= P(O-*i*-Pr)$_3$, 80719-05-7; **1**, L = CO, 12078-25-0; **2a**, 80719-07-9; **2**, L = PEt$_3$, X = I, 80719-08-0; **2**, L = PEt$_3$, X = BF$_4$, 80719-10-4; **2**, L = PEt$_3$, X = Br, 80719-11-5; **2**, L = PPh$_2$Et, X = BF$_4$, 80719-13-7; **2**, L = DPPE, X = Br, 80719-14-8; **2**, L = DPPE, X = I, 80719-15-9; **2**, L = P(O-*i*-Pr)$_3$, X = BF$_4$, 80719-17-1; **2**, L = P(OPh)$_3$, X = BF$_4$, 80719-19-3; **3a**, 72859-67-7; **3**, L = PPh$_3$, X = Br, 80719-20-6; **3**, L = PPh$_3$, X = I, 80719-21-7; **3**, L = PEt$_3$, X = Cl, 80719-22-8; **4**, L = CO, X = I, 12012-77-0; **4**, L = PPh$_3$, X = CN, 38531-03-2; **5**, L = PPh$_3$, X = BF$_4$, 80719-24-0; **6**, L = PEt$_3$, X = Cl, BF$_4$, 80719-26-2; **7**, L = PEt$_3$, X = BF$_4$, 80719-28-4; **8**, L = P(OMe)$_3$, X = BF$_4$, 80737-24-2; **8**, L = P(OEt)$_3$, X = BF$_4$, 80737-26-4; **8**, L = P(O-*i*-Pr)$_3$, X = BF$_4$, 80719-30-8; (Ph$_3$P)$_3$CoCl, 26305-75-9; (Et$_3$P)$_2$CoI$_2$, 31933-55-8; (η-C$_5$H$_5$)$_2$Co, 1277-43-6; (Ph$_3$P)$_2$CoCl$_2$, 14126-40-0; (Ph$_3$P)$_2$CoBr$_2$, 14126-32-0; (Ph$_3$P)$_2$CoI$_2$, 14056-93-0; (Et$_3$P)$_2$CoCl$_2$, 14784-62-4; (Et$_3$P)$_2$CoBr, 14784-57-7; (Ph$_2$EtP)$_2$CoBr$_2$, 14916-44-0; (Ph$_2$EtP)$_2$CoI$_2$, 31880-18-9; (Ph$_2$EtP)$_2$CoCl$_2$, 14916-45-1; (DPPE)CoBr$_2$, 34775-49-0; (DPPE)CoI$_2$, 34775-39-8; ((EtO)$_3$P)$_3$CoCl, 15488-43-4.

Contribution from the Laboratoire de Chimie de l'Ecole Normale Supérieure,
associé au CNRS, 24 rue Lhomond, 75231 Paris Cedex 05, France

A New Route to Thiocarbonyl–Iron Complexes: Preparation of Fe^{II}[porphyrin][C(Cl)SR] Carbene Complexes and Their Conversion to Fe^{II}[porphyrin][CS] Complexes

JEAN-PAUL BATTIONI, JEAN-CLAUDE CHOTTARD, and DANIEL MANSUY*

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The reaction of trichloromethyl–thioalkyl compounds including the widely used fungicides Captan and Folpet with iron(II) porphyrins in the presence of a reducing agent in excess leads to the formation of new carbene complexes, Fe[porphyrin][C(Cl)SR], whose stabilities are strongly dependent on the nature of the R substituent. Upon treatment by a catalytic amount of FeCl$_2$ or CuCl$_2$, some of them are decomposed into thiocarbonyliron(II)–porphyrin complexes, Fe[porphyrin][CS], in nearly quantitative yields. Various Fe[porphyrin][CS][L] complexes have thus been obtained by this method and characterized by UV–visible, IR, and ^{1}H and ^{13}C NMR spectroscopy. They are very stable to dioxygen and nucleophiles but react with primary amines R'NH$_2$ in excess to give the Fe[porphyrin][CNR'][R'NH$_2$] complexes. Reduction of C$_6$H$_5$SCHCl$_2$ by iron(II) tetraphenylporphyrin, Fe[TPP], leads to the Fe[TPP][CHSC$_6$H$_5$] complex, which is the first example of an iron(II) porphyrin complex bearing a secondary CHR carbene.

Introduction

Polyhalogenated compounds are widely used as industrial solvents, insecticides, fungicides, or volatile anaesthetics. It has been indicated[1] that they lead to cytochrome P450–iron(II)–carbene complexes upon reductive metabolization (eq 1).

$$\underset{\mathbf{1}}{RCCl_3} + Fe[P] \xrightarrow[-2Cl^-]{2e^-} \underset{\mathbf{2}}{Fe[P][C(Cl)R]} \qquad (1)$$

P = porphyrin or cytochrome P450

This has been recently confirmed by the preparation of carbene–iron(II) porphyrin complexes (**2**) upon reduction of polyhalogenated compounds by iron(II) porphyrins in the presence of an excess of reducing agent (eq 1).[2,3] The carbenic structure of complexes **2** has been established by their elemental analysis and various spectroscopic studies as well as by an X-ray diffraction analysis[3b] in the case of the dichlorocarbene complex Fe[TPP][CCl$_2$][H$_2$O].[3a,4]

Various organic compounds containing the SCCl$_3$ moiety display fungicidal activity. Among them, Folpet **3a**[4] and especially Captan **3b**[4] are broad spectra, nonpersistent fungicides, which are widely used for various fungus diseases of seeds, plants, and fruits.[5] Their activities have been related to the presence of the SCCl$_3$ group, which is metabolized in part into thiophosgene and carbonyl sulfide.[6]

We have studied the reduction of RSCCl$_3$ compounds by iron(II) porphyrins in order to mimic their reductive metabolism by cytochrome P450–iron(II) and also to have an access to the unknown carbene complexes of the type Fe^{II}[P][C(Cl)SR] that one could expect from eq 1.

We report, in this paper,[7] the preparation and properties of such carbene complexes, Fe[TPP][C(Cl)SR], and a new simple method of preparation of iron thiocarbonyl complexes based on the unexpected property of the aforementioned carbene complexes to eliminate RCl upon treatment by FeCl$_2$ or CuCl$_2$. The properties of some thiocarbonyl–iron(II) porphyrin complexes, Fe[P][CS][L], obtained by this reaction are also discussed.

Results and Discussion

(I) Reaction of Iron(II) Porphyrins with RSCCl$_3$ and RSCHCl$_2$ in the Presence of an Excess of Reducing Agent. The reduction of the RSCCl$_3$ compounds **3a**–**3d** and of dichloromethyl benzyl thioether, **3e**, by iron(II) tetraphenylporphyrin has been done under argon in a biphasic medium (CH$_2$Cl$_2$ or C$_6$H$_6$–H$_2$O) with sodium dithionite as a reducing agent (method A). Compounds **3d** and **3e** can also be reduced in dichloromethane–methanol solutions with iron powder as a

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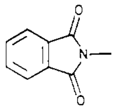
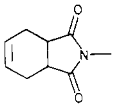
0020-1669/82/1321-2056$01.25/0

$$RSCXCl_2 + Fe[TPP] \xrightarrow[\text{or B: } Fe^0,\ CH_2Cl_2-CH_3OH]{\text{A: } Na_2S_2O_4,\ H_2O-C_6H_6} \underset{4}{Fe[TPP][C(X)SR]} \qquad (2)$$

3a, X = Cl,



3b, X = Cl,



c, X = Cl, R = $C_6H_5CH_2$
d, X = Cl, R = C_6H_5
e, X = H, R = C_6H_5

Table I. Spectral Characteristics of the Carbene Complexes [Fe][TPP][C(Cl)SR] 4

compd	UV[a] λ, nm ($10^{-5}\epsilon$)	visible[a] λ, nm ($10^{-3}\epsilon$)		δ (vs. Me_4Si) ^1H NMR signals of carbene ligand[b,c]			^{13}C NMR[b,d]
4a	408 (2.1)	520 (16.5)	544 sh	7.33 (s, 4 H)			264.3
4b	411[e]	521[e]	544 sh	5.95 (m, 2 H)	3.55 (m, 2 H)	2.91–2.41 (m, 4 H)	f
4c	412 (2.0)	520 (17)	545 sh	6.88 (m, 3 H)	5.81 (m, 2 H)	2.71 (s, 2 H)	266.4
4d	411 (1.9)	520 (17)	548 sh	6.65 (m, 3 H)	5.55 (m, 2 H)		288.5
4e	413 (1.9)	521 (18.7)	545 sh	6.61 (m, 3 H)	5.56 (m, 2 H)	13.83 (s, 1 H)	f

[a] C_6H_6 solution. [b] $DCCl_3$ solution. [c] At 34 °C. [d] δ for the carbene carbon, at 20 °C. [e] Too unstable for the determination of ε. [f] Too unstable for reasonable acquisition times.

reducing agent (method B). The formation of complexes **4** was followed by visible spectroscopy on samples of the reaction mixture diluted in deaerated benzene.

Complexes **4** were obtained by crystallization from mixtures of noncoordinating (CH_2Cl_2, $CHCl_3$, C_6H_6) and weakly coordinating (CH_3OH, C_2H_5OH) solvents. Depending upon these crystallization conditions, they are obtained either as pentacoordinated, Fe[TPP][C(Cl)SR], or as hexacoordinated complexes, Fe[TPP][C(Cl)SR][L] with L = ROH or H_2O, in the solid state. However, in the noncoordinating solvents used for the study by visible and ^1H and ^{13}C NMR spectroscopy, they are always in the pentacoordinated state because of the low affinity of the ROH or H_2O ligand (vide infra).

Complexes **4** all exhibit almost identical visible spectra (Table I) and ^1H and ^{13}C NMR signals for the porphyrin ring (see Experimental Section). The spectral characteristics (i) visible spectra with two peaks around 410 and 520 nm, (ii) ^1H NMR porphyrin signals with a sharp singlet for the pyrrole protons around 8.70 ppm (8 H) and two signals for the phenyl protons around 8.10 (8 H) and 7.70 (12 H), and (iii) ^{13}C NMR porphyrin signals between 146 and 120 ppm have been previously found for Fe[TPP][carbene] complexes,[2,3] the NMR spectra being indicative of low-spin iron(II) complexes with an axial symmetry.

The specific NMR characteristics of their carbene ligands are reported in Table I. The ^1H NMR signals of the protons of the R group are shifted upfield because of the ring-current effect of the porphyrin.[8] The chemical shifts of their carbene carbons (264–288 ppm) are those expected for Fe[TPP][carbene][3] as well as for transition-metal–carbene complexes.[9]

With mass spectrometry (70 eV, 230 °C), complexes **4** are generally too unstable to give molecular peaks, except for complexes **4c** and **4d** (M^+ respectively at 838 and 824 for ^{35}Cl and ^{32}S). Complexes **4** all exhibit a peak at *m/e* 668 corresponding to $Fe[TPP]^+$.

Chemical Properties of Complexes 4, Fe[TPP][C(Cl)SR]. Reaction with Nucleophilic Ligands. Addition of limited amounts of ligands L such as pyridine or *N*-methylimidazole to the Fe[TPP][carbene] complexes gives the corresponding hexacoordinated compexes where the L ligand is bound in trans position to the carbene ligand. With the conditions of visible spectroscopy studies (complex 10^{-4} M, 25 °C), addition of an excess of L ligands (above 10^4 molar excess) affords within a few minutes the corresponding hemochromes, $Fe[TPP][L]_2$, according to eq 3. We have not checked what happened to the carbene ligand.

$$Fe[TPP][carbene] + L \overset{K}{\rightleftarrows} Fe[TPP][carbene][L] \xrightarrow{L} Fe[TPP][L]_2 \qquad (3)$$

By titration of complex **4d**, dissolved in benzene, with increasing amounts of pyridine, we have been able to determine the equilibrium constant of formation of the corresponding hexacoordinated complex $Fe[TPP][C(Cl)SC_6H_5][py]$: K = 1500 L mol^{-1} at 25 °C, λ = 424 nm (ε 2.2×10^5 M^{-1} cm^{-1}), 544 (14×10^3). *N*-methylimidazole exhibits a greater affinity [*K* = 7500 L mol^{-1}, λ = 427 nm (ε 2.5×10^5), 539 (14×10^3)] at 25 °C. Complex **4e** (~ 8×10^{-5} M in benzene) is rapidly decomposed into $Fe[TPP][py]_2$ during addition of the first 5 equiv of pyridine. In the same conditions, complexes **4a**–**4c** are partially decomposed into Fe[TPP][CS][py] (vide infra) (the equilibrium constant of formation of $Fe[TPP][C(Cl)SCH_2C_6H_5][py]$ from **4c** can be evaluated during the first stage of the titration with pyridine and is ca. 1500 L mol^{-1} at 25 °C).

Reaction with Dioxygen. Complexes **4** react with dioxygen leading to an irreversible oxidation of the iron with quantitative formation of Fe^{III}[TPP][Cl] in the case of **4a**–**4c** and of the μ-oxo dimer $[Fe^{III}(TPP)]_2O$ in the case of complex **4e**. Their half-lives in aerated benzene are greatly dependent upon the substituents of the carbene carbon and vary from less than 30 s for **4e** to 0.5, 5, and 4.5 h respectively for complexes **4a**, **4c**, and **4d**.

Decomposition of Complexes 4 into Fe[TPP][CS]. Upon treatment of complex **4c** in $CDCl_3$ by a catalytic amount of cupric or ferrous chloride in CH_3CN, its ^1H NMR signals are progressively replaced by those of Fe[TPP][CS] (**5a**) (pyrrole hydrogens at 8.88 ppm) and of benzyl chloride (7.26 and 4.46 ppm). The structure of complex **5a** is established by com-

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Table II. Spectral Characteristics of the Thiocarbonyl-Iron(II) Porphyrin Complexes 5

	porphyrin	UV[a] λ, nm ($10^{-5}\epsilon$)	visible[a] λ, nm ($10^{-3}\epsilon$)		^{1}H NMR signals of the porphyrin ring[b] δ (vs. Me_4Si) (*J*, Hz)	IR[c] ν(C=S), cm^{-1}
5a	TPP	409 (2.2)	523 (17)	550 sh	8.88 (s, 8 H), 8.11 (m, 8 H), 7.71 (m, 12 H)	1310
5b	T(*p*-Cl)PP	409 (2.05)	523 (17)	548 sh	8.83 (s, 8 H), 8.06 (d, *J* = 7.5, 8 H), 7.71 (d, *J* = 7.5, 8 H)	1310
5c	TTP[d]	409 (2.2)	523 (17)	548 sh	8.85 (s, 8 H), 8.05 (d, *J* = 9, 8 H), 7.65 (d, *J* = 9, 8 H), 2.72 (s, 12 H)	1300
5d	OEP[d]	390 (1.8)	516 (10)	553 (27)	9.95 (s, 4 H), 4.01 (q, *J* = 7.5, 16 H), 1.90 (t, *J* = 7.5, 24 H)	1290

[a] C_6H_6 solution. [b] $DCCl_3$ solution at 34 °C. [c] KBr pellets. [d] See also ref 13.

Table III. Spectral Characteristics of the Fe[TPP][CS][L] Complexes 6

					^{1}H NMR[d]			
						phenyl		
	L	UV-visible[a] λ, nm	IR[b] ν(CS), cm^{-1}	*K*,[c] L mol^{-1}	pyrrol	o[h]	m, p[h]	L
5a	none	409, 523, 550	1310		8.88	8.11	7.71[e]	
6a	CH_3OH	419, 535	1295	10				
6b	C_2H_5OH	419, 535	1295	6	8.70	8.07	7.65[f]	1.93, 0.17–0.73[g]
6c	morpholine	424, 542, 576	1285					
6d	*i*-$C_3H_7NH_2$	424, 544, 580		34				
6e	py	424, 543, 577	1282	5600	8.75	8.08	7.71[e]	2.66, 5.53, 6.35
					8.73	8.15–8.01	7.69[f]	1.75, 5.25, 6.15
6f	*N*-CH_3Imid	425, 547, 583	1278	12 000	8.69	8.15–8.02	7.69[f]	0.93, 1.41, 4.70, 2.12
6g	$[CH_3CH_2]_3P$	441, 566, 602	1270					

[a] C_6H_6 solution. [b] KBr pellets. [c] Formation constants of complexes 6 at 25 °C, in benzene solution (equilibrium 6). [d] $DCCl_3$ solution; δ vs. Me_4Si. [e] At 34 °C. [f] At –60 °C. For **6e** and **6f** one observes a splitting of the ortho protons of the phenyl groups, indicating that their rotation is hindered. [g] Average value for δ, with equilibrium 6 being not completely displaced to the right. [h] Key: o = ortho phenyl protons; m = meta, and p = para.

parison with an authentic sample obtained by direct reduction of thiophosgene by iron(II) porphyrin as previously described.[10] With $FeCl_2$, the reaction (eq 4) is complete within 3 h at 34 °C. Formation of complex **5a** was also observed by similar decomposition of complexes **4a** and **4b** while complexes **4d** and **4e** remained unchanged under the same conditions. It is noteworthy that this conversion to **5a** also occurs for complex **4b** in the absence of added $FeCl_2$ during its crystallization from the reaction medium and for complex **4c** during its study by ^{13}C NMR spectroscopy which requires a rather long accumulation time (70% yield of **5a** in 20 h from **4c**, 8×10^{-2} M in $CDCl_3$ at 20 °C).

$$\underset{\mathbf{4c}}{\mathrm{Fe[TPP][C(Cl)SCH_2C_6H_5]}} \xrightarrow{\mathrm{FeCl_2}} \underset{\mathbf{5a}}{\mathrm{Fe[TPP][CS]}} + \mathrm{C_6H_5CH_2Cl} \qquad (4)$$

The occurrence of this reaction explains various results obtained during preparation of complexes **4**. For instance, complex **4c** can be obtained almost quantitatively by reduction of **3c** by Fe^{II}[TPP] in the presence of sodium dithionite (method A) whereas Fe[TPP][CS] is obtained, in nearly quantitative yields, when iron powder is used as a reducing agent (method B). Under the latter conditions, $FeCl_2$ is formed upon reduction of Fe^{III}[TPP][Cl] by iron powder and catalyzes efficiently the conversion of complex **4c**, formed in a first step, to Fe[TPP][CS]. Because of their greater ability to decompose into **5a**, complexes **4a** and **4b** were always obtained as mixtures with **5a** even by method A.

(II) Preparation and Properties of Thiocarbonyl–Iron(II) Porphyrin Complexes. Different methods of preparation of thiocarbonyl–metal complexes are now available[11] including the substitution of both thiophosgene chlorine atoms by metal carbonyl dianions.[12] In a preliminary communication we have described the preparation of thiocarbonyl–iron(II) porphyrin complexes by direct reduction of thiophosgene by Fe^{II}[TPP] in the presence of iron powder as a reducing agent.[10] Independently and at the same time, Buchler and co-workers have reported the same reaction using Hg/Na amalgam as a reducing agent.[13]

Decomposition of thiobenzylchlorocarbene–iron(II) porphyrin complexes catalyzed by $FeCl_2$ is a convenient method to obtain with nearly quantitative yields the corresponding thiocarbonyl–iron(II) porphyrin complexes **5** from $C_6H_5CH_2SCCl_3$. This prompted us to prepare some of them according to eq 5, by method B, without isolation of the intermediate carbene complexes.

$$\mathrm{Fe[P]} + \underset{\mathbf{3c}}{\mathrm{C_6H_5CH_2SCCl_3}} \xrightarrow{\text{method B}} \underset{\substack{\mathbf{5a},\ \mathrm{P = TPP} \\ \mathbf{5b},\ \mathrm{P = T(\mathit{p}\text{-}Cl)PP} \\ \mathbf{5c},\ \mathrm{P = TTP} \\ \mathbf{5d},\ \mathrm{P = OEP}}}{\mathrm{Fe[P][CS]}} \qquad (5)$$

The low-spin iron(II) state of complexes **5** is shown by the ^{1}H NMR characteristics of their porphyrin ring and by their visible spectra (Table II). The presence of the thiocarbonyl ligand in complexes **5** is shown by their characteristic IR band around 1300 cm^{-1} and by their mass spectra which exhibit molecular peaks at *m*/*e* 712, 848 (for ^{35}Cl) and 632 respectively for **5a**, **5b**, and **5d**.[14]

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(14) An X-ray analysis of a crystal of Fe[T(*p*-Cl)PP][CS][H_2O] has been done (B. Chevrier and R. Weiss, Université Louis Pasteur, Strasbourg, France). It confirms the linear S–C–Fe–O arrangement but the quality of the crystal did not allow a satisfactory determination of the bond distances.

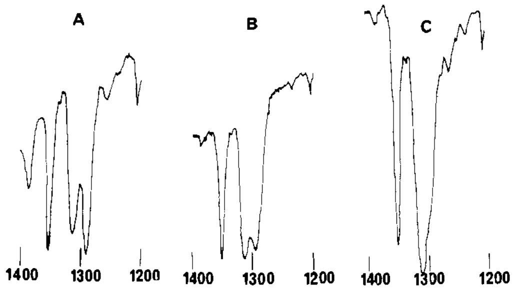

Figure 1. IR spectra of solid samples of complex **5a** (KBr pellets), depending upon its preparation method. (A) Sample prepared from the method described in the Experimental Section and recrystallized from DMF–H_2O–C_6H_6: the 1310 and 1290 cm^{-1} bands correspond respectively to the pentacoordinate Fe[TPP][CS] and hexacoordinate Fe[TPP][CS][H_2O or DMF] species. (B) Previous sample treated 5 h at 150 °C (10^{-2} mmHg). (C) Sample after 10 h at 150 °C (10^{-2} mmHg). After elimination of H_2O and DMF under vacuum, the pentacoordinate Fe[TPP][CS] complex is now largely predominant.

Coordination State of 5a in the Solid State and in Solution. Hexacoordinated complexes **6** are formed upon addition of various ligands to Fe[TPP][CS], owing to equilibrium 6.

$$\underset{\textbf{5a}}{\mathrm{Fe[TPP][CS]}} + \mathrm{L} \overset{K}{\rightleftarrows} \underset{\textbf{6}}{\mathrm{Fe[TPP][CS][L]}} \qquad (6)$$

In the solid state, IR spectroscopy is a good method for determining the coordination state of thiocarbonyl–iron(II) porphyrin complexes which, depending upon their preparation procedure, can be either pentacoordinate (**5**) or hexacoordinate (**6**) complexes with weak ligands such as H_2O or ROH coming from the solvents used for their preparation. Actually, as shown in Table III, ν(CS) is dependent upon the presence and nature of the ligand in trans position to CS. The thiocarbonyl complex of Fe[TPP] presents, after recrystallization from DMF–H_2O–C_6H_6, two IR bands at 1310 and 1295 cm^{-1} (KBr), which should correspond respectively to Fe[TPP][CS] (**5a**) and Fe[TPP][CS][L] with L = DMF or H_2O. After 10 h at 150 °C under 10^{-2} mmHg, the sixth ligand is almost completely removed (Figure 1).

IR ν(CS) frequencies indicated in Table III have been obtained for complexes **6** prepared by crystallization of **5a**, at −30 °C, from CH_2Cl_2–C_5H_{12} solutions in the presence of an excess of L. The increase of electron density provided by coordination of L in the trans position to CS results in a weakening of the CS bond ($\Delta\nu$ = 15 cm^{-1} for L = ROH and 40 cm^{-1} for L = $P(C_2H_5)_3$). The cis effect of the porphyrin ring on the CS stretching frequency is comparable to that observed for Fe[porphyrin][CO][py] complexes:[15] ν(CS) decreases according to the sequence TPP < TTP < OEP (Table II).

In solution, various methods can be used to determine the coordination state: (i) the electronic spectra of complexes **5** and **6** are very different (Table III) and allow for a precise determination of their proportions; (ii) the chemical shift of the pyrrole protons is slightly different in complexes **5** and **6** (Table III); (iii) finally, it has been found recently that a band is present in the resonance Raman spectra of Fe[TPP] complexes which seems characteristic of pentacoordination. This 1375-cm^{-1} band is present in the spectrum of complex **5** but not in that of the Fe[TPP][CS][py] complex.[16]

As shown in Table III, complex **5a** exhibits a low affinity for weak oxygen-containing ligands such as alcohols and a considerably greater affinity for aromatic nitrogen-containing heterocycles such as pyridine or *N*-methylimidazole. The variation of this affinity with the nature of L is very similar to that previously observed for Fe[TPP][CCl_2].[2,3b] Because of the low affinity of alcohols or water for complex **5a**, equilibrium 6 is always almost completely displaced to the left when solid Fe[TPP][CS][ROH or H_2O] is dissolved in noncoordinating solvents under the conditions used for the determination of its visible spectrum. The visible spectra of complexes **6** reported in Table III have thus been obtained upon addition of a large excess (when L = ROH) or limited amounts (when L = pyridine or *N*-methylimidazole) of ligand L to complex **5a**. The position of the Soret and α and β bands greatly depends upon the electron-donating ability of L, the red-shift of these bands being greatest for L = phosphine.

At room temperature, the exchange between free and bound L is fast relative to the ^1H NMR time scale, the observed chemical shifts being average values depending upon the position of equilibrium 6. At −60 °C, this exchange is slow with L = pyridine or *N*-methylimidazole, the signals of free and bound L being simultaneously observed. This allows the determination of ^1H NMR resonances of some complexes **6** which are indicated in Table III. A slight upfield shift of the pyrrole protons is noticeable when one goes from **5a** (8.88) to **6e** (8.73) and **6f** (8.69), indicating an increase of electron density in the porphyrin ring due to a cis effect of L.[15] With L = alcohols or ethers, the exchange remains fast even at −60 °C.

Reactivity of the Fe–CS Bond. The Fe–CS bond in complexes **5** is very strong as emphasized by the remarkable stability of these complexes toward dioxygen; no oxidation of complex **5a** is observed after 20 h of oxygen bubbling in its benzene solution. Complexes **5** can thus be handled in air and even purified without decomposition by silica gel column or thin-layer chromatography. The Fe–CS bond of complex **5a** is not dissociated upon dilution (2×10^{-8} M) or after heating at 150 °C under 10^{-2} mmHg for 4 h.

Moreover, complex **5a** is considerably less reactive toward nucleophiles such as pyridine than other carbene– or nitrosoalkane–iron(II) porphyrin complexes. After 24 h, less than 5% of complex **5a**, initially 5×10^{-5} M in benzene in the presence of 1 M pyridine at 25 °C, is transformed into bis(pyridine)hemochrome, Fe[TPP][py]$_2$, whereas Fe[TPP][CCl_2][3a] and Fe[TPP][*i*-C_3H_7NO][py][17] are half-transformed into Fe[TPP][py]$_2$ in 1.5 and 6 h under the same conditions.

However, more basic ligands such as primary amines (*n*-$C_4H_9NH_2$) in excess react with **5a** to give the isocyanide complex Fe[TPP][CN-*n*-C_4H_9][NH_2-*n*-C_4H_9] (λ = 431, 535, 568 nm in C_6H_6; ν(CN) = 2110 cm^{-1}) (eq 7). The rate of this reaction is much lower than that observed with Fe[TPP][CCl_2].[18]

$$\mathrm{Fe[TPP][CS]} \xrightarrow{n\text{-}C_4H_9NH_2} \mathrm{Fe[TPP][CS][NH_2\text{-}\mathit{n}\text{-}C_4H_9]} \xrightarrow{n\text{-}C_4H_9NH_2} \mathrm{Fe[TPP][CN\text{-}\mathit{n}\text{-}C_4H_9][NH_2\text{-}\mathit{n}\text{-}C_4H_9]} \qquad (7)$$

Formation of isonitrile–metal complexes from thiocarbonyl complexes are also known for other nonporphyrinic transition-metal complexes via unstable mercaptocarbene complexes.[19]

The Fe–CS bond of complex **5a** (6×10^5 M in benzene) is also dissociated upon its reaction with one-electron oxidants

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such as ferric chloride (3 equiv, 1.4 × 10^{-4} M in acetonitrile) with complete formation of Fe^{III}[TPP][Cl] within 2.5 h at 25 °C.

Conclusion

Though several examples of transition-metal carbene complexes bearing a thioalkyl group on the carbenic carbon have been reported in the literature,[9] there has been no example of a metal complex with a C(X)SR carbene ligand (X = halogen). The reduction of $RSCCl_3$ compounds by iron(II) porphyrins in the presence of an excess of reducing agent is a general route of preparation of Fe[porphyrin][C(X)SR] carbene complexes. The same reaction of $C_6H_5SCHCl_2$ gives the Fe[TPP][$CHSC_6H_5$] complex, which is the first isolated stable complex of an iron porphyrin bearing a secondary CHR carbene ligand.[20]

The quantitative conversion of some Fe[TPP][C(Cl)SR] complexes to Fe[TPP][CS] and RCl (particularly when R = $CH_2C_6H_5$), upon their treatment by a catalytic amount of $FeCl_2$ or $CuCl_2$, is a new reaction in coordination chemistry. It constitutes a simple route of preparation of thiocarbonyliron(II) porphyrin complexes from readily available and stable $RSCCl_3$ precursors. For instance, in a one-pot reaction, Fe[TPP][CS] is obtained by reduction of $C_6H_5CH_2SCCl_3$ by Fe[TPP] in the presence of an excess of iron powder (vide supra), within 1 h at room temperature, in 90% yield. This reaction has been recently used for the preparation of selenocarbonyliron(II) porphyrin complexes[21] by reduction of the stable and readily available precursor $C_6H_5CH_2SeCCl_3$. It is noteworthy that the other possible precursor $CSeCl_2$ is not stable, contrary to $CSCl_2$, and therefore the reduction of $C_6H_5CH_2SeCCl_3$ is the only described method of preparation of Fe[porphyrin][CSe] complexes.

The fungicides containing the $SCCl_3$ group, Folpet and Captan, are reduced by iron(II) porphyrins to give the corresponding carbene complexes **4a** and **4b**. These complexes are particularly prone to decompose into Fe[TPP][CS]. Actually complex **4b** was never obtained in a completely pure state because of this reaction. It is very likely that these fungicides could be reduced, as other polyhalogenated compounds,[1b,22] by cytochrome P450 in its ferrous state, the first step of the reaction being the formation of the $RS\dot{C}Cl_2$ radical. Our results suggest that a possible evolution of this system is the formation of cytochrome P450-Fe$^{II}\leftarrow$C(Cl)SR and P450-Fe$^{II}\leftarrow$CS complexes. It has been shown that the free radical $\cdot CCl_3$ and the cytochrome P450-Fe$\leftarrow CCl_2$ complex, formed upon metabolic reduction of CCl_4, are responsible for the toxic effects of CCl_4 because of their irreversible reactions with cell macromolecules.[22,23] The toxic effects of Folpet and Captan could be similarly due to the free radicals $RS\dot{C}Cl_2$ and the cytochrome P450-Fe$^{II}\leftarrow$C(Cl)SR complexes possibly formed upon their metabolic reduction.

Experimental Section

Physical Measurements. Visible spectra were obtained in benzene solution on a Super Scan 3 Varian or Aminco DW2 spectrometer. Data are given with wavelengths in nanometers, and ϵ (M^{-1} cm^{-1}) were determined by reaction of complexes with an excess of pyridine and comparison with known ϵ of the hemochrome Fe[porphyrin][py]$_2$. Infrared spectra are recorded as KBr pellets on a Perkin-Elmer 599 spectrophotometer (wavelengths in cm^{-1}). ^{1}H NMR spectra were run on a Varian EM 390 spectrometer operating at 90 MHz; chemical shifts are reported in parts per million downfield of tetramethylsilane (Me_4Si) for $CDCl_3$, ca. 10^{-2} M solutions at 34 °C. ^{13}C NMR spectra were recorded on a Bruker WH 90 spectrometer (sweep width 6000 Hz, 80000–200000-45° pulses, 8K point memory blocks, acquisition time 2 s). Samples containing ~80 mg of compound in 1.5 mL of $CDCl_3$ in 10-mm tubes were run at a probe temperature of ca. 20 °C. In some cases, Cr(acac)$_3$ (0.04 M in $DCCl_3$) has been added to the sample to decrease the carbon T_1 relaxation times of the porphyrin complexes.[29] The tubes are prepared under argon and sealed under high vacuum. ^{13}C chemical shifts are reported relative to Me_4Si, with the central line of the $CDCl_3$ triplet as a standard with a chemical shift of 76.99 ppm. Mass spectra were performed on a Varian CH7 mass spectrometer (70 eV) using a direct introduction temperature of ca. 230 °C. Elemental analysis were performed by the Service de Microanalyse du CNRS at Gif-sur-Yvette.

Starting Material. Benzaldehyde, *p*-chlorobenzaldehyde, *p*-methylbenzaldehyde, and pyrrole (Aldrich Chemicals) were distilled immediately before use. Benzyl thiocyanate, thioanisole (Aldrich Chemicals), *N*-(trichloromethylthio)phthalimide (Folpet), and *N*-(trichloromethylthio)-1,2,3,6-tetrahydrophtalimide (Captan)(Riedel de Haën) were used without further purification.

Benzyl trichloromethyl thioether (**3c**) was prepared from benzyl thiocyanate by the Makosza procedure:[24] bp 85–90 °C (0.1 mmHg); mp 36 °C (lit. respectively 128–129 °C (7 mmHg) and 37–39 °C);[24] ^{1}H NMR 7.30 (5 H), 4.37 (2 H); ^{13}C NMR 132.9, 129.3, 128.6, 127.9, 97.3, 41.7; mass spectrum (70 eV, 30 °C) *m*/*e* 244, 242, 240, with the good isotopic ratio for three chlorine atoms.

Phenyl dichloromethyl thioether[25] (**3e**) and phenyl trichloromethyl thioether[25] (**3d**) were prepared from thioanisole by direct chlorination with an excess of phosphorus(V) chloride: $C_7H_6Cl_2S$, bp 110 °C (20 mmHg) [lit. 117–118 °C (15 mmHg)];[25] ^{1}H NMR 6.80 (1 H), 7.60 (3 H), 7.77 (2 H); ^{13}C NMR 135.0, 130.0, 129.7, 129.0, 75.8; mass spectrum (70 eV, 80–200 °C) *m*/*e* 192, 194, 190, with the good isotopic ratio for two chlorine atoms. For $C_7H_5Cl_3S$: bp 58 °C (0.01 mmHg); mp 36 °C (lit. respectively 124 °C (16 mmHg) and 35.5 °C);[25] ^{1}H NMR 7.51 (3 H), 7.75 (2 H); ^{13}C NMR 132.9, 129.3, 128.6, 127.9, 97.3, 41.7; mass spectrum (70 eV, 80–200 °C) *m*/*e* 226 (for ^{35}Cl).

Preparation of the Porphyrins. The tetraarylporphyrins $TPPH_2$, $TTPH_2$ and T(*p*-Cl)PPH$_2$ were prepared by Adler's method[26] and made chlorin free by Smith's procedure.[27] A gift of $OEPH_2$ from Professor R. Guilard, University of Dijon, Dijon, France, is grateful acknowledged. The insertion of iron atom into the free base was done with $FeCl_2 \cdot 4H_2O$ with dimethylformamide as solvent.[26,28] The iron porphyrin complexes were characterized by their visible spectra in benzene.

Preparation of Carbene and Thiocarbonyl–Iron(II) Porphyrin Complexes. Owing to the sensitivity of most complexes to dioxygen, all manipulations and measurements were performed under pure argon. Two different standard procedures were used for the preparation of carbene or thiocarbonyliron(II) porphyrin complexes with either a saturated aqueous solution of sodium dithionite (method A) or iron powder (method B) as reducing agent.

Iron(II) Tetraphenylporphyrin (Thiobenzyl)chlorocarbene (4c). Method A. To a solution of 0.346 g (0.492 mmol) of Fe^{III}[TPP][Cl] in 70 mL of C_6H_6 was added 25 mL of a saturated aqueous solution of $S_2O_4Na_2 \cdot H_2O$. The reaction mixture was stirred for 0.25 h during which time the solution changed from brown-green to red. An electronic spectrum of a sample was recorded to confirm the reduction of Fe^{III}[TPP][Cl] to Fe[TPP]. Then a solution of 0.149 g (0.615 mmol) of **3c** in 10 mL of C_6H_6 was added and the reaction mixture vigorously stirred for 2 h. The color changed gradually from red to brown-red. The end of the reaction was checked by recording the

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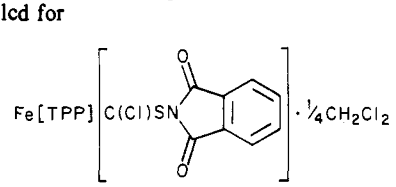
electronic spectra of different samples. The new species was characterized by peaks at 412 and 520 nm (in C_6H_6). The aqueous solution was removed, the organic layer washed two times with distilled and deaerated water, and benzene removed by argon bubbling (0.37 g, ~90% yield).

All attempts of recrystallization partially decomposed **4c** with formation of Fe[TPP][CS] (see text). The physical measurements were made on the crude product. Anal. Calcd for Fe[TPP][C(Cl)$SCH_2C_6H_5$] ($C_{52}H_{35}N_4FeClS$): C, 74.46; H, 4.17; N, 6.68; S, 3.81. Found: C, 74.59; H, 4.28; N, 6.03; S, 3.89. ^{1}H NMR: 8.69 (8 H), 8.11 (8 H), 7.71 (12 H), 6.88 (3 H), 5.81 (2 H), 2.71 (2 H). ^{13}C NMR: 144.8, 140.3, 132.3, 131.3, 126.5, 125.6, and 120.9 for chemical shifts of porphyrin carbons, and 28.9, 127.6, 127.4, 126.6 (one signal of the phenyl substituent of the carbene ligand is superimposed on those of the porphyrin ring), and 266.4 for the carbene carbon. IR: ν(C–Cl) = 875 cm^{-1}.

Iron(II) Tetraphenylporphyrin (Thiophthalimido)chlorocarbene (4a). This complex was prepared as was **4c** from a solution of 0.337 g (0.48 mmol) of Fe^{III}[TPP][Cl] in 50 mL of CH_2Cl_2 and a solution of 0.143 g (0.482 mmol) of Folpet in 5 mL of CH_2Cl_2. The crude product was dissolved in a minimum amount of CH_2Cl_2 and crystallized by adding an excess of CH_3OH. Fine purple crystals were collected by filtration and washed two times with CH_3OH (0.34 g, 80% yield). Actually, the crystals retained CH_2Cl_2 (0.25 mol/mol of complex) as shown by their ^{1}H NMR spectrum.

Anal. Calcd for



($C_{53.25}H_{32.5}N_5FeO_2SCl_{1.5}$): C, 69.89; H, 3.55; N, 7.65; S, 3.50; Cl, 5.74. Found: C, 70.34; H, 3.99; N, 7.29; S, 3.64; Cl, 6.30. ^{1}H NMR: 8.73 (8 H), 8.15 (8 H), 7.71 (12 H), 7.33 (4 H). ^{13}C NMR: 145.8, 141.5, 133.7, 132.5, 127.3, 126.5, and 121.5 for chemical shifts of porphyrinic carbons; 162.7, 132.9, 130.4, 133.0, and 264.3 for the carbene ligand. IR: ν(C—Cl) = 870 cm^{-1}; ν(C=O) = 1720 cm^{-1}.

Iron(II) Tetraphenylporphyrin (1,2,3,6-Tetrahydrothiophthalimido)chlorocarbene (4b). Complex **4b** was prepared as above by using a solution of 0.068 g (0.096 mmol) of Fe^{III}[TPP][Cl] and of 0.07 g (0.23 mmol) of Captan. All attempts of crystallization partially decomposed **4b** with formation of Fe[TPP][CS] (see text). The physical measurements were made on the crude product. ^{1}H NMR: 8.72 (8 H), 8.11 (8 H), 7.71 (12 H), 5.95 (2 H), 3.55 (2 H), 2.91–2.41 (4 H). IR: ν(C—Cl) = 880 cm^{-1}; ν(C=O) = 1730 cm^{-1}.

Iron(II) Tetraphenylporphyrin (Thiophenyl)chlorocarbene (4d). Method B. To a solution of 0.365 g (0.52 mmol) of Fe^{III}[TPP]Cl in 50 mL of CH_2Cl_2 and 5 mL of DMF was added ca. 3 g of iron powder. The reaction mixture was vigorously stirred for 15 min; the solution turned from brown to red, and an electronic spectrum of a sample was recorded to confirm the reduction of Fe[TPP][Cl] to Fe^{II}[TPP]. Then a solution of 0.147 g (0.65 mmol) of **3d** in 5 mL of CH_2Cl_2 was added. The color changed gradually from red to brown-red. A new species characterized by peaks at 412 and 520 nm (in C_6H_6) was formed after 2 h of stirring. The solution was filtered and CH_2Cl_2 evaporated. The crude product was dissolved in chloroform and filtered. After solvent evaporation, crystallization was achieved by dissolving the product in a minimum amount of CH_2Cl_2 and adding an excess of CH_3OH. Fine purple crystals were collected by filtration and washed with CH_3OH (0.36 g, 85% yield based on starting Fe^{III}[TPP][Cl]). The presence of 1 molecule of H_2O was actually detected from ^{1}H NMR (δ 1.58, which disappears upon D_2O addition). Anal. Calcd for Fe[TPP][C(Cl)SC_6H_5][H_2O] ($C_{51}H_{35}N_4FeSClO$): C, 72.68; H, 4.15; N, 6.65; S, 3.80; Cl, 4.15. Found: C, 72.12; H, 4.19; N, 6.71; S, 3.67; Cl, 4.60. ^{1}H NMR: 8.75 (8 H), 8.11 (8 H), 7.71 (12 H), 6.65 (3 H), 5.55 (2 H). ^{13}C NMR: 145.5, 140.9, 132.5, 131.8, 126.6, 125.8, and 120.3 for the carbons of porphyrin ring, 288.5 for the carbene carbon. It is not possible to assign the other phenyl signals of the carbene ligand since they are superimposed on those of the porphyrin ring. IR: ν(C–Cl) = 880 cm^{-1}.

Iron(II) Tetraphenylporphyrin (Thiophenyl)carbene (4e). Complex **4e** was prepared as **4d** (method B) with a solution of 0.311 g (0.442 mmol) of Fe^{III}[TPP][Cl] in 50 mL of CH_2Cl_2 and 3 mL of CH_3OH. After the reduction of Fe[TPP][Cl], 200 μL (~1.5 mmol) of deaerated **3e** was added. Fine purple crystals were obtained by crystallization in CH_2Cl_2 and CH_3OH (0.3 g, 85% yield). Anal. Calcd for Fe[TPP][$CHSC_6H_5$] ($C_{51}H_{36}N_4FeS$): C, 77.46; H, 4.33; N, 7.08; S, 4.05. Found: C, 77.18; H, 4.22; N, 6.74; S, 4.14. ^{1}H NMR: 8.61 (8 H), 8.08 (8 H), 7.71 (12 H), 6.61 (3 H), 5.56 (2 H), 13.83 (1 H). ^{13}C NMR: 146.3, 141.9, 133.1, 131.8, 126.9, 126.0, 120.7. **4e** is not soluble enough to give significant ^{13}C NMR signals for the carbene ligand within reasonable acquisition times.

Iron(II) Tetraphenylporphyrin Thiocarbonyl (5a). (1) Method B. Complex **5a** was prepared as was **4d** with 0.291 g (0.413 mmol) of Fe^{III}[TPP][Cl] in 50 mL of CH_2Cl_2 and 5 mL of CH_3OH and with 2 g of iron powder. After the formation of Fe^{II}[TPP], 0.21 g (0.87 mmol) of **3c** in 5 mL of CH_2Cl_2 was added. Fine purple crystals were obtained by crystallization from a CH_2Cl_2–C_2H_5OH mixture (0.290 g, 90% yield). The crystals were found to retain CH_2Cl_2 as shown by ^{1}H NMR spectroscopy. Anal. Calcd for Fe[TPP][CS][C_2H_5OH]·$^1/_8$$CH_2Cl_2$: C, 73.57; H, 4.49; N, 7.78; S, 4.17; Cl, 1.15. Found: C, 73.25; H, 4.47; N, 7.24; S, 4.10; Cl, 1.41. ^{1}H NMR: 8.88 (8 H), 8.11 (8 H), 7.71 (12 H), 3.61 (2 H), 1.21 (3 H). ^{13}C NMR: 145.7, 141.7, 133.6, 132.5, 127.6, 126.7, and 120.8 for the carbons of the porphyrin ring, 57.9 and 17.9 for the carbons of C_2H_5OH, and 313.5 for the thiocarbonyl carbon. IR: ν(CS) = 1310 cm^{-1}.

(2) Decomposition of 4c in the Presence of Ferrous Chloride in Acetonitrile. To a solution of 0.028 g (0.034 mmol) of **4c** in 0.8 mL of $CDCl_3$ was added 10 μL of a saturated solution of $FeCl_2{\cdot}4H_2O$ in CH_3CN. The reaction was followed by ^{1}H NMR spectroscopy with examination of the ratio of the pyrrole protons of **5a** (δ 8.88) vs. those of **4c** (δ 8.69) + **5a**. After 0.25, 1.75, and 3 h, this ratio was respectively 0.37, 0.77, and 1.

During this time, new signals corresponding to the formation of $C_6H_5CH_2Cl$ appear at 7.26 and 4.46 ppm. After solvent evaporation and crystallization from a CH_2Cl_2–C_2H_5OH mixture, **5a** was obtained quantitatively as shown by its electronic and infrared spectra.

Iron(II) Tetrakis(*p*-chlorophenyl)porphyrin Thiocarbonyl (5b). Complex **5b** was prepared as **5a** from a solution of 0.251 g (0.298 mmol) of Fe^{III}[T(*p*-Cl)PP][Cl] in 50 mL of CH_2Cl_2 and 2 mL of CH_3OH and a solution of 0.142 g (0.59 mmol) of **3c** in 3 mL of CH_2Cl_2. **5b** was crystallized from a CH_2Cl_2–CH_3OH mixture (0.250 g, 98% yield). ^{1}H NMR: 8.83 (s, 8 H), 8.06 (d, J = 7.5 Hz, 8 H), 7.72 (d, J = 7.5 Hz, 8 H). ^{13}C NMR: 144.3, 138.5, 133.2, 133.0, 131.0, 125.8, and 119.1 for the chemical shifts of the porphyrin carbons. **5b** is not enough soluble to give a significant signal for the thiocarbonyl carbon within reasonable acquisition times. IR: ν(C=S) = 1310 cm^{-1}.[14]

Iron(II) Tetratolylporphyrin Thiocarbonyl (5c). Complex **5c** was prepared as **5a** from a solution of 0.205 g (0.27 mmol) of Fe^{III}[TTP][Cl] in 50 mL of CH_2Cl_2 and 2 mL of CH_3OH and a solution of 0.13 g (0.54 mmol) of **3c** in 3 mL of CH_2Cl_2 and crystallized from a CH_2Cl_2–CH_3OH mixture (0.198 g, 95% yield). The analytical data (see Table II) are similar to those previously described.[13b]

Iron(II) Octaethylporphyrin Thiocarbonyl (5d). Complex **5d** was prepared as was **5a** from a solution of 0.155 g (0.25 mmol) of Fe^{III}[OEP][Cl] in 60 mL of CH_2Cl_2 and 5 mL of CH_3OH and a solution of 0.12 g (0.52 mmol) of **3c** in 5 mL of CH_2Cl_2. The crude product was purified by thin-layer chromatography (silica gel Merck 60 F 254; hexane-CH_2Cl_2 1/1) and crystallized from a CH_2Cl_2–CH_3OH mixture (0.135 g, 87% yield). The analytical data (see Table II) are similar to those previously described.[13b]

Hexacoordinated Thiocarbonyl–Iron(II) Tetraphenylporphyrin Complexes (6). A general procedure to obtain complexes **6** has been used. With L = CH_3OH or C_2H_5OH, complex **5a** is dissolved in CH_2Cl_2 and a large excess of L was added until precipitation of the corresponding **6a** or **6b** complexes occurred. With L = nitrogen or phosphorus ligand, 0.1 mL of L was added to 0.05 g of **5a** in 2 mL of CH_2Cl_2. The solution was cooled to −30 °C, and an excess of pentane was added. Complexes **6** have been obtained by rapid filtration and characterized in the solid state by their IR spectra. UV–visible spectra were done by dissolution of the solid complexes **6** in C_6H_6 and addition of few microliters of ligand L to obtain a complete formation of hexacoordinated complexes (see Table III). ^{1}H NMR of solid complexes **6**, in $DCCl_3$ solution, showed the characteristic signals of Fe[TPP][CS] and L in a 1:1 ratio.

Registry No. **3c**, 2976-37-6; **3d**, 701-65-5; **3e**, 5533-18-6; **4a**, 80697-72-9; **4b**, 80697-73-0; **4c**, 80697-74-1; **4d**, 80719-01-3; **4e**, 80697-75-2; **5a**, 67583-11-3; **5b**, 80697-76-3; **5c**, 80052-14-8; **5d**, 69306-31-6; **6a**, 80697-77-4; **6b**, 67551-66-0; **6c**, 80697-78-5; **6d**, 80719-02-4; **6e**, 67670-43-3; **6f**, 80697-79-6; **6g**, 80719-03-5; Fe^{III}[TPP][Cl], 16456-81-8; **3a**, 133-07-3; **3b**, 133-06-2; Fe^{III}[T(*p*-Cl)PP][Cl], 36965-70-5; Fe^{III}[TTP][Cl], 19496-18-5; Fe^{III}[OEP][Cl], 28755-93-3; n-$C_4H_9NH_2$, 109-73-9; Fe[TPP][CN-n-C_4H_9][NH_2-n-C_4H_9], 80719-68-2.

Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201

Synthesis and Characterization of Some Ruthenium–Phosphoniodithiocarboxylate Complexes

THOMAS R. GAFFNEY and JAMES A. IBERS*

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Addition of CS_2 to $RuClH(CO)(PCy_3)_2$ affords the cation $[RuH(CO)(S_2CPCy_3)(PCy_3)_2]^+$, which has been isolated as the tetraphenylborate salt. The closely related complex $[RuCl(CO)(S_2CPCy_3)(PCy_3)_2][BPh_4]$ is formed when the zwitterion ligand S_2CPCy_3 is added to a methanol suspension of $RuCl_2(CO)(PCy_3)_2$ and $NaBPh_4$. The reaction of carbonyl sulfide with $RuClH(CO)(PCy_3)_2$ results in the formation of $RuClH(CO)_2(PCy_3)_2$.

Carbon disulfide is known to insert into metal–hydride bonds to give metal dithioformates.[1-5] Recently it has become apparent that metal–phosphoniodithiocarboxylate complexes, $M(S_2CPR_3)L_n$, may be formed from the addition of CS_2 to metal–phosphine complexes.[6-8] We report the syntheses of several ruthenium–phosphoniodithiocarboxylate complexes and one reaction in which formation of a phosphoniodithiocarboxylato ligand is favored over formation of a dithioformato ligand when a polar solvent is employed.

Results and Discussion

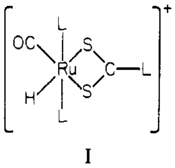
While CS_2 inserts into the RuH bond of $RuClH(CO)(PCy_3)_2$ (Cy = cyclohexyl) to afford $RuCl(S_2CH)(CO)(PCy_3)_2$,[2] we find that in a polar solvent (ethanol) a different reaction occurs. When CS_2 is added to an ethanol suspension of $RuClH(CO)(PCy_3)_2$, the yellow-orange solid dissolves and a purple solution is formed. Addition of $NaBPh_4$ to the solution precipitates $[RuH(CO)(S_2CPCy_3)(PCy_3)_2][BPh_4]$ (eq 1). The yield of the salt is low, as expected since some of the $RuClH(CO)(PCy_3)_2$ starting material must serve as a source of PCy_3.

$$RuClH(CO)(PCy_3)_2 + CS_2 \xrightarrow[NaBPh_4]{EtOH} [RuH(CO)(S_2CPCy_3)(PCy_3)_2][BPh_4] \quad (1)$$

Coordination of CS_2 and subsequent transfer of a PCy_3 ligand to the carbon atom of CS_2 could lead to the formation of the phosphoniodithiocarboxylato ligand. Alternatively, phosphine dissociation could lead to the formation of the zwitterion adduct S_2CPR_3, which could then react with $RuClH(CO)(PCy_3)_2$ to give the insertion product. We have found that direct addition of a zwitterion adduct, S_2CPR_3 (R = Cy, Et), to $RuClH(CO)(PCy_3)_2$ results in the facile formation of the cation $[RuH(CO)(S_2CPR_3)(PCy_3)_2]^+$, which we have isolated as the tetraphenylborate salt (R = Cy, **1**; R = Et, **2**), as shown in eq 2. Although the formation of the phosphoniodithiocarboxylato ligand could be regarded as an insertion of CS_2 into a RuP bond, we believe from (2) that it is more likely that reaction 1 proceeds via disproportionation.

$$RuClH(CO)(PCy_3)_2 + S_2CPR_3 \xrightarrow[NaBPh_4]{MeOH} [RuH(CO)(S_2CPR_3)(PCy_3)_2][BPh_4] \quad (2)$$

The infrared spectra of **1** and **2** exhibit one terminal carbonyl stretching vibration and a band between 1050 and 950 cm^{-1} that we suggest is $\nu(CS)$ of the S_2CPR_3 ligand[7] (Table I). Each complex also exhibits a very weak band at ~2000 cm^{-1} that may be attributed to $\nu(Ru\text{–}H)$, but the low intensity of this absorption precludes a definite assignment. The complexes exhibit several strong bands between 750 and 700 cm^{-1} that might be attributed to $\nu(CS_2)_{sym}$.[5] However, these bands are apparently not observed in other phosphoniodithiocarboxylate complexes. The $^{31}P\{^1H\}$ NMR spectra of **1** and **2** consist of an A_2X pattern, consistent with the presence of two magnetically equivalent and one magnetically inequivalent PR_3 group. The small values of the coupling constants (see Table I) are indicative of long-range coupling.[6,7] Three isomers that should exhibit similar spectra are



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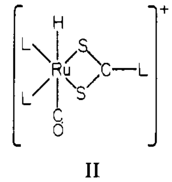
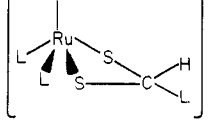


II



III

Although phosphonium–betaine ligands (isomer III) are formed when CS_2 is added to similar metal complexes,[7,9] the ^1H NMR spectra are consistent only with isomers I and II as the spectra exhibit a hydride resonance (Figure 1) that is split into a triplet by two equivalent PR_3 ligands and further split into a doublet by a more distant PR_3 group. The betaine proton of isomer III would be expected to appear further downfield[7,9] ($\delta \simeq 6$) and should couple more strongly to the

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