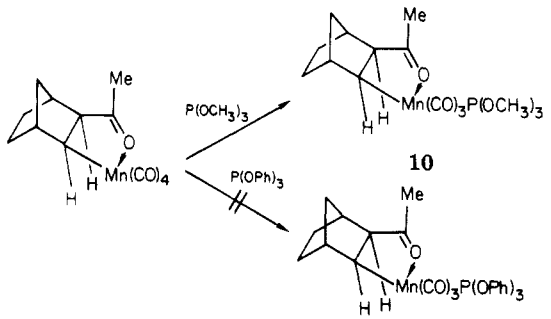
Halocarbon binding in [Ir(cod)(.eta.2-o-BrC6H4PPh2)]SbF6

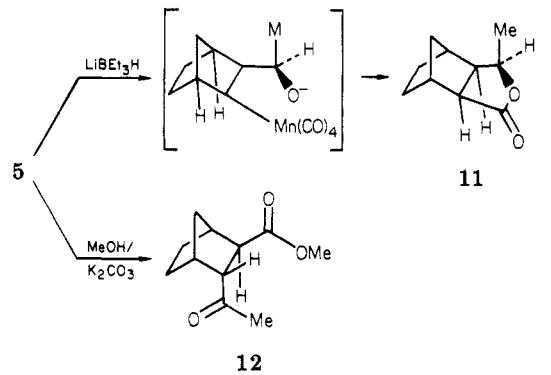
Mark J. Burk, Robert H. Crabtree, and Elizabeth M. Holt

Organometallics, **1984**, 3 (4), 638-640• DOI: 10.1021/om00082a026 • Publication Date (Web): 01 May 2002



10

48% yield. This reaction allows for the preparation of



5 11 12

highly substituted butyrolactones by a direct "annulation" of an olefin—a reaction for which there is no equivalent in organic synthesis.

Alternatively,when **5** was stirred in methanol containing a catalytic amount of K_2CO_3, the keto ester **12** was isolated in modest (30%) yield. This reaction demonstrates that manganacycles such as **5** can also serve as precursors to 1,4-dicarbonyl systems via biscarbonylation of an olefin.

A single diastereomer of **11** was obtained from the reduction of **5** with $LiBEt_3H$; it was assigned the stereochemistry shown from ^1H NMR spectroscopy. The proton H-3 appears as a broad singlet at δ 2.43, width at half-height of 8 Hz. Irradiation of the bridgehead proton, H-6, results in sharpening of the H-3 signal into a doublet with J = 6.7 Hz: H-3 must be endo and syn to H-4. Therefore, we propose that **5** arises from syn addition of the acylmanganese moiety onto the exo face of norbornylene.

In conclusion, it has been demonstrated that high-pressure techniques are useful in the preparation of manganacycles **5–7** from the reaction of alkylmanganese pentacarbonyl complexes and olefins and that complexes **5–7** can be readily converted into butyrolactones and 1,4-dicarbonyl compounds.

Acknowledgment. We acknowledge the financial support of the National Institutes of Health (GM 30743) and numerous helpful discussions with Professors G. Geoffroy and A. Sen of this department. Partial support for the purchase of a Bruker WP-200 NMR spectrometer from the National Science Foundation is also acknowledged.

Registry No. 1 (R = Me), 13601-24-6; 1 (R = CH_2Ph), 14049-86-6; **5**, 88996-56-9; **6**, 88996-57-0; **7**, 89016-71-7; **8**, 13963-91-2; **9**, 14058-20-9; **10**, 88996-58-1; **11**, 89063-56-9; **12**, 88996-59-2; CO, 630-08-0; $LiBEt_3H$, 22560-16-3; K_2CO_3, 584-08-7; $P(OCH_3)_3$, 121-45-9; norbornylene, 498-66-8; cyclopentene, 142-29-0.

Supplementary Material Available: Spectroscopic data (^1H NMR, ^{13}C NMR, IR, mass spectral) for the compounds reported (7 pages). Ordering information is given on any current masthead page.

Halocarbon Binding in $[Ir(cod)(\eta^2\text{-}o\text{-}BrC_6H_4PPh_2)]SbF_6$

Mark J. Burk,[1] Robert H. Crabtree,*[1] and Elizabeth M. Holt*[2]

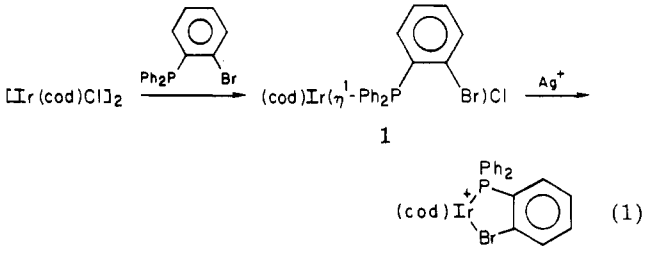
Departments of Chemistry, Yale University New Haven, Connecticut 06511, and Oklahoma State University, Stillwater, Oklahoma 74078

Received December 9, 1983

Summary: In the complex $[Ir(cod)(\eta^2\text{-}L)]SbF_6$ (**2**, L = o-$BrC_6H_4PPh_2$), L chelates to Ir via P and the Br bound to the aromatic ring. Complex **2** was formed from $Ir(cod)(\eta^1\text{-}L)Cl$ (**1**) with $AgSbF_6$. **2** reacts with Cl^- to give **1**, with MeCN to give $[Ir(cod)(MeCN)(\eta^1\text{-}L)]SbF_6$ reversibly, and with H_2 to give $[IrH_2(cod)(\eta^2\text{-}L)]SbF_6$, a hydrogenation catalyst.

We recently showed[3] that intact halocarbons such as o-$C_6H_4X_2$ (X = Cl, Br, I) or MeI can bind to transition metals via X to give complexes in which X plays the role of a neutral 2e donor, much like P in PR_3 or S in SR_2 complexes. Although the formation of halocarbon complexes had previously been proposed,[4] no definitive crystallographic evidence was obtained to support these formulations.

We wondered why our halocarbon complexes were stable and did not undergo oxidative addition. Since all our examples had involved Ir(III), it could be argued that oxidation to Ir(V) might be unfavorable. We therefore decided to try to make Ir(I) halocarbon complexes because this argument would not then apply, oxidative addition to Ir(I) to give Ir(III) being commonplace.[5] This paper describes preliminary results on the chelation of o-$BrC_6H_4PPh_2$ to Ir(I) via Br and P. $[Ir(cod)Cl]_2$ (300 mg, cod = 1,5-cyclooctadiene) reacts at 20 °C with o-$BrC_6H_4PPh_2$ (305 mg) in CH_2Cl_2 (20 mL) for 24 h to give $[Ir(cod)(\eta^1\text{-}BrC_6H_4PPh_2)Cl]$ (1) in 80% yield. We assign to this complex the unchelated P-bound structure 1 (eq 1), on the basis of two empirical spectroscopic criteria that



1 (1) 2

have emerged from our work (see below). In chelated systems, the ^{31}P NMR resonance of the phosphorus nucleus lies at δ +45–60 (ppm to low field of external H_3PO_4); in unchelated ones it lies at δ +15–30. Entirely analogous findings for chelating diphosphines have been reviewed by Garrou.[6a] In the case of five-membered chelate di-

(1) Yale University.
(2) Oklahoma State University.
(3) (a) Crabtree, R. H.; Faller, J. W.; Mellea, M. F.; Quirk, J. M. *Organometallics* **1982**, *1*, 1361. (b) Crabtree, R. H.; Mellea, M. F.; Quirk, J. M. *J. Chem. Soc., Chem. Commun.* **1981**, 1217.
(4) (a) Lawson, D. N.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1733. (b) A crystallographic study[4c] failed to support the binding of MeI proposed in ref 4a. (c) Troughton, P. G. H.; Skapski, A. C. *J. Chem. Soc., Chem. Commun.* **1968**, 575. (d) Beck, W.; Schloter, K. *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **1978**, *33B*, 1214.
(5) Vaska, L., *Acc. Chem. Res.* **1968**, *1*, 335.

0276-7333/84/2303-0638$01.50/0

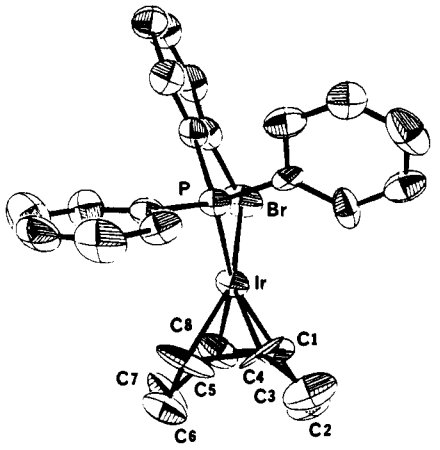
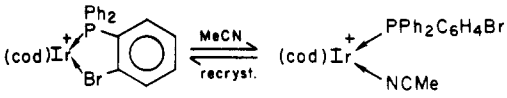


Figure 1. Chelating structure of the (*o*-bromophenyl)phosphine, coordinating via P and Br without C–Br bond cleavage or other rearrangement, in the complex $[Ir(cod)(\eta^2\text{-}PPh_2C_6H_4Br)]SbF_6$. The anion is not shown for clarity and C4 and C5 show the effects of disorder. In spite of the disorder, the key feature, the chelating nature of the phosphine binding, is unequivocally established.

phosphine rings, chelation shifts of δ +25–33 are observed; we obtain shifts of δ +28.6–32.8.[6b] Our second criterion is the appearance at δ 6.8–7.2 in the ^1H NMR spectrum of a complex multiplet only in the unchelated systems. This feature corresponds to one proton in intensity and is always clear of the other aromatic protons at δ 7.2–7.8. It can probably be assigned to the proton ortho to Br or to P. In chelated systems this absorption apparently becomes part of the aromatic multiplet at ca. δ 7.7.

Treatment of 1 (570 mg) with $AgSbF_6$ (288 mg) at 20 °C in CH_2Cl_2 (20 mL) and filtration of the solution on Celite gives a solution from which $[Ir(cod)(\eta^2\text{-}BrC_6H_4PPh_2)]SbF_6$ was isolated with Et_2O in 90% yield as yellow-orange prisms. Our proposed spectral criteria both show that the phosphine is chelating via Br in solution. The ^{31}P NMR spectral resonance at δ +52.7 (chelate shift relative to 1: +32 ppm) is consistent with chelation, as is the observation only of a single aromatic multiplet at δ 7.55–8.0 by ^1H NMR. The structure in the solid state was studied by X-ray methods, and appears to be identical. Unfortunately, disorder of the F atoms in the SbF_6 and of C4–5 in the cod group lessened the quality of the structure; the final *R* factor was 9.6%. However, the main features of the phosphine binding are well established: the chelate ring involving P and Br (see Figure 1). The major distances and angles observed (Ir–Br, 2.473(4) Å; C–Br, 1.86 (4) Å; and C–Br–Ir, 102.2 (9)°) all appeared to be normal.[3a,8,9] The cod groups, although partially disordered in the solid state, showed ^1H NMR resonances for the cod vinyl groups trans to P[10] at δ 5.65 and to Br at δ 3.55.

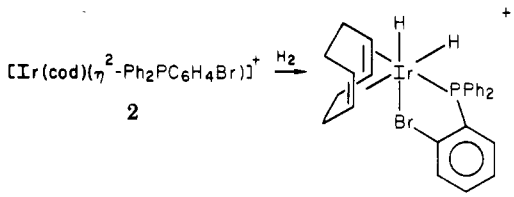
We hoped the chelating ligand might be able to open up easily to allow ligands to bind, a property that would be useful in catalysis. Indeed this is the case: reaction of chelate 2 with NaCl regenerates the chloro complex 1. The complex 2 reversibly cordinates MeCN (eq 2). When 1



2 3 (2)

molar equiv of this ligand is added to a CD_2Cl_2 solution of 2, the ^{31}P NMR resonance shifts to δ +19.56 (a nonchelating position). The product may be 3, but we were not able to study it in detail because on crystallization with Et_2O, 2 was precipitated.

Hydrogen adds to 2 to give the corresponding dihydride 4 (eq 3). This is revealed by the ^1H NMR spectrum, which



2 4 (3)

shows Ir–H resonances at δ –12.6 and –17.6, both doublets (J(P,H) = 17.7 and 12.4 Hz, respectively). These positions are appropriate for H trans to C=C and BrAr, respectively.[3a,10] The phosphorus nucleus resonates at δ +42.5, a "chelating" chemical shift. Complex 2 in CH_2Cl_2 is a hydrogenation (H_2: 1 atm) catalyst for 1-methylcyclohexene at 25 °C, a temperature at which 4 is unstable under H_2 and decomposes to give the active catalyst and cyclooctane. Reduction rates are only about 5% as fast as are found for the related catalysts[11] $[Ir(cod)PCy_3(py)]BF_4$, however.

The rhodium analogues of 1 and 2 have also been prepared in the same way. They appear to resemble their iridium analogues. Coupling to rhodium is observed in the ^{31}P NMR (Rh analogue of 1 δ +28.25 (d), J(P,Rh) = 145 Hz; of 2 δ +59 (d), J(P,Rh) = 141 Hz).

o-$ClC_6H_4PPh_2$[12] reacts with $[Ir(cod)Cl]_2$ in the same way as the bromo analogue to give the anlogous $[Ir(cod)(\eta^1\text{-}PPh_2C_6H_4Cl)Cl]$ (^{31}P NMR δ +17.31), which on treatment with $AgSbF_6$ closes to $[Ir(cod)(\eta^2\text{-}PPh_2C_6H_4Cl)]SbF_6$ (^{31}P NMR δ +45.9).

1 is recovered unchanged after reflux in toluene for 16 h, so the unchelated bromoarene group does not give oxidative addition even under these vigorous conditions. Any such addition product would easily be detectedby the characteristic three-membered chelate ring ^{31}P NMR shift[6] of ca. –50 ppm that it would have. The remarkable resistance to oxidation shown by 1 and 2 may therefore primarily be due to the electron-withdrawing cod group.

We expect that the coordination chemistry of halocarbons will prove to be extensive, especially when part of a chelating ligand, as described here.

Acknowledgment. We thank the Petroleum Research Fund and the National Science Foundation for support.

(6) (a) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (b) The ^{31}P NMR chelation shifts (ppm) cited arise as follows: $[Ir(cod)(\eta^1\text{-}L_1)Cl]$ at δ 17.31 and $[Ir(cod)(\eta^2\text{-}L_1)]SbF_6$ at δ 45.86 give a chelation shift of 28.6; $[Ir(cod)(\eta^1\text{-}L_2)Cl]$ at δ 19.94 and $[Ir(cod)(\eta^2\text{-}L_2)]$ at δ 52.72 give a shift of 32.8 (L_1 = *o*-$ClC_6H_4PPh_2$, L_2 = *o*-$BrC_6H_4PPh_2$).

(7) The compound crystallises in the space group $P\bar{1}$ with lattice constants a = 13.127 (1) Å, b = 10.239 (4) Å, c = 12.007 (8) Å, α = 68.12 (4)°, β = 77.07 (4)°, γ = 104.16 (2)°, V = 1360.3 Å^3, ρ_{calcd} = 2.14 g cm^{-3}, Z = 2. Matrix for conversion to reduced cell (α, β, γ > 90°):

$$\begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{matrix}$$

Diffraction data were collected on a Syntex P3 diffractometer with Mo Kα radiation at 25 °C. The structure was solved by using 3213 reflections, and the non-hydrogen atoms were anisotropically refined. The final *R* value was 9.6%. A full description appears in the supplementary data along with tables of structure factors, positional parameters, thermal parameters, distances, and angles.

(8) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* 19, *103*, 5984.

(9) Furmanora, N. G.; Batsanov, A. S.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1979**, *20*, 294.

(10) Crabtree, R. H.; Felkin, H.; Fillebeen-Khan, T. Morris, G. E. *J. Organomet. Chem.* **1979**, *168*, 183.

(11) Crabtree, R. H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *135*, 395. Crabtree, R. H.; Felkin, H.; Morris, G. E. *Ibid.* **1977**, *141*, 205.

(12) Hart, F. A. *J. Chem. Soc.* **1960**, 3324.

Robert H. Crabtree thanks the Camille and Henry Dreyfus Foundation for a Fellowship, and Johnson Matthey for the loan of iridium.

Supplementary Material Available: A figure showing the complete molecular structure and tables of structure factors, positional parameters, anisotropic thermal parameters, and selected bond lengths and angles (18 pages). Ordering information is given on any current masthead page.

Fragmentation and Carbonylation of Dithioformate via Addition of Electrophilic Alkynes to Fe(η^2-HCS_2Me) Complexes. X-ray Crystal Structure of $FeCH(SMe)COC(CO_2Me)=C(CO_2Me)S(CO)(PMe_3)_2$

Daniel Touchard*

Institut Universitaire de Technologie
44600 Saint-Nazaire, France

Pierre H. Dixneuf*

Laboratoire de Chimie de Coordination Organique
Université de Rennes, Campus de Beaulieu
35042 Rennes Cedex, France

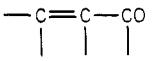
Richard D. Adams and Brigitte E. Segmüller

Department of Chemistry, Yale University
New Haven, Connecticut 06511

Received November 22, 1983

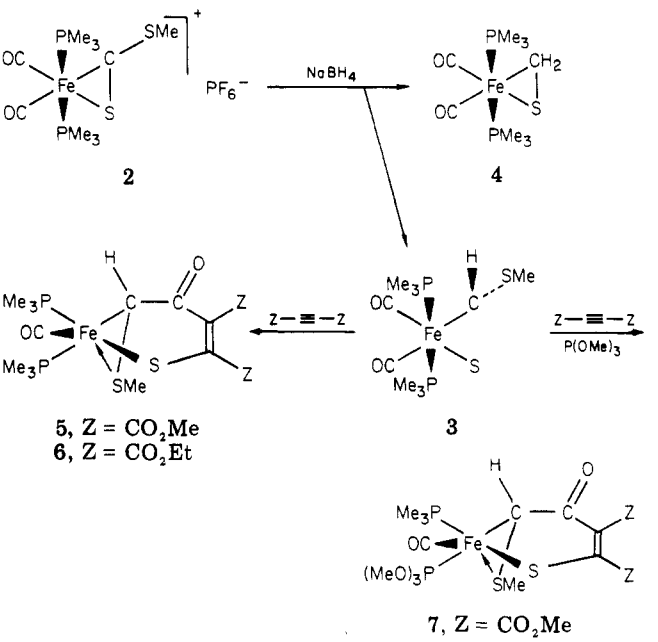
Summary: The complex Fe(η^2-HCS_2Me)$(CO)_2(PMe_3)_2$ has been obtained from a Fe(η^2-CS_2) precursor. It reacts with electrophilic alkynes with cleavage of the coordinated C=S bond, and insertion of both the C≡C bond and carbon monoxide takes place to afford six-membered metallacycle derivatives. Fe(η^2-$CH(SMe)COC(CO_2Me)$-$=C(CO_2Me)S(CO)(PMe_3)_2$ crystallizes in the triclinic space group $P\bar{1}$ (No. 2), with a = 8.957 (2) Å, b = 10.440 (2) Å, c = 14.005 (2) Å, α = 70.60 (1)°, β = 83.40 (2)°, γ = 67.96 (2)°, and Z = 2.

Fragmentation of sulfur–carbon bonds by transition-metal centers has attracted interest recently in the search for processes allowing the desulfurization of substrates such as thiocarbonates to afford dioxolanylidene–iron complexes[1] and thioketones to offer new applications to organic synthesis[2] or of dithioesters,[3] dithiocarbonates,[3] and thiolates[4] to produce new polymetallic species from metal carbonyls. We report here a novel reaction which involves the cleavage, via electrophilic addition, of a coordinated carbon–sulfur double bond, with concomitant insertion of an alkyne and of carbon monoxide, and which affords a new six-membered ring corresponding to the formal insertion of a



fragment into the C=S bond of a coordinated dithioformate.

Scheme I



The addition of sodium borohydride to a THF solution of the cationic complex **2**, obtained directly from Fe(η^2-CS_2)$(CO)_2(PMe_3)_2$ (**1**),[5] led to the formation of two yellow derivatives, **3** and **4** (Scheme I). The main product, **3**,[6] was isolated in 51% yield by crystallization in pentane whereas complex **4** was obtained in 5% yield by thick-layer chromatography of the crystallization solution.[7] Complex **3** has been identified as an η^2-dithioformateiron complex rather than the expected iron hydride derivative analogous to Os(H)(η^1-CS_2Me)$(CO)_2(PPh_3)_2$ obtained under similar conditions[8] (^{13}C NMR δ ($CHSMe$) = 60.9 (dt, $^1J_{CH}$ = 56 Hz, $^2J_{PC}$ = 9.9 Hz)[9]).

In order to study the activation by the iron center of the coordinated η^2-HCS_2Me group the reaction of **3** with alkynes has been examined. Although no reaction was observed with diphenylacetylene or 3-hexyne, complex **3** reacted in benzene with 1 equiv of dimethyl acetylenedicarboxylate to afford after 1 h at room temperature, a red complex isolated in 70% yield with thick-layer chromatography and identified as the metallacycle **5**[10] (Scheme

(1) Daub, J.; Endress, G.; Erhardt, U.; Jogun, K. H.; Kappler, J.; Laumer, A.; Pfiz, R.; Stezowski, J. J. *Chem. Ber.* **1982**, *115*, 1787.
(2) Alper, H.; Root, W. G. *J. Am. Chem. Soc.* **1975**, *97*, 4251. Laycock, D. E.; Alper, H. *J. Org. Chem.* **1981**, *46*, 289.
(3) Patin, H.; Mignani, G.; Van Hulle, M. T. *Tetrahedron Lett.* **1979**, 2441. Patin, H.; Mignani, G.; Benoit, A.; Le Marouille, J. Y.; Grandjean, D. *Inorg. Chem.* **1981**, *20*, 4351.
(4) Adams, R. D.; Yang, L. W. *J. Am. Chem. Soc.* **1982**, *104*, 4115. Adams, R. D.; Katahira, D. A.; Yang, L. W. *Organometallics*, **1982**, *1*, 235. Adams, R. D. *Acc. Chem. Res.* **1983**, *16*, 67.

(5) (a) Le Bozec, H.; Dixneuf, P. H.; Carty, A. J.; Taylor, N. J. *Inorg. Chem.* **1978**, *17*, 2568. (b) Touchard, D.; Le Bozec, H.; Dixneuf, P. H.; Carty, A. J.; Taylor, N. J. *Ibid.* **1981**, *20*, 1811.
(6) **3**: mp 101–102 °C; IR (Nujol) 1962, 1892 cm^{-1}; mass spectrum, m/e 355.990 (calcd for M^+ ($C_{10}H_{22}O_2P_2S_2Fe$), 355.989). Anal. Found: C, 34.14; H, 6.19; P, 17.33; S, 17.63. Calcd for $C_{10}H_{22}O_2P_2S_2Fe$: C, 33.72; H, 6.22; P, 17.39; S, 18.00.
(7) **4**: mp 81–82 °C; IR (Nujol) 1955, 1887 cm^{-1}; mass spectrum, m/e 310.002 (calcd for M^+, 310.001). Anal. Found: C, 34.93; H, 6.64; S, 10.18. Calcd for $C_9H_{20}O_2P_2SFe$: C, 34.85; H, 6.50; S, 10.33. ^1H NMR (60 MHz) δ (C_6D_6) 2.82 (t, CH_2S, J_{PH} = 5.2 Hz).
(8) Collins, T. J.; Roper, W. R.; Town, K. G. *J. Organomet. Chem.* **1976**, *121*, C41.
(9) Additional NMR data for **3**: ^1H NMR (60 MHz) 4.67 (d, CH, $^3J_{PH}$ = 7.0 Hz), 2.47 (s, SMe), 1.24 (d), and 0.90 (d, PMe_3, $^2J_{PH}$ = 8.2 Hz); ^{13}C NMR (20.115 MHz) δ (C_6D_6) 218.4 (t, CO, $^2J_{PC}$ = 28.0 Hz), 215.9 (t, CO, $^2J_{PC}$ = 28.7 Hz), 24.5 (s, SMe); ^{31}P NMR (32.38 MHz) δ (C_6D_6) 20.98 and 8.18 ($^2J_{PP}$ = 185.5 Hz).
(10) **5**: mp 172–174 °C. Anal. Found: C, 38.51; H, 5.64; S, 13.09. Calcd for $C_{16}H_{28}O_6P_2S_2Fe$: C, 38.57; H, 5.66; S, 12.87. Mass spectrum, m/e 478 (M^+), 450.018 (calcd for (M − CO)$^+$, 450.020).

0276-7333/84/2303-0640$01.50/0