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Novel Route to Iron-Carbene Derivatives via Addition of Alkynes to Carbon Disulfide-Iron Complexes. Rearrangement of (1,3-Dithiol-2-ylidene)iron Complexes into Heterometallacycles

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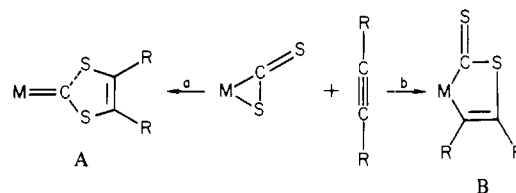
Addition of a variety of alkynes, containing a formyl, acyl, or carboxylate group, to a benzene solution of $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2[\text{P}(\text{OMe})_3]_2$ produces carbene-iron complexes (A), the (1,3-dithiol-2-ylidene)iron derivatives **2** resulting from the bonding of both sulfur atoms to the alkyne carbons. The reaction of dimethyl acetylenedicarboxylate with $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2\text{L}_2$ affords the carbene complex A which is stable when L is $\text{P}(\text{OMe})_3$ or PPh_3 but isomerizes into a heterometallacycle (B) for L = PMe_3 and gives the $\text{A} \rightleftharpoons \text{B}$ equilibrium when L = PMe_2Ph . The cycloaddition of the alkyne to the CS_2 ligand is shown to be reversible. The $\text{A} \rightleftharpoons \text{B}$ equilibrium constant and the rate of the isomerization of A increase with the electron-donating capability of the ligand L. 1,3-Dipolar cycloaddition of the alkyne to the FeCS_2 moiety may account for these reactions.

Introduction

The activation of heteroallenes such as carbon disulfide by coordination is of interest from two points of view: (i) in providing information on the fixation and the activation of carbon dioxide¹⁻³ and (ii) in designing syntheses of heterocyclic molecules by the reaction of unsaturated molecules with a coordinated heteroallene.⁴⁻⁶

Recent studies on $\eta^2\text{-CS}_2$ metal complexes have shown the dual nature of their reactivity as electrophilic or nucleophilic reagents. The coordinated sulfur atom is likely to be the site of nucleophilic attack by tertiary phosphine, leading to phosphine sulfide elimination and formation of thio-carbonylmetal complexes.⁷ On the other hand nucleophilicity of the uncoordinated sulfur atom has been demonstrated by nucleophilic substitution of alkyl halides—an initial step in the formation of other thio-carbonylmetal complexes.^{8,9} This dual behavior is also supported by an X-ray diffraction structural study of $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2(\text{PMe}_3)(\text{PPh}_3)$ ¹⁰ which indicates 1,3-dipolar character for the FeCS_2 moiety.

The present paper deals with the addition of electrophilic alkynes to several $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2\text{L}_2$ complexes which are known to accept a variety of phosphorus ligands L.¹⁰ While addition of dimethyl acetylenedicarboxylate to $\text{Rh}(\eta^2\text{-CS}_2)(\text{PPh}_3)(\text{C}_5\text{H}_5)$ has been reported to lead to the formation of a heterometallacycle of type B,⁶ in contrast we found that the addition of activated alkynes to the $\text{Fe}^0(\eta^2\text{-CS}_2)$ complexes, $\text{Fe}(\text{CS}_2)(\text{CO})_2\text{L}_2$, gives rise to novel (1,3-dithiol-2-ylidene)-metal complexes of type A.¹¹



Although a number of routes to carbene-metal complexes involving the transformation of a coordinated ligand¹² or even of the coordinated carbon disulfide ligand¹³ are known, reaction a provides the first example of the formation of sulfur-containing carbene-metal derivatives of type A and a novel method of generation of carbene-metal complexes by cycloaddition of an unsaturated unit to a ligand. The behavior of the carbene-iron complexes depends markedly on the nature of the phosphorus ligands L bonded to iron; they can isomerize into heterometallacycles of type B with donating groups L.

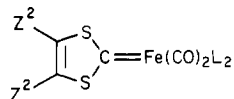
Experimental Section

All the reactions were carried out under an inert atmosphere. Carbon disulfide-iron(0) complexes were prepared according to the literature;¹⁰ the alkynes were commercial grade (Aldrich) or synthesized by the methods described in the literature.¹⁸

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- (13) 1,3-Dithiocarbene-metal complexes have been formed by alkylation of dithioester complexes¹⁴ or from $\eta^2\text{-CS}_2$ -metal derivatives of osmium^{8,12} or platinum¹⁶ which undergo two successive nucleophilic substitution of alkyl halides; in the later case the transformation corresponds to an increase of the formal oxidation number of the metal which does not occur when alkynes add to the $\eta^2\text{-CS}_2$ ligand. Other 1,3-dithio-carbene-metal complexes have been obtained from a bis mercapto ligand complex^{17a} or by transfer of the dithiocarbene moiety to the metal.^{17b,c}
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Infrared spectral determinations were with use of a Perkin-Elmer 157 G or a Pye Unicam SP 1100 spectrophotometer. NMR spectra were recorded on a Varian EM 360 or a Varian A60 (^1H NMR: C_6D_6 solution with Me_4Si internal standard) and a Bruker WP 80 spectrometer (^{13}C NMR: C_6D_6 solution unless otherwise noted). Mass spectra were determined at 70 eV with use of a Varian MAT 311 double-focusing spectrometer (Centre de Mesures Physiques, Rennes).

Preparation of Bis(phosphine)dicarbonyl(1,3-dithiol-2-ylidene)iron(0) Complexes:



A slight excess of the alkyne, as a pure liquid or as a solution in benzene, was added with a syringe, to approximately 1 mmol of the suitable $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2\text{L}_2$ complex in 10 mL of air-free dry benzene. The solution was stirred at room temperature till completion as indicated by the disappearance of the carbonyl absorption bands in the infrared of the $\text{Fe}(\text{CS}_2)(\text{CO})_2\text{L}_2$ complexes, the time depending on the nature of Z^1 , Z^2 , and L groups. The solution was then concentrated under vacuum, and a brown oil was isolated with use of silica-gel column chromatography under an inert atmosphere (column length = 25 cm, diameter = 4 cm, eluant = hexane progressively enriched with ether).

The NMR spectra were recorded with use of C_6D_6 solutions, and the same solutions were used for mass spectrometry.

2a ($\text{Z}^1, \text{Z}^2 = \text{CO}_2\text{Me}, \text{L} = \text{P}(\text{OMe})_3$): 0.3 mL of alkyne a, 700 mg of **1** (1.6 mmol) for 1 h, obtained 790 mg of **2a** (87%). *m/e*: (M) $^+$ 577.9550 (calcd 577.9534), ($\text{M} - \text{CO}$) $^+$ 550, ($\text{M} - 2\text{CO}$) $^+$ 522, (TTF) $^+$ 436, ($\text{M} - 2\text{CO} - \text{P}(\text{OMe})_3$) $^+$ 398. IR (benzene): 1928, 1880, 1737 cm^{-1} . ^1H NMR: δ 3.30 (s, CO_2Me), 3.40 (t, $^3J_{\text{PH}} = 13.0$ Hz, $\text{P}(\text{OMe})_3$). ^{13}C NMR: δ 145.1 (s, $>\text{C}=\text{C}<$), 158.8 (s, $>\text{C}=\text{O}$), 220.7 (t, $^2J_{\text{PC}} = 37.6$ Hz, FeCO), 239.4 (s, $\text{FeC}(\text{S})\text{S}$).

2b ($\text{Z}^1 = \text{H}, \text{Z}^2 = \text{CO}_2\text{Et}, \text{L} = \text{P}(\text{OMe})_3$): 0.3 mL of alkyne b, 436 mg of **1** (1 mmol) for 15 h, obtained 500 mg of **2b** (94%). *m/e*: (M) $^+$ 533.9635 (calcd 533.9638), ($\text{M} - \text{CO}$) $^+$ 506, ($\text{M} - 2\text{CO}$) $^+$ 478, ($\text{M} - 2\text{CO} - \text{P}(\text{OMe})_3$) $^+$ 354, (TTF) $^+$ 348. IR (benzene): 1930, 1870, 1730 cm^{-1} . ^1H NMR: δ 0.93 (t, CH_3), 3.62 (t, $^3J_{\text{PH}} = 11.5$ Hz, $\text{P}(\text{OMe})_3$), 4.02 (q, OCH_2), 7.95 (s, $\text{HC}=\text{C}$). ^{13}C NMR: δ 247.3 (s, $>\text{C}=\text{O}$), 219.6 (t, $^2J_{\text{PC}} = 36$ Hz, FeCO), 250.7 (s, $\text{FeC}(\text{S})\text{S}$).

2c ($\text{Z}^1 = p\text{-ClC}_6\text{H}_4, \text{Z}^2 = \text{CHO}, \text{L} = \text{P}(\text{OMe})_3$): 320 mg of alkyne c, 700 mg of **1** (1.6 mmol) for 12 h, obtained 830 mg of **2c** (87%). *m/e*: (M) $^+$ 600, ($\text{M} - 2\text{CO}$) $^+$ 544, ($\text{M} - 2\text{CO} - \text{P}(\text{OMe})_3$) $^+$ 419.911 (calcd 419.911). IR (benzene): 1925, 1880, 1660 cm^{-1} . ^1H NMR: δ 3.50 (t, $^3J_{\text{PH}} = 12$ Hz, $\text{P}(\text{OMe})_3$), 6.80 (q, $p\text{-ClC}_6\text{H}_4$), 7.63 (s, CHO). ^{13}C NMR: δ 146.1 (s), 164.6 (s, $=\text{C}(\text{S})$), 179.0 (s, $>\text{C}=\text{O}$), 222.8 (t, $^2J_{\text{PC}} = 35.9$ Hz, FeCO), 239.7 (t, $^2H_{\text{PC}} = 6.7$ Hz, $\text{FeC}(\text{S})\text{S}$).

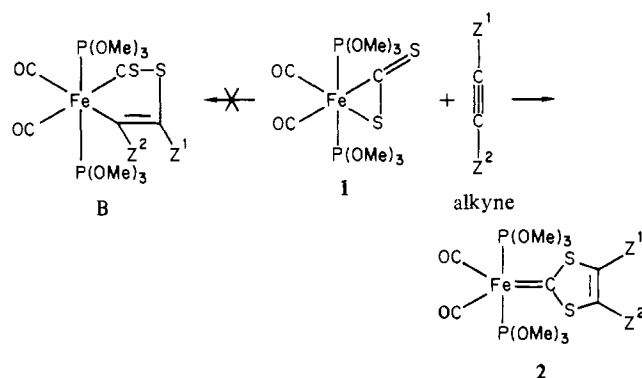
2d ($\text{Z}^1 = \text{Ph}, \text{Z}^2 = \text{COCH}_3, \text{L} = \text{P}(\text{OMe})_3$): 0.33 mL of alkyne d, 1.0 g of **1** (2.3 mmol) for 24 h, obtained 850 mg of **2d** (64%). *m/e*: (M) $^+$ 580, ($\text{M} - \text{CO}$) $^+$ 552, ($\text{M} - 2\text{CO}$) $^+$ 523.992 (calcd 523.994). IR (benzene): 1905, 1855, 1665 cm^{-1} . ^1H NMR: δ 1.50 (s, CH_3), 3.60 (t, $^2J_{\text{PH}} = 12.0$ Hz, $\text{P}(\text{OMe})_3$), 7.60 (C_6H_5).

2e ($\text{Z}^1 = \text{CH}(\text{OEt})_2, \text{Z}^2 = \text{CHO}, \text{L} = \text{P}(\text{OMe})_3$): 36 mg of alkyne e, 100 mg of **1** (0.23 mmol) for 1 h, obtained 127 mg of **2e** (93%). *m/e*: (M) $^+$ 592.0048 (calcd 592.0054), ($\text{M} - \text{CO}$) $^+$ 564, ($\text{M} - 2\text{CO}$) $^+$ 536.0143 (calcd 536.0156). IR (benzene): 1930, 1870, 1670 cm^{-1} . ^1H NMR: δ 0.93 (t, $^3J_{\text{HH}} = 8.0$ Hz, CH_3), 3.37 (q, OCH_2), 3.50 (t, $^3J_{\text{PH}} = 11.0$ Hz, $\text{P}(\text{OMe})_3$), 5.33 (s, $\text{HC}=\text{C}$), 9.97 (s, CHO). ^{13}C NMR: δ 148.5 (s), 165.3 (s, $=\text{C}(\text{S})$), 179.1 (s, $\text{C}=\text{O}$), 222.1 (t, $^2J_{\text{PC}} = 35.0$ Hz, FeCO), 245.7 (s, $\text{FeC}(\text{S})\text{S}$).

8 ($\text{Z}^1, \text{Z}^2 = \text{CO}_2\text{Me}, \text{L} = \text{PPh}_3$): 80 mg of alkyne a and 60 mg of **4** (0.5 mmol) for 1 h led to 260 mg of **8** (60%). IR (benzene): 1915, 1850, 1740 cm^{-1} . ^1H NMR: δ 3.30 (s, CO_2Me), 7.90 (C_6H_5). ^{13}C NMR (CD_2Cl_2): δ 147.5 (s, $>\text{C}=\text{C}<$), 159.6 (s, $\text{C}=\text{O}$), 221.2 (t, $^2J_{\text{PC}} = 32.8$ Hz, FeCO), 247.8 (t, $^2J_{\text{PC}} = 7.0$ Hz, $\text{FeC}(\text{S})\text{S}$).

9 ($\text{Z}^1, \text{Z}^2 = \text{CO}_2\text{Me}, \text{L}^1 = \text{PMe}_3, \text{L}^2 = \text{P}(\text{OMe})_3$): 29 mg of alkyne a, 80 mg of **5** (0.21 mmol) for 15 min, quantitative yield by ^1H NMR. IR (benzene): 1900, 1860, 1735 cm^{-1} . ^1H NMR: δ 1.30 (dd, $^2J_{\text{PH}} = 9.5$ Hz, $^4J_{\text{PH}} = 0.4$ Hz, PMe_3), 3.43 (s, CO_2Me), 3.50 (d, $^3J_{\text{PH}} = 12.4$ Hz, $\text{P}(\text{OMe})_3$).

Scheme I



a: $\text{Z}^1 = \text{Z}^2 = \text{CO}_2\text{Me}$. b: $\text{Z}^1 = \text{H}, \text{Z}^2 = \text{CO}_2\text{Et}$.
c: $\text{Z}^1 = p\text{-ClC}_6\text{H}_4, \text{Z}^2 = \text{CHO}$. d: $\text{Z}^1 = \text{C}_6\text{H}_5, \text{Z}^2 = \text{COCH}_3$. e: $\text{Z}^1 = \text{CH}(\text{OEt})_2, \text{Z}^2 = \text{CHO}$

10 ($\text{Z}^1, \text{Z}^2 = \text{CO}_2\text{Me}, \text{L} = \text{PMe}_2\text{Ph}$): 26 mg of alkyne a, 86 mg of **6** (0.19 mmol) for 5 min, quantitative yield ^1H NMR, nonisolable product due to facile isomerization. *m/e*: ($\text{M} - \text{CO}$) $^+$ 578.154 (calcd 578.0203), ($\text{M} - 2\text{CO}$) $^+$ 550.0245 (calcd 550.0253), (TTF) $^+$ 436. IR (benzene): 1890, 1845, 1740 cm^{-1} . ^1H NMR: δ 1.53 (t, $^2J_{\text{PH}} = 8.0$ Hz, PMe_2Ph), 3.37 (s, CO_2Me).

11 ($\text{Z}^1, \text{Z}^2 = \text{CO}_2\text{Me}, \text{L} = \text{PMe}_3$): 42 mg of alkyne a, 100 mg of **7** (0.29 mmol) for 5 min, quantitative yield by ^1H NMR, nonisolable product due to facile isomerization. *m/e*: (M) $^+$ 482, ($\text{M} - \text{CO}$) $^+$ 453.9887 (calcd 453.9890), ($\text{M} - 2\text{CO}$) $^+$ 426. IR (benzene): 1890, 1835, 1710 cm^{-1} . ^1H NMR: δ 1.27 (t, $^2J_{\text{PH}} = 8.5$ Hz, PMe_3), 3.45 (s, CO_2Me).

3 ($\text{Z}^1, \text{Z}^2 = \text{CO}_2\text{Me}, \text{L} = \text{CO}$). Dimethyl acetylenedicarboxylate (a) (0.3 mL) was added to a suspension of 1.1 g of $\text{Fe}_2(\text{CO})_9$ (3 mmol) in 30 mL of carbon disulfide, and the mixture was stirred overnight at room temperature. After chromatography 220 mg of the brown oil **3** was obtained. *m/e*: (M) $^+$ 385.885 (calcd 385.888), ($\text{M} - \text{CO}$) $^+$ 358, ($\text{M} - 2\text{CO}$) $^+$ 330, ($\text{M} - 3\text{CO}$) $^+$ 302, ($\text{M} - 4\text{CO}$) $^+$ 247 (calcd 435.942) (calcd for the corresponding tetrathiafulvalene 435.941). IR (thin film): 2080, 1990, 1960, 1740 cm^{-1} .

Preparation of Heterometallacycles 12–14. Dimethyl acetylenedicarboxylate (a) (29 mg) was added to 1 equiv of complex **5** (80 mg) in solution in 0.5 mL of deuterated benzene, and the mixture was allowed to stand 4 days at room temperature. Compound **12** was formed in 15% yield as indicated by ^1H NMR. ^1H NMR: δ 1.28 (dd, $^2J_{\text{PH}} = 10.8$ Hz, $^4J_{\text{PH}} = 2.0$ Hz, PMe_2), 3.55 (d, $^3J_{\text{PH}} = 11.2$ Hz, $\text{P}(\text{OMe})_3$), 3.80 (s), 3.43 (s, CO_2Me).

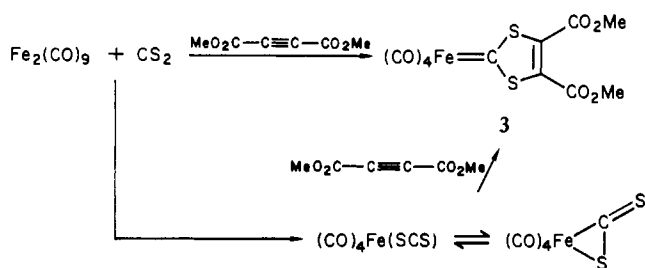
13. Dimethyl acetylenedicarboxylate (a) (26 mg) was added to 1 equiv of complex **6** (86 mg) in solution in 0.5 mL of deuterated benzene, and the mixture was allowed to stand 1 day at room temperature. Compound **13** was formed in more than 80% yield as indicated by ^1H NMR. *m/e*: ($\text{M} - \text{CO}$) $^+$ 578.0211 (calcd 578.0253), ($\text{M} - 2\text{CO}$) $^+$ 550, ($\text{M} - 2\text{CO} - \text{PMe}_2\text{Ph}$) $^+$ 412. IR (benzene): 2025, 1980, 1720 cm^{-1} . ^1H NMR: δ 1.63 (t, $^2J_{\text{PH}} = 9.5$ Hz, PMe_2Ph), 3.46 (s), 3.78 (s, CO_2Me). ^{13}C NMR: δ 50.7 (s), 51.3 (s, OCH_3), 142 (s), 158.9 (s, $\text{C}=\text{C}$), 176.1 (s, $>\text{C}=\text{O}$), 210.9 (t, $^2J_{\text{PC}} = 12.5$ Hz, $\text{FeC}=\text{S}$), 207.8 (t, $^2J_{\text{PC}} = 18.7$ Hz, FeCO), 194.7 (t, $^2J_{\text{PC}} = 22.6$ Hz, FeCO).

14. Dimethyl acetylenedicarboxylate (a) (42 mg) was added to 1 equiv of complex **7** (100 mg) in solution in 0.5 mL of deuterated benzene, and the mixture was allowed to stand 1 h at room temperature. Compound **14** was formed quantitatively as indicated by ^1H NMR and was crystallized from pentane-dichloromethane (mp 170 $^\circ\text{C}$). *m/e*: (M) $^+$ 482, ($\text{M} - \text{CO}$) $^+$ 453.9887 (calcd 453.9890), ($\text{M} - 2\text{CO}$) $^+$ 426. IR (Nujol): 2020, 1960, 1725, 1700 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{24}\text{FeO}_6\text{P}_2\text{S}_2$: C, 37.34; H, 4.98; P, 12.86; S, 13.28. Found: C, 37.30; H, 5.00; P, 12.66; S, 14.18. ^1H NMR: δ 1.23 (t, $^2J_{\text{PH}} = 9.0$ Hz, PMe_3), 3.46 (s), 3.78 (s, CO_2Me). ^{13}C NMR: δ 50.8 (s, OCH_3), 51.5 (s, OCH_3), 140.2 and 159 (s, $\text{C}=\text{C}$), 176.4 (s), 176.5 (s, $>\text{C}=\text{O}$), 212.0 (t, $^2J_{\text{PC}} = 14.7$ Hz, $\text{FeC}=\text{S}$), 207.9 (t, $^2J_{\text{PC}} = 19.5$ Hz, FeCO), 196.6 (t, $^2J_{\text{PC}} = 24.4$ Hz, FeCO).

Results and Discussion

1. Formation of (1,3-Dithiol-2-ylidene)iron(0) Complexes. The orange $\eta^2\text{-CS}_2$ iron complex **1** in benzene solution under

Scheme II



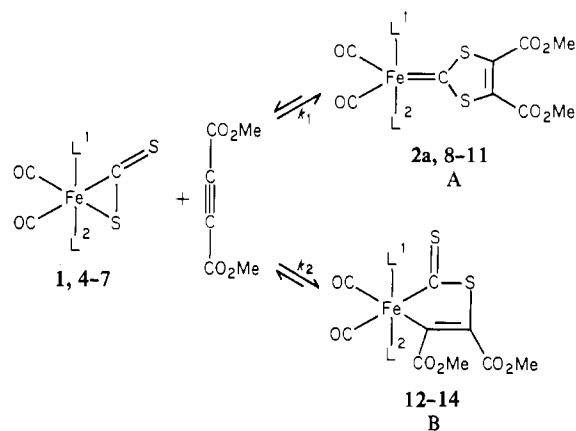
an inert atmosphere reacts very easily at room temperature with 1 equiv of the electrophilic alkynes a–e to afford almost quantitatively compounds **2a–2e** (Scheme I) which were thermally stable but very air sensitive and were isolated in 67–95% yield with use of a silica-gel column chromatography under nitrogen. The addition reaction is effective only with alkynes bearing at least one electron-withdrawing group such as a formyl, acyl, or carboxylate group; no reaction could be observed with toluene using the same conditions whereas the reaction was completed within a few seconds with the dimethyl acetylenedicarboxylate (a) and in approximately 15 h with ethyl propiolate (b) at room temperature.

The air sensitivity of complexes **2a–2e** prevented their analysis, but for each of them the mass spectrum showed the molecular peak, ions corresponding to the loss of one and two carbonyls, and the ion corresponding to the tetrathiafulvalene resulting from the dimerization of the carbene ligand. The spectroscopic data allowed us to establish unambiguously the carbene–metal structure of type A and eliminated the heterometallacycle moiety B for compounds **2a–2e**. The infrared spectra exhibited two carbonyl absorption bands at very low frequencies [ν , cm^{-1} (C_6H_6): **2a**, 1928, 1880; **2b**, 1930, 1870; **2c**, 1925, 1880; **2d**, 1905, 1855; **2e**, 1930, 1870] as compared to those of the parent $\eta^2\text{-CS}_2$ iron derivative [ν , cm^{-1} (THF): **1**, 2020, 1964¹⁰]. Such a lowering of frequencies is consistent with the presence of a strong electron-donating ligand such as the carbene ligand containing heteroatoms bonded to the carbene carbon.²⁰ On the other hand with a metallacycle geometry such as B, high frequencies would have been expected for the absorption of carbonyls bonded to iron(II). The $\text{P}(\text{OMe})_3$ ligands of compounds **2** gave an apparent triplet in ^1H and ^{13}C NMR; these data are consistent with equivalent phosphite groups bonded to iron in the trans position. It thus appears that the addition of the alkynes to the $\eta^2\text{-CS}_2$ -iron derivative **1** takes place without modifying significantly the geometry of the ligands bonded to iron.²¹

The nature of a carbene–metal complex, rather than a metallacycle geometry B, was established by ^{13}C NMR of compound **2a**: the carbonyls, the CO_2Me groups, and the olefinic carbons are equivalent.¹¹ Moreover, the ^{13}C nucleus originating from the CS_2 ligand was observed at low field (240–250 ppm)²² in a range usually expected for a ^{13}C chemical shift corresponding to a carbene carbon atom bonded to a metal.^{12a,23}

It has been reported by Hartzler²⁴ that activated alkynes react with uncoordinated carbon disulfide in more drastic

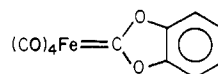
Scheme III



L^1, L^2	$\text{Fe}(\eta^2\text{CS}_2)$	A	B
$\text{P}(\text{OMe})_3$	1	2a	
PPh_3	4	8	
$\text{P}(\text{OMe})_3, \text{PMe}_3$	5	9	12
PMe_2Ph	6	10	13
PMe_3	7	11	14

conditions and the resulting products were explained by the initial formation of the 1,3-dithiol-2-ylidene carbene. The formation of **2a** which is instantaneous at room temperature shows that carbon disulfide is activated toward alkynes by coordination.

The preparation of the iron–carbene complexes above was extended to the synthesis of derivative **3** (Scheme II). The reaction of $\text{Fe}_2(\text{CO})_9$ with carbon disulfide has already been reported and gives the adduct $\text{SCSFe}(\text{CO})_4$ with only one sulfur atom coordinated to iron.¹⁹ The reaction of dimethyl acetylenedicarboxylate with a solution of $\text{Fe}_2(\text{CO})_9$ in carbon disulfide was then investigated at room temperature. An air-sensitive, violet derivative was isolated in poor yield with use of column chromatography and identified as **3** on the basis of (i) the infrared spectrum which showed low-frequency carbonyl absorption bands [$\nu(\text{CO})$, cm^{-1} (benzene): 2080, 1990, 1960] similar to those observed for



[$\nu(\text{CO})$, cm^{-1} (THF): 2066, 1994, 1968],²⁵ (ii) the ^1H NMR spectrum which exhibited one singlet for the methyl protons [$\delta(\text{C}_6\text{D}_6)$ 3.37], and (iii) the mass spectrum which indicated the molecular peak, ions resulting from the successive loss of four carbonyls, and the tetrathiafulvalene ion arising from the dimerization of the 1,3-dithiol-2-ylidene ligand, a process usually observed in the mass spectra of compounds **2**. This result is apparently inconsistent with the initial formation of the $\text{Fe}(\eta^1\text{-CS}_2)(\text{CO})_4$ derivative,¹⁹ but this compound may be in equilibrium with the less stable $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_4$ complex which can account for the formation of compound **3**, as indicated in Scheme II.

2. Isomerization Carbene–Metal (A) = Metallacycle (B). It was shown recently that the electron-withdrawing $\eta^2\text{-CS}_2$ ligand allows the introduction of iron on a variety of phosphorus ligands¹⁰ and that the nature of the L group in $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2\text{L}_2$ derivatives modifies significantly the behavior of the FeCS_2 entity.²⁶ This led us to study the addition of one reactive alkyne on $\eta^2\text{-CS}_2$ -iron complexes **4–7** which showed that the nature of the phosphorus ligand could promote

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(21) However, the ^1H NMR triplet due to *trans*- $\text{P}(\text{OMe})_3$ groups in compounds **2** is less sharp than that of precursor **1**,¹⁰ and the reaction may take place with a modification of the trigonal bipyramid into a square-pyramid geometry.

(22) The signal showing the coupling of the (carbene) ^{13}C nucleus with two identical ^{31}P nuclei was only observed for compound **2c** ($^2J_{\text{PC}} = 6.7$ Hz) and **8** ($^2J_{\text{PC}} = 7.0$ Hz).

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Table I

L ¹	P(OMe) ₃	PPh ₃	P(OMe) ₃	PMe ₂ Ph	PMe ₃
L ²	P(OMe) ₃	PPh ₃	PMe ₃	PMe ₂ Ph	PMe ₃
A/B ^a	100/0	100/0	85/15	18/82	0/100
relative rate			1	2.5	50

^a Measured by ¹H NMR spectroscopy using C₆D₆ solutions at 37 °C.

the isomerization of the (1,3-dithiol-2-ylidene)iron complexes.

The treatment at room temperature, under inert atmosphere, of a benzene solution of compounds 4–7 with 1 equiv of dimethyl acetylenedicarboxylate (a) gave, within a few seconds, quantitative yields of air-sensitive (1,3-dithiol-2-ylidene)iron complexes 8–11, respectively (Scheme III).

These derivatives were characterized by mass spectroscopy, by infrared analysis which showed two carbonyl absorption bands at low frequencies [ν , cm⁻¹ (C₆H₆): 8, 1915, 1850; 9, 1900, 1860; 10, 1890, 1845; 11, 1890, 1835], and by ¹H NMR, which indicated equivalent CO₂Me groups.

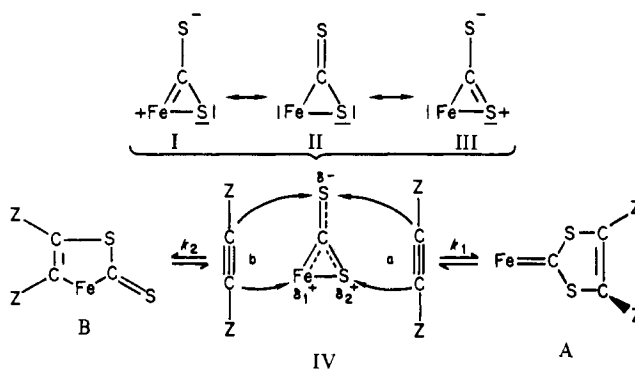
While the compounds 2a and 8, containing the weaker electron-donor groups P(OMe)₃ and PPh₃, respectively, are thermally stable, the derivative 11, containing the stronger electron-donating group PMe₃, is rapidly converted into the stable metallaheterocycle isomer 14. Complexes of type A (9 and 10) lead slowly to an equilibrium mixture with the corresponding metallacycles of type B (12 and 13) (Table I). These new metallaheterocycles (12–14) were identified by their mass and infrared spectra. In the IR spectra two carbonyl absorption bands were observed at much higher frequencies than their corresponding carbene iron precursors [ν , cm⁻¹ (C₆H₆): 13, 2025, 1980; 14, 2002, 1980]. This frequency shift is in agreement with the transformation of an iron(0) derivative into an iron(II) complex. In contrast to the parent carbene-iron complexes, the derivatives 12–14 have nonequivalent CO₂Me groups in the NMR spectra, indicating nonsymmetrical incorporation of the alkyne into the complexes.²⁷ The ¹³C NMR spectrum of 14 exhibits different lines for the six ¹³C nuclei originating from the alkyne part, in addition to two different carbonyl carbon nuclei coupled with two identical phosphorus nuclei.

The A ⇌ B isomerization reaction was studied by ¹H NMR techniques with use of C₆D₆ solutions of 9–11 at 37 °C.²⁸ The ratio A:B displayed in Table I, where the electron-donating effect of ligands L¹ and L² increase from left to right, indicates clearly that the more L¹ and L² are electron releasing the less the carbene-iron compounds are stable and the more the equilibrium is shifted toward the metallacycle B.

The relative rates of the transformation A → B were approximately determined by ¹H NMR and were in the range 1:2.5:50, respectively, starting from 9, 10, and 11 and showed that the electron-donor character of L not only increases the equilibrium constant of A ⇌ B but also increases the rate which leads to this equilibrium.

The addition of 1 equiv of the η^2 -CS₂Fe complex 6 to a benzene solution of the carbene-iron complex 11 led to a mixture of the η^2 -CS₂Fe derivative 7 and the carbene-iron complex 10. Moreover, the addition of diethyl acetylenedicarboxylate to the carbene complex 10 in C₆D₆ solution led to the release of dimethyl acetylenedicarboxylate (a) with

Scheme IV



formation of two metallaheterocycles of type B (L¹, L² = PMe₂Ph) containing the carboxylate groups CO₂Me (13) and CO₂Et, as observed by ¹H NMR.

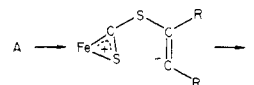
These reactions demonstrated the reversibility of the addition of alkyne to the η^2 -CS₂ complex when the molecule of type A was unstable and suggested that the A ⇌ B isomerization might proceed by initial retrocycloaddition from A to the η^2 -CS₂-iron complex, followed by the 1,3-dipolar cycloaddition of the alkyne to the η^2 -CS₂ moiety according to Scheme IV.²⁹ Structural¹⁰ and reactivity²⁶ information suggested that the canonical forms I–III could account for the electron distribution of Fe(η^2 -CS₂) complexes. The superposition of these forms gives the situation IV which shows high electron density on the uncoordinated sulfur atom with electron deficiency shared by the coordinated sulfur atom and the iron atom. Therefore the reversible 1,3-dipolar cycloaddition of the alkyne according to the route a could lead to the complex A, and competitive cycloaddition according to the route b could lead to complex B; cycloaddition would imply that the rate constant k₁ is higher than k₂ (Scheme IV), e.g., that complexes of type A (9–11) are the kinetic products and that derivatives 12–14 are the thermodynamically stable products. In the case of 2a and 8 the carbene complexes are likely to be the thermodynamic products as well, preventing the reversibility of reaction a.

The present study shows the activation by coordination of carbon disulfide toward alkynes and the dual behavior of the metal-CS₂ moiety according to the nature of the phosphorus ligands which can then be selected to produce thermally stable (1,3-dithiol-2-ylidene)iron complexes or to promote their isomerization into heterometallacyclic derivatives.

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Registry No. 1, 64424-66-4; 2a, 67228-20-0; 2b, 67228-18-6; 2c, 67228-19-7; 2d, 77357-83-6; 2e, 74334-32-0; 3, 77357-84-7; 4, 64424-68-6; 5, 66808-75-1; 6, 64424-57-3; 7, 64424-58-4; 8, 68587-53-1; 9, 68587-54-2; 10, 68587-55-3; 11, 68587-56-4; 12, 68628-48-8; 13, 68587-57-5; 14, 68587-58-6; a, 762-42-5; b, 623-47-2; c, 67228-76-6; d, 1817-57-8; e, 74149-25-0; Fe₂(CO)₉, 15321-51-4; CS₂, 75-15-0.

(29) An intramolecular rearrangement via an intermediate such as



could also contribute.

(27) The ¹H NMR showed a pattern consistent with two identical trans phosphorus ligands for 13 and 14.

(28) Le Bozec, H.; Gorgues, A.; Dixneuf, P. *J. Chem. Soc., Chem. Commun.* 1978, 573–574.