1772 *Organometallics* **1986,** *5,* 1772-1777

Formation of Donor–Acceptor Fe(0)→Hg(II) Bond for the Stabilization of Carbene–Iron(0) Complexes: Synthesis, Characterization, Reactivity toward Sulfur Donor Molecules, and X-ray Structure of $Cl_2HgFe(CO)_2(PMe_2Ph)_2(CS_2C_2(CO_2Me)_2)$

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Received January 23, 1986

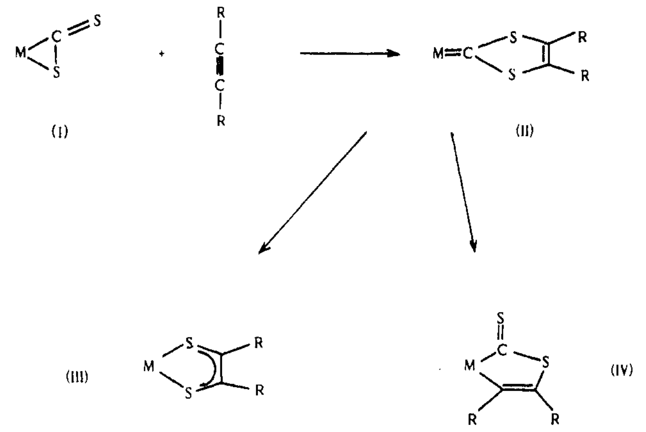
Mercury chloride reacts with the 1,3-dithiol-2-ylidene iron complexes **2** to produce stable new mixed bimetallic carbene complexes $Cl_2HgFe(CO)_2(L)_2(CS_2C_2(CO_2Me)_2)$ [**3a**, L = PMe_2Ph; **3b**, L = PMe_3; **3c**, L = $P(OMe)_3$; **3d**, L = PPh_3]. These compounds were characterized by infrared and ^1H, ^{31}P, and ^{13}C NMR spectroscopy which indicated the trans position of the carbonyls and of the phosphorus ligands. Cis coupling constants between ^{31}P and ^{199}Hg nuclei were determined by ^{31}P NMR in the range 742–894 Hz. The enhancement of the electrophilicity of the carbene carbon center was revealed by the easier reaction of **3c** vs. **2c** toward sulfur and cyclohexene sulfide which gave the 1,3-dithiole-2-thione **6**. The compound $Cl_2HgFe(CO)_2(PMe_2Ph)_2(CS_2(CO_2Me)_2)$ crystallizes in space group $C2/c$ with a = 35.059 (5) Å, b = 11.706 (1) Å, c = 17.600 (2) Å, α = 90.00°, β = 101.96 (1), γ = 90.00°, and Z = 8. The structure was solved and refined (3253 reflections) to the final values for the residual R_F = 0.044 and R_{wF} = 0.058. The stereochemistry of the iron atom is octahedral with the Lewis acid $HgCl_2$ in an equatorial site trans to the electron-releasing carbene ligand, with Hg–Fe and Fe–C(carbene) bond lengths of 2.546 (1) and 1.912 (7) Å, respectively.

Introduction

The cycloaddition of an alkyne to a metal η^2-CS_2 complex (I)[1] has been shown to provide a novel route to the cyclic carbene–transition-metal complexes of type II. This simple reaction appears to be general for carbene–metal complexes II, and derivatives of Fe(0),[1,2] Mn(1),[3] Cr(0),[4] W(0),[5] and Ni(0)[6,7] have now been prepared (Scheme I).

Among these carbene–metal complexes II, the 1,3-dithiol-2-ylidene iron(0) derivatives **2** have been obtained from **1**, for a variety of phosphorus ligands L[1,2] and have been found to be useful intermediates for the synthesis of tetrathiafulvalenes,[8] thiones,[9] or dithiolene metal derivatives.[10] However, they show an instability that is related to the electron-releasing capability of the cyclic carbene ligand. For instance complexes **2** behave as electron-rich complexes and are easily oxidized by air to yield dithiolene metal derivatives of the type III.[10] When the phosphorus groups L are very basic (PMe_2Ph, PMe_3), isomerization takes place affording the metallocycle iron(II) compounds of type IV.[2,11] This allows the release of the excess electron density from the iron center.

Scheme I



The instability and/or the reactivity of complexes **2** prevented their structural characterization by X-ray diffraction. One possible way to stabilize the carbene–iron complex **2** was to reduce the electron density on the iron atom without bringing about its oxidation. This was expected to be achieved by formation of a donor–acceptor bond involving the basic iron center. Donor–acceptor complexes involving 18-valence-electron, low-valent transition-metal complexes with Lewis acids, such as HgX_2,[12,13] or 16-electron organometallic species[14] are now well-documented.

Here we report the synthesis of carbene–Fe(0)→Hg(II) donor–acceptor complexes **3** for the phosphorus ligands L (PMe_3, PMe_2Ph, PPh_3, $P(OMe)_3$). One of which has

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[1] Le Bozec, H.; Gorgues, A.; Dixneuf, P. H. *J. Am. Chem. Soc.* **1978,** *100,* 3946.

[2] Le Bozec, H.; Gorgues, A.; Dixneuf, P. H. *Inorg. Chem.* **1981,** *20,* 2486.

[3] Le Marouille, J. Y.; Lelay, C.; Benoit, A.; Grandjean, D.; Touchard, D.; Le Bozec, H.; Dixneuf, P. H. *J. Organomet. Chem.* **1980,** *191,* 133.

[4] Frazier, C. C.; Magnussen, N. D.; Osuji, L. N.; Parker, K. O. *Organometallics* **1982,** *1,* 903.

[5] Schenk, W. A.; Schwietzke, T.; Muller, H. *J. Organomet. Chem.* **1982,** *232,* C41.

[6] Bianchini, C.; Meli, A.; Scapacci, G. *Organometallics* **1985,** *4,* 264.

[7] Bianchini, C.; Meli, A. *J. Chem. Soc., Chem. Commun.* **1983,** 1309.

[8] Le Bozec, H.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1983,** 1462.

[9] Ngounda, M.; Le Bozec, H.; Dixneuf, P. H. *J. Org. Chem.* **1982,** *47,* 4000.

[10] Carty, A. J.; Dixneuf, P. H.; Gorgues, A.; Hartstock, F.; Le Bozec, H.; Taylor, N. J. *Inorg. Chem.* **1981,** *20,* 3929.

[11] Le Bozec, H.; Gorgues, A.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1978,** 573.

[12] Shriver, D. F. *Acc. Chem. Res.* **1970,** *3,* 231.

[13] Burlitch, J. M. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 6, Chapter 42, p 983.

[14] Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1983,** 854. Einstein, F. W. B.; Jones, T.; Pomeroy, R. K.; Rushman, P. *J. Am. Chem. Soc.* **1984,** *106,* 2707.

0276-7333/86/2305-1772$01.50/0

been described previously in a communication.[15] We also show the formation of the Fe(0)→Hg(II) bond in these compounds (i) allows the stabilization of the carbene–iron unit and the X-ray characterization of $Cl_2HgFe(CS_2C_2(CO_2Me)_2)(CO)_2(PMe_2Ph)_2$ (3) but (ii) at the same time enhances the reactivity of the carbene carbon toward the sulfur donor cyclohexene sulfide, in the formation of a thione derivative.

Experimental Section

All reactions were carried out under an argon atmosphere using Schlenk techniques. Infrared spectra were recorded on a Pye-Unicam SP 1100 infrared spectrometer. NMR spectra were obtained on Brucker WP 80 FT (^1H, ^{31}P) and on Brucker AM 300 WB (^{13}C) instruments at the Centre Regional de Mesures Physiques de l'Ouest, Université de Rennes.

Materials. Ether was distilled from sodium/benzophenone ketyl, methylene chloride was distilled from P_2O_5, and methanol was distilled from magnesium methoxide. Dimethyl acetylenedicarboxylate, mercury dichloride, cyclohexene sulfide (Janssen), and benzene (Merck) were used as purchased.

Preparation of $Cl_2HgFeCS_2C_2(CO_2Me)_2(CO)_2L_2$ (3a,b). One equivalent of dimethyl acetylenedicarboxylate was added to a stirred solution of complex **1a**,**b**[16] in 50 mL of ether. The red solution immediately turned brown with the formation of iron–carbene intermediate **2a**,**b**.[1] After 2 min of stirring at room temperature, 1 equiv of mercury dichloride was added. A yellow complex, **3a**,**b**, immediately precipitated at room temperature, was isolated by filtration on a frit, washed with ether, and slowly crystallized from methanol–ether under inert atmosphere.

3a (L = PMe_2Ph): 0.31 g (82%) obtained from 0.20 g of **1a** (0.43 mmol), 1.1 mL of dimethyl acetylenedicarboxylate (0.05 M solution in CH_2Cl_2), and 0.13 g of $HgCl_2$ (0.45 mmol); IR (Nujol) ν_{CO} 1940, $\nu_{C=O}$ 1740 cm^{-1}, $\nu_{C=C}$ 1560 cm^{-1}; ^1H NMR (CD_2Cl_2, 80 MHz, 309 K) δ 7.40 (m, C_6H_5), 3.92 (s, CO_2Me), 2.10 (d, $|^2J_{PH} + {}^4J_{PH}| = 8$ Hz, PMe); ^{31}P NMR (CD_2Cl_2, 32.38 MHz, 309 K) δ 21.87 (s + symmetrical d, $^2J_{^{31}P\text{–}^{199}Hg} = 742$ Hz); ^{13}C NMR (CD_3OD, 75.47 MHz, 297 K) δ 266.9 (t, $^2J_{PC} = 16.2$ Hz, $FeC(S–)_2$), 213.9 (t, $^2J_{PC} = 23.0$ Hz, Fe–CO), 159.0 (s, >C=O), 154.4 (s, >C=C<). Anal. Calcd for $C_{25}H_{28}Cl_2FeHgO_6P_2S_2 \cdot 0.25Et_2O$: C, 34.82; H, 3.41; Cl, 7.90; P, 6.92; S, 7.14. Found: C, 34.96; H, 3.45; Cl, 7.32; P, 6.09; S, 6.62.

3b (L = PMe_3): 0.74 g (98%) obtained from 0.34 g (1 mmol) of **1b**, 2.5 mL of dimethyl acetylenedicarboxylate (0.05 M solution in CH_2Cl_2), and 0.28 g (1 mmol) of $HgCl_2$; IR (Nujol) ν_{CO} 1940, $\nu_{C=O}$ 1740 cm^{-1}; ^1H NMR (CD_2Cl_2, 80 MHz, 309 K) δ 3.39 (s, CO_2Me), 1.59 (d, $|^2J_{PH} + {}^4J_{PH}| = 9.3$ Hz, PMe); ^{31}P NMR (CD_2Cl_2, 32.38 MHz, 309 K) 10.34 (s + symmetrical d, $^2J_{^{31}P\text{–}^{199}Hg} = 801$ Hz). Anal. Calcd for $C_{15}H_{24}Cl_2FeHgO_6P_2S_2$: C, 23.89; H, 3.18. Found: C, 23.70; H, 3.00.

Preparation of $Cl_2HgFe(CS_2C_2(CO_2Me)_2)(CO)_2(P(OMe)_3)_2$ (3c). One equivalent of dimethyl acetylenedicarboxylate (2.5 mL, 0.05 M solution in CH_2Cl_2) was added to a stirred solution of 0.436 g of **1c** (1 mmol) in 50 mL of ether at room temperature. The red solution immediately turned brown. After 15 min of stirring, 0.28 g of mercury dichloride was added (1 mmol) and the solution was stirred for 1 h. The yellow precipitate was then isolated by filtration on a frit and washed with ether. Slow crystallization in methanol–ether gave 0.76 g of **3c** (89%): IR (Nujol) ν_{CO} 1955, $\nu_{C=O}$ 1730 cm^{-1}; ^1H NMR (CD_2Cl_2, 80 MHz, 309 K) δ 4.00 (s, CO_2Me), 3.78 (t, $|^3J_{PH} + {}^5J_{P'H}| = 11.5$ Hz, $P(OCH_3)_3$); ^{31}P NMR (CD_2Cl_2, 32.38 MHz, 308 K) δ 153,4 (s + symmetrical d, $^2J_{^{31}P\text{-}^{199}Hg} = 894$ Hz). Anal. Calcd for $C_{15}H_{24}Cl_2FeHgO_{12}P_2S_2$: C, 21.39; H, 2.82. Found: C, 21.20; H, 2.85.

Preparation of $Cl_2HgFe(CS_2C_2(CO_2Me)_2)(CO)_2(PPh_3)_2$ (3d). Analogous to the preparation of **3c**, 0.90 g (79%) of **3d** was obtained from 0.71 g of **1d** (1 mmol), 2.5 mL of dimethyl acetylenedicarboxylate (0.05 M solution in CH_2Cl_2), and 0.28 g (1 mmol) of mercury dichloride in a mixture of 20 mL of CH_2Cl_2 and 30 mL of benzene. Complex **3d** was crystallized from CH_2Cl_2–ether under inert atmosphere at −20 °C: IR (Nujol) ν_{CO} 1960, $\nu_{C=O}$ 1740 cm^1.

Preparation of $FeC(CO_2Me){=}C(CO_2Me)SC(SHgCl_2)$-$(CO)_2(PMe_3)_2$ (5b). One equivalent of dimethyl acetylenedicarboxylate (2.5 mL, 0.05 M solution in CH_2Cl_2) was added to a stirred solution of 0.34 g of **1b** (1 mmol) in 50 mL of ether–CH_2Cl_2 (1:1) at room temperature. After 6 h of stirring, 0.28 g of mercury dichloride was added (1 mmol) and the solution was stirred for two additional hours. The yellow precipitate was then isolated by filtration on a frit and washed with ether. Slow crystallization in methanol–ether under inert atmosphere afforded 0.65 g of **5b** (86%): IR (Nujol) ν_{CO} 2030, 1985, $\nu_{C=O}$ 1755, 1740 cm^{-1}; ^1H NMR (CD_2Cl_2, 80 MHz, 309 K) δ 3.83 (s, CO_2Me), 3.76 (s, CO_2Me), 1.55 (d, $|^2J_{PH} + {}^4J_{PH}| = 10.0$ Hz PMe); ^{31}P NMR (CD_2Cl_2, 32.38 MHz, 309 K) δ 10.6 (s). Anal. Calcd for $C_{15}H_{24}C_{12}FeHgO_6P_2S_2$: C, 23.9; H, 3.2; P, 8.2. Found: C, 23.7; H, 3.0; P, 8.4.

Preparation of $S{=}\overline{CSC(CO_2Me){=}C(CO_2Me)S}$ (6). Method A. Reaction of 2c and 3c with Cyclohexene Sulfide. From 2c. Dimethyl acetylenedicarboxylate (0.2 mL) was added to a stirred solution of 0.34 g of **1c** (1 mmol) in 25 mL of CH_2Cl_2, at room temperature. After 5 min, 0.3 mL (2 mmol) of cyclohexene sulfide was added. The reaction was followed by thin-layer chromatography. After 24 h of stirring at room temperature, no reaction occurred. The solution was then refluxed for 1 h. After filtration and evaporation of the solvent to dryness, the crude product was chromatographed on a silica gel column (eluent hexane–ether). The yellow compound **6** was obtained (0.12 g, 48%): IR (Nujol) $\nu_{C=O}$ 1735, 1720, $\nu_{C=C}$ 1530 cm^{-1}; mp 84–86 °C; ^1H NMR ($CDCl_3$, 60 MHz, 309 K) δ 3.80 (s, CO_2Me) [Lit.[17] mp 86–87 °C; ^1H NMR (Me_2SO-d_6) δ 3.83 (s, CO_2Me)].

From 3c. To a solution of 0.4 g of **3c** (0.5 mmol) in 25 mL of CH_2Cl_2 was added 0.3 mL of cyclohexene sulfide (2 mmol). After 20 min of stirring at room temperature, the solvent was evaporated to dryness. The yellow compound **6** was isolated by using a silica gel column chromatography (eluent hexane–ether); obtention of 0.11 g of **6** (88%).

Method B. Reaction of 2c and 3c with Sulfur. From 2c. Dimethyl acetylenedicarboxylate (0.2 mL) was added to a stirred solution of 0.34 g of **1c**[16] (1 mmol) in 25 mL of CH_2Cl_2, at room temperature. After 5 min, 1 g of sulfur was added. The reaction was followed by thin-layer chromatography. After 24 h of stirring at room temperature, no reaction occurred. The solution was then refluxed for 72 h. After filtration and evaporation of the solvent to dryness, the crude product was chromatographed on a silica gel column (eluent hexane–ether); obtention of 0.05 g of **6** (22%).

From 3c. To a solution of 0.4 g of **3c** (0.5 mmol) in 25 mL of CH_2Cl_2 was added 1 g of sulfur. After 24 h of stirring at room temperature, the solvent was evaporated to dryness. The yellow compound **6** was isolated by using a silica gel column chromatography (eluent hexane–ether); obtention of 0.1 g of **6** (78%).

Crystallographic Analysis. Yellow crystals suitable for X-ray diffraction measurements were grown by diffusion of ether into a methanol solution of the complex. The data crystal was mounted in thin-walled glass capillary. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated diffractometer and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines. The space group *C2/c* was established from the pattern of systematic absences observed during the data collection. Crystal data and data collection parameters are listed in Table I. All data processing was performed on a Digital Equipment Corp. PDP 11/45 computer using the Enraf-Nonius SDP program library (version 18). An absorption correction of a Gaussian integration type was applied to all data. Neutral atom scattering factors were calculated by the standard procedures.[18a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[18b] Full-matrix least-squares refinements minimized the function: $\sum_{hk} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o{}^2)/2F_o$, and $\sigma(F_o{}^2) = [\sigma(I_{raw})^2 + (pF_o{}^2)^2]^{1/2}/Lp$.

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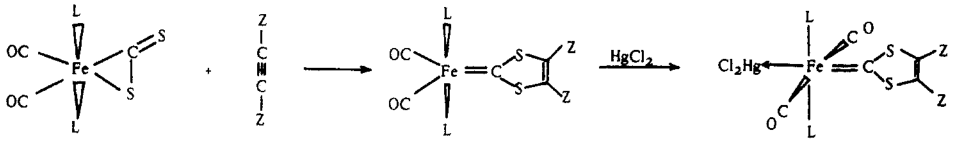
(15) Le Bozec, H.; Dixneuf, P. H.; Adams, R. D. *Organometallics* **1984**, *3*, 1919.

(16) Le Bozec, H.; Dixneuf, P. H.; Carty, A. J.; Taylor, N. J. *Inorg. Chem.* **1978**, *14*, 2568.

(17) Melby, R. L.; Hartzler, H. D.; Sheppard, W. A. *J. Org. Chem.* **1974**, *39*, 2456.

(18) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV; (a) Table 2.2 B, pp 99–101; (b) Table 2.3.1, pp 149–150.

Scheme II



1a–d Z = CO$_2$Me 2a–d 3a–d

a = PMe$_2$Ph
b = PMe$_3$
c = P(OMe)$_3$
d = PPh$_3$

The structure was solved by combination of direct methods and difference Fourier techniques. The iron and mercury atoms were located in an electron density map based on the phasing (MULTAN) of 412 reflections ($E_{\min}$ = 1.73). Only atoms heavier than oxygen were refined anisotropically. Hydrogen atoms were ignored. The values of the final fractional atomic coordinates are listed in Table II. Tables III and IV list interatomic distances and angles with estimated standard deviations obtained from the inverse matrix on the final cycle of refinement.

Table I. Crystallographic Data for X-ray Diffraction Studies

(A) Crystal Data	
formula	$HgFeCl_2S_2P_2O_6C_{25}H_{28}$
temp, (±3 °C)	23
space group	C_2/c, No. 15
a, Å	35.059 (5)
b, Å	11.706 (1)
c, Å	17.600 (2)
α, deg	90.00
β, deg	101.96 (1)
γ, deg	90.00
V, Å^3	7067 (3)
M_r	877.9
Z	8
P_{calcd}, g cm^3	1.65
(B) Measurement of Intensity Data	
radiatn	Mo K$\bar{\alpha}$(0.710 73Å)
monochromator	graphite
detector aperture (mm)	
Horizontal ($A + B$ tan θ)	
A	3.0
B	1.2
vertical	4.0
cryst faces	100, $\bar{1}00$, $11\bar{1}$, $\bar{1}11$, 001, $00\bar{1}$
crystal size, mm	0.22 × 0.29 × 0.30
cryst orientatn directn; deg from ϕ axis	112; 0.0
reflectns measd	$h,k,\pm l$
max 2θ	46°
scan type	moving crystal–stationary counter
ω-scan width (A + 0.347 tan θ)°	1.0
bkgd	$^1/_4$ additional scan at each end of scan
ω-scan rate (variable)	
max, deg/min	10.0
min, deg/min	1.5
no. of reflectns measd	5250
data used ($F^2 > 3.0\sigma(F^2)$)	3253
(C) Treatment of Data	
abs correctn:	
coeffi, cm	51.4
grid	8 × 14 × 8
transmissn coeff	
max	0.38
min	0.31
decay correctn	
max	1.04
min	0.99
p factor	0.03
final residuals	
R_F	0.044
R_{wF}	0.058
esd of unit weight observn	2.47
largest shift/error value of final cycle	0.03
largest peak in final diff Fourier, e/A^3	1.14

Results and Discussion

Synthesis of Complexes 3. We have already shown that |η^2-CS$_2$| iron complexes **1a–d** readily reacted with dimethyl acetylenedicarboxylate under inert atmosphere and at room temperature to produce the thermally stable **2c,d**[1,2] and the isomerizable **2a,b**[2,11] 1,3-dithiol-2-ylidene iron derivatives (Scheme II). We have studied their behavior toward the Lewis acid HgCl$_2$ which was added in situ and have shown that their reactivity is dependent on the nature of the phosphorus ligands L. Thus, the thermally stable carbene complexes **2c,d** bearing weak donor phosphorus derivatives slowly reacted with mercury(II) chloride in dichloromethane at room temperature to afford almost quantitatively the new bimetallic complexes **3c,d** as a yellow precipitate: **3c** (89%); **3d** (79%). The reaction which was completed after 1 h of stirring, contrasted with the very fast formation of complexes **3a,b** bearing alkylphosphines. Addition of 1 equiv of dimethyl acetylenedicarboxylate to a solution of complexes **1a,b** in ether was rapidly followed by the addition of 1 equiv of mercury chloride to prevent the isomerization of the intermediates **2a,b** into the heterometallocycles of type III.[2,11] A bright yellow precipitate of **3a,b** *immediately* formed in quantitative yields: **3a** (82%); **3b** (98%). The difference in the rate of addition of the Lewis acid to basic complexes **2** is consistent with an increase of the electron density on the iron atom according to the donor capability of the phosphorus groups in the sequence P(OMe)$_3$ < PPh$_3$ < PMe$_2$Ph < PMe$_3$. By contrast to the air sensitivity and to the isomerization ability of the precursors **2**, the Hg(II)←Fe(0) bimetallic complexes **3** are air-stable and do not isomerize in any cases. Therefore, the reaction **2** → **3** provides an excellent method to stabilize the reactive carbene complex **2**.

The necessity of adding HgCl$_2$, as soon as the intermediates **2a** and **2b** were formed, was demonstrated by the following experiment. As the carbene–iron complex **2b** isomerized rapidly into the heterometallocyclic iron(II) complex **4b**[2,11] (Scheme III), the addition of dimethyl acetylenedicarboxylate to **1b** was followed by a 6 h of stirring at room temperature before addition of HgCl$_2$. A yellow precipitate appeared slowly which was obtained in 86% yield and identified as derivative **5b**, resulting from the bonding of HgCl$_2$ to a sulfur atom of **4b**.

Spectroscopic Characterization. Compounds **3** were characterized on the basis of their analyses, infrared and NMR spectroscopies, and the crystallographic structure determination for **3a**. They are only soluble in dichloromethane and methanol, except for complex **3d** of which

Table II. Final Positional Parameters for $Cl_2HgFe(CO)_2(PMe_2Ph)_2[CS_2C_2(CO_2Me)_2]$ (3a)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Hg	0.84239 (2)	0.10433 (4)	0.08553 (3)	C7	0.9434 (5)	0.5599 (15)	0.5423 (9)
Fe	0.85502 (4)	0.1672 (1)	0.22703 (8)	C8	0.7819 (4)	0.2662 (12)	0.6051 (7)
Cl(1)	0.7852 (1)	0.0157 (3)	−0.0018 (2)	C9	0.8613 (3)	0.2116 (9)	0.3334 (6)
Cl(2)	0.8845 (1)	0.1647 (4)	−0.0069 (2)	C11	0.8150 (3)	0.4260 (9)	0.2529 (6)
S1	0.89149 (8)	0.3172 (2)	0.3744 (1)	C12	0.8415 (4)	0.5129 (11)	0.2467 (7)
S2	0.83466 (9)	0.1571 (3)	0.3956 (2)	C13	0.8485 (4)	0.6008 (14)	0.3057 (9)
P1	0.80989 (9)	0.3063 (3)	0.1857 (2)	C14	0.8302 (4)	0.5949 (13)	0.3664 (9)
P2	0.90221 (9)	0.0341 (3)	0.2610 (2)	C15	0.8031 (4)	0.5093 (13)	0.3722 (8)
O1	0.9148 (2)	0.3143 (7)	0.1840 (5)	C16	0.7954 (4)	0.4225 (11)	0.3138 (7)
O2	0.7954 (3)	−0.0065 (8)	0.2268 (5)	C17	0.7589 (4)	0.2623 (13)	0.1719 (8)
O3	0.8875 (3)	0.4261 (8)	0.5807 (5)	C18	0.8122 (4)	0.3745 (12)	0.0924 (8)
O4	0.9244 (2)	0.4611 (7)	0.4964 (5)	C21	0.9401 (3)	0.0816 (9)	0.3417 (6)
O5	0.8535 (2)	0.1778 (7)	0.6041 (5)	C22	0.9373 (3)	0.0574 (11)	0.4178 (7)
O6	0.8028 (2)	0.2792 (7)	0.5394 (4)	C23	0.9660 (4)	0.1035 (12)	0.4810 (8)
C1	0.8906 (3)	0.2558 (10)	0.2000 (6)	C24	0.9962 (4)	0.1725 (13)	0.4658 (8)
C2	0.8189 (3)	0.0643 (10)	0.2255 (7)	C25	0.9983 (4)	0.1946 (12)	0.3910 (8)
C3	0.8800 (3)	0.3187 (9)	0.4661 (6)	C26	0.9701 (4)	0.1524 (11)	0.3279 (7)
C4	0.8532 (3)	0.2432 (9)	0.4752 (6)	C27	0.8857 (4)	−0.1030 (11)	0.2922 (7)
C5	0.8972 (3)	0.4055 (10)	0.5204 (7)	C28	0.9296 (3)	−0.0074 (10)	0.1868 (7)
C6	0.8369 (3)	0.2313 (10)	0.5481 (6)				

Table III. Interatomic Distances (Å) with Esd's for $Cl_2HgFe(CO)_2(PMe_2Ph)_2[CS_2C_2(CO_2Me)_2]$ (3a)

Hg–Fe	2.546 (1)	O(4)–C(7)	1.487 (12)
Hg–Cl(1)	2.486 (2)	C(4)-C(6)	1.514 (9)
Hg–Cl(2)	2.514 (2)	C(6)–O(5)	1.210 (8)
Fe–P(1)	2.282 (2)	C(6)–O(6)	1.303 (8)
Fe–P(2)	2.260 (2)	O(6)–C(8)	1.499 (9)
Fe–C(1)	1.761 (8)	P(1)–C(11)	1.819 (7)
Fe–C(2)	1.744 (8)	P(1)–C(17)	1.828 (9)
Fe–C(9)	1.912 (7)	P(1)–C(18)	1.842 (10)
C(9)–S(1)	1.688 (7)	P(2)–C(21)	1.819 (7)
C(9)–S(2)	1.704 (7)	P(2)–C(27)	1.829 (8)
C(3)–S(1)	1.743 (7)	P(2)–C(28)	1.840 (8)
C(4)–S(2)	1.739 (7)	C(1)–O(1)	1.170 (8)
C(3)–C(4)	1.324 (9)	C(2)–O(2)	1.171 (8)
C(3)–C(5)	1.438 (10)	$C–C_{av}(11–16)$	1.40 (3)
C(5)–O(3)	1.206 (9)	$C–C_{av}(21–26)$	1.40 (3)
C(5)–O(4)	1.295 (9)		

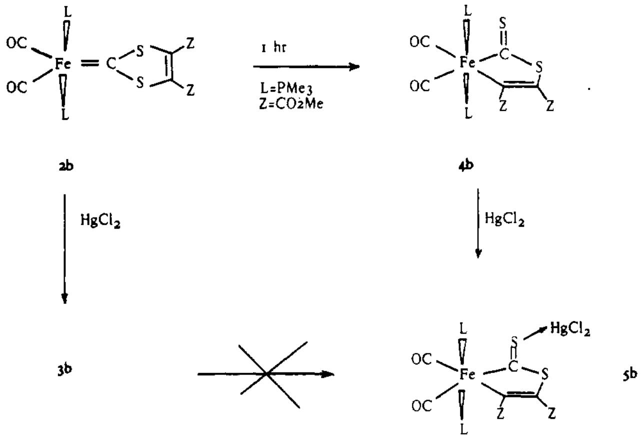
Table IV. Interatomic Angles (deg) with Esd's for $Cl_2HgFe(CO)_2(PMe_2Ph)_2[CS_2C_2(CO_2Me)_2]$ (3a)

Hg–Fe–C(9)	176.5 (2)	C(9)–S(2)–C(4)	97.9 (3)
Hg–Fe–P(1)	85.73 (6)	S(1)–C(3)–C(4)	114.3 (5)
Hg–Fe–P(2)	91.68 (6)	S(1)–C(3)–C(5)	118.5 (5)
Hg–Fe–C(1)	84.0 (2)	S(2)–C(4)–C(3)	116.4 (5)
Hg–Fe–C(2)	78.9 (2)	S(2)–C(4)–C(6)	119.1 (5)
P(1)–Fe–P(2)	175.60 (8)	C(4)–C(3)–C(5)	127.0 (6)
P(1)–Fe–C(1)	88.6 (2)	C(3)–C(4)–C(6)	124.4 (6)
P(1)–Fe–C(2)	92.0 (3)	C(3)–C(5)–O(3)	124.8 (7)
P(1)–Fe–C(9)	92.9 (2)	C(3)–C(5)–O(4)	112.0 (7)
P(2)–Fe–C(1)	87.6 (2)	C(5)–O(4)–C(7)	119.4 (7)
P(2)–Fe–C(2)	91.0 (3)	C(4)–C(6)–O(5)	122.4 (7)
P(2)–Fe–C(9)	89.9 (2)	C(4)–C(6)–O(6)	111.1 (6)
C(1)–Fe–C(2)	162.8 (3)	C(6)–O(6)–C(8)	116.8 (6)
C(1)–Fe–C(9)	99.2 (3)	Fe–C(1)–O(1)	178.2 (6)
C(2)–Fe–C(9)	98.0 (3)	Fe–C(2)–O(2)	177.7 (7)
Fe–Hg–Cl(1)	132.86 (6)	Fe–P(1)–C(11)	112.0 (2)
Fe–Hg–Cl(2)	123.05 (7)	Fe–P(1)–C(17)	115.8 (3)
Cl(1)–Hg–Cl(2)	102.89 (9)	Fe–P(1)–C(18)	116.0 (3)
Fe–C(9)–S(1)	123.6 (4)	Fe–P(2)–C(21)	111.9 (2)
Fe–C(9)–S(2)	124.0 (4)	Fe–P(2)–C(27)	115.1 (3)
S(1)–C(9)–S(2)	112.2 (4)	Fe–P(2)–C(28)	117.1 (3)
C(9)–S(1)–C(3)	99.1 (3)		

its insolubility in all common solvents prevented its NMR characterization.

In contrast to the infrared spectra of the carbene–metal precursors **2** which exhibit two carbonyl absorption bands at very low frequencies,[2] the infrared spectra of the Hg(II)←Fe(0) complexes **3** show only one strong carbonyl absorption band between 1940 and 1960 cm^{-1}, consistent with trans carbonyl ligands. The ^1H NMR spectra show equivalent CO_2Me groups compatible with the symmetry of the carbene moiety. The methyl groups of the phosphorus ligands are equivalent and appear as a triplet due to virtual coupling for **3c** and as a doublet for compounds **3a** and **3b**. The ^{31}P NMR spectra of compounds **3a–c** show a signal corresponding to a singlet with two symmetrical lines in the approximate ratio 1:10:1. This signal is consistent with equivalent ^{31}P nuclei but with a coupling with ^{199}Hg nucleus in 16% of molecules. The magnitude of the $^2J_{^{31}P-^{199}Hg}$ value (**3a**, 742 Hz; **3b**, 801 Hz; **3c**, 894 Hz) is compatible with two phosphorus ligands cis to mercury(II). Such $^2J_{^{31}P-^{199}Hg}$ coupling constants have been previously observed in iridium–mercury and rhodium–mercury complexes with cis and trans ^2J values of about 300–400 and 3500–4000 Hz, respectively.[19]

Scheme III



Unlike complexes **3**, the infrared spectrum of compound **5b** shows carbonyl absorption bands at 2030 and 1985 cm^{-1}; which are at slightly higher frequencies than in the starting complex **4b** (2020, 1960 cm^{-1}).[11] The ^1H NMR spectrum of **5b** indicates the inequivalency of the CO_2Me groups as in the precursor complex **4b** which is consistent with the unsymmetrical incorporation of the alkyne into the complex. The ^{31}P NMR exhibits a single line, with no observable $^{31}P-^{199}Hg$ coupling and is in agreement with the proposed structure where the mercury is bonded to the sulfur rather than to the iron atom.

The ^{13}C NMR spectra of derivative **3a** shows the equivalency of the carbonyls, the CO_2Me groups, and the olefinic carbons, but the carbene carbon appears at low field as a triplet due to coupling with two identical

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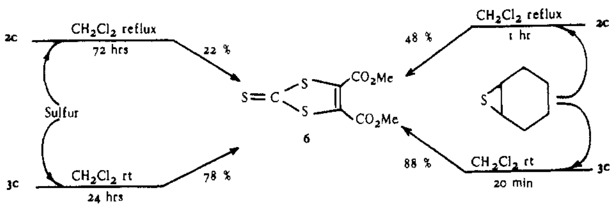
[19] Van Vliet, P. I.; Kuyper, J.; Vrieze, K. *J. Organomet. Chem.* **1975**, *122*, 99.

Scheme IV



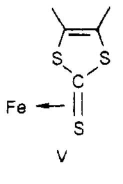
phosphorus nuclei (δ (CD_3OD) 267 (t, $^2J_{P-C}$ = 16.2 Hz)). The corresponding resonance of carbene carbon of the precursor **2a** lies at much higher field and appears to be weakly coupled with the two phosphorus nuclei (δ (C_6D_6) 242 (t, $^2J_{P-C}$ = 2.7 Hz). This comparison suggests that the coordination of $HgCl_2$ trans to the carbene ligand in **3a** produces a reduction of the electron density at the carbene carbon atom, as compared to that in precursor **2a**. Consequently an enhancement of the electrophilicity of the carbene carbon atom upon formation of the trans donor–acceptor Hg(II)←Fe(0) bond should be expected.

Reactivity of 2c and 3c toward Sulfur and Cyclohexene Sulfide. The previous spectroscopic studies have suggested a possible enhancement of the electrophilicity of the carbene carbon atom by coordination of $HgCl_2$ trans to the 1,3-dithiol-2-ylidene ligand. To illustrate this point, we have studied the reactivity of carbene–iron complex **2c** and of its $HgCl_2$ adduct **3c** toward sulfur and cyclohexene sulfide (Scheme IV).

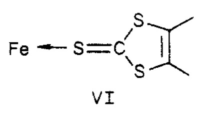
We have previously described a simple route to a variety of 1,3-dithiole-2-thione, which are one of the main precursors of tetrathiofulvalene derivatives, by displacement of the 1,3-dithiol-2-ylidene ligand from carbene–iron complexes **2d** (L = PPh_3) with elemental sulfur.[9] Thus the thione **6** was obtained in 64% yield by heating **2d** with an excess of sulfur to reflux in toluene. Under similar conditions the carbene **2c** gave only a 25% yield.[9] However, complex **3c** reacts with sulfur at *room temperature* in dichloromethane to give the thione **6** in 78% yield after 24 h. Compound **2c** failed to react under the same experimental conditions, but small amounts of compound **6** were formed in a lower yield (22%) when **2c** and sulfur were refluxed in dichloromethane for 72 h.

Recently cyclohexene sulfide has been used as a sulfur donor atom by Gladysz et al.[20] for the synthesis of a η^2-thioformaldehyde complex from an electrophilic methylidene–rhenium complex. We have compared the reactivity, of this sulfur donor with the carbene–iron complex **2c** and its $HgCl_2$ adduct **3c**. Compound **2c** did not react with cyclohexene sulfide at room temperature but did give **6** in 48% yield after 1 h of heating to reflux in dichloromethane. By contrast **3c** reacted rapidly at room temperature, within half an hour, and gave **6** (88%).

The mechanism of formation of compound **6** from sulfur and cyclohexene sulfide has not been elucidated. However, it is proposed that the first step is the nucleophilic addition of the sulfur atom to the carbene carbon atom. This explains the faster reaction with **3c**, where the carbon center is more electrophilic, than with **2c**. In the case of reaction with cyclohexene sulfide, this step must be accompanied by the loss of cyclohexene. The second step may provide the formation of either an η^2-thione intermediate, V, or an η^1-thione intermediate, VI.



V



VI

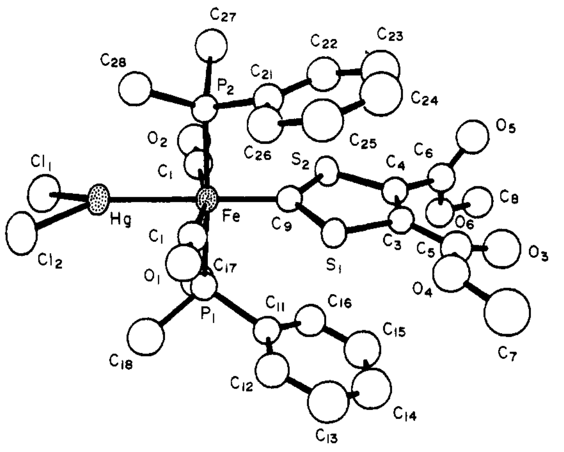


Figure 1. Perspective view of the structure of $Cl_2HgFe(CO)_2(PMe_2Ph)_2[CS_2C_2(CO_2Me)_2]$ (**3a**).

Complex V is comparable with the η^2-formaldehyde–rhenium complex made by Gladysz et al.,[20] whereas intermediate VI is supported by the recent isolation of a $(OC)_5W\leftarrow S{=}CR_2$ complex by treatment of a Fischer-type carbene–chromium compound with sulfur.[21] This latter carbene derivative was also previously known to give thio ester with elemental sulfur.[22] Finally these two intermediates could lead to **6** by decoordination of the η^2- or η^1-thione.

Description and Discussion of the Structure of 3a. An ORTEP plot of one molecule without hydrogen atoms is illustrated in Figure 1. Bond lengths and angles are listed in Tables III and IV. The geometry around the iron center can be described in terms of an octahedron with trans phosphines and trans carbonyls and by a $HgCl_2$ ligand trans to the cyclic carbene ligand. This description is supported by the values of the angles P(1)–Fe–P(2) = 175.60 (8)°, C(1)–Fe–C(2) = 162.8 (3)°, and Hg–Fe–C(9) = 176.5 (2)°. The average Fe–P bond length (2.271 Å) is comparable to that in other iron alkylphosphine complexes such as in $Fe(PMe_3)_2(CO)_2(CS_2CH_2Ph)^+(PF6)^-$ (average 2.276 Å)[23] or in $(Me_3P)(OC)\overline{FeCH(SMe)COC(CO_2Me)=C(CO_2Me)S}$ (average 2.238 Å).[24] The Hg–Fe bond length (2.546 (1) Å) is similar to that in known Hg–Fe complexes containing different HgX_2 moieties such as in $Fe(CO)_4(HgClpy)_2$[25] (2.553 (8) Å), $[Fe(CO)_4(HgCl)(HgCl_2)]^-(AsPh_4)^+$[26] (2.560 (3) and 2.516 (4) Å), or $Hg[Fe(CO)_2NO(PEt_3)]_2$[27] (2.534 (2) Å). The Hg atom is 0.157 Å out of the plane [Cl(1),Cl(2),Fe], and the [Cl(1),Cl(2),Hg)][(FeC(1),C(2),C(9)] dihedral angle is 18.2°. The two Hg–Cl bond lengths are similar [2.486 (2) and 2.514 (2) Å], but the Cl–Hg–Fe angles are significantly different [132.86 (6) and 123.05 (7)°].

The (carbene)C–Fe distance (1.912 (7) Å) is comparable to that in the dioxanylidene–iron complex $(OC)_4\,Fe{=}\overline{COC(R)C(R)O}$ (1.905 (1) Å)[28] but is markedly shorter than

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[20] Buhro, W. E.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A.; McCormick, F. B.; Etter, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 1056.

[21] Fischer, H. *J. Organomet. Chem.* **1981**, *219*, C34.

[22] Fischer, E. O.; Riedmuller, S. *Chem. Ber.* **1978**, *107*, 915.

[23] Touchard, D.; Le Bozec, H.; Dixneuf, P. H.; Carty, A. J.; Taylor, N. J. *Inorg. Chem.* **1981**, *20*, 1811.

[24] Touchard, D.; Dixneuf, P. H.; Adams, R. D.; Segmueller, B. E. *Organometallics* **1984**, *3*, 640.

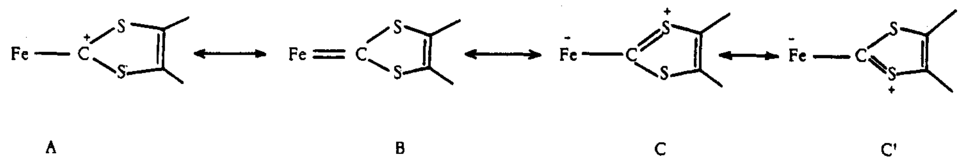
[25] Baker, R. W.; Pauling, P. J. *J. Chem. Soc., Chem. Commun.* **1970**, 573.

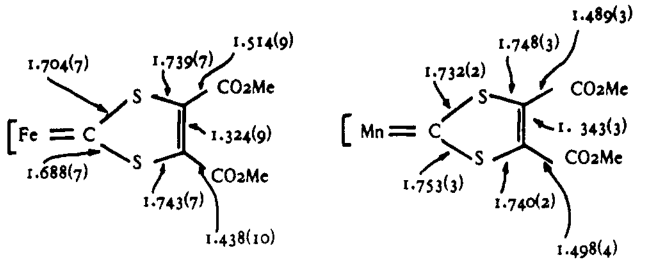
[26] Botherton, P. D.; Kepert, D. L.; White, A. H.; Wild, S. B. *J. Chem. Soc., Dalton. Trans.* **1976**, 1870.

[27] Stephens, F. S. *J. Chem. Soc., Dalton. Trans.* **1972**, 2257.

[28] Daub, J.; Endress, G.; Erhardt, U.; Jogun, K. H.; Kappler, J.; Laumer, A.; Pfiz, R.; Stezowski, J. J. *Chem. Ber.* **1982**, *115*, 1787.

Scheme V





3a 7

Figure 2.

in $(OC)_4\,Fe{=}\overline{CN(Me)CH_2CH_2N}{-}Me$ (2.007 (5) Å).[29] This difference can be attributed to a greater π-donor character of an amino group, as compared to an oxy or thio group, and this reduces back-bonding from the metal to the carbene and thus lengthens the iron–C(carbene) distance. Of special interest is the cyclic carbene ligand itself which is approximately planar. Its structural parameters can be directly compared with those of the same ligand bonded to manganese(I) in $(C_5H_5)(CO)(P(OMe)_3)$-$Mn{=}\overline{CSC(CO_2Me){=}C(CO_2Me)S}$ (7),[3] which is the only carbene–metal complex of type II for which crystallographic data have been obtained previously (Figure 2). The C(3)–C(4) bond length (1.324 (9) Å) is slightly shorter than in the manganese complex 7[3] (1.343 (3) Å) and corresponds to that expected for a carbon–carbon double bond. This is also evidence against the aromatic nature of the ring which would induce a lengthening of this bond. Although the two (olefinic)C–$C(CO_2Me)$ bond distances C(3)–C(5) (1.438 (10) Å) and C(4)–C(6) (1.514 (9) Å) are significantly different, the average (1.476 Å) can be favorably compared with the expected $C(sp^2)$–$C(sp_2)$ single bond (1.48 Å) and is an indication of the nonconjugation of the CO_2Me groups with the carbene ligand. The carbene carbon–sulfur bond distances (C(9)–S(1) = 1.688 (7) Å and C(9)–S(2) = 1.704 (7) Å) are significantly shorter than the two olefinic carbon–sulfur bond lengths C(9)–S(1) = 1.743 (7) Å and C(4)–S(2) = 1.739 (7) Å. They are also markedly shorter than the corresponding C–S bond lengths in **7** (average 1.744 Å) which, unlike **3a**, shows only slight differences between the four carbon–sulfur bond distances. This result implies that considering the classical valence bond representation A ⇄ B ⇄ C for a Fischer-type metal–carbene complex (Scheme V), there is a greater contribution to **3a** from the canonical forms C and C′. This also suggests that the formation of a donor–acceptor Fe→Hg(II) bond trans to the carbene ligand reduces the iron–carbene back-donation, thus reduces the electron density at the carbene carbon atom, and induces an increase of the electron transfer from the sulfur atoms toward the carbene carbon atom.

Conclusion

The present results show that the formation of a donor–acceptor mercury(II)←iron(0) bond can be used (i) to trap unstable carbene iron(0) derivatives and thus prevent their air oxidation or their isomerization, (ii) to allow their X-ray diffraction study, and (iii) to enhance the electron deficiency on the carbene carbon atom. Thus the formation of Hg(II)←M(0) adduct provides a new method of stabilization of electron-rich unstable metal complexes but can also be used to increase selectively the reactivity of their ligands.

Acknowledgment. D.V.K. is grateful to the CNRS for financial support.

Registry No. **1a**, 64424-57-3; **1b**, 64424-58-4; **1c**, 64424-66-4; **1d**, 64424-68-6; **3a**, 93110-78-2; **3b**, 103191-62-4; **3c**, 103191-63-5; **3d**, 103224-46-0; **5b**, 103191-64-6; **6**, 7396-41-0; $HgCl_2$, 7487-94-7; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5; cyclohexene sulfide, 286-28-2.

Supplementary Material Available: A table of thermal parameters (1 page); a table of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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(29) Huttner, G.; Gartzke, W. *Chem. Ber.* **1972**, *105*, 2714.