26 *Organometallics* 1988, 7, 26-33

Reactions of Iron(II) Complexes Modulated by the Unsymmetrical Chelating Alkenethiolato–Phosphine Ligand. Elaboration of a Novel Carbenethiolato–Phosphine Tripodal Ligand. X-ray Structure Determinations of $[Fe(\eta^2\text{-}Ph_2PCH_2C(t\text{-}Bu){=}S)(\eta^2\text{-}SCOMe)(PPh_3)(CO)](PF_6)$ and $ClFe[\eta^3\text{-}Ph_2PCH_2C(t\text{-}Bu)(S)(SCOMe)](PPh_3)(CO)$ Complexes

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Received February 23, 1987

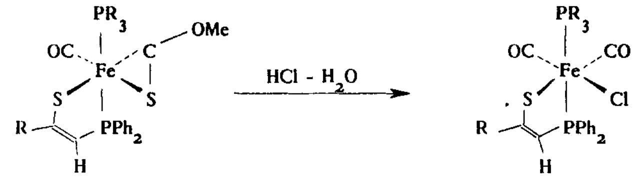
Protonation of neutral complexes $Fe(\eta^2\text{-}Ph_2PCH{=}C(R)S)(\eta^2\text{-}SCOMe)(PPh_3)(CO)$ (**1a**, R = *t*-Bu; **1b**, R = Ph) with HBF_4 and HPF_6 occurs reversibly at the chelating $Ph_2PCH{=}C(R)S^-$ anionic ligand to give the cationic derivatives $[Fe(\eta^2\text{-}Ph_2PCH_2C(R){=}S)(\eta^2\text{-}SCOMe)(PPh_3)(CO)]^+$ (**2**, **3**). With HCl or HBr and **1a**, the coordination of the halide and further intramolecular coupling of the sulfur-containing groups take place to afford a novel tripodal ligand in $XFe[\eta^3\text{-}Ph_2PCH_2C(t\text{-}Bu)(S)(SCOMe)](PPh_3)(CO)$ (**5**, X = Cl; *and* **6**, X = Br). When the same reaction is performed in the presence of water, the formal replacement of the SCOMe group by CO and Cl ligands affords $ClFe(\eta^2\text{-}Ph_2PCH{=}C(t\text{-}Bu)S)(PPh_3)(CO)_2$ (**7**). Complexes **1a** and **1b** react with trimethylphosphine to give the $\eta^1\text{-}C(OMe){=}S$ derivatives $Fe(\eta^2\text{-}Ph_2PCH{=}C(R)\text{-}S)(\eta^1\text{-}C(OMe){=}S)(PMe_3)_2(CO)$ (**8a,b**) which on protonation with HBF_4 or HCl undergo methanol elimination and formation of cationic iron thiocarbonyl complexes $[Fe(\eta^2\text{-}Ph_2PCH{=}C(R)S)(PMe_3)_2(CO)(CS)]^+$ (**10**, **11**). The crystal structures of the compounds $[Fe(\eta^2\text{-}Ph_2PCH_2C(t\text{-}Bu){=}S)(\eta^2\text{-}SCOMe)(PPh_3)(CO)](PF_6)$ (**3a**) and $ClFe[\eta^3\text{-}Ph_2PCH_2C(t\text{-}Bu)(S)(SCOMe)](PPh_3)(CO)$ (**5**) have been determined. Crystal data for **3a** are as follows: $a = 18.969$ (6) Å, $b = 10.779$ (4) Å, $c = 9.183$ (4) Å, $\alpha = 69.10$ (3)°, $\beta = 85.73$ (2)°, $\gamma = 82.87$ (2)°, triclinic $P\bar{1}$, $Z = 2$, $R = 0.062$. Crystal data for **5** are as follows: $a = 15.213$ (7) Å, $b = 20.969$ (7) Å, $c = 13.083$ (6) Å, $\beta = 99.44$ (3)°, monoclinic, $P2_1/n$, $Z = 4$, $R = 0.073$. The structure of **3a** has the pseudooctahedral geometry of a d^8 L_4M system, η^2 coordinated by a heteroallene group. The structure of **5** shows that the metal atom is six-coordinate, using three donor atoms (P, S, and C) of the newly formed tripodal ligand $Ph_2PCH_2C(t\text{-}Bu)(S)(SCOMe)$ together with chloride, CO, and PPh_3.

Introduction

Functionalized phosphines of the type $R_2PCH{=}C(R)O^-$ [1-6] can serve as unsymmetrical bidentate chelating ligands with one phosphorus and one oxygen donor atom. Metal complexes containing these mixed chelates exhibit interesting reactivity. For example, nickel complexes of such ligands are olefin polymerization and oligomerization catalysts.[2,3] Reversible carbon–carbon coupling reactions with carbon dioxide can be achieved with similar systems.[6] In contrast, the properties of the corresponding $Ph_2PCH{=}C(R)S^-$ metal complexes have not been investigated since straightforward methods of access are lacking. We have shown that (2-phosphinoalkenethiolato)iron complexes of type I (Scheme I) can be readily obtained[7] (in two steps from $Fe(CO)_5$) via the methanol-induced intramolecular coupling reaction of a phosphinoalkyne with a $Fe(\eta^2\text{-}CS_2)$ moiety.[8] Our preliminary studies[9] of complexes I have led to the formation of one example of compound II, on treatment with aqueous hydrochloric acid. This apparently straightforward transformation suggested the inertness of the $Ph_2PCH{=}C(R)S^-$ chelating ligand with respect to that of the (η^2-SCOR) group.

We now wish to report how the reactivity of complexes I is modulated by the alkenethiolato–phosphine ligand. The latter plays the role of an ancillary ligand in conversion of I to other $(Ph_2PCH{=}C(R)S)Fe$ complexes such as thiocarbonyl-metal compounds. More importantly this ligand itself can be site of protonation allowing access to new chloro–iron derivatives probably via a novel carbenethiolato–phosphine tripodal ligand–iron complex. The X-ray diffraction studies of two complexes, $[Fe(\eta^2\text{-}Ph_2PCH_2C(t\text{-}Bu){=}S)(\eta^2\text{-}SCOMe)(PPh_3)(CO)]PF_6$ (**3a**)

Scheme I



(I) (II)

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(1) Carty, A. J.; Jacobson, S. E.; Simpson, R. J.; Taylor, N. J. *J. Am. Chem. Soc.* **1975**, *97*, 7254.

(2) (a) Keim, W.; Howaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466. (b) Keim, W.; Behr, A.; Limbäcker, B.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 503. (c) Keim, W.; Behr, A.; Gruber, B.; Hoffmann, B.; Kowaldt, F. H.; Kürschner, V.; Limbäcker, B.; Sistig, F. P. *Organometallics* **1986**, *5*, 2356.

(3) Klabunde, U.; Ittel, S. D. *Abstracts of the 5th International Symposium on Homogeneous Catalysis*, Kobe, 1986; p 9.

(4) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 299.

(5) Braustein, P.; Matt, D.; Dusausoy, Y.; Protas, J. *J. Chem. Soc., Chem. Commun.* **1979**, 763.

(6) (a) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115. (b) Bonaoud, S. E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1986**, *25*, 3765.

(7) Le Bozec, H.; Fournier, J.; Samb, A.; Dixneuf, P. H. *Organomet. Synth.* **1986**, *3*, 297.

(8) Robert, P.; Le Bozec, H.; Dixneuf, P. H.; Hartstock, F.; Taylor, N. J.; Carty, A. J. *Organometallics* **1982**, *1*, 1148.

(9) Robert, P.; Demerseman, B.; Dixneuf, P. H. *Organometallics* **1984**, *3*, 1771.

0276-7333/88/2307-0026$01.50/0

and ClFe[η^3-Ph$_2$PCH$_2$C(*t*-Bu)(S)(SCOMe)](PPh$_3$)(CO) (**5**), resulting from the reaction of Fe(η^2-Ph$_2$PCH═(*t*-Bu)-S)(η^2-SCOMe)(PPh$_3$)(CO) (**1a**) with HPF$_6$ and HCl, respectively, are reported.

Experimental Section

Syntheses. General Comments. All operations were carried out under a nitrogen atmosphere by using Schlenk tube techniques. IR spectra were recorded on a Perkin-Elmer Model 225 infrared spectrophotometer. NMR spectra were recorded on a Bruker WP 80 DS spectrometer. Microanalyses were performed at the Service Central de Microanalyses du CNRS, Villeurbanne, France. Hexane was dried over calcium hydride and dichloromethane over P$_2$O$_5$ and then distilled under nitrogen. Diethyl ether was distilled under nitrogen from sodium–benzophenone. Fe(PPh$_3$)$_2$(CO)$_2$(CS$_2$) was prepared according to a published method.[7] The preparation of Ph$_2$PC≡CR (R = *t*-Bu or Ph), was adapted from published methods.[10]

Ph$_2$PC≡CR (R = *t*-Bu and Ph). To a cooled (−78 °C) solution of 30 mL of *tert*-butylacetylene or 24 mL of phenylacetylene (0.24 mol) in 400 mL of hexane was added 150 mL of a 1.6 M solution of *n*-BuLi in hexane, while the mixture was efficiently stirred. The white resulting suspension was stirred for 2 h until it warmed to about 0 °C. After the solution was cooled again to −78 °C with vigorous stirring, 40 mL (0.22 mol) of freshly distilled PPh$_2$Cl was added. The reaction mixture was stirred overnight at room temperature and then left to stand for 2 days. The supernatant was decanted from solid materials, and this solution was filtered through a short alumina column (3 × 10 cm). The residue was washed twice with 50 mL of hexane. These washing solutions were filtered also, reduced to ca. 100 mL by evaporation under vacuum, and then cooled to −30 °C overnight. White needles formed that were separated by decantation and dried under vacuum. Yields: 81% (48 g), R = *t*-Bu; 79% (50 g), R = Ph.

Fe(η^2-Ph$_2$PCH═C(*t*-Bu)S)(η^2-SCOMe)(PPh$_3$)(CO) (1a).[8] (PPh$_3$)$_2$(CO)$_2$(CS$_2$)Fe (30 g, 42.1 mmol) and 12 g (45 mmol) of Ph$_2$PC≡C-*t*-Bu were heated at reflux for 12 h in a mixture of 250 mL of methanol and 250 mL of diethyl ether. After the solution was cooled to room temperature, the resulting red precipitate was separated by filtration, washed twice with 100 mL of methanol, and dried under vacuum. Yield: 69% (21 g). The product retains a small amount of the starting iron complex but could be used as such for the preparation of its derivatives. ^{1}H NMR[8] (CDCl$_3$, 80 MHz): δ 7.50 (m, 25 H, Ph), 6.05 (d, 1 H, $^2J_{PH}$ = 10 Hz, PCH═), 3.57 (s, 3 H, OMe), 1.52 (s, 9 H, *t*-Bu). ^{31}P NMR (CDCl$_3$, 32.38 MHz): δ 81.50 (d, PPh$_2$), 48.60 (d, PPh$_3$, $^2J_{PP}$ = 181 Hz).

Fe(η^2-Ph$_2$PCH═C(Ph)S)(η^2-SCOMe)(PPh$_3$)(CO) (1b). (PPh$_3$)$_2$(CO)$_2$(CS$_2$)Fe (40 g, 56.2 mmol) and 20 g (70.0 mmol) of Ph$_2$PC≡CPh were treated at reflux for 20 h in a mixture of 350 mL of methanol and 150 mL of diethyl ether. After the solution was cooled to room temperature, the resulting red precipitate was separated by filtration, washed twice with 100 mL of methanol, and dried under vacuum. Yield: 80% (33.2 g). Recrystallization of the product from dichloromethane–hexane solution afforded red-brown crystals of Fe(η^2-Ph$_2$PCH═C(Ph)S)(η^2-SCOMe)-(PPh$_3$)(CO)·1.25CH$_2$Cl$_2$: ^{1}H NMR (CDCl$_3$) δ 7.50 (m, 30 H, Ph), 6.33 (d, 1 H, $^2J_{PH}$ = 8.0 Hz, PCH═), 3.46 (s, 3 H, OMe); ^{31}P NMR (CDCl$_3$) δ 81.30 (d, PPh$_2$), 49.50 (d, PPh$_3$, $^2J_{PP}$ = 176 Hz). Anal. Found (Calcd): C, 59.66 (59.93); H, 4.30 (4.34); P, 7.15 (7.31); S, 6.83 (7.57).

[Fe(η^2-Ph$_2$PCH$_2$C(*t*-Bu)═S)(η^2-SCOMe)(PPh$_3$)(CO)]$^+$-(BF$_4$)$^-$ (2a) and [Fe(η^2-Ph$_2$PCH$_2$C(*t*-Bu)═S)(η^2-SCOMe)-(PPh$_3$)(CO)]$^+$(PF$_6$)$^-$ (3a). To 1.5 g (2.1 mmol) of **1a** in 30 mL of dichloromethane were added 1.5 mL (10.8 mmol) of Et$_2$O·HBF$_4$ and then 100 mL of diethyl ether. After being stirred for a short time, the reaction mixture was left at room temperature overnight. The resulting orange needles of **2a** were separated, washed with 20 mL of methanol, and dried under vacuum. Yield: 83% (1.4 g). **3a** was prepared similarly except that a 60% (by weight) aqueous solution of HPF$_6$ was used. The resulting aqueous layer was discarded before crystallization of **3a** which was obtained in 85% yield (1.5 g). Anal. Found (Calcd) for **2a**:[11] C, 56.84 (57.94); H, 4.77 (4.86); P, 7.59 (7.66); S, 6.60 (7.93). **3a**: ^{1}H NMR (CD$_2$Cl$_2$) δ 7.53 (m, 25 H, Ph), 4.23–4.03 (m, 2 H, PCH$_2$–), 3.30 (s, 3 H, OMe), 1.13 (s, 9 H, *t*-Bu). Anal. Found (Calcd) for **3a**: P, 10.42 (10.72).

[Fe(η^2-Ph$_2$PCH$_2$C(Ph)═S)(η^2-SCOMe)(PPh$_3$)(CO)]$^+$(BF$_4$)$^-$ (2b) and [Fe(η^2-Ph$_2$PCH$_2$C(Ph)═S)(η^2-SCOMe)(PPh$_3$)-(CO)]$^+$(PF$_6$)$^-$ (3b). Complexes **2b** and **3b** were obtained in yields of ca. 80% starting from **1b** and using procedures identical with those used for complexes **2a** and **3a**. Anal. Found (Calcd) for **2b**:[11] C, 57.25 (59.44); H, 4.28 (4.26); P, 7.21 (7.48); S, 7.76 (7.74). Anal. Found (Calcd) for **3b**:[11] C, 54.02 (55.54); H, 4.69 (3.98); P, 11.07 (10.48); S, 6.74 (7.23).

Recovery of Complexes 1 from 2 or 3. A typical procedure is as follows: to a solution of 0.79 g (0.97 mmol) of **2a** in 20 mL of CH$_2$Cl$_2$ was added 10 mL of a saturated aqueous solution of NaHCO$_3$. After the solution was stirred for a short time, the organic layer was separated and washed twice with water, leading to the recovery of 0.67 g (95%) of red **1a**.

ClFe(η^1-Ph$_2$PCH$_2$C(Ph)═S)(η^2-SCOMe)(PPh$_3$)(CO) (4). Complex **4** can be obtained from **1b**, following the procedures described for complex **5**, with equivalent yields. A violet solid was isolated. IR (Nujol): ν 1940 (CO), 1335 (η^2-SCOMe) cm^{-1}.[12] It decomposed slowly turning to a yellow solid.

XFe(η^3-Ph$_2$PCH$_2$C(*t*-Bu)(S)(SCOMe))(PPh$_3$)(CO) (5, X = Cl; 6, X = Br). To a solution of 0.9 g (1.25 mmol) of **1a** in 10 mL of CH$_2$Cl$_2$ were added successively 80 mL of Et$_2$O and 10 mL of an approximately 6 M solution of anhydrous HCl in Et$_2$O. The solution was homogenized and left overnight at 0 °C. The resulting orange crystals were decanted, washed with 20 mL of Et$_2$O, and dried under vacuum. Yield: 69% (0.65 g). Anal. Found (Calcd): C, 61.54 (61.87); H, 5.24 (5.19); P, 8.40 (8.18); Cl, 5.57 (4.68).

5 (or **6**) was also obtained in a 85% yield as an orange precipitate by stirring for 3 h a suspension of 2.0 g (2.8 mmol) of **1a** in 100 mL of diethyl ether with 20 mL of a 6 M aqueous HCl (or HBr) solution. The products were isolated by filtration and dried under vacuum. Anal. Found (Calcd) for **6**: Br, 9.69 (9.97). When **5** was reacted with aqueous NaHCO$_3$ solution, as described above for **2a**, **1a** was recovered in 50% yield.

ClFe(η^2-Ph$_2$PCH═C(*t*-Bu)S)(PPh$_3$)(CO)$_2$ (7). A solution of 10 g (13.9 mmol) of crude complex **1a** in 75 mL of CH$_2$Cl$_2$ was stirred at room temperature for 20 h with 20 mL of a 12 M aqueous HCl solution. Then 100 mL of water were added. The organic layer was separated and the aqueous solution washed with 20 mL of CH$_2$Cl$_2$. The organic solution was dried over CaCl$_2$ and filtered, and 50 mL of heptane was added. The slow evaporation of the solvents under vacuum left an orange crystalline solid which was washed twice with 75 mL of hexane and dried under vacuum: yield 87% (8.6 g); ^{1}H NMR (CDCl$_3$, 80 MHz) δ 7.50 (m, 25 H, Ph), 5.95 (d, 1 H, $^2J_{PH}$ = 10 Hz, PCH═), 1.48 (s, 9 H, *t*-Bu); ^{31}P NMR (CDCl$_3$, 32.38 MHz) δ 71.93 (d, PPh$_2$), 35.79 (d, PPh$_3$, J_{PP} = 177 Hz). Anal. Found (Calcd): C, 64.13 (64.36); H, 4.97 (4.94); P, 7.99 (8.75); S, 4.99 (4.51); Cl, 5.44 (5.01).

Fe(η^2-Ph$_2$PCH═C(*t*-Bu)S)(η^1-C(OMe)S)(PMe$_3$)$_2$(CO) (8a). **1a** (10.0 g, 13.9 mmol) was stirred for 2 days at room temperature with an excess (4 mL) of PMe$_3$ in 75 mL of diethyl ether. The resulting yellow crystalline precipitate was isolated by filtration, washed twice with 30 mL of diethyl ether, and dried under vacuum: yield 66% (5.6 g). ^{1}H NMR (CDCl$_3$, 80 MHz) δ 7.36 (m, 10 H, Ph), 6.30 (d, 1 H, $^2J_{PH}$ = 5 Hz, PCH═), 4.14 (s, 3 H, OMe), 1.50 (s, 9 H, *t*-Bu), 1.00 (t, 18 H, $|^2J_{PH} + {}^4J_{PH}|$ = 8.0 Hz, PMe$_3$). Anal. Found (Calcd): C, 52.82 (53.12); H, 6.43 (6.77); P, 14.98 (15.22).

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(10) (a) Carty, A. J.; Hota, N. K.; Ng, T. W.; Patel, H. A.; D'Connor, T. J. *Can. J. Chem.* **1975**, *49*, 2706. (b) Charrier, C.; Chodkiewicz, W.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1966**, 1002.

(11) A low percentage of carbon was invariably obtained probably because the isolation of these salts requires the presence of a large excess of acid. However these analyses remained consistent with the formation of 1/HA adducts.

(12) Although no satisfactorily analytical or NMR data could be obtained for **4**, the proposed structure was based on the assumption that chloride is coordinated to iron, as suggested by a lower carbonyl absorption frequency as compared to those of **2b** and **3b**, and on the reversibility of the formation of **4** which indicated that no loss of ligand had occurred. Infrared data showed the retention of the η^2-SCOMe moiety and the protonation of the Ph$_2$PCH═C(Ph)S group.

Table I. Summary of Crystal Data for Compounds 5 and 3a

	5	**3a**
formula	$C_{39}H_{39}ClP_2O_2S_2Fe$	$C_{39}H_{39}F_6P_3O_2S_2Fe$
mol wt	757.2	866.6
cryst form	polyhedra	parallelepiped
cryst size, mm	0.2 × 0.3 × 0.4	0.15 × 0.25 × 0.25
cryst system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a, Å	18.969 (6)	15.213 (7)
b, Å	10.779 (4)	20.969 (7)
c, Å	9.183 (4)	13.083 (6)
α, deg	69.10 (2)	90.0
β, deg	85.73 (2)	99.44 (3)
γ, deg	82.87 (2)	90.0
V, Å^3	1843.7 (3)	4117.0
Z	2	4
d_{calcd}, g cm^{-3}	1.36	1.378
μ(Mo Kα), cm^{-1}	6.5	5.5
radiation	graphite–monochromated Mo Kα, λ = 0.71069 Å	
scan type	$\theta/2\theta$	$\theta/2\theta$
2θ range, deg	5–50	5–45
scan width	1.0 + 0.3 tan θ	0.85
scan speed, deg s^{-1}	0.04	0.04
total data	6477	5815
unique data, $I > 3(\sigma)$	4636	2031
no. of parameters	231	255
R	0.062	0.073
R_w	0.071	0.076

Table II. Atomic Coordinates and Temperature Factors for Compound 3a

atom	x	y	z	U, Å^2
Fe[a]	4009 (1)	461 (1)	2416 (2)	33 (1)
S1	4997 (3)	−59 (2)	1385 (4)	50 (2)
S2	3163 (3)	1180 (2)	1374 (3)	46 (2)
P1	4944 (3)	1296 (2)	2670 (3)	36 (2)
P2	2877 (3)	−256 (2)	1950 (3)	34 (2)
P3	1655 (3)	1657 (3)	6044 (4)	59 (3)
C1	3796 (10)	449 (8)	3688 (16)	47 (9)
C2	4858 (9)	−135 (7)	2596 (12)	36 (8)
C3	5922 (11)	−966 (10)	3143 (14)	73 (12)
C4	4804 (9)	1656 (7)	1363 (11)	43 (9)
C5	3845 (9)	1696 (7)	966 (12)	40 (9)
C6	3511 (11)	2208 (9)	218 (13)	54 (11)
C7	4061 (13)	2215 (10)	−653 (14)	81 (17)
C8	3629 (14)	2847 (9)	819 (17)	93 (17)
C9	2545 (11)	2109 (10)	−315 (16)	82 (12)
O1	3702 (8)	421 (7)	4522 (10)	71 (10)
O2	5221 (7)	−512 (5)	3350 (8)	47 (6)
F1	2185 (7)	1549 (5)	5129 (9)	94 (4)
F2	1735 (10)	943 (8)	6287 (12)	146 (5)
F3	1542 (9)	2393 (7)	5753 (10)	127 (5)
F4	1094 (9)	1797 (7)	6933 (11)	125 (5)
F5	759 (9)	1542 (6)	5275 (10)	123 (5)
F6	2524 (9)	1808 (7)	6775 (11)	129 (5)
C1 1	6139 (7)	1160 (5)	3030 (7)	34 (4)
C2 1	6765 (7)	1439 (5)	2501 (7)	54 (5)
C3 1	7671 (7)	1324 (5)	2822 (7)	63 (5)
C4 1	7951 (7)	931 (5)	3672 (7)	60 (5)
C5 1	7325 (7)	652 (5)	4202 (7)	64 (5)
C6 1	6419 (7)	767 (5)	3880 (7)	50 (5)
C1 2	4694 (6)	1962 (5)	3466 (9)	37 (4)
C2 2	3938 (6)	1968 (5)	3942 (9)	52 (5)
C3 2	3764 (6)	2492 (5)	4534 (9)	81 (6)
C4 2	4347 (6)	3011 (5)	4650 (9)	76 (6)
C5 2	5103 (6)	3005 (5)	4174 (9)	66 (6)
C6 2	5277 (6)	2481 (5)	3582 (9)	63 (5)
C1 3	1930 (7)	−195 (4)	2618 (9)	36 (4)
C2 3	1712 (7)	387 (4)	3030 (9)	63 (5)
C3 3	961 (7)	433 (4)	3511 (9)	74 (6)
C4 3	429 (7)	−102 (4)	3580 (9)	62 (5)
C5 3	647 (7)	−683 (4)	3168 (9)	65 (5)
C6 3	1398 (7)	−730 (4)	2687 (9)	50 (5)
C1 4	2355 (7)	−187 (6)	583 (8)	43 (4)
C2 4	1445 (7)	−60 (6)	330 (8)	68 (6)
C3 4	1073 (7)	85 (6)	−690 (8)	90 (7)
C4 4	1610 (7)	104 (6)	−1457 (8)	68 (6)
C5 4	2520 (7)	−23 (6)	−1204 (8)	76 (6)
C6 4	2893 (7)	−168 (6)	−184 (8)	56 (5)
C1 5	3224 (7)	−1078 (6)	2175 (6)	40 (4)
C2 5	3284 (7)	−1517 (6)	1388 (6)	63 (5)
C3 5	3611 (7)	−2129 (6)	1635 (6)	90 (7)
C4 5	3880 (7)	−2302 (6)	2668 (6)	88 (7)
C5 5	3821 (7)	−1862 (6)	3455 (6)	85 (7)
C6 5	3493 (7)	−1251 (6)	3208 (6)	44 (5)

[a] Coordinates multiplied by 10^4. Temperature factors multiplied by 10^3. Temperature factors for atoms Fe through O2 are given as U(eq).

Fe(η^2-Ph$_2$PCH=C(Ph)S)(η^1-C(OMe)S)(PMe$_3$)$_2$(CO) (8b). **8b** was obtained in 68% yield from **1b** following the procedure described for **8a**: ^{1}H NMR (CDCl$_3$, 80 MHz) δ 7.87–7.27 (m, 15 H, Ph), 6.57 (d, 1 H, $^2J_{PH}$ = 7.1 Hz, PCH=), 4.08 (s, 3 H, OMe), 1.03 (t, 18 H, $|^2J_{PH} + {}^4J_{PH}|$ = 7.1 Hz); ^{31}P NMR (CDCl$_3$, 32.38 MHz) δ 56.21 (t, PPh$_2$), 10.45 (d, PMe$_3$, $^2J_{PP}$ = 34.18 Hz). Anal. Found (Calcd): C, 55.27 (55.24); H, 6.05 (5.92); P, 14.36 (14.74); S, 9.79 (10.17).

[Fe(η^2-Ph$_2$PCH=C(t-Bu)S)(PMe$_3$)$_2$(CO)(CS)](BF$_4$) (10). To a stirred solution of 1.1 g (1.8 mmol) of **8a** in 30 mL of CH$_2$Cl$_2$ was added 0.5 mL (3.6 mmol) of Et$_2$O·HBF$_4$. The mixture was stirred for 12 h at room temperature and became dark green. Water (100 mL) was then added. The organic layer was separated and dried over CaCl$_2$. Diethyl ether (50 mL) and 100 mL of hexane were then added. The resulting yellow crystals were collected and dried under vacuum: yield 58% (0.7 g); ^{1}H NMR (CDCl$_3$, 80 MHz) δ 7.56 (m, 10 H, Ph), 6.28 (d, 1 H, $^2J_{PH}$ = 7.6 Hz, PCH=), 1.80 (d, 9 H, $^2J_{PH}$ = 10.0 Hz, PMe$_3$), 1.44 (s, 9 H, t-Bu), 1.29 (d, 9 H, $^2J_{PH}$ = 9.8 Hz, PMe$_3$); ^{31}P NMR (CDCl$_3$, 32.38 MHz) δ 58.51 (dd, P$_{(1)}$Ph$_2$), 11.56 (dd, P$_{(2)}$Me$_3$), −0.09 (t, P$_{(3)}$Me$_3$): J_{PP} = 84 Hz (1,2), 65 Hz (1,3), 60 Hz (2,3). Anal. Found (Calcd): C, 45.94 (46.87); H, 5.75 (5.75); P, 14.56 (13.95); S, 9.03 (9.62).

[Fe(η^2-Ph$_2$PCH=C(Ph)S)(PMe$_3$)$_2$(CO)(CS)]Cl (11b). To a solution of 1.0 g (1.6 mmol) of **8b** in 30 mL of CH$_2$Cl$_2$ was added 1 mL of a 6 M solution of anhydrous HCl in diethyl ether. The reaction mixture became immediately violet and then rapidly turned to yellow-brown. Anhydrous diethyl ether (75 mL) was then added. On standing, yellow *hygroscopic* crystals of **11b** formed. They were decanted and dried under vacuum: yield 75% (0.7 g).

[Fe(η^2-Ph$_2$PCH=C(t-Bu)S)(PMe$_3$)$_2$(CO)(CS)]Cl (11a). This thiocarbonyl complex was prepared as the homologous complex **11b** with an equivalent yield, as a yellow crystalline *hygroscopic* solid, starting from **8a**.

X-ray Diffraction Studies. Crystal data for both compounds **3a** and **5** are summarized in Table I. A Philips PW 1100 automated four-circle diffractometer with graphite-monochromated radiation was used for the experimental work. A set of 2θ high-angle reflections was used for the centering procedure of each crystal. As a general procedure, three standard reflections were collected every 2 h (no appreciable decay of intensities was observed in any case). The data were corrected for Lorentz and polarization effects. Numerical absorption corrections were applied with transmission factors ranging between 0.97–0.87 and 0.99–0.83 for **3a** and **5**, respectively. Atomic scattering factors were those tabulated by Cromer and Waber[13] with anomalous dispersion corrections taken from ref 14. The computational work was essentially performed by using the SHELX76 system.[15] Refinements were performed by full-matrix least-squares calculations. The function minimized was $\sum w(|F_o| - |F_c|)^2$.

[Fe(η^2-Ph$_2$PCH$_2$C(t-Bu)=S)(η^2-SCOMe)(PPh$_3$(CO)]$^+$(PF$_6$)$^-$ (3a). The structure was solved by the Patterson method and Fourier techniques. During the refinement rigid-body models (D_{6h}) were used for the carbons of the phenyl rings. The hydrogen atoms were introduced at calculated positions (C–H = 1.0 Å). Anisotropic thermal parameters were used for all of the non-hydrogen atoms except fluorine and the carbon atoms of the phenyl groups. The PF$_6$ anion is affected by some disorder as

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(13) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(14) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(15) *SHELX76. Program for Crystal Structure Determinations*: University Cambridge: Cambridge, 1976.

Table III. Atomic Coordinates and Temperature Factors for Compound 5[a]

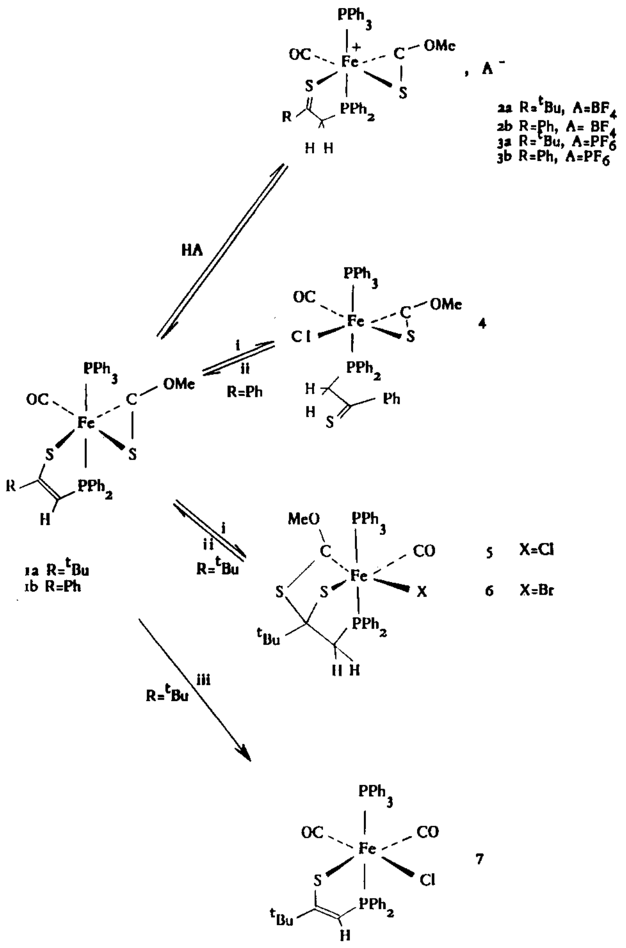
atom	x	y	z	U, Å^2
Fe	2168 (1)	4797 (1)	1175 (1)	28 (1)
P1	1714 (1)	3082 (1)	3007 (2)	28 (1)
P2	2766 (1)	6428 (1)	−558 (2)	35 (1)
S1	3216 (1)	2197 (2)	1465 (2)	41 (1)
S2	3109 (1)	4344 (1)	2725 (2)	36 (1)
Cl	1573 (1)	6487 (2)	1980 (2)	48 (1)
O1	908 (3)	5332 (5)	−589 (5)	55 (3)
O2	2416 (3)	3438 (4)	−761 (5)	49 (3)
C1	1414 (3)	5120 (5)	74 (6)	35 (3)
C2	2590 (3)	3489 (5)	491 (6)	31 (3)
C3	2727 (6)	2409 (10)	−1319 (10)	81 (7)
C4	2487 (3)	2044 (6)	4034 (6)	37 (3)
C5	3173 (3)	2554 (6)	3221 (6)	36 (3)
C6	3863 (3)	1814 (7)	4076 (7)	46 (3)
C7	3850 (5)	2049 (9)	5520 (10)	75 (5)
C8	3899 (4)	304 (7)	4418 (10)	71 (5)
C9	4528 (4)	2347 (10)	3160 (11)	79 (4)
C1 1	1263 (2)	1998 (4)	2355 (5)	35 (1)
C2 1	1585 (2)	740 (4)	2427 (5)	52 (2)
C3 1	1242 (2)	−49 (4)	1877 (5)	72 (2)
C4 1	579 (2)	420 (4)	1253 (5)	83 (3)
C5 1	257 (2)	1677 (4)	1180 (5)	69 (2)
C6 1	600 (2)	2466 (4)	1731 (5)	48 (2)
C1 2	1135 (2)	3369 (4)	4487 (4)	32 (1)
C2 2	1417 (2)	4018 (4)	5297 (4)	45 (1)
C3 2	1033 (2)	4201 (4)	6501 (4)	59 (2)
C4 2	366 (2)	3735 (4)	6895 (4)	55 (2)
C5 2	84 (2)	3086 (4)	6085 (4)	50 (2)
C6 2	469 (2)	2903 (4)	4881 (4)	41 (1)
C1 3	3279 (3)	7486 (5)	28 (4)	39 (1)
C2 3	3749 (3)	8264 (5)	−994 (4)	58 (2)
C3 3	4142 (3)	9089 (5)	−598 (4)	71 (2)
C4 3	4064 (3)	9137 (5)	819 (4)	74 (2)
C5 3	3594 (3)	8359 (5)	1841 (4)	74 (2)
C6 3	3201 (3)	7534 (5)	1446 (4)	52 (2)
C1 4	2167 (3)	7662 (4)	−1899 (5)	41 (1)
C2 4	1854 (3)	7277 (4)	−2916 (5)	56 (2)
C3 4	1352 (3)	8161 (4)	−3865 (5)	70 (2)
C4 4	1163 (3)	9432 (4)	−3798 (5)	74 (2)
C5 4	1476 (3)	9817 (4)	−2781 (5)	70 (2)
C6 4	1978 (3)	8932 (4)	−1832 (5)	56 (2)
C1 5	3469 (2)	5800 (5)	−1648 (4)	43 (1)
C2 5	4029 (2)	4954 (5)	−842 (4)	50 (2)
C3 5	4566 (2)	4371 (5)	−1545 (4)	64 (2)
C4 5	4545 (2)	4634 (5)	−3053 (4)	79 (2)
C5 5	3985 (2)	5479 (5)	−3859 (4)	84 (3)
C6 5	3447 (2)	6062 (5)	−3156 (4)	64 (2)

[a] Coordinates multiplied by 10^4. Temperature factors multiplied by 10^3. Temperature factors for atoms Fe through C9 are given as U(eq).

shown by the temperature factors of the fluorine atoms which are somewhat, but not unreasonably, high. No attempt was made to rationalize the disorder by refining a double model of the anion. The final difference Fourier map has the largest peaks and depths of absolute values of 0.8–0.9 e/Å^3, some of which appear in the PF_6 region. Final coordinates of all the non-hydrogen atoms are reported in Table II.

ClFe(η^3-Ph_2PCH_2C(t-Bu)(S)(SCOMe))(PPh_3)(CO) (5). The structure was solved by the Patterson method and Fourier techniques. During the least-squares refinement all of the non-hydrogen atoms, except those belonging to the phenyl rings, were allotted anisotropic temperature factors. The phenyl rings were treated as rigid bodies. The hydrogen atoms were introduced at calculated positions. A final difference map was essentially featureless with peaks less than |0.1| e/Å^3. Final coordinates of all non-hydrogen atoms are reported in Table III.

Scheme II[a]



[a] i, HX (X = Cl or Br); ii, $NaHCO_3$; iii, aqueous 12 M HCl.

Results and Discussion

Protonation of Fe(η^2-$Ph_2PCH{=}C$(R)S)(η^2-SCOMe) Complexes. In order to understand the transformation of complexes I into derivatives II by reaction of HCl in the presence of water[9] (Scheme I), the protonation of complexes 1 (Scheme II) with strong acids either containing a noncoordinating anion, HA (HBF_4, HPF_6), or a coordinating anion, HX (HCl, HBr), was investigated.

The addition of an excess of $HBF_4 \cdot OEt_2$ (anhydrous conditions) or concentrated aqueous solution of HPF_6 to a dichloromethane solution of **1a** or **1b** led to an immediate color change from dark red to orange (**1a**) or to violet (**1b**). The addition of diethyl ether to the solution led to the formation of crystals of the salts **2a,b** (HBF_4) and **3a,b** (HPF_6). Attempts to recrystallize these salts in a neutral medium (CH_2Cl_2/Et_2O) led to the recovery of substantial amounts of complexes 1, thus indicating the ready reversibility of the protonation reaction. Complexes 1 were recovered in an essentially quantitative yield by treatment of the salts 2 and 3 in weakly basic medium, such as by stirring their solution in CH_2Cl_2 with an excess of aqueous $NaHCO_3$. Given the weakly basic character of complexes 1, the salts 2 and 3 could only be isolated in the presence of a large excess of the corresponding acids and elemental analyses of these salts were consistent with the formation of 1/HA (1/1) adducts.[11] As the deprotonation occurred by simple dissolution, especially in the case of derivative **1b**, ^1H NMR spectra could not provide detailed information. However, they did show the disappearance of the olefinic proton of **1a** and the presence of a broad signal at ca. δ 4 which is consistent with that of a CH_2P group. The infrared spectra of the complexes 2 and 3 (Table IV) showed an increase of both carbonyl and η^2-SCOMe absorption frequencies with respect to those of the precursors 1. The lack of the strong absorption band at 1520 cm^{-1}, attributable to the C=C bond of the chelating ligand, also

Table IV. Infrared Data of Complexes 1–11[a]

	CO (vs)	PCH=C (m)	η^2-SCOMe (s)	CS (vs)	A$^-$ (vs)
1a	1928	1520	1285		
1b	1920	1525	1280		
2a	1955		1325		1055
2b	1960		1335		1055
3a	1955		1325		840
3b	1960		1335		840
4	1940		1335		
5	1975				
6	1975				
7	2025 1975	1520			
8a	1914	1500			
8b	1918	1525			
10	2012	1507		1285	1055
11a	2017	1515		1280	
11b	2043	1510		1275	

[a] Complexes as Nujol mulls; ν, cm^{-1}. Abbreviations: vs, very strong; s, strong; m, medium.

suggested that protonation occurred at the olefinic carbon linked to phosphorus.

Unambiguous evidence of the site of protonation in **1** was provided by an X-ray diffraction study of **3a**. It showed that protonation occurred at the chelating ligand, at the olefinic carbon α to the thiocarbonyl group.

Complexes **1a** and **1b** showed different behavior upon reaction with acids containing a coordinating anion. The addition of an excess of anhydrous HCl to a dichloromethane solution of **1b** led immediately to a violet product, **4**, which was precipitated on addition of ether. Complex **4** was unstable at room temperature (even in the solid state), but on treatment with an aqueous solution of $NaHCO_3$ **1b** was recovered in 74% yield. The infrared spectrum of **4** showed the absence of the C=C absorption band of the chelating ligand and that the η^2-SCOMe moiety was retained (Table IV). Accordingly, the structure $ClFe(\eta^1\text{-}Ph_2PCH_2C(Ph){=}S)(\eta^2\text{-}SCOMe)(PPh_3)(CO)$ was assumed for **4**.[12]

The same reaction of anhydrous HCl with **1a** in dichloromethane developed in a different way. Addition of ether led to the isolation of 69% of the orange complex **5**. Alternatively, complexes **5** and **6** were quantitatively obtained by stirring a suspension of **1a** in diethyl ether with an excess of a 6 M aqueous solution of HCl and HBr, respectively (Scheme II).

Complexes **5** and **6** were found to be stable in the solid state but decomposed on dissolution in dichloromethane. The resulting dark red solution contained the precursor **1a** as indicated by its infrared spectrum. Complex **1a** was recovered in 50% yield after treatment of this solution with aqueous $NaHCO_3$. Infrared spectra of **5** and **6** showed no absorptions corresponding to the C=C double bond and, by contrast to that of **4**, to the η^2-SCOMe moiety (however, a new strong absorption appeared at 1200 cm^{-1}). Therefore both the protonation of the chelating ligand and the modification of the η^2-SCOMe group were expected to be involved in the transformation of **1a** into **5** and **6**.

The X-ray diffraction study of **5** showed that the chloride ligand in coordination sphere of the metal and formation of the novel tripodal ligand carbenethiolato–phosphine (Scheme II). The polyfunctional phosphine of **5** arises formally from the protonation of the $Ph_2PCH{=}C(R)S$ ligand α to the C–S bond followed by intramolecular coupling of the SCOMe sulfur atom with the thiocarbonyl carbon of the protonated chelating ligand. It thus appears that the coupling reaction requires the coordination of the chloride to the iron, since the structure of **3a**, containing the noncoordinating PF_6^- anion, showed that such a coupling was not involved.

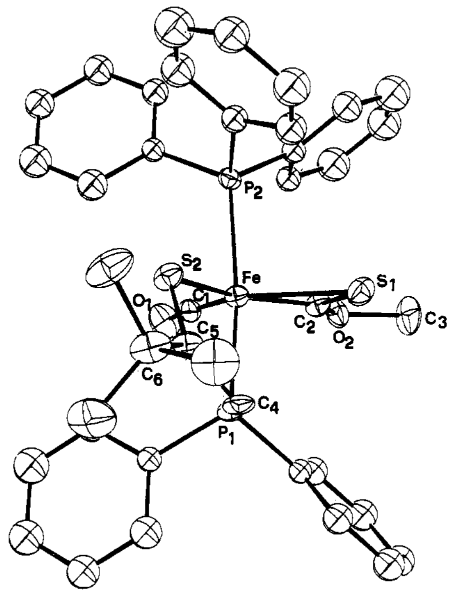


Figure 1. ORTEP drawing of $[Fe(\eta^2\text{-}Ph_2PCH_2C(t\text{-}Bu){=}S)(\eta^2\text{-}SCOMe)(PPh_3)(CO)](PF_6)$ (**3a**).

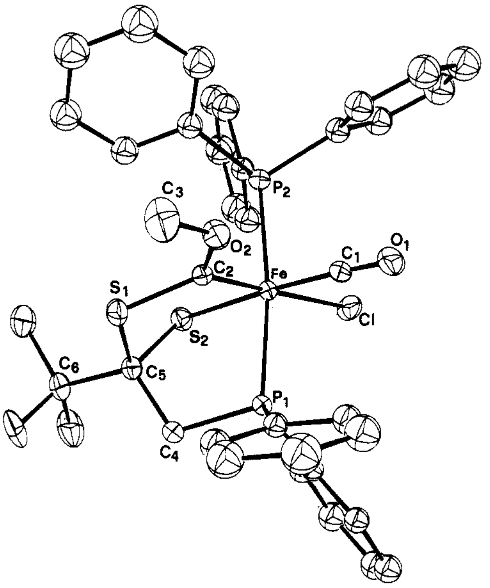


Figure 2. ORTEP drawing of $ClFe[\eta^3\text{-}Ph_2PCH_2C(t\text{-}Bu)(S)(SCOMe)](PPh_3)(CO)$ (**5**).

Description and Discussion of the Structures of $[Fe(\eta^2\text{-}Ph_2PCH_2C(t\text{-}Bu){=}S)(\eta^2\text{-}SCOMe)(PPh_3)(CO)]^+(PF_6)^-$ (3a) and $ClFe(\eta^3\text{-}Ph_2PCH_2C(t\text{-}Bu)(S)(SCOMe))(PPh_3)(CO)$ (5). ORTEP drawings of the cation in compound **3a** and of the complex molecule **5** are shown in Figures 1 and 2, respectively. Table V compares a selection of bond lengths and angles in the two structures. The complex cation in **3a** can be described as formed by two fragments: a metal fragment of the type ML_4 with pseudo C_{2v} symmetry and a η^2-coordinated methylated heteroallene (SCOMe). All of the non-hydrogen atoms of the latter group lie almost exactly in the equatorial plane formed by the metal, the CO ligand, and the sulfur atom of the ligand $Ph_2PCH_2C(t\text{-}Bu){=}S$. This type of structure is typical for d^8 $ML_4(\eta^2\text{-}CS_2)$ complexes.[16] The compound

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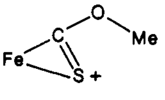
[16] Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Stereochemistry of Organometallic and Inorganic Compounds*: Bernal, I., Ed.; Elsevier,: Amsterdam, 1986; Vol. 1, p 146.

Table V. Selected Bond Lengths (Å) and Angles (deg) for Compounds 5 and 3a

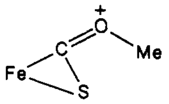
	5	3a
	Bond Lengths	
Fe–C1	1.741 (6)	1.748 (20)
Fe–C2	1.817 (6)	1.785 (14)
Fe–Cl	2.337 (2)	
Fe–S1		2.436 (5)
Fe–S2	2.261 (2)	2.284 (4)
Fe–P1	2.225 (2)	2.246 (4)
Fe–P2	2.268 (2)	2.292 (4)
C1–O1	1.130 (8)	1.124 (17)
C2–O2	1.241 (8)	1.314 (15)
C3–O2	1.429 (12)	1.488 (17)
C2–S1	1.734 (5)	1.641 (15)
C5–S1	1.780 (7)	
C5–S2	1.807 (6)	1.647 (14)
C5–C4	1.515 (8)	1.470 (18)
C4–P1	1.827 (5)	1.850 (14)
C5–C6	1.554 (8)	1.483 (19)
P3–F(av)		1.562 (25)
	Bond Angles	
Cl–Fe–C1	82.0 (2)	
Cl–Fe–C2	177.0 (2)	
Cl–Fe–S2	96.6 (1)	
Cl–Fe–P1	97.4 (1)	
Cl–Fe–P2	85.9 (1)	
S1–Fe–P1		89.8 (2)
S1–Fe–P2		93.7 (2)
S1–Fe–S2		107.7 (2)
S1–Fe–C1		138.5 (5)
S1–Fe–C2		42.3 (5)
P1–Fe–P2	172.7 (1)	168.8 (2)
P1–Fe–C1	90.9 (2)	94.7 (5)
P1–Fe–C2	82.4 (2)	95.7 (4)
P1–Fe–S2	86.5 (1)	81.7 (1)
P2–Fe–C1	96.0 (2)	89.7 (5)
P2–Fe–C2	94.7 (2)	94.1 (4)
P2–Fe–S2	86.7 (1)	87.1 (2)
S2–Fe–C1	176.9 (2)	113.8 (5)
S2–Fe–C2	86.4 (2)	150.0 (5)
C1–Fe–C2	95.1 (3)	96.1 (7)
P1–C4–C5	111.3 (4)	107.9 (9)
C4–C5–S2	109.2 (4)	122 (1)
C4–C5–S1	104.3 (4)	
C4–C5–C6	115.4 (5)	119 (1)
S1–C5–S2	108.6 (3)	
S1–C2–O2	113.7 (5)	133 (1)
Fe–C2–S1	126.3 (3)	90.5 (7)
Fe–C2–O2	119.9 (5)	137 (1)
C2–O2–C3	121.4 (6)	118 (1)
Fe–C1–O1	177.2 (5)	176 (1)
Fe–S2–C5	95.5 (2)	
C2–S1–C5	96.3 (3)	

Fe($Ph_2PCH{=}C$(*t*-Bu)S)(η^2-SCOMe)(PR_3)(CO) (**1c**, R = OMe)[8], can be considered as the unprotonated precursor of **3a** if, in the first approximation, the monofunctional triphenylphosphine ligand is considered equivalent to $P(OMe)_3$. Since the structure of **1c** is available,[8] it becomes interesting to evaluate from a structural viewpoint the effect of the protonation both on the chelate ligand and on the coordination sphere about the metal. As expected, the most remarkable geometrical differences occur within the metallacycle formed by the bifunctional ligand. Upon protonation the C–C linkage loses the double-bond character and elongates from 1.346 (8) in **1c** to 1.470 (18) Å in **3a**. At the same time the C–S bond is shortened from 1.764 (5) to 1.647 (14) Å. The C–P bond is also elongated in **3a** [1.770 (6) vs 1.850 (14) Å] probably because of the loss of conjugation. The bond angle at the protonated carbon atom C_4, 107.9 (9)°, also reflects the loss of sp^2 hybridization. Within the $\overline{\text{Fe–P–C–C–S}}$ metallacycle there is no other major variation as the Fe–P and Fe–S distances are very comparable to those in **1c** and **3a** [2.256 (1) vs 2.246 (4) Å] and [2.307 (2) vs 2.284 (4) Å], respectively. It is surprising that the bond to the metal formed by the sulfur atom of the thiocarbonyl group is almost as strong as that formed by the thiolato group which is presumed to be a better donor. Another notable difference between the structures **3a** and **1c** is relative to the Fe–S bond involving the η^2-coordinated C–S linkage [2.436 (5) and 2.512 (2) Å, respectively]. Thus the iron atom, which is likely less electron-rich in **3a**, shows a stronger interaction with the sulfur donor of the heteroallene.

Of particular interest are the structural data relative to complex **5** which contains the novel tripodal ligand Ph_2PCH_2C(*t*-Bu)(S)(SCOMe). The overall geometry about the metal is close to octahedral. In spite of the different nature of the three arms of the tripod, the bond angles at the iron center are nearly those for a regular octahedron, being close to 90 or 180° (see Table V). The P_1–C_4 and C_4–C_5 bond distances [1.827 (5) and 1.515 (8) Å] as well as the angular values at atoms C_4 and C_5 confirm sp^3 hybridization for both of them. The C_5–S_2 bond of 1.807 (6) Å corresponds to a single-bond value and is almost equal to the newly formed bond C_5–S_1 [1.780 (7) Å]. There is also a geometrical readjustment of the heteroallene SCO fragment in going from the η^2 (in **3a**) to η^1 (in **5**) coordination: a shortening of the C_2–O_2 bond [1.314 (15) vs 1.241 (8) Å] and a lengthening of the C_2–S_1 bond [1.641 (15) vs 1.734 (5) Å]. Irrespective of the fact that S_1 forms a new bond to C_5 in **5**, the longer C–O bond in **3a** suggests that the resonance structure A is the major contributor relative to B, as previously suggested.[16] Conversely the double-bond character is more equally shared between the C–O and C–S linkages in the η^1 coordination. Also a certain amount of Fe=C double-bond character should be expected in the carbene-like complex **5**. However, as observed in other cases,[16] the Fe–C bond is not shorter in the η^1 coordination compared to η^2. On the contrary Fe–C_2 is slightly shorter in **3a** than in **5** [1.785 (14) vs 1.817 (6) Å]. (Although this fact is not totally understood, σ rather than π effects seem to be responsible for such a feature.[16])



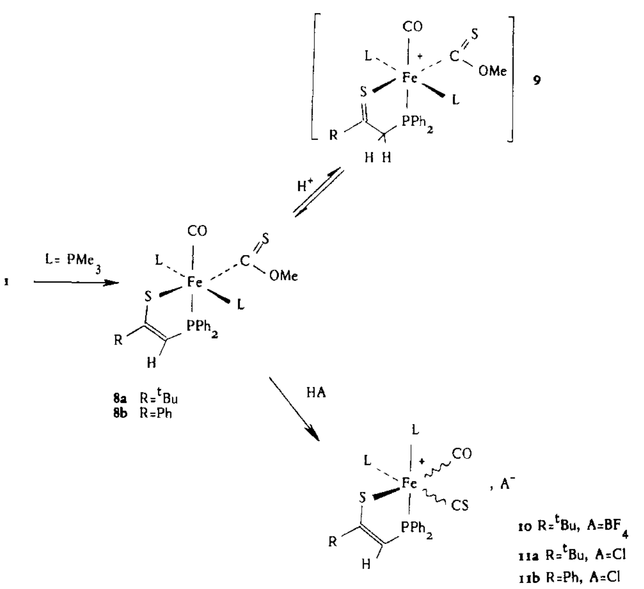
A



B

Protonation of Fe(η^2-$Ph_2PCH{=}C$(R)S)(η^1-C(OMe)S) Complexes. The reaction of complexes **1** with PMe_3 led to derivatives **8** by both displacement of PPh_3 and conversion of the coordinated mode of the SCOMe group from η^2 to η^1.[9] This transformation retains the basic chelating ligand without significant modification of the electron density at the iron center as shown by the slight variation of the carbonyl IR absorption frequency (Table IV). Therefore the protonation of the complexes Fe($Ph_2PCH{=}C$(R)S)(η^1-C(OMe)S) was investigated. Complexes **8a** and **8b** were readily obtained in about 65% yield from the corresponding complexes **1a** and **1b**, on treatment with an excess of PMe_3 in diethyl ether at room temperature. Complexes **8a** and **8b** in dichloromethane solution showed a strong carbonyl absorption at 1915 cm^{-1} in the infrared. The addition of $HBF_4 \cdot OEt_2$ to these solutions led immediately to a new absorption frequency at 1960 cm^{-1}. The increase of the frequency by about 45 cm^{-1} suggested that protonation of the $Ph_2PCH{=}C$(R)S ligand had occurred to give the complexes **9** (Scheme III). At this stage, the starting complex **8** was easily recovered by filtration of the resulting acidic solution through a short alumina column. Prolonged reaction of **8a** with acid (12 h) led to the formation of a yellow complex, **10**, isolated

Scheme III



in 58% yield. The ^1H NMR spectrum of complex **10** showed the retention of the $Ph_2PCH{=}C(R)S$ ligand and the disappearance of the methoxy resonance. The IR spectrum showed a very strong absorption at 1280 cm^{-1} consistent with the formation of a thiocarbonyl ligand. Similarly, complex **8a** reacted in dichloromethane with anhydrous HCl to produce, on addition of ether, the yellow crystalline complex **11a**. **11a** was hygroscopic but had the same IR spectrum as that of **10** (except for the BF_4^- absorption). Analogously, complex **11b** was obtained as a yellow crystalline solid from **8b**. The η^1-C(OMe)S ligand has already been reported to be a precursor of the thiocarbonyl ligand on protonation, as shown in the following equation:[17]

$$CpFe(CO)_2(\eta^1\text{-}C(OMe){=}S) + H^+ \rightarrow [CpFe(CO)_2(CS)]^+ + MeOH$$

Consequently, the protonation of $Fe(Ph_2PCH{=}C(R)S)(\eta^1\text{-}C(OMe){=}S)$ complexes (**8**) can be understood in terms of competitive protonations of the $\eta^2\text{-}Ph_2PCH{=}C(R)S$ and the η^1-C(OMe)S ligands leading either reversibly to derivatives **9** or irreversibly to the thiocarbonyliron complexes **10** and **11**.

Discussion on the Formation of $XFe(\eta^3\text{-}Ph_2PCH_2C(t\text{-}Bu)(S)(SCOMe))(PPh_3)(CO)$ Derivatives (5 and 6). The structure of **3a** shows that the protonation of the complexes $Fe(Ph_2PCH{=}C(R)S)(\eta^2\text{-}SCOMe)$ (**1**) takes place at the carbon linked to the phosphorus atom within the chelating $Ph_2PCH{=}C(R)S$ ligand. Therefore in complex **1a** the $Ph_2PCH{=}C(R)S$ ligand behaves as a reversible proton acceptor to give the neutral four-electron $Ph_2PCH_2C(R){=}S$ group in the presence of a noncoordinating anion. The coordination of a halide ligand (Cl^- or Br^-) to the iron center of the protonated species **2a** or **3a** promotes the coupling of the $Ph_2PCH_2C(R){=}S$ ligand with the SCOMe group to give complex **5** or **6**.

Our study of **1a** indicated a facile rearrangement from η^2 to η^1 coordination of the SCOMe ligand, upon coordination of a basic phosphine ligand. The transformation of the bonding mode of coordinated heteroallenes is known to be promoted by a simultaneous change of the nature of the supporting metal fragment. Typically a d^8 ML_4 (C_{2v} symmetry) adds an extra ligand and transforms into a square-pyramidal d^8 ML_5 fragment.[16] Therefore, to form complex **5**, the chloride ligand could enter the coordination sphere of the cation **3a** in the equatorial plane of the trigonal bipyramid (or octahedron) in between the C_1 and C_2 atoms (see Figure 1). As a consequence, the methylated heteroallene group (SCOMe) would be forced to rearrange its coordination mode from η^2 to η^1. This would allow the originally coordinated S_1 atom to quench its nucleophilicity over the sp^2-carbon atom of the ligand $Ph_2PCH_2C(R){=}S$. There are two suitable conditions to achieve such a coupling. (i) As seen in the structure of complex **3a**, the S_1 and C_5 atoms lie in close proximity and, upon achievement of η^1 coordination of the methylated heteroallene, unhindered rotation of the group about the Fe–C_2 bond is expected to favor the process. (ii) The C_5 atom of the thiocarbonyl group is electrophilic since much electron density is polarized away from C_5 toward the S_2 atom which must act as a donor toward the metal.

Table VI. ^{31}P NMR Data of Complexes 1–10[a]

	PPh_2	PPh_3	PMe_3	$^2J_{PP}$
1a[b]	81.50 (d)	48.60 (d)		181
1b[b]	81.30 (d)	49.50 (d)		176
2a[c]	97.53 (d)	48.54 (d)		166
2b[c]	95.74 (d)	48.37 (d)		167
3a[c]	96.70 (d)	49.28 (d)		166
7[b]	72.99 (d)	36.12 (d)		173
8b[b]	56.21 (t)		10.45 (d)	34
10[b]	58.51 (dd)		11.56 (dd), −0.09 (t)	84, 60, 65

[a] Chemical shifts in δ and coupling constants in Hz. [b] Solution in $CDCl_3$ at 309 K. [c] Solution in CH_2Cl_2–$CDCl_3$ (2:1) mixture at 223 K.

The fact that no similar coupling is obtainable from the protonation of compound **8**, but compound **9** is formed (Scheme III), can be explained from a stereochemical point of view. In complex **8**, the trans position of the two PMe_3 groups forces a trans arrangement of the η^1-C(OMe)S carbon atom with respect to the electrophilic carbon atom of the chelating ligand, thus hindering a close approach of the sulfur atom of the η^1-C(OMe)S group.[18]

Formation of $ClFe(\eta^2\text{-}Ph_2PCH{=}C(t\text{-}Bu)S)(PPh_3)(CO)_2$ (7). The formation of **5** with aqueous HCl was solvent-dependent as **5** was quantitatively obtained in diethyl ether, whereas in CH_2Cl_2 (or $CHCl_3$) the orange complex **7** was isolated in 87% yield after a prolonged stirring of 20 h. It can be assumed that the insolubility of **5** in diethyl ether prevented further hydrolysis. Complex **7** was found to be monomeric in benzene solution, and a structure with cis carbonyls and trans phosphorus groups was assigned to **7** on the basis of its infrared spectra (Table IV) and a large $^2J_{PP}$ (173 Hz) coupling constant value (Table VI). The high yield of **7** demonstrates unambiguously that the new carbonyl ligand derives from the SCOMe fragment, likely via addition of water to the electrophilic carbon atom, as summarized by the following formula[19] equation:

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[17] Busseto, L.; Angelici, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 3283.

[18] When complex **1a** was reacted with slightly less than 1 equiv of PMe_3, a red oily product resulted that was identified as $Fe(\eta^2\text{-}Ph_2PCH{=}C(t\text{-}Bu)S)(\eta^2\text{-}SCOMe)(PMe_3)(CO)$ [IR (CH_2Cl_2) ν 1910 ($C{\equiv}O$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.60–7.19 (m, 10 H, Ph), 5.95 (d, 1 H, PCH=, $^2J_{PH}$ = 9.8 Hz), 4.14 (s, 3 H, OMe), 1.49 (s, 9 H, *t*-Bu), 1.40 (d, PMe_3, $^2J_{PH}$ = 11 Hz)]. By treatment of this complex with anhydrous HCl, following the same procedure as described for **5**, yellow crystals were first obtained. On standing, and in about the same amount, additional orange crystals formed. The orange product has the same IR spectrum (except the bands due to PMe_3) as that of **5** whereas IR and ^1H NMR data of the yellow product [IR (Nujol) ν 2000 ($C{\equiv}O$, vs), 1510 (C=C(S), m), 1285 ($C{\equiv}S$, vs) cm^{-1}], which show the transformation Fe(C(OMe)S) → Fe(CS), were consistent with the formulation $ClFe(\eta^2\text{-}Ph_2PCH{=}C(t\text{-}Bu)S)(PMe_3)(CO)(CS)$. This indicates that the formation of a tripodal or a thiocarbonyl ligand via a η^1-C(OMe)S intermediate are competitive.

$$\mathrm{Fe}(\eta^2\text{-}\mathrm{Ph_2PCH{=}C}(t\text{-}\mathrm{Bu})\mathrm{S})(\eta^2\text{-}\mathrm{SCOMe})(\mathrm{PPh_3})(\mathrm{CO}) + \mathrm{HCl} + \mathrm{H_2O} \rightarrow \mathrm{ClFe}(\eta^2\text{-}\mathrm{Ph_2PCH{=}C}(t\text{-}\mathrm{Bu})\mathrm{S})(\mathrm{PPh_3})(\mathrm{CO})_2 + \mathrm{H_2S} + \mathrm{MeOH}$$

Although there was no direct evidence for this, it seems probable that the formation of **7** results from the hydrolysis of **5**, following the sequence **1** → **2** → **5** → **7**.

Conclusions

The results that are reported here show that the chelating $Ph_2PCH{=}C(R)S^-$ ligand is a reversible proton acceptor and that its neutral iron complexes **1** and **8** behave as weak bases. The protonation of the $Ph_2PCH{=}C(R)S$ chelating ligand of $Fe(\eta^2\text{-}SCOMe)$ complexes **1** promotes the coordination of a halide anion to iron via displacement of its sulfur atom to give the unstable complex **4** or via interconversion of the heteroallene coordination mode from η^2 to η^1, leading finally to a novel tripodal ligand containing iron complex **5**. The iron–chloro derivative **7** can be considered as resulting from the hydrolysis of this tripodal ligand, with regeneration of the initial $Ph_2PCH{=}C(t\text{-}Bu)S^-$ chelating ligand. The protonation appears as a competitive but reversible pathway in the transformation of the $Fe(\eta^1\text{-}C(OMe)S)$ complexes **8** into the thiocarbonyliron derivatives **10** and **11**. Finally, the readily available $Ph_2PCH{=}C(t\text{-}Bu)S$ chloro–iron derivative **7** appears particularly attractive for conversion to other $Ph_2PCH{=}C(t\text{-}Bu)S$ iron derivatives.

Acknowledgment. This work was supported by CNRS and the "Progetto bilaterale" approved by Italian CNR. Thanks are due to Dante Masi for technical assistance during the X-ray work.

Registry No. **1a**, 82264-89-9; **1b**, 82247-29-8; **2a**, 110614-72-7; **2b**, 110614-75-0; **3a**, 110614-73-8; **3b**, 110614-76-1; **4**, 110614-77-2; **5**, 110614-78-3; **6**, 110637-29-1; **7**, 92543-95-8; **8a**, 92543-92-5; **8b**, 110614-79-4; **10**, 110614-81-8; **11a**, 110614-83-0; **11b**, 110614-82-9; $Ph_2PC{\equiv}C\text{-}t\text{-}Bu$, 33730-51-7; $Ph_2PC{\equiv}CPh$, 7608-17-5; PPh_2Cl, 1079-66-9; $(PPh_3)_2(CO)_2(CS_2)Fe$, 86196-40-9; *tert*-butylacetylene, 917-92-0; phenylacetylene, 536-74-3.

Supplementary Material Available: Tables of anisotropic thermal parameters and positional parameters of hydrogen atoms (4 pages); listings of structure factors (20 pages). Ordering information is given on any current masthead page.

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(19) The evolved H_2S was quantitatively determined by precipitation as ZnS or HgS. The formation of **7** has been found to be slow as compared to those of **5** under similar acidic conditions, and it could be assumed that **7** arises from the hydrolysis of **5**. When $CHCl_3$ was used instead of CH_2Cl_2 for the preparation of **7**, an orange crystalline product resulted which showed in the solid state two IR carbonyl frequencies (2013, 1962 cm^{-1}) different from those (2025, 1975 cm^{-1}) showed by the product obtained from CH_2Cl_2 conditions. The same ^1H and ^{31}P NMR and IR spectra were found in solution [IR (cyclohexane solution) 2025, 1977 cm^{-1}]. Analysis shows that from $CHCl_3$, **7** crystallized as $7\cdot CHCl_3$. Anal. Found (Calcd) C, 56.61 (56.54); H, 4.44 (4.38); P, 6.79 (7.48); S, 2.83 (3.87); Cl, 17.25 (17.12).

Synthesis and Complexation of a New Chelating Bis(phosphite) Ligand, pinacop. Structural Characterization of (2,4-Dimethylpentadienyl)M(pinacop) Complexes (M = Co, Rh)[1]

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Received March 30, 1987

A new chelating bis(phosphite) ligand, $\overline{\mathrm{OCMe_2CMe_2OP}}\mathrm{OCMe_2CMe_2O}\overline{\mathrm{POCMe_2CMe_2O}}$ or "pinacop", has been synthesized via condensation of pinacol with phosphorus trichloride. The addition of pinacop to the low-temperature reaction product of $CoCl_2$ and 2 equiv of potassium 2,4-dimethylpentadienide yields (2,4-dimethylpentadienyl)Co(pinacop) (**1**), which has been structurally characterized. **1** crystallizes in the monoclinic space group *Cc* with $a = 13.964$ (7) Å, $b = 16.018$ (5) Å, $c = 13.775$ (3) Å, $\beta = 108.58$ (3)°, $V = 2921$ (2) Å^3, and $Z = 4$. The pinacop ligand is oriented with one phosphorus atom eclipsing the open edge and the other phosphorus atom eclipsing the central carbon, C3, of the U-shaped η^5-dimethylpentadienyl group. (2,4-Dimethylpentadienyl)Rh(pinacop) (**2**) has been synthesized by reacting $[(pinacop)RhCl]_2$ with 2 equiv of potassium 2,4-dimethylpentadienide and has been structurally characterized. **2** crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.609$ (3) Å, $b = 25.241$ (6) Å, $c = 11.500$ (1) Å, $\beta = 104.36$ (2)°, $V = 2983$ (1) Å^3, and $Z = 4$. The dimethylpentadienyl ligand in **2** is bonded to the Rh center in an η^3 fashion and adopts an anti-rotated (sickle shaped) geometry. The overall coordination geometry for 16 e^- **2** is square planar with C1 and C3 of the dimethylpentadienyl ligand and P1 and P2 of the pinacop ligand occupying the four coordination sites. In solution, **2** exists as an equilibrium mixture of *anti*-η^3- and *syn*-η^3-2,4-dimethylpentadienyl isomers. The anti isomer undergoes a fluxional process, which exchanges the ends of the dimethylpentadienyl ligand via an 18 e^- (η^5-2,4-dimethylpentadienyl)Rh(pinacop) intermediate.

Introduction

Chelating ligands can dramatically influence the reactivity of transition-metal complexes.[2] For this reason, considerable effort has been directed toward synthesizing metal complexes containing chelating poly(tertiary phosphine) ligands.[2,3] In contrast, there have been no reports

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[1] Pentadienyl-Metal-Phosphine Chemistry. 13. For the previous paper in this series, see Bleeke, J. R.; Peng, W.-J. *Organometallics* **1987**, *6*, 1576.

(2) Pignolet, L. H. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum: New York, 1983.

(3) McAuliffe, C. A.; Levason, W. *Phosphine, Arsine, and Stibine Complexes of the Transition Elements*; Elsevier: Amsterdam, 1979.

0276-7333/88/2307-0033$01.50/0