
C(10)–O(6)–C(11)	116.3 (7)	O(7)–C(12)–C(8)	125.4 (8)
C(12)–O(8)–C(13)	114.9 (7)	O(8)–C(12)–C(8)	112.1 (7)
C(14)–N–C(15)	120.4 (7)	O(8)–C(13)–H(13A)	112 (4)
C(14)–N–C(16)	122.5 (6)	O(8)–C(13)–H(13B)	114 (5)
C(15)–N–C(16)	116.9 (7)	O(8)–C(13)–H(13C)	108 (5)
Fe–C(1)–O(1)	178.7 (9)	H(13A)–C(13)–H(13B)	96 (6)
Fe–C(2)–O(2)	172.6 (8)	H(13A)–C(13)–H(13C)	134 (6)
Fe–C(3)–O(3)	177.3 (8)	H(13B)–C(13)–H(13C)	86 (7)
C(5)–C(4)–C(8)	104.1 (6)	S–C(14)–N	123.1 (6)
C(5)–C(4)–C(9)	109.8 (6)	S–C(14)–C(5)	116.2 (6)
C(5)–C(4)–H(4)	113 (3)	N–C(14)–C(5)	120.7 (6)
C(8)–C(4)–C(9)	111.0 (6)	N–C(15)–H(15A)	121 (3)
C(8)–C(4)–H(4)	109 (3)	N–C(15)–H(15B)	110 (4)
C(9)–C(4)–H(4)	109 (4)	N–C(15)–H(15C)	104 (7)
C(4)–C(5)–C(6)	106.3 (6)	H(15A)–C(15)–H(15B)	84 (5)
C(4)–C(5)–C(14)	111.7 (6)	H(15A)–C(15)–H(15C)	104 (7)
C(4)–C(5)–H(5)	111 (4)	H(15B)–C(15)–H(15C)	131 (8)
C(6)–C(5)–C(14)	109.0 (6)	N–C(16)–C(17)	118.4 (7)
C(6)–C(5)–H(5)	112 (4)	N–C(16)–C(21	117.6 (8)
C(14)–C(5)–H(5)	106 (4)	C(17)–C(16)–C(21)	124.0 (8)
O(4)–C(6)–C(5)	125.2 (6)	C(16)–C(17)–C(18)	119.2 (9)
O(4)–C(6)–C(7)	128.4 (7)	C(16)–C(17)–C(17)	131 (4)
C(5)–C(6)–C(7)	106.4 (6)	C(18)–C(17)–C(17)	119 (4)
Fe–C(7)–C(6)	106.9 (5)	C(17)–C(18)–C(19)	117.0 (10)
Fe–C(7)–C(8)	71.0 (4)	C(17)–C(18)–H(18)	119 (4)
Fe–C(7)–C(10)	120.0 (5)	C(19)–C(18)–H(18)	122 (4)
C(6)–C(7)–C(8)	110.2 (6)	C(18)–C(19)–C(20)	122.5 (9)
C(6)–C(7)–C(10)	112.7 (6)	C(18)–C(19)–C(19)	117.8 (14)
C(8)–C(7)–C(10)	128.4 (6)	C(20)–C(19)–H(19)	120.7 (13)
Fe–C(8)–C(4)	115.9 (5)	C(19)–C(20)–C(21)	118.6 (9)
Fe–C(8)–C(7)	68.0 (4)	C(19)–C(20)–H(20)	107.8 (11)
Fe–C(8)–C(12)	112.0 (5)	C(21)–C(20)–H(20)	133.6 (12)
C(4)–C(8)–C(7)	109.4 (6)	C(16)–C(21)–C(20)	118.7 (9)
C(4)–C(8)–C(12)	115.4 (6)	C(16)–C(21)–H(21)	128 (4)
C(7)–C(8)–C(12)	127.5 (7)	C(20)–C(21)–H(21)	112 (4)

Experimental Section

General Data. Melting point determinations were made on a Gallenkamp apparatus. The following instrumentation was used to record spectra: Perkin-Elmer 783 (infrared), VG7070E (mass), and Varian-XL300 (nuclear magnetic resonance) spectrometers. Gas chromatography was effected by using a Varian 3400 instrument equipped with a 2-m column packed with 3% OV-100 having a 10-m DB-1 column. Elemental analyses were carried out by either MHW Laboratories, Phoenix, AZ, or by Guelph Chemical Laboratories, Guelph, Ontario. Reagents and reactants were purchased from commercial sources and were used as received. Solvents were dried and distilled prior to use. All reactions were effected under nitrogen.

Preparation of α,β-Unsaturated Thiocarbonyls. *N*,*N*-Diethyl-3-phenylpropenethioamide (1′). 3-Phenylpropenoyl chloride (60 mmol) was added dropwise to a stirred solution of *N*,*N*-diethylamine (240 mmol) in 5% KOH (150 mmol) at 0 °C.[19] After the acid chloride was added, the solution was allowed to warm to room temperature and stirred overnight. The solution was then extracted with ether (4 × 100 mL), the combined organic fractions were washed with distilled water (3 × 100 mL), dried (Na_2SO_4), and filtered, and the filtrate was concentrated, leaving 11.33 g (93%) of a white solid, *N*,*N*-diethyl-3-phenylpropenamide, which was characterized by IR and ^{1}H NMR spectroscopy.

The amide (20 mmol) was converted to the thioamide with Lawesson's reagent (12 mmol) by refluxing in toluene under N_2 for 1 h.[18] After cooling to room temperature, silica (~15 g) was added, and rotary evaporation gave a powder. The solid was added to the top of a dry-packed silica column, and elution with hexane–ether (9:1) gave 1′. Recrystallization from ethanol afforded 1′ in 96% yield. Mp: 47–49 °C (lit. mp 48–50 °C[27]). MS (*m*/*e*): 239 (M)$^+$. ^{1}H NMR ($CDCl_3$): δ 1.32 (t, 3 H, ^3J = 7.4 Hz, $\mathrm{CH_2}CH_3$), 1.33 (t, 3 H, ^3J = 7.4 Hz, $\mathrm{CH_2}CH_3$), 3.70 (q, 2 H, ^3J = 7.4 Hz, $CH_2\mathrm{CH_3}$), 4.09 (q, 2 H, ^3J = 7.4 Hz, $CH_2\mathrm{CH_3}$), 7.07 (d, 1 H, ^3J = 15.3 Hz, β-*CH*), 7.33, 7.49 (m, 5 H, aromatic protons), 7.85 (d, 1 H, ^3J = 15.3 Hz, γ-*CH*) ppm. ^{13}C NMR ($CDCl_3$): δ 11.54 ($\mathrm{CH_2}C\mathrm{H_3}$), 13.83 ($\mathrm{CH_2}C\mathrm{H_3}$), 46.46 ($C\mathrm{H_2CH_3}$), 48.55 ($C\mathrm{H_2CH_3}$), 124.85 (β-*C*H), 127.85, 128.80, 129.44 (aromatic *C*H), 135.61 (quaternary aromatic C), 143.82 (γ-*C*H), 193.65 (C═S) ppm.

***N*,*N*-Diethyl-2,3-Diphenylpropenethioamide (2′).** 2,3-Diphenylpropenoic acid (70 mmol) was refluxed in a benzene solution of thionyl chloride (270 mmol) for 1 h. The solvent was removed by rotary evaporation, leaving a yellow oil (93% yield). IR analysis confirmed the absence of the starting material, and the acid chloride was converted to the amide (96% yield) as described for the amide above (characterized by IR and ^{1}H NMR spectroscopy).

The thioamide was prepared from the amide (20 mmol) by refluxing in tolune with Lawesson's reagent (12 mmol) for 40 min. Purification on a dry-packed silica column using hexanes–ether (1:1) gave a yellow solid after solvent removal. Yield from amide: 90%. Mp: 56–58 °C. MS (*m*/*e*): 295 (M)$^+$. ^{1}H NMR ($CDCl_3$): δ 0.82 (t, 3 H, ^3J = 7.2 Hz, $\mathrm{CH_2}CH_3$), 1.37 (t, 3 H, ^3J = 7.1 Hz, $\mathrm{CH_2}CH_3$), 3.53 (overlapping dq, 2 H, $C\mathrm{H_2CH_3}$), 4.02 (dq, 1 H, ^3J = 7.2 Hz, ^2J = 7.1 Hz, $C\mathrm{H_2CH_3}$), 4.23 (dq, 1 H, ^3J = 7.2 Hz, ^2J = 7.1 Hz, $CH_2\mathrm{CH_3}$), 6.72 (s, 1 H, γ-*CH*), 7.35, 7.60 (m, 10 H, aromatic protons) ppm. ^{13}C NMR ($CDCl_3$): δ 10.42 ($\mathrm{CH_2}C\mathrm{H_3}$), 12.82 ($\mathrm{CH_2}C\mathrm{H_3}$), 44.94 ($C\mathrm{H_2CH_3}$), 47.59 ($C\mathrm{H_2CH_3}$), 123.59 (β-*C*), 126.29, 127.66, 127.93, 128.17, 128.49, 128.93 (aromatic CH), 135.46, 138.19 (quaternary aromatic carbons), 141.07 (γ-C*H*), 196.62 (C═S) ppm.

***N*-Phenyl-*N*-(2-propenyl)-3-phenylpropenethioamide (3′).** The required amide was prepared (94% yield) by using the procedure leading to 1′. The thioamide was obtained from the amide (20 mmol) by refluxing in toluene with Lawesson's reagent (12 mmol) for 17 h. Purification on a dry-packed silica column using hexane–ether (3:7) gave an orange solid, which was spectroscopically pure but gave a broad mp range. Yield from amide: 81%. Mp: 56–77 °C. MS (*m*/*e*): 279 (M)$^+$. ^{1}H NMR ($CDCl_3$): δ 5.03 (d, 2 H, ^3J = 6.3 Hz, $\mathrm{N}C\mathrm{H_2CHCH_2}$), 5.15 (dd, 1 H, ^3J = 20.0 Hz, ^2J = 1.4 Hz, $\mathrm{NCH_2CH}CH_2$), 5.20 (dd, 1 H, ^3J = 10.3 Hz, ^2J = 1.4 Hz, $\mathrm{NCH_2CH}C\mathrm{H_2}$), 6.04 (ddt, 1 H, ^3J = 20.0, 10.3, 6.3

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[27] Kaesz, H. D.; Lavigne, G. *J. Am. Chem. Soc.* 1984, *106*, 4647.

Hz, $NCH_2\mathit{CH}CH_2$), 6.56 (d, 1 H, ${}^3J$ = 15.0 Hz, β-*CH*), 7.17 (m, 2 H, aromatic protons), 7.24 (s, 5 H, Ph), 7.42 (m, 3 H, aromatic protons), 7.91 (d, 1 H, γ-*CH*) ppm. ^{13}C NMR ($CDCl_3$): δ 59.19 ($N\mathit{C}H_2CH{=}CH_2$), 118.7 ($NCH_2CH{=}\mathit{CH_2}$), 125.94, 126.52 (β-*CH* and $NCH_2\mathit{CH}{=}CH_2$), 127.11, 127.43, 128.01, 129.10, 129.25, 130.66 (aromatic *CH*), 134.99, 143.30 (quaternary aromatic *C*), 144.03 (γ-*CH*), 194.79 (C=S) ppm.

N,N-Diethylbut-2-enethioamide (4′). The required amide was prepared from crotyl chloride (97% yield) and diethylamine. The thioamide was obtained from the amide (20 mmol) by refluxing in toluene with Lawesson's reagent (12 mmol) for 2 h. Purification on a dry-packed silica column using hexanes–ether gave a yellow oil. Yield from amide: 45%. Bp: 192–194 °C. MS (*m*/*e*): 157 $(M)^+$. ^1H NMR ($CDCl_3$): δ 1.79 (2 overlapping t, 6 H, ${}^3J$ = 7.1 Hz, $CH_2\mathit{CH_3}$), 1.80 (dd, 3 H, ${}^3J$ = 6.9 Hz, ${}^4J$ = 1.6 Hz, $\mathit{CH_3}$), 3.53 (q, 2 H, ${}^3J$ = 7.1 Hz, $\mathit{CH_2}CH_3$), 3.93 (q, 2 H, ${}^3J$ = 7.1 Hz, $\mathit{CH_2}CH_3$), 6.38 (d, 1 H, ${}^3J$ = 14.6 Hz, β-*CH*), 6.92 (dq, 1 H, ${}^3J$ = 14.6 Hz, ${}^3J$ = 6.9 Hz, γ-*CH*) ppm. ^{13}C NMR ($CDCl_3$); δ 10.94 ($CH_2\mathit{C}H_3$), 13.11 ($CH_2\mathit{C}H_3$), 18.02 ($\mathit{CH_3}$), 45.69 ($\mathit{C}H_2CH_3$), 47.55 ($\mathit{C}H_2CH_3$), 128.40 (β-*C*H), 141.97 (γ-*C*H), 193.37 (C=S) ppm.

N,N-Diethyl-2-methylpent-2-enethioamide (5′). The acid chloride was prepared in 89% yield by treating 2-methylhexenoic acid (70 mmol) in refluxing benzene with thionyl chloride (270 mmol) for 1 h. Reaction of the acid halide with diethylamine afforded the amide in 90% yield.

The thioamide was prepared from the amide (20 mmol) by refluxing in toluene with Lawesson's reagent (12 mmol) for 40 min. Purification on silica using hexanes–ether (9:1) gave 5′ as a yellow oil in 65% yield. Bp: 170 °C/10 mmHg. MS (*m*/*e*): 185 $(M)^+$. ^1H NMR ($CDCl_3$): δ 0.91 (t, 3 H, ${}^3J$ = 7.5 Hz, $CH_2\mathit{CH_3}$), 1.16 (t, 3 H, ${}^3J$ = 7.2 Hz, $CH_2\mathit{CH_3}$), 1.24 (t, 3 H, ${}^3J$ = 7.1 Hz, $\mathit{CH_3}$), 1.66 (m, 2 H, $\mathit{CH_2}CH_3$), 1.90 (d, 3 H, ${}^4J$ = 1.3 Hz, $\mathit{CH_3}$), 3.46 (dq, 1 H, ${}^3J$ = 7.1 Hz, ${}^2J$ = 7.0 Hz, $\mathit{CH_2}CH_3$), 4.09 (dq, 1 H, ${}^3J$ = 7.1 Hz, ${}^2J$ = 7.0 Hz, $\mathit{CH_2}CH_3$), 5.01 (m, 1 H, γ-*CH*) ppm. ^{13}C NMR $(CDCl)_3$: δ 11.11 ($\mathit{C}H_3$), 13.02 ($\mathit{C}H_3$), 22.51 ($\mathit{C}H_3$), 44.54 ($\mathit{C}H_2CH_3$), 46.53 ($\mathit{C}H_2CH_3$), 126.49 (γ-*C*H), 137.00 (β-*C*), 200.76 (C=S) ppm.

N,N-Diethyl-3-methylbut-2-enethioamide (6′). The acid chloride, prepared in 86% yield from 3-methylbutenoic acid (70 mmol) in refluxing benzene with thionyl chloride (270 mmol) for 1 h, was converted to the amide in 89% yield using *N,N*-diethylamine.

The thioamide was prepared from the amide (20 mmol) by refluxing in toluene with Lawesson's reagent (12 mmol) for 5 h. Purification on silica gel using hexanes–ether (9:1) gave 6′ in 80% yield as a yellow oil. Bp: 130 °C/12 mmHg. MS (*m*/*e*): 171 $(M)^+$. ^1H NMR ($CDCl_3$): δ 1.04 (t, 3 H, ${}^3J$ = 7.2 Hz, $CH_2\mathit{CH_3}$), 1.15 (t, 3 H, ${}^3J$ = 7.1 Hz, $CH_2\mathit{CH_3}$), 1.59 (s, 3 H, $\mathit{CH_3}$), 1.66 (s, 3 H, $\mathit{CH_3}$), 3.46 (q, 2 H, ${}^3J$ = 7.2 Hz, $\mathit{CH_2}CH_3$), 3.87 (q, 2 H, ${}^3J$ = 7.2 Hz, $\mathit{CH_2}CH_3$), 5.79 (s, 1 H, β-*CH*) ppm. ^{13}C NMR ($CDCl_3$): δ 10.61 ($CH_2\mathit{C}H_3$), 12.66 ($CH_2\mathit{C}H_3$), 18.66 ($\mathit{CH_3}$), 24.41 ($\mathit{CH_3}$), 44.95 ($\mathit{C}H_2CH_3$), 46.17 ($\mathit{C}H_2CH_3$), 125.01 (β-*C*H), 134.66 (γ-C), 195.73 (C=S) ppm.

N-Methyl-N-phenylbut-2-enethioamide (7′). The amide was prepared in 96% yield from crotonyl chloride and *N*-methylaniline. The thioamide was then formed from the amide (20 mmol) by refluxing in toluene with Lawesson's reagent (12 mmol) for 23 h. Purification on silica gel using hexanes–ether (9:1) gave orange 7′ in 73% yield. Mp: 82–83 °C. MS (*m*/*e*): 191 $(M)^+$. ^1H NMR ($CDCl_3$): δ 1.62 (dd, 3 H, ${}^3J$ = 7.0 Hz, ${}^4J$ = 1.6 Hz, $\mathit{CH_3}$), 3.71 (s, 3 H, $N\mathit{CH_3}$), 5.85 (d, 1 H, ${}^3J$ = 15.0 Hz, β-*CH*), 7.10 (m, 3 H, γ-*CH* and two aromatic protons), 7.40 (m 3 H, aromatics) ppm. ^{13}C NMR ($CDCl_3$): 18.28 ($\mathit{C}H_3$), 45.46 ($N\mathit{C}H_3$), 125.71, 127.88, 129.42 (aromatic *C*H), 129.83 (β-*C*H), 143.34 (γ-*C*H), 195.58 (C=S) ppm.

N-Methyl-N-phenyl-2-methylprop-2-enethioamide (8′). The amide was obtained in 85% yield from acryloyl chloride and *N*-methylaniline. The thioamide was prepared from the amide (20 mmol) by refluxing in toluene with Lawesson's reagent (12 mmol) for 23 h. Silica gel chromatography using hexanes–ether (9:1) gave 8′ as an orange oil in 58% yield. Bp: 238 °C (lit. bp 70 °C/0.7 mmHg).[28] MS (*m*/*e*): 191 $(M)^+$. ^1H NMR ($CDCl_3$): δ 1.82 (s, 3 H, CH_3), 3.74 (s, 3 H, $N\mathit{CH_3}$), 4.78 (s, 2 H, $\mathit{CH_2}$), 7.11–7.38 (m, 5 H, aromatics) ppm. ^{13}C NMR ($CDCl_3$): δ 22.60 ($\mathit{C}H_2$), 44.98 (NCH_3), 115.00 ($\mathit{C}H_2$), 125.00, 127.60, 129.60 (aromatic *C*H), 146.82 (quaternary *C*), 190.82 (C=S) ppm.

N,N-Diethyl-3-methylprop-2-enethioamide (9′). The amide was formed in 83% yield from acryloyl chloride and diethylamine. The thioamide was prepared from the amide (20 mmol) by refluxing in toluene with Lawesson's reagent (12 mmol) for 2 h. Purification on a dry-packed silica column using hexanes–ether (9:1) gave 9′ in 27% yield. Bp: 218–220 °C. MS (*m*/*e*): 157 $(M)^+$. ^1H NMR ($CDCl_3$): δ 1.19 (t, 3 H, ${}^3J$ = 7.2 Hz, $NCH_2\mathit{CH_3}$), 1.24 (t, 3 H, ${}^3J$ = 7.2 Hz, $NCH_2\mathit{CH_3}$), 2.01 (dd, 3 H, ${}^4J$ = 1.6, 1.0 Hz, $\mathit{CH_3}$), 3.55 (q, 2 H, ${}^3J$ = 7.2 Hz, $N\mathit{CH_2}CH_3$), 3.93 (q, 2 H, ${}^3J$ = 7.2 Hz, $N\mathit{CH_2}CH_3$), 4.81 (m, 1 H, γ-$\mathit{CH_2}$), 4.86 (m, 1 H, γ-$\mathit{CH_2}$) ppm. ^{13}C NMR ($CDCl_3$): 11.03 ($NCH_2\mathit{C}H_3$), 14.10 ($NCH_2\mathit{C}H_3$), 45.02 ($N\mathit{C}H_2CH_3$), 47.10 ($N\mathit{C}H_2CH_3$), 111.09 (γ-$\mathit{C}H_2$), 146.79 (β-*C*), 201.45 (C=S) ppm.

Ethyl 3-Phenylpropenethioate (10′). Ethyl cinnamate (50 mmol) was refluxed for 16 h in a solution of Lawesson's reagent (30 mmol) in toluene (150 mL). Workup as described for 1′ gave 10′ in 70% yield. Bp: 135 °C/10 mmHg (lit.[18] 40 °C/12 mmHg). MS (*m*/*e*): 192 $(M)^+$. ^1H NMR ($CDCl_3$): δ 1.50 (t, 3 H, ${}^3J$ = 7.1 Hz, $CH_2\mathit{CH_3}$), 4.63 (q, 2 H, ${}^3J$ = 7.1 Hz, $\mathit{CH_2}CH_3$), 7.02 (d, 1 H, ${}^3J$ = 15.7 Hz, β-*CH*), 7.38 (m, 5 H, Ph), 7.69 (d, 1 H, ${}^3J$ = 15.7 Hz, γ-*CH*) ppm. ^{13}C NMR ($CDCl_3$): δ 13.79 ($CH_2\mathit{C}H_3$), 67.71 ($\mathit{C}H_2CH_3$), 113.80 (β-*C*H), 128.10, 128.69, 129.99 (aromatic CH), 140.09 (γ-*C*H), 163.85 (quaternary aromatic C), 209.87 (C=S) ppm.

Ethyl But-2-enethioate (11′). Ethyl crotonate (44 mmol) was refluxed for 2 h in a solution of Lawesson's reagent (44 mol) in *p*-xylene (40 mL). The sample was cooled and placed directly on a dry-packed silica column and eluted with hexanes–ether (9:1). The volatile solvents were removed by rotary evaporation with no heating. Distillation of the remaining liquid gave an impure yellow oil. The oil was purified on a dry-packed silica column with hexanes–ether (9:1) and distilled to give pure 11′ in 50% yield. Bp: 130 °C/0.25 mmHz (lit.[18] 60 °C/ 10 mmHg). MS (*m*/*e*): 130 $(M)^+$. ^1H NMR ($CDCl_3$): δ 1.39 (t, 3 H, ${}^3J$ = 7.1 Hz, $CH_2\mathit{CH_3}$), 1.82 (dd, 3 H, ${}^3J$ = 6.9 Hz, ${}^3J$ = 1.7 Hz, $\mathit{CH_3}$), 4.51 (q, 2 H, ${}^3J$ = 7.1 Hz, $\mathit{CH_2}CH_3$), 6.38 (d, 1 H, ${}^3J$ = 15.6 Hz, β-*CH*), 6.96 (dq, 1 H, ${}^3J$ = 15.6 Hz, ${}^4J$ = 6.6 Hz, γ-*CH*) ppm. ^{13}C NMR ($CDCl_3$): δ 13.78 ($CH_2\mathit{C}H_3$), 18.02 ($\mathit{C}H_3$), 67.55 ($\mathit{C}H_2CH_3$), 133.63 (β-*C*H), 140.46 (γ-*C*H), 210.68 (C=S) ppm.

General Methods for the Preparation of Complexes 1–11. Method A. To a stirred suspension of $[Fe_2(CO)_9]$ (1.5 equiv) in freshly distilled benzene was added, dropwise, a solution of the α,β-unsaturated thiocarbonyl (1 equiv) in benzene. The mixture was stirred for 48 h or until the formation of extraneous products as indicated by TLC. (Reactions which were carried out at 40 °C generally required less time.) The solution was then filtered, and the solvent was reduced by rotary evaporation. Column chromatography on silica using 9:1 hexanes–ether or on neutral alumina using hexane as eluant gave two fractions. The first fraction which was deep red was characterized as $[S_2Fe_2(CO)_6]$ by IR and ^{13}C NMR spectroscopy. The second fraction which was orange corresponded to the desired organometallic complex.

Method B. To a stirred solution of $[Fe(CO)_5]$ (1.2 equiv) in degassed cyclohexane was added a cyclohexane solution of the α,β-unsaturated thiocarbonyl (1 equiv). The solution was photolyzed (medium-pressure, 450-W Hanovia mercury lamp), and the reaction was followed by IR spectroscopy and TLC. Generally, the reaction required 18 h, the solution was then filtered, and the solvent was concentrated by rotary evaporation. Column chromatography on Florisil using hexane as eluant gave two fractions. The first fraction was orange and corresponded to the desired organometallic complex. A second fraction was collected and identified as unreacted thiocarbonyl.

Complex 1. Complex 1 was isolated in 44% yield by method A, and in 22% yield by method B.

Purification on silica gel using hexane as eluant gave an orange oily solid. Dissolving the latter in pentane and cooling to −78 °C afforded an orange powder, which, on recrystallization from pentane at −30 °C, gave needlelike crystals of 1. Mp: 67–70 °C. Anal. Calcd for $C_{16}H_{17}NO_3SFe$: C, 53.48; H, 4.74; N, 3.90; S, 8.91. Found: C, 53.80; H, 4.89; N, 3.94; S, 9.33. MS (*m*/*e*): 303 $(M - 2CO)^+$, 275 $(M - 3CO)^+$, 219 $(Ligand)^+$. IR ($CHCl_3$): ν(CO) 2030 (s), 1965 (vs, br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.30 (t, 6 H, ${}^3J$ = 6.9 Hz, $CH_2\mathit{CH_3}$), 3.47 (d, 1 H, ${}^3J$ = 7.7 Hz, γ-*CH*), 3.55 (dq, 2

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[28] Bonnans-Plaisance, C.; Levesque, G. *Macromol. Chem., Rapid Commun.* **1985**, *6*, 145.

H, ^3J = 6.9 Hz, ^2J = 6.9 Hz, CH_2CH_3), 3.77 (dq, 2 H, ^3J = 6.9 Hz, ^2J = 6.9 Hz, CH_2CH_3), 5.04 (d, 1 H, ^3J = 7.7 Hz, β-CH), 7.25 (m, 5 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ 11.59 (CH_2CH_3), 45.76 (CH_2CH_3), 52.42 (γ-CH), 63.93 (β-CH), 125.74, 126.20, 128.51 (aromatic CH), 142.30 (quaternary aromatic C), 161.69 (C=S), 210.50 (C=O) ppm.

Complex 2. Complex **2** was isolated in 22% yield by using method A at 40 °C.

Purification on silica gel using hexane–ether (9:1) gave an oily solid, which on treatment with pentane at −78 °C became an orange solid. Recrystallization from pentane at −30 °C gave needlelike crystals. Mp: 105–108 °C. Anal. Calcd for $C_{22}H_{21}NO_3SFe$: C, 60.69; H, 4.83; N, 3.22; S, 7.36. Found: C, 61.12; H, 5.20; N, 3.34; S, 7.17. MS (m/e): 295 (Ligand)$^+$. IR ($CHCl_3$): ν(CO) 2020 (s), 1950 (vs, br) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 0.36 (t, 3 H, ^3J = 7.2 Hz, CH_2CH_3), 1.11 (t, 3 H, ^3J = 7.1 Hz, CH_2CH_3), 3.02 (m, 2 H, CH_2CH_3), 3.66 (dq, 1 H, ^3J = 7.2 Hz, ^2J = 7.1 Hz, CH_2CH_3), 3.94 (dq, 1 H, ^3J = 7.2 Hz, ^2J = 7.1 Hz, CH_2CH_3), 5.17 (s, 1 H, γ-CH), 7.14 and 7.64 (m, 10 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ 10.51 (CH_2CH_3), 12.91 (CH_2CH_3), 45.02 (CH_2CH_3), 47.66 (CH_2CH_3), 66.18 (γ-C), 126.77, 127.68, 128.02, 128.75, 129.55, 130.30 (aromatic CH), 135.57, 138.31 (quaternary aromatic C), 141.20 (C=S); 210.00 (C=O) ppm.

Complex 3. Complex **3** was isolated in 66% yield by using method B.

Purification on a neutral alumina column using hexane–ether (8:2) afforded an orange solid. Recrystallization from pentane at −30 °C resulted in needlelike crystals. Mp: 85 °C dec. Anal. Calcd for $C_{21}H_{17}NO_3SFe$: C, 60.16; H, 4.09; N, 3.34; S, 7.64. Found: C, 60.57; H, 4.14; N, 3.21; S, 7.13. MS (m/e): 363 (M − 2CO)$^+$, 335 (M − 3CO)$^+$. IR ($CHCl_3$): ν(CO) 2045 (s), 1983 (vs, br) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 3.63 (d, 1 H, ^3J = 8.2 Hz, γ-CH), 3.96 (dd, 1 H, ^3J = 15.4 Hz, ^2J = 6.1 Hz, NCH_2CHCH_2), 4.57 (dd, 1 H, ^3J = 15.4 Hz, ^2J = 6.1 Hz, NCH_2CHCH_2), 4.90 (m, 2 H, NCH_2CHCH_2), 5.11 (d, 1 H, ^3J = 8.2 Hz, β-CH), 5.69 (ddt, 1 H, ^3J = 15.4 Hz, ^3J = 6.0 Hz, NCH_2CHCH_2), 6.88 (m, 2 H, aromatics), 7.03 (s, 5 H, aromatics) ppm. ^{13}C NMR (benzene-d_6): δ 57.28 ($NCH_2CH{=}CH_2$), 60.16 (γ-CH), 63.30 (β-CH), 118.79 ($NCH_2CH{=}CH_2$), 126.51 ($NCH_2CH{=}CH_2$), 127.25, 128.03, 128.33, 128.94, 130.39, 131.86 (aromatic CH), 141.30, 143.61 (quaternary aromatic C), 155.85 (C=S), 209.43 (C=O) ppm.

Complex 4. Complex **4** was isolated in 29% yield by using method A, and in 22% yield by using method B.

Purification by column chromatography on neutral alumina using hexanes afforded an orange oil, which was crystallized from pentane at −78 °C. Mp: 36–39 °C. Anal. Calcd for $C_{11}H_{15}NO_3SFe$: C, 44.44; H, 5.05; N, 4.71; S, 10.71. Found: C, 44.31; H, 5.20; N, 4.75; S, 10.72. MS (m/e): 297 (M)$^+$, 269 (M − 1CO)$^+$, 241 (M − 2CO)$^+$, 213 (M − 3CO)$^+$, 157 (Ligand)$^+$. IR ($CHCl_3$): ν(CO) 2025 (s), 1955 (vs) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 0.74 (t, 6 H, ^3J = 7.1 Hz, CH_2CH_3), 1.44 (d, 3 H, ^4J = 6.3 Hz, CH_3), 2.53 (dq, 1 H, ^3J = 7.3 Hz, ^4J = 6.3 Hz, γ-CH), 2.70 (2 overlapping q, 2 H, ^3J = 7.1 Hz, CH_2CH_3), 3.04 (2 overlapping q, 2 H, ^3J = 7.1 Hz, CH_2CH_3), 4.10 (d, 1 H, ^3J = 7.3 Hz, β-CH) ppm. ^{13}C NMR ($CDCl_3$): δ 11.48 (CH_2CH_3), 19.99 (CH_3), 45.46 (CH_2CH_3), 58.78 (γ-CH), 59.85 (β-CH), 159.69 (C=S), 210.39 (C=O) ppm.

Complex 5. Complex **5** was isolated in 5.5% yield by using method A, and in 49% yield by using method B.

Purification by column chromatography on neutral alumina using hexanes resulted in isolation of an oil. Orange thermally sensitive crystals were obtained at 0 °C, but the solid melted and decomposed at room temperature. MS (m/e): 297 (M − 1CO)$^+$, 269 (M − 2CO)$^+$, 241 (M − 3CO)$^+$, 185 (Ligand)$^+$. IR ($CHCl_3$): ν(CO) 2050 (s), 2020 (s, sh), 2010 (s), 1980 (s, sh), 1960 (vs) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 0.74 (m, 9 H, CH_2CH_3, β-CH_3), 1.13 (m, 1 H, γ-CH), 1.48 (s, 1 H, γ-CH_2CH_3), 2.81 (m, 2 H, CH_2CH_3), 2.95 (dq, 1 H, ^3J = 7.1 Hz, ^2J = 6.7 Hz, CH_2CH_3), 3.17 (dq, 1 H, ^3J = 7.1 Hz, ^2J = 6.7 Hz, CH_2CH_3) ppm. ^{13}C NMR (benzene-d_6): δ 11.75 (CH_2CH_3), 14.72 (CH_2CH_3), 27.00 (CH_3), 44.32 (CH_3), 44.95 (CH_2CH_3), 46.22 (γ-CH), 92.52 (β-C), 143.01 (C=S), 211.40 (C=O) ppm.

Complex 6. Preparation by method A at room temperature gave **6** in only 2% yield, but method B afforded **6** in 67% yield.

Purification by column chromatography on neutral alumina using hexanes–ether (7:3) gave an oil, which could be crystallized as an orange solid at 0 °C. When warmed to room temperature, **6** melted and decomposed. MS (m/e): 451 (M)$^+$, 423 (M − 1CO)$^+$, 395 (M − 2CO)$^+$, 367 (M − 3CO)$^+$, 339 (M − 4CO)$^+$, 171 (Ligand)$^+$. IR ($CHCl_3$): ν(CO) 2050 (m), 2010 (s), 1985 (s), 1960 (s, sh), 1940 (sh, m) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 0.47 (t, 3 H, ^3J = 7.2 Hz, CH_2CH_3), 0.70 (s, 3 H, CH_3), 0.96 (t, 3 H, ^3J = 7.2 Hz, CH_2CH_3), 1.73 (s, 3 H, CH_3), 2.41 (m, 2 H, CH_2CH_3), 2.63 (s, 1 H, β-CH), 3.33 (dq, 1 H, ^3J = 6.8 Hz, ^2J = 6.7 Hz, CH_2CH_3), 3.65 (dq, 1 H, ^3J = 6.8 Hz, ^2J = 6.7 Hz, CH_2CH_3) ppm. ^{13}C NMR (benzene-d_6): δ 12.94 (CH_2CH_3), 13.01 (CH_2CH_3), 30.98 (CH_3), 40.32 (CH_3), 46.02 (CH_2CH_3), 46.42 (CH_2CH_3), 49.55 (β-CH), 54.45 (γ-C) ppm.

Complex 7. Complex **7** was isolated in 60% yield by using method B.

Purification by column chromatography on neutral alumina using hexane–ether (8:2) gave an orange oil, which was crystallized from pentane at −78 °C. Mp: 39–41 °C. Anal. Calcd for $C_{14}H_{13}NO_3SFe$: C, 50.57; H, 3.93; N, 4.23. Found: C, 50.35; H, 4.18; N, 4.28. MS (m/e): 331 (M)$^+$, 303 (M − 1CO)$^+$, 275 (M − 2CO)$^+$, 247 (M − 3CO)$^+$, 191 (Ligand)$^+$. IR ($CHCl_3$): ν(CO) 2025 (s), 1975 (vs, br) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 1.11 (d, 3 H, ^3J = 6.1 Hz, γ-CH_3), 2.28 (dq, 1 H, ^3J = 7.8 Hz, ^3J = 6.1 Hz, γ-CH), 2.98 (s, 3 H, NCH_3), 4.41 (d, 1 H, ^3J = 7.8 Hz, β-CH), 7.02 (m, 5 H, Ph) ppm. ^{13}C NMR (benzene-d_6): δ 19.24 (CH_3), 42.21 (NCH_3), 60.85 (β-CH), 67.59 (γ-CH), 125.93, 127.34, 130.24 (aromatic CH), 145.37 (aromatic quaternary C), 152.95 (C=S), 209.98 (C=O) ppm.

Complex 8. Complex **8** was isolated in 58% yield by using method B.

Purification by column chromatography on neutral alumina using hexane–ether (8:2) gave an oil, which crystallized as an orange solid from pentane at −78 °C. Mp: 74–76 °C. Anal. Calcd for $C_{14}H_{13}NO_3SFe$: C, 50.76; H, 3.93; N, 4.23; S, 9.67. Found: C, 50.71; H, 4.13; N, 3.91; S, 9.79. Chemical Ionization MS (m/e): 332 (M + 1)$^+$, 276 (M + 1 − 2CO)$^+$, 248 (M + 1 − 3CO)$^+$, 192 (Ligand + 1)$^+$. IR ($CHCl_3$): ν(CO) 2060 (s), 1990 (vs, br) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 1.44 (s, 3 H, CH_3), 1.62 (s, 1 H, CH_2), 1.93 (s, 1 H, CH_2), 3.12 (s, 3 H, NCH_3), 6.72–6.96 (m, 5 H, Ph) ppm. ^{13}C NMR (benzene-d_6): δ 23.98 (CH_3), 43.22 (NCH_3), 51.45 (γ-C), 92.85 (β-C), 123.04, 123.90, 129.54 (aromatic CH), 148.96 (C=S), 208.22 (C=O) ppm.

Complex 9. Complex **9** was isolated in 30% yield by using method B.

Purification by column chromatography on neutral alumina using hexane–ether (8:2) afforded an orange oil, which was crystallized from pentane at −78 °C. Mp: 23 °C. MS (m/e): 297 (M)$^+$, 269 (M − 1CO)$^+$, 241 (M − 2CO)$^+$, 213 (M − 3CO)$^+$, 157 (Ligand)$^+$. Anal. Calcd for $C_{11}H_{15}NO_3SFe$: C, 44.46; H, 5.09; N, 4.71. Found: C, 44.81; H, 5.06; N, 5.01. IR ($CHCl_3$): ν(CO) 2040 (s), 1965 (vs, br) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 0.74 (t, 6 H, ^3J = 7.1 Hz, NCH_2CH_3), 1.75 (s, 3 H, CH_3), 2.21 (s, 1 H, γ-CH_2), 2.28 (s, 1 H, γ-CH_2), 2.91 (dq, 2 H, ^3J = 7.1 Hz, ^2J = 7.1 Hz, NCH_2CH_3), 3.01 (dq, 2 H, ^3J = 7.1 Hz, ^2J = 7.1 Hz, NCH_2CH_3) ppm. ^{13}C NMR (benzene-d_6): δ 12.85 (NCH_2CH_3), 26.11 (CH_3), 46.47 (NCH_2CH_3), 54.07 (γ-CH_2), 67.30 (β-C), 148.07 (C=S), 210.77 (C=O) ppm.

Complex 10. Complex **10** was isolated in 51% yield by using method A.

Purification by column chromatography on Florisil using hexanes–ether (9:1) gave an orange oil, which crystallized from pentane at −78 °C. MS (m/e): 332 (M)$^+$, 304 (M − 1CO)$^+$, 276 (M − 2CO)$^+$, 248 (M − 3CO)$^+$, 192 (Ligand)$^+$. Anal. Calcd for $C_{14}H_{12}NO_4SFe$: C, 50.60; H, 3.61; N, 9.64. Found: C, 50.84; H, 3.67; N, 9.94. IR ($CHCl_3$): ν(CO) 2050 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.40 (overlapping dd, 3 H, ^3J = 7.1 Hz, CH_2CH_3), 2.70 (d, 1 H, ^3J = 8.8 Hz, γ-CH), 3.95 (dq, 1 H, ^3J = 7.1 Hz, ^2J = 3.4 Hz, CH_2CH_3), 6.18 (d, 1 H, ^3J = 8.8 Hz, β-CH), 7.27 (m, 5 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ 14.36 (CH_2CH_3), 63.30 (γ-CH), 67.24 (CH_2CH_3), 71.53 (β-CH), 126.55 (aromatic CH), 126.77 (quaternary aromatic C), 128.71, 139.08 (aromatic CH), 155.00 (C=S), 207.87 (C=O) ppm.

Complex 11. Complex **11** was isolated in 36% yield by using method A.

Purification by column chromatography on silica using hexanes–ether (9:1) resulted in an orange oil, which could not be solidified. MS (m/e): 270 (M)$^+$, 242 (M − 1CO)$^+$, 214 (M − 2CO)$^+$, 186 (M − 3CO)$^+$, 130 (Ligand)$^+$. IR ($CHCl_3$): ν(CO) 2025 (s), 1993 (vs) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 0.99 (t, 3 H, ^3J = 7.1 Hz, CH$_2$CH$_3$), 1.06 (d, 3 H, ^3J = 6.4 Hz, γ-CH$_3$), 1.45 (dq, 1 H, ^3J = 8.3 Hz, ^3J = 6.4 Hz, γ-CH), 3.68 (dq, 1 H, ^3J = 7.1 Hz, ^3J = 7.0 Hz, CH$_2$CH$_3$), 3.97 (dq, 1 H, ^3J = 7.1 Hz, ^3J = 7.0 Hz, CH$_2$CH$_3$), 5.16 (d, 1 H, ^3J = 8.3 Hz, β-CH) ppm. ^{13}C NMR (benzene-d_6): δ 14.45 (CH$_2$CH$_3$), 18.49 (γ-CH$_3$), 59.84 (γ-CH), 67.22 (CH$_2$CH$_3$), 77.79 (β-CH), 155.52 (C=S), 209.00 (C=O) ppm.

Reaction of 1, 7, or 10 with PPh$_3$. 13: R = Ph, X = NEt$_2$. Triphenylphosphine (0.84 mmol) was added to a stirred solution of complex 1 (0.84 mmol) in dry benzene (50 mL). The solution was refluxed for 2 h, cooled to room temperature, and concentrated. Purification of the residue on a neutral alumina column using hexanes–ether (8:2) afforded 13 (R = Ph, X = NEt$_2$) as an orange solid in 26% yield. Mp: 95 °C decomp. Anal. Calcd for C$_{33}$H$_{32}$NO$_2$PSFe: C, 66.78; H, 5.40; S, 2.36. Found: C, 66.67; H, 5.47; S, 2.27. CI-MS (m/e): 374 [Fe(CO)$_2$(PPh$_3$)]$^+$. IR (CHCl)$_3$: ν(CO) 1977 (vs), 1917 (s) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 0.99 (t, 6 H, ^3J = 7.1 Hz, CH$_2$CH$_3$), 2.59 (apparent t, 1 H, ^3J = 8.1 Hz, γ-CH), 2.94 (dq, 1 H, ^3J = 7.1 Hz, ^2J = 7.0 Hz, CH$_2$CH$_3$), 3.48 (dq, 1 H, ^3J = 7.0 Hz, CH$_2$CH$_3$), 5.23 [dd, 1 H, ^3J = 8.1 Hz, ^3J(HP) = 2.7 Hz, β-CH], 6.81–7.58 (m, 20 H, aromatics) ppm. ^{13}C NMR (benzene-d_6): δ 11.89 (CH$_2$CH$_3$), 45.56 (CH$_2$CH$_3$), 59.38 (γ-CH), 66.18 (β-CH), 124.79, 126.12, 127.86, 128.82, 129.55, 133.99, 134.25 (aromatic CH), 136.82, 144.92 (quaternary aromatic carbons), 152.87 (C=S), 211.24 [^2J(PC) = 5.6 Hz, C=O], 215.50 [^2J(PC) = 12.0 Hz, C=O] ppm. ^{31}P NMR (benzene-d_6): δ 55.95 ppm.

13: R = Me, X = N(Ph)Me. A solution of PPh$_3$ (0.90 mmol) in THF (4 mL) was added to a stirred degassed solution of complex 7 (0.90 mmol) in C$_6$H$_{12}$ (16 mL). The solution was photolyzed for 22 h. The solvent was reduced by rotary evaporation and the solution was chromatographed on neutral alumina with hexanes–ether (3:2). Recrystallization from ether–hexanes at −10 °C resulted in the formation of deep orange crystals in 85% yield. Mp: 134–137 °C. MS (m/e): 537 (M − PPh$_3$)$^+$, 481 (M − PPh$_3$ − 2CO)$^+$, 191 (Ligand)$^+$. IR (CHCl$_3$): ν(CO) 1975 (s), 1914 (s) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 0.96 (d, 3 H, ^3J = 6.1 Hz, 1 CH$_3$), 1.32 (m, 1 H, ^3J = 6.6, 6.1 Hz, β-CH), 3.33 (s, 3 H, NCH$_3$), 4.75 (d, 1 H, ^3J = 6.6 Hz, β-CH), 7.04–7.79 (20 H, aromatic protons) ppm. ^{13}C NMR (benzene-d_6): δ 18.44 ppm (CH$_3$), 42.22 (NCH$_3$), 61.92 (γ-CH), 72.86 (β-CH), 126.34, 129.64, 130.02, 131.53, 132.33, 132.45, 132.69, 132.85, 133.36, 133.50 (aromatic CH), 136.80, 137.29 (aromatic quaternary C), 147.02 (C=S), 216.53, 210.39 (C=O) ppm. ^{31}P NMR (benzene-d_6): δ 61.99 ppm.

13: R = Ph, X = OEt. Triphenylphosphine (1.60 mmol) was added to a stirred solution of complex 10 (1.60 mmol) in dry benzene (50 mL). The solution was refluxed for 2 h, cooled, and concentrated. The sample was purified on a neutral alumina column with hexanes–ether (8:2) affording 13 as an orange solid in 76% yield. Mp: 143–146 °C. Anal. Calcd for C$_{31}$H$_{27}$O$_3$PSFe: C, 65.73; H, 4.80; S, 5.66. Found: C, 65.55; H, 4.87; S, 6.02. MS (m/e): 262(PPh$_3$)$^+$. IR (CHCl$_3$): ν(CO) 1995 (s), 1939 (s) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 1.17 (t, 3 H, ^3J = 7.1 Hz, CH$_2$CH$_3$), 2.02 (m, 1 H, γ-CH), 4.08 (m, 1 H, CH$_2$CH$_3$), 4.31 (m, 1 H, CH$_2$CH$_3$), 6.23 (d, 1 H, ^3J = 9.0 Hz, β-CH), 6.96 (s, 13 H, aromatics), 6.54 (s, 2 H, aromatics), 7.46 (m, 5 H, aromatics) ppm. ^{13}C NMR (benzene-d_6): δ 14.80 (CH$_2$CH$_3$), 65.67 (γ-CH), 66.76 (CH$_2$CH$_3$), 75.62 (β-CH), 125.51, 126.52, 128.56, 129.90, 133.40, 133.53 (aromatic CH), 135.95, 142.00 (quaternary aromatic C), 151.45 (C=S), 208.14, 212.99 (C=O) ppm. ^{31}P NMR (benzene-d_6): δ 54.33 ppm (s).

Ligand Recovery Using [Ce(NH$_4$)$_2$(NO$_3$)$_6$]. To a stirred aqueous acetone solution of the complex, 0.3 mmol of 1, 4, or 10 cooled to 0 °C, was added [Ce(NH$_4$)$_2$(NO$_3$)$_6$] in small portions until bubbling ceased. The solution was then extracted with ether (3 × 100 mL), and the combined organic layers were washed with water (3 × 100 mL), dried (MgSO$_4$), and concentrated to give the thioamide or thioester.

Reaction of 1, 4, or 7 with Alkynes. Complex 14. To a cold (0 °C) stirred solution of complex 7 (0.222 g, 0.67 mmol) dissolved in THF (6 mL) under a CO atmosphere was added, dropwise, a THF (12 mL) solution of dimethylacetylenedicarboxylate (DMAD, 0.67 mmol). The solution was allowed to warm to room temperature and then refluxed with stirring for 2 h. The solvent was reduced by rotary evaporation, and the sample was purified on a neutral alumina column with CHCl$_3$–ether (1:1), giving two fractions. The first fraction, which was orange, corresponded to unreacted complex 7 and the yellow second fraction was the desired product. The resulting yellow oil was crystallized from CHCl$_3$–ether at 0 °C to give 14 in 69% yield. Mp: 130 °C. Anal. Calcd for C$_{21}$H$_{19}$NO$_8$SFe: C, 50.30; H, 3.79; N, 2.79; S, 6.39. Found: C, 50.52; H, 3.99; N, 2.90; S, 6.06. IR (CHCl$_3$): ν(CO) 2060 (s), 1998 (s, sh), 1985 (s), 1690 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.12 (d, 3 H, ^3J = 7.0 Hz, CHCH$_3$), 2.59 (q, 1 H, ^3J = 7.0 Hz, CHCH$_3$), 2.63 (s, 3 H, NCH$_3$), 2.82 (s, 1 H, CH), 3.73 (s, 3 H, OCH$_3$), 3.74 (s, 3 H, OCH$_3$), 7.45 (m, 5 H, Ph) ppm. ^{13}C NMR (benzene-d_6): δ 20.98 (CHCH$_3$), 42.34 (CHCH$_3$), 43.58 (NCH$_3$), 50.94 (OCH$_3$), 53.07 (OCH$_3$), 63.46 (CH), 66.52, 67.06 (olefin carbons), 127–129 (aromatic CH), 143.19 (aromatic quaternary C), 169.23, 173.85 (ester carbonyls), 205.32, 206.47, 208.86, 210.38 (ketone, 3M − CO, and CS) ppm.

Complex 15. To a solution of thioamide iron complex 7 (0.67 mmol, 0.67 mmol) in THF (5 mL) was added dropwise a solution of n-butyl propynoate (0.67 mmol) in THF (10 mL) at room temperature (CO atmosphere). The solution was refluxed for 2 h, and the solvent was removed by rotary evaporation. Purification on neutral alumina with CHCl$_3$–ether (1:1) gave unreacted starting material followed by 15, which was purified by crystallization from CHCl$_3$–ether at 0 °C. Yield: 11%. Mp: 130 °C. Anal. Calcd for C$_{22}$H$_{23}$NO$_6$SFe: C, 54.43; H, 4.96; N, 2.89; S, 6.60. Found: C, 54.62; H, 5.07; N, 2.96; S, 6.53. IR (CHCl$_3$): ν(CO) 2085 (w), 2050 (s), 1985 (s), 1970 (s), 1720 (m), 1690 (m, br) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 0.68 (d, 3 H, ^3J = 7.0 Hz, CHCH$_3$), 0.82 [t, 3 H, ^3J = 7.3 Hz, O(CH$_2$)$_3$CH$_3$], 1.42 [tq, 2 H, ^3J = 7.3 Hz, ^3J = 6.5 Hz, O(CH$_2$)$_2$CH$_2$CH$_3$], 1.58 (m, 2 H, OCH$_2$CH$_2$CH$_2$CH$_3$), 2.11 (q, 1 H, ^3J = 7.1 Hz, CHCH$_3$), 2.55 (s, 1 H, CH), 2.62 (s, 3 H, NCH$_3$), 4.15 [dt, 1 H, ^2J = 10.9 Hz, OCH$_2$(CH$_2$)$_2$CH$_3$], 4.23 [dt, 1 H, OCH$_2$(CH$_2$)$_2$CH$_3$], 4.60 (s, 1 H, olefinic proton), 6.73–6.78 (m, 5 H, Ph) ppm.

Complex 16. To a stirred solution of thioamide iron complex 7 (1.00 g, 0.30 mmol) in ether (30 mL) at room temperature was added methyl propynoate (0.05 g, 0.60 mmol). Carbon monoxide was bubbled through the solution for 15 h at reflux temperature. Workup was effected by rotary evaporation and column chromatography of the residue on neutral alumina using CHCl$_3$ as the eluant. Complex 16 was obtained as yellow crystals in 78% yield. Mp: 135 °C dec. Anal. Calcd for C$_{19}$H$_{17}$NO$_6$SFe: C, 51.47; H, 3.84; N, 3.16. Found: C, 51.21; H, 4.04; N, 2.95. CI-MS (m/e): 444 (M + 1)$^+$, 416 (M + 1 − CO)$^+$, 388 (M + 1 − 2CO)$^+$, 360 (M + 1 − 3CO)$^+$, 304 (Ligand + 1)$^+$. IR (CHCl$_3$): ν(CO) 2060 (s), 1990 (s), 1975 (s), 1725 (m), 1695 (m) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 0.67 (d, 3 H, ^3J = 7.0 Hz, CH$_3$), 2.10 (q, 1 H, ^3J = 7.0 Hz, CH), 2.54 (s, 1 H, CH), 2.60 (s, 3 H, NCH$_3$), 3.54 (s, 3 H, OCH$_3$), 4.57 (s, 1 H, olefin CH), 6.75 (m, 5 H, Ph) ppm. ^{13}C NMR (benzene-d_6): δ 23.22 (CH$_3$); 40.37 (CH$_2$CH), 43.24 (NCH$_3$), 51.22 (OCH$_3$), 54.86 (quaternary olefin C), 62.72 (CH), 63.67 (CH), 127–130 (aromatic CH), 143.08 (aromatic quaternary C), 170.43 [C(=O)OCH$_3$], 203.93, 205.87, 207.57, 208.38, 209.67 (ketone C=O, 3 M − CO's, C=S) ppm.

Complex 17. To a stirred solution of thioamide iron complex 4 (0.20 g, 0.67 mmol) in THF (30 mL) at room temperature was added dimethylacetylenedicarboxylate, DMAD, (1.35 mmol). Carbon monoxide was bubbled through the solution, which was heated to reflux for 6 h. Purification of the residue from rotary evaporation of THF by column chromatography on the neutral alumina with CHCl$_3$–ether (1:1) as eluant, gave yellow crystals of 17 in 81% yield. Mp: 120 °C dec. Anal. Calcd for C$_{18}$H$_{21}$NO$_8$SFe: C, 46.25; H, 4.50; N, 3.00. Found: C, 46.37; H, 4.75; N, 2.86. CI-MS (m/e): 468 (M + 1)$^+$, 412 (M + 1 − 2CO)$^+$, 384 (M + 1 − 3CO)$^+$, 328 (Ligand + 1)$^+$. IR (CHCl$_3$): ν(CO) 2065 (s), 2000 (s, sh), 1988 (s), 1728 (m), 1695 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.25 (m, 3 H, NCH$_2$CH$_3$), 1.33 (m, 3 H, NCH$_2$CH$_3$), 1.42 (d, 3 H, ^3J = 6.0 Hz, CH$_3$), 2.56 (q, 1 H, ^3J = 6.0 Hz, CH), 3.05 (s, 1 H, CH), 3.61 (m, 3 H, NCH$_2$CH$_3$), 3.74 (s, 6 H, OCH$_3$), 3.92 (m, 1 H, NCH$_2$CH$_3$) ppm. ^{13}C NMR (CDCl$_3$): δ 11.61 (CH$_3$), 15.11 (CH$_3$), 21.67 (CH$_3$), 41.90 (CH), 48.59 (NCH$_2$CH$_3$), 48.74 (NCH$_2$CH$_3$), 51.17 (CO$_2$CH$_3$), 61.85 (CH), 65.59 (olefin quaternary C), 169.23 (CO$_2$CH$_3$), 173.95 (CO$_2$CH$_3$), 203.77, 205.13, 206.98, 207.17, 208.84 (ketone C=O, 3 M − CO's, C=S) ppm.

Complex 18. To a stirred solution of thioamide iron complex 1 (0.100 g, 0.28 mmol) in cyclohexane (20 mL) at room temperature was added 0.040 g (0.28 mmol) of dimethylacetylenedicarboxylate (CO atmosphere). The solution was photolyzed for 3 h, and filtered, and the filtrate was concentrated. Purification of the residue by column chromatography on neutral alumina [$CHCl_3$–ether (1:1)] gave yellow crystals of **18** in 22% yield. Mp: 130 °C dec. Anal. Calcd for $C_{23}H_{23}NO_8SFe$: C, 52.17; H, 4.35; N, 2.65. Found: C, 52.09; H, 4.48; N, 2.69. CI-MS (*m/e*): 530 $(M + 1)^+$, 474 $(M + 1 - 2CO)^+$, 446 $(M + 1 - 3CO)^+$, 390 $(\text{Ligand} + 1)^+$. IR ($CHCl_3$): ν(CO) 2065 (s), 1998 (br, s), 1695 (m, br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.15 (t, 3 H, ^3J = 7.0 Hz, CH_2CH_3), 1.28 (t, 3 H, ^3J = 7.0 Hz, CH_2CH_3), 3.29 (s, 1 H, *CH*), 3.42 (s, 3 H, CO_2CH_3), 3.50 (m, 2 H, CH_2CH_3), 3.63 (s, 1 H, *CH*), 3.68 (m, 2 H, CH_2CH_3), 3.87 (s, 3 H, CO_2CH_3), 7.22–7.42 (m, 5 H, Ph) ppm.

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Supplementary Material Available: Tables of anisotropic temperature factors and torsion angles for 1, 2, and 14 (7 pages); listings of structure factors for 1, 2, and 14 (39 pages). Ordering information is given on any current masthead page.

Synthesis and Properties of Novel Organozinc Enolates of N,N-Disubstituted Glycine Esters. Molecular Structure of $[\mathrm{Et\overline{ZnOC(OMe){=}C(H)N}}(t\text{-}\mathrm{Bu})\mathrm{Me}]_4$

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This report describes the first detailed characterization of synthetically useful organozinc ester enolates both in the solid state and in solution. Reactions of *N*-(ethylzincio)diisopropylamine with *N,N*-dialkylglycine esters afford pure ethylzinc ester enolates $\mathrm{Et\overline{ZnO(RO)C{=}C(H)N}R^1R^2}$ (**4**) in almost quantitative yields. The ester enolate anions are chelate-bonded to the metal center through covalent Zn–O and dative Zn–N bonds. The strength of the Zn–N bond, and consequently the thermostability of the zinc enolates **4**, is influenced by the electronic properties of the amino-nitrogen substituents. A crystal structure determination of the ethylzinc enolate (**4b**) of *N*-methyl-*N-tert*-butyl-glycine methyl ester shows a tetrameric associate of four crystallographically independent $\overline{\mathrm{ZnOCCN}}$ units (average Zn–O = 2.065 (4) Å) that are linked via Zn–O–Zn bridges (average Zn–O = 2.032 (2) Å). The title compound crystallizes as colorless crystals in the monoclinic space group $P2_1/n$ with a = 20.063 (1) Å, b = 12.875 (1) Å, c = 20.414 (1) Å, β = 101.72 (1)°, V = 5163.2 (6) $Å^3$, Z = 4, and T = 295 K. Blocked full-matrix least-squares refinement converged at R = 0.061 and R_w = 0.055. Chlorozinc enolates **3** were prepared by transmetalation of α-amino lithium ester enolates $\mathrm{LiO(RO)C{=}C(H)NR^1R^2}$ (**2**) with $ZnCl_2$. Characterization of these enolates shows the presence of several aggregates, including mixed aggregates that contain both lithium and zinc cations. The structures and degree of association of zinc enolates **3** and **4** in solution are influenced by the presence of Lewis acids (Et_2Zn, EtZnCl) as well as Lewis bases (THF, pyridine). In solution, the title compound is present as a mixture of dimeric and tetrameric associates that are in an equilibrium which is slow on the NMR time scale. Furthermore, it is shown that in solution α-amino zinc ester enolates are present as *Z*-isomers containing an intramolecular Zn–N coordination bond. An exception to this generalization is zinc enolate **3e**, in which Zn–N coordination is absent (the amino nitrogen has a planar geometry and therefore is a poor Lewis base), and consequently this enolate is predominantly present as the *E*-isomer. Our findings reveal some of the factors that control the chemo- and stereoselectivity of the reactions of zinc ester enolates with imines that afford 2-azetidinones.

Introduction

In recent years metal enolates have become the most widely used reagents for carbon–carbon bond formation in organic synthesis. Especially alkylation[1] and aldol-type reactions[2,3] have been extensively developed. In view of controlling the stereochemistry of these reactions, the need for specific generation and characterization of the intermediate metal enolates has become a major challenge for synthetic chemists. Particularly the synthesis and characterization of alkali-metal enolates has received much attention, and nowadays the chemistry of these alkali-metal enolates is well-known.[4,5]

In contrast, still very little is known about the structure and nature of the enolates derived from less electropositive main-group metals, e.g. magnesium, aluminum, zinc, and tin.[6] This is illustrated by the fact that, whereas the

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