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# $\eta^2$-Alkoxythiocarbonyl and Chelating $Ph_2PCH{=}C(R)S$-Ligands *via* Intramolecular Coupling of Co-ordinated $CS_2$ and $Ph_2PC{\equiv}CR$; *X*-Ray Crystal Structure of $Fe(CO)[P(OMe)_3]$-$[Ph_2PCH{=}C(Bu^t)S][CS(OMe)]$

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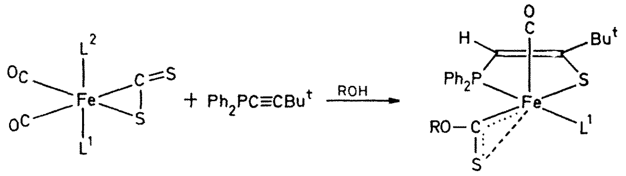
*Summary* Reaction of $\eta^2$-$CS_2$ complexes, $Fe(CS_2)(CO)_2(L^1)(L^2)$ with a phosphino-alkyne $Ph_2PC{\equiv}CBu^t$ in alcohols, generates, *via* intramolecular coupling and $CS_2$ fragmentation, novel derivatives containing $\eta^2$-alkoxythiocarbonyl and chelating $Ph_2PCH{=}C(Bu^t)S$-ligands; $Fe(CO)[P(OMe)_3][Ph_2PCH{=}C(Bu^t)S][CS(OMe)]$ has been characterised by *X*-ray diffraction.

In $\eta^2$-$CS_2$ complexes[1] the unco-ordinated sulphur atom has nucleophilic character and is susceptible to attack by electrophiles.[2,3] Thus, electrophilic, activated alkynes react readily with $\eta^2$-$CS_2$ iron complexes.[4] Since the unco-ordinated acetylene in phosphorus bound phosphinoalkyne complexes[5] is subject to easy nucleophilic addition, we have attempted to use these reactivity patterns to cause intramolecular coupling of $CS_2$ and $Ph_2PC{\equiv}CR$ ligands held proximate in a zerovalent iron complex. We here describe the synthesis of complexes of the type (**1**) and the characterisation of $Fe(CO)[P(OMe)_3][Ph_2PCH{=}C(Bu^t)S][CS(OMe)]$ (**1a**), suggesting that this approach may be used for the elaboration of co-ordinated $CS_2$, a topic of considerable current interest, and the synthesis of anionic 1-phosphino-2-sulphido alkene ligands. To our knowledge the intramolecular trapping of both fragments derived from a single $\eta^2$-$CS_2$ molecule in a mononuclear complex is unprecedented although very recently trinuclear osmium[6] and cobalt[7] clusters containing derived fragments have been described.



(**2**) $L^1{=}L^2{=}P(OMe)_3$
(**3**) $L^1{=}PMe_2Ph$, $L^2{=}PPh_3$

(**1**)
**a**, $L^1{=}P(OMe)_3$; $R{=}Me$
**b**, $L^1{=}PMe_2Ph$; $R{=}Me$
**c**, $L^1{=}PMe_2Ph$; $R = Et$

Scheme 1.

Reaction of $Fe(CO)_2[P(OMe)_3]_2(CS_2)$ (**2**) (0·5 g) with $Ph_2PC{\equiv}CBu^t$ (0·3 g) in methanol (12 ml), followed by thick layer chromatography on silica gel (eluant hexane:ether 9:1) afforded a red product (**1a**) which was recrystallized from hexane {120 mg; 16%; m.p. 121 °C; i.r. Nujol ν(CO) 1935 cm$^{-1}$; mass spectrum, *m/e* 582 ($M^+$), 554 $(M - CO)^+$, 430 $[M - CO - P(OMe)_3]^+$; $^1H$ n.m.r. ($CDCl_3$), δ 1·57 (s, $Bu^t$), 3·83 [d, $P(OMe)_3$, $^3J_{P-H}$ 11 Hz], 4·33 (s, OMe), and 6·20 (dd, P–CH=, $^2J_{P-H}$ 9·5 Hz, $^4J_{P-H}$ 2·6 Hz); $^{31}P$ n.m.r.†

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† All $^{31}P$ n.m.r. spectra are with reference to external $H_3PO_4$.

(CDCl$_3$) δ 160·4 [P(OMe)$_3$] and 78·6 p.p.m. (PPh$_2$–C=, $^2J_{PP}$ 262 Hz)}. A comparable reaction sequence starting with (**3**), which has been shown to lead to the easy, selective replacement of the PPh$_3$ ligand,[1] afforded higher yields of a similar product (**1b**) in methanol or (**1c**) in ethanol (Scheme 1). Compound (**1b**) [68%; m.p. 125 °C; i.r. Nujol ν(CO) 1905 cm$^{-1}$; $^1$H n.m.r. (CDCl$_3$), δ 1·53 (s, Bu$^t$), 3·70 (s, OMe), 1·87 and 1·73 (d, PMe$_2$, $^2J_{P-H}$ 9·5 Hz), and 6·04 (d, P–CH=, $^2J_{P-H}$ 10 Hz); $^{31}$P n.m.r.† (CDCl$_3$), δ 78·9 (Ph$_2$P–C) and 26·7 p.p.m. (PMe$_2$Ph, $^2J_{P-P}$ 176 Hz)]; (**1c**) [57%; m.p. 155 °C; i.r. Nujol ν(CO) 1912 cm$^{-1}$; $^1$H n.m.r. (CDCl$_3$) δ 1·57 (s, Bu$^t$), 4·10 (m, OCH$_2$), 1·07 (t, CH$_2$*CH$_3$*, $^3J_{H-H}$ 8 Hz), 1·90 and 1·80 (d, PMe$_2$, $^2J_{P-H}$ 9·5 Hz), 6·20 (d, P–CH=, $^2J_{P-H}$ 10 Hz)].‡

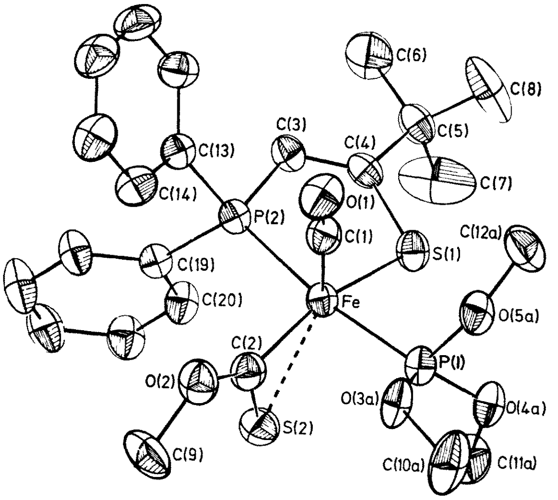
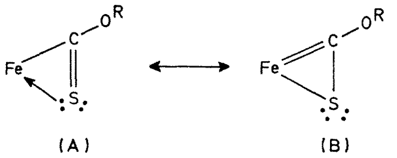
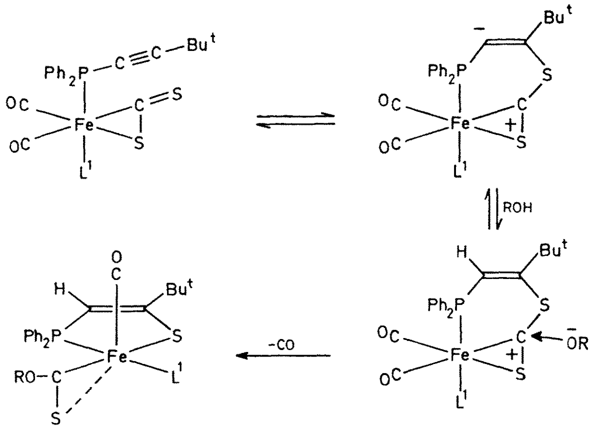


FIGURE. ORTEP plot of (**1a**).

Single crystals of Fe(CO)[P(OMe)$_3$][Ph$_2$PCH=C(Bu$^t$)S]-[CSOMe] (**1a**) are triclinic, space group $P\bar{1}$, with $a$ = 11·115(1), $b$ = 11·347(1), $c$ = 12·882(1) Å, $\alpha$ = 97·80(1), $\beta$ = 64·90(1), $\gamma$ = 83·97(1)°; $Z$ = 2, $D_m$ = 1·34 g cm$^{-3}$, $F$(000) = 608, $\mu$ = 8·22 cm$^{-1}$. The structure was solved and refined using 2647 observed [$I \geqslant 3\sigma(I)$] intensities measured on a Syntex $P2_1$ diffractometer with Mo-$K_\alpha$ radiation. Full matrix least squares refinement gave $R$ and $R_w$ values of 0·042 and 0·051.§ An ORTEP plot (Figure) illustrates that reaction of the co-ordinated phosphino-alkyne and CS$_2$ ligands has resulted in cleavage of the CS$_2$ group, with formation of a rigid chelating 1-diphenylphosphino-2-sulphido-3,3-dimethylbutene ligand which occupies two basal sites of a distorted square pyramidal molecule. The remaining co-ordination sites around the iron atom are occupied by an axial carbonyl group, a trimethyl phosphite ligand *trans* to the phosphorus atom P(2) of the chelating ligand, and a novel alkoxythiocarbonyl ligand derived from a CS fragment of the original CS$_2$ group and a methoxide ion of the solvent methanol. The short Fe–C(2) bond length [1·800(6) Å], the acute Fe-C(2)–S(2) angle [92·9(0)°], and the Fe–S(2) distance [2·512(2) Å] strongly suggest that the –C(=S)OMe ligand is behaving as a 3-electron donor with a major contribution to bonding from the carbene-like canonical form B rather than from the canonical form A.



Bonding of this type is rare although an analogy might be drawn with the bridging Me$_2$NCS ligand in Fe$_4$(CO)$_{12}$(S)(Me$_2$-NC)(Me$_2$NCS),[8] where, however, the Fe–C(carbene) bond length [Fe(4)–C(13) 2·023 Å] is much longer than in the present case.



SCHEME 2.

Formation of (**1**), which depends on the ease of the substitution of ligand L by the phosphino-acetylene, can be adequately rationalised in terms of the chemistry of co-ordinated phosphinoalkynes and $\eta^2$-CS$_2$ (Scheme 2). Nucleophilic attack by sulphur at the $\beta$-carbon of the alkyne and proton transfer to the $\alpha$-carbon has a close analogy in the addition of secondary phosphines to co-ordinated phosphino-alkynes yielding olefinic diphosphines.[9] Subsequent nucleophilic displacement by RO$^-$ at the electrophilic carbon atom generates Ph$_2$PCH=C(Bu$^t$)S– and –C(=S)OR ligands. Further efforts to exploit intramolecular coupling for the elaboration of $\eta^2$-CS$_2$ are in

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‡ Satisfactory analytical data were obtained for (**1b**) and (**1c**).

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

progress Finally we note that the potentially useful, formally anionic, rigid chelating ligands $R_2PCH{=}C(R)S^-$ have not yet found extensive application in co-ordination chemistry presumably owing to the difficulty of their synthesis

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