W≡W bond energy, within the range of values consistent with thermochemical data[11] (ca. 80–230 kcal/mol), a choice toward the high end of the range might be justified.

Acknowledgment. We thank the National Science Foundation for financial support.

Registry No. $(Me_3CO)_3WCC_6H_5$, 82228-87-3.

Supplementary Material Available: Tables of atomic positional and thermal parameters, crystallographic data, bond lengths, bond angles, and structure factors (24 pages). Ordering information is given on any current masthead page.

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[11] See ref 9, p 353.

Access to Novel [2-(Diphenylphosphino)alkenethiolato]iron Complexes via Reactions of the η^2-Alkoxythiocarbonyl Ligand

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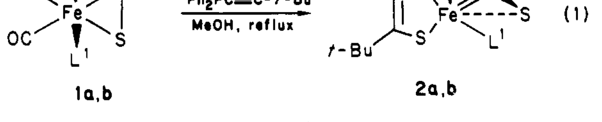
Received July 19, 1984

Summary: Complexes of type $Fe(\eta^2\text{-CSOMe})(CO)(PR_3)(P\frown S)$ [**2**, $P\frown S$ = $Ph_2PCH{=}C(t\text{-Bu})S$] on treatment with basic phosphines L give $Fe(\eta^1\text{-CSOMe})(CO)(L)_2(P\frown S)$ (**3**, **4**). **3** reacts with CH_3I/PF_6^- (aqueous) to lead to $[Fe(P\frown S)(CO)_2(PMe_2Ph)_2]PF_6$ **5**. On reaction with concentrated HCl **2** affords $FeCl(CO)_2(PPh_3)(P\frown S)$ (**6**), which is a precursor to $Fe(P\frown S)$ complexes, such as $Fe(P\frown S)(CO)(\eta^5\text{-}C_5H_5)$ (**7**) obtained by reaction of **6** with NaC_5H_5.

Although chelating ligands of type ($R_2PCH{=}CHS$) are potentially useful as ancillary ligands owing to both their rigidity and electron-donor capability, as suggested by the chemistry of analogous [$RPCH{=}C(R)Y$] metal complexes (Y = O[1,2] and NH[3]), their use has been limited by the lack of good methods for the preparation of their complexes. Recently, the intramolecular coupling of phosphinoalkyne and η^2-carbon disulfide ligands, in the presence of an alcohol, has offered a ready route (in only two steps from $Fe(CO)_5$ and via complexes **1**) to the (2-phosphinoalkenethiolato)iron derivatives **2**[4] that contain an η^2-alkoxythiocarbonyl ligand (eq 1). We now report that whereas the $Ph_2PCH{=}C(R)S$ ligand is inert and strongly bonded to the iron atom, the three-electron η^2-CSOR group is the reactive site in complexes **2**. It can be easily transformed, thus opening a route to a variety of [$Ph_2PCH{=}C(R)S$] Fe complexes.

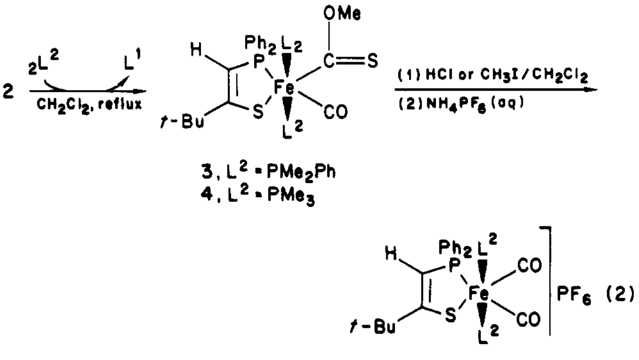


(1)

1a,b **2a,b**

a, L¹ = PPh₃; **b**, L¹ = PMe₂Ph

Although the Fe–S bond length of the $Fe(\eta^2\text{-CSOMe})$ moiety in complexes **2** is very long [2.512 (2) Å in **2c** (L^1 = $P(OMe)_3$)],[4] its sulfur atom is strongly coordinated in iron. The sulfur atom was displaced at the same time as the ligand L^1 only when complexes **2** were heated with an excess of a very basic phosphine. Thus the yellow $Fe(\eta^1\text{-CSOMe})$ complexes **3** (66%) and **4** (60%) were obtained from **2a** with PMe_2Ph and from **2b** with PMe_3, respectively[5,6] (eq 2). No reaction was observed on treatment of **2a** with the less basic phosphorus compounds PPh_3 and $P(OMe)_3$. The trans position of the equivalent ligands L^2 was indicated by the ^1H NMR spectra of **3** and **4**[6] and the ^{31}P NMR spectrum of **3** [^{31}P NMR (32.38 MHz, $CDCl_3$) δ (referenced to H_3PO_4) 54.06 (t, PPh_2), 13.76 (d, PMe_2Ph), $^2J_{PP}$ = 32.3 Hz].

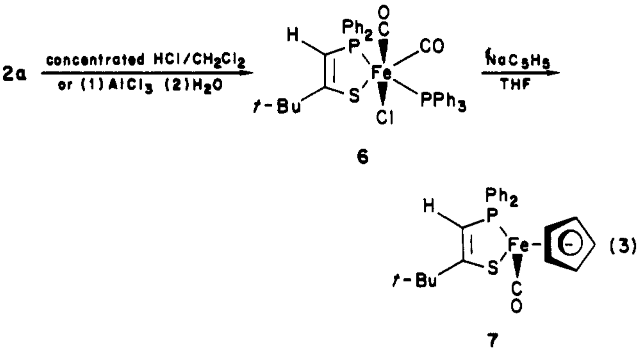


(2)

3, L² = PMe₂Ph
4, L² = PMe₃

5, L² = PMe₂Ph

The protonation of complexes **2** was investigated on the assumption that protonation of the sulfur atom of the $Fe(\eta^2\text{-CSOMe})$ moiety would facilitate its displacement by a small ligand such as carbon monoxide. The protonation of **2a** in dichloromethane, by HPF_6 in ether, is reversible; no coordination of CO takes place and complex **2a** is recovered after addition of water to the solution. In contrast, concentrated HCl reacts with **2a** in dichloromethane to afford, even in the absence of a carbon monoxide atmosphere and at room temperature, a yellow product that was isolated in 90% yield and identified as complex **6**[7] (eq 3)



(3)

6

7

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

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[3] Braunstein, P.; Matt, D. *J. Soc., Chem. Commun.* **1979**, 763.

[4] Robert, P.; Le Bozec, H.; Dixneuf, P. H.; Hartstock, F.; Taylor, N. J.; Carty, A. J. *Organometallics* **1982**, *1*, 1148.

[5] A related complex $(C_5H_5)(OC)_2$ $Fe(\eta^1\text{-CSOEt})$ was obtained previously by reaction of $[(C_5H_5)(OC)_2Fe]$ Na with ClCSOEt. Busetto, L.; Angelici, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 3283.

[6] **3**: mp 133–136 °C; IR (Nujol) 1935 cm^{-1} (C≡O), 1585 cm^{-1} (C=C); ^1H NMR (60 MHz, $CDCl_3$) δ 7.20 (m, C_6H_5), 6.19 (d, PCH=, $^2J_{PH}$ = 4.0 Hz), 3.31 (s, OMe), 1.57 (s, *t*-Bu), 1.23 (dt, PMe_2, $|^2J_{PH} + {}^4J_{PH}|$ = 9.0 Hz). Anal. Calcd for $C_{37}H_{45}O_2P_3S_2Fe$: C, 60.49; H, 6.13; P, 12.67. Found: C, 60.16; H, 6.08; P, 12.44. **4**: mp 118–121 °C; IR (Nujol) 1925 (C≡O), 1585 cm^{-1} (C=C); ^1H NMR (60 MHz, $CDCl_3$) δ 7.36 (m, C_6H_5), 6.30 (d, PCH=, $^2J_{PH}$ = 5.0 Hz), 4.14 (s, OMe), 1.50 (s, *t*-Bu) 1.00 (t, PMe_3, $|^2J_{PH} + {}^4J_{PH}|$ = 8.0 Hz). Anal. Calcd for $C_{27}H_{41}O_2P_3S_2Fe$: C, 53.12; H, 6.77; P, 15.22. Found: C, 52.82; H, 6.43; P, 14.98.

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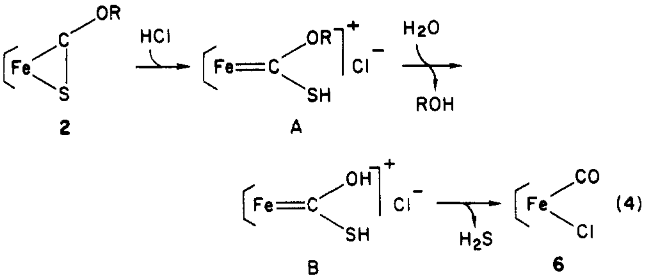
for which the trans position of the phosphorus atom has been established [**6**: ^{31}P NMR (32.38 MHz, $CDCl_3$) δ 72.40 (PPh_2), 36.28 (PPh_3), $^{2}J_{PP}$ = 177.0 Hz] by the large $^{2}J_{PP}$ value, similar to that of the trans phosphorus nuclei in complexes **2**.[4]

The reaction **2a** → **6** corresponds to the formal replacement of the three-electron η^2-CSOMe group by one carbonyl and one chloro group, but the high yield (90%) indicates that the new carbonyl ligand arises from the η^2-alkoxythiocarbonyl group. We suggest that eq 4 may account for this transformation: (i) protonation of the sulfur atom of **2** to produce a cationic iron–carbene intermediate (A), (ii) nucleophilic addition of water (from concentrated HCl) to displace methanol, and (iii) coordination of chloride and elimination of H_2S. This mechanism is supported by the fact that compound **2a** reacts also with Lewis acids such as $AlCl_3$ in dichloromethane to produce, after addition of water, the same compound **6** in 66% yield.



(4)

A similar transformation of the η^1-CSOMe group of complex **3** into a carbonyl group could be achieved. The treatment of **3** in dichloromethane with concentrated HCl at room temperature for 1 h followed by the addition of an aqueous solution of NH_4PF_6 afforded a 65% yield of the orange salt **5**[8] (eq 2) in which the stereochemistry of **3** was retained as shown by ^{31}P NMR [(32.38 MHz, $CDCl_3$) δ 65.37 (t, PPh_2), 9.08 (d, PMe_2Ph), $^{2}J_{PP}$ = 56.2 Hz)], but with a very clear diastereotopy of the methyl groups bonded to each phosphorus atom.[8,9] Complex **5** was also obtained, but in lower yield (30%) by treatment of **3** with an excess of methyl iodide followed by addition of aqueous NH_4PF_6. The formation of **5** is consistent with the methylation (or protonation) of the sulfur atom of **3** to give the unstable cationic iron carbene moiety $[Fe{=}C(SMe)OMe]^+$, similar to the formation of $[(C_5H_5)(OC)_2Fe{=}C(SMe)SR]^+$.[10] We may expect that the addition of water to this cationic species would release thiomethanol, and then methanol, to afford **5**.

Besides the novelty of the facile transformation **2a** → **6**, compound **6** may be an useful intermediate for the preparation of the new 2-phosphinoalkenethiolato derivative of iron by direct substitution of the chloride, whereas we were not able to achieve direct nucleophilic displacement of the alkoxythiocarbonyl group of derivative **2** or **3**. To illustrate this possibility, compound **6** was treated with an excess of NaC_5H_5 in THF and an orange derivative was isolated in 38% yield by using thick-layer chromatography and identified as the new chiral cyclopentadienylcarbonyliron complex **7**.[11]

The above reactions show that the transformation of an η^1- or η^2-alkoxythiocarbonyl ligand into a carbonyl group by reaction with an electrophilic reagent allows preparation of iron derivatives containing the inert, strongly bonded $Ph_2CH{=}C(R)S$ ligand, which shows potential as an electron-donating ancillary ligand.

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[7] **6**: mp 130–135 °C; IR (Nujol) 2025, 1966 (C≡O), 1585 cm^{-1} (C=C); ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.50 (m, C_6H_5), 5.95 (dd, PCH=, $^{2}J_{PH}$ = 10.0 Hz, $^{4}J_{PH}$ = 2.6 Hz), 1.48 (s, *t*-Bu). Anal. Calcd for $C_{38}H_{35}ClO_2P_2SFe$: C, 64.36; H, 4.94; Cl, 5.01; S, 4.51; P, 8.75. Found: C, 64.13; H, 4.97; Cl, 5.44; S, 4.99; P, 7.99.

[8] **5**: mp 175–178 °C; IR (Nujol) 2060, 2000 (C≡O), 1595 (C=C), 840 cm^{-1} (PF_6^-); ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.65 (m, C_6H_5), 6.80 (d, PCH=, $^{2}J_{PH}$ = 8.8 Hz), 1.71 (s, *t*-Bu), 1.70 (t, PMe(1), $|^{2}J_{PJ} + {}^{4}J_{PH}|$ = 8.6 Hz), 1.30 (t, PMe(2), $|^{2}J_{PH} + {}^{4}J_{PH}|$ = 8.6 Hz). Anal. Calcd for $C_{36}H_{42}F_6O_2P_4SFe$; C, 51.92; H, 5.04; P, 14.90. Found: C, 51.89; H, 5.01; P, 14.74.

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[11] **7**: mp 150–153 °C; IR (Nujol) 1967 cm^{-1} (C≡O); ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.65 (m, C_6H_5), 6.10 (d, PCH=, $^{2}J_{PH}$ = 11 Hz), 4.52 (s, C_5H_5), 1.31 (s, *t*-Bu). Anal. Calcd for $C_{24}H_{25}OPSFe$: C, 64.28; H, 5.35; P, 6.91; S, 7.14. Found: C, 63.54; H, 5.55; P, 6.75; S, 7.28.

First Heterobimetallic Complexes with Bridging and Chelating $Ph_2PCH_2Ph_2$ (dppm): Crystal Structure of $[(\eta\text{-}C_5H_4Me)Mo(CO)_2(\mu\text{-dppm})Pt(dppm)]_2[Mo_2O_7]$. Air Oxidation of the Anions $[(\eta\text{-}C_5H_4R)Mo(CO)_3]^-$ into $[Mo_2O_7]^{2-}$.

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Received July 7, 1984

Summary: The reactions of *trans*-$Pt[M(CO)_3(\eta\text{-}C_5H_4R)]_2(PhCN)_2$ (M = Mo, R = H, Me; M = W, R = H) with dppm afford the complexes $[(\eta\text{-}C_5H_4R)M(CO)_2(\mu\text{-dppm})Pt(dppm)]^+[(\eta\text{-}C_5H_4R)M(CO)_3]^-$ (**1–3**) in which the cation contains a bridging and a chelating dppm ligand. Easy air oxidation of the anions with M = Mo affords $[Mo_2O_7]^{2-}$, leading to $[(\eta\text{-}C_5H_4Me)Mo(CO)_2(\mu\text{-dppm})Pt(dppm)]_2[Mo_2O_7]$ (**4**), the structure of which was determined by X-ray diffraction. Reaction of the heterobimetallic cations with $NaBH_4$ affords the neutral heterobimetallic hydrides $[(\eta\text{-}C_5H_4R)M(CO)_2(\mu\text{-dppm})Pt(H)(\eta^1\text{-dppm})]$ (**10–12**) in which the terminal hydride occupies a coordination site liberated by the chelating dppm ligand.

We recently described the first mixed-metal clusters containing the $Ph_2PCH_2PPh_2$ (dppm) ligand.[1,2] The general interest for the synthesis, structure, and reactivity of heteropolymetallic complexes can be further enhanced by the introduction of one or more dppm ligands in such molecules, because of the unique properties often conferred by this ligand to polymetallic systems.[3]

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0276-7333/84/2303-1772$01.50/0