Journal of Organometallic Chemistry, 135 (1977) C29—C32
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Preliminary communication

CARBON DISULPHIDE IRON CARBONYL COMPLEXES: X-RAY CRYSTAL STRUCTURE OF $Fe(\eta^2\text{-}CS_2)(CO)_2(PMe_3)(PPh_3)$

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(Received April 22nd, 1977)

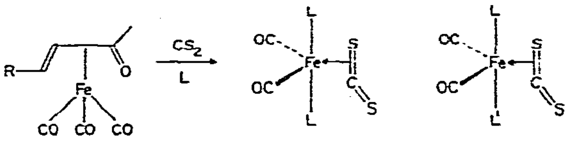
Summary

A series of η^2-CS_2 iron carbonyl complexes $Fe(CS_2)(CO)_2LL'$, where L and L' are tertiary phosphines or phosphites, have been synthesised from $Fe(CO)_3$-(α-enone) derivatives or via displacement of PPh_3 from $Fe(CS_2)(CO)_2(PPh_3)_2$; an X-ray study of $Fe(CS_2)(CO)_2(PMe_3)(PPh_3)$ has revealed a η^2-CS_2 molecule coordinated in the equatorial plane of a trigonal bipyramid.

Despite the utility of π-CS_2 complexes as precursors for thiocarbonyl compounds [1], relatively few CS_2 derivatives of the first row transition metals have been characterised [2]. Recently it was shown that nucleophilic phosphines and phosphites add readily to $Fe(CO)_3$ (α-enone) complexes I forming stable adducts by displacement of the ketonic carbonyl only [3]. We now report that these heterodiene complexes I provide a convenient source of π-CS_2 iron carbonyl derivatives, for which an important synthetic role can be anticipated.

The readily accessible benzylidene acetone iron tricarbonyl [4] of type I reacted readily with carbon disulphide, but no stable derivative could be isolated. Addition of tertiary phosphites to the solution resulted in complete displacement of the heterodiene and formation of CS_2 complexes IIa, b. Spectroscopic data for IIa, b were consistent with the presence of two carbonyl groups and a mutual *trans* disposition of the phosphorus ligands. For example, IIa exhibited a parent ion in the mass spectrum (M^+ 435.929; calcd. 435.927) and a virtually coupled $P-CH_3$ resonance in the ^1H NMR spectrum.

The reaction is effective with phosphines and phosphites which do not form zwitterionic adducts $R_3\overset{+}{P}-\overset{-}{C}S_2$. Thus the triphenylphosphine complex IIc, which has also been prepared by another route [2], was obtained in 90% yield. Alkylphosphines (PBu_3, PMe_2Ph, PMe_3) which react with CS_2 gave low yields of



I

II a, L=P(OMe)$_3$
II b, L=P(OEt)$_3$
II c, L=PPh$_3$
II d, L=PBu$_3$
II e, L=PMe$_2$Ph
II f, L=PMe$_3$

III L=PPh$_3$
L'=PMe$_3$

IV L=PPh$_3$
L'=PMe$_2$Ph

SCHEME 1

complexes IId—f via the $Fe(CO)_3$ (α-enone) method. However, complexes IId—f can be prepared in 70—90% yields by replacement of triphenylphosphine in IIc with an excess of alkylphosphine. ^1H NMR data indicate retention of the *trans* configuration for the phosphines on substitution. Unsymmetrical bis(phosphine) complexes III (74%) and IV (55%) were isolated by selective replacement of one triphenylphosphine ligand of IIc by trimethylphosphine or dimethylphenylphosphine. The infrared $\nu(CO)$ spectra of complexes III and IV are similar to those of derivatives IIa—f, with two strong absorptions appearing at ~2000 cm^{-1} and 1950 cm^{-1}. All of these compounds exhibit $\nu(C{=}S)$ bands near 1150 cm^{-1}. The ^{31}P FT NMR spectrum of III (δ, ppm downfield from H_3PO_4) —54.87 (PPh_3), —21.67 (PMe_3); $^2J(PP)$ 161 Hz) shows a large value of $^2J(PP)$, typical [5] of *trans* phosphines.

To establish the η^2-bonding of CS_2 in these compounds and to provide the first accurate structural data for a first row transition metal CS_2 derivative an X-ray analysis of III was carried out. From CH_2Cl_2, $Fe(CS_2)(CO)_2(PMe_3)(PPh_3)$ crystallises in the acentric monoclinic space group *Pc* with $a = 9.309(4)$, $b = 13.640(12)$, $c = 11.390(5)$ Å, $\beta = 120.43(5)°$; $Z = 2$; $\rho_c = 1.402$, $\rho_m = 1.39$ g cm^{-3}. $F(000) = 544$; $\mu(Mo\text{-}K_\alpha) = 9.28$ cm^{-1}. The intensities of 2202 reflections ($2\theta < 50°$) were measured on a Datex automated GE-XRD6 diffractometer using Mo-K_α radiation ($\lambda = 0.7107$ Å) and a θ—2θ scan. Of these reflections, 1881 were counted as observed and used in the solution and refinement. Standard heavy atom and full matrix least squares refinement methods were used. All non-hydrogen atoms were refined anisotropically. Current R and R_w values are 0.036 and 0.042. An ORTEP II plot of the structure is shown in Fig. 1. The best stereochemical description of the molecule is in terms of a trigonal bipyramid with the mid-point of the C(3)—S(1) bond of the η^2-CS_2 molecule defining one equatorial position of the polyhedron. The remaining coordination positions are occupied by *cis* CO groups C(1)—O(1) and C(2)—O(2) and *trans* phosphorus atoms P(1) and P(2). The atoms C(1), C(2), Fe, C(3), S(1) and S(2) are almost coplanar with deviations of —0.074, 0.104, —0.048, 0.011, —0.074, 0.082 Å respectively from the best plane. Within the η^2-CS_2 molecule the C(3)—S(1) distance (1.671(9) Å) can be compared with the corresponding but less accurate value of 1.72(5) Å in $Pt(CS_2)(PPh_3)_2$ [6], the incompletely refined value of 1.66 Å in $[Ru(CS_2Me)(CO)_2(PPh_3)_2]^+$ [7] and the C—S bond length of 1.554 Å in free CS_2 [8]. The "free" C(3)—S(2)

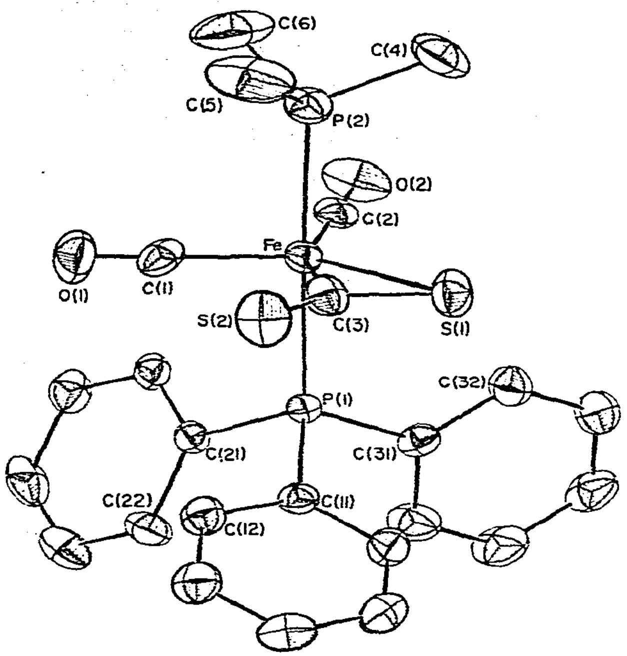


Fig. 1. A perspective view of the molecular structure of $Fe(CS_2)(CO)_2(PMe_3)(PPh_3)$ showing the atomic numbering.

bond in III (1.623(10) Å) is also considerably longer than in the uncoordinated molecule. This result serves to emphasise the nucleophilic character of the uncoordinated sulphur atom in these η^2-CS_2 complexes, a feature of obvious relevance to their chemistry. The structure of III also bears a strong resemblance to that of $Fe_2(CO)_6(Ph_2PC{\equiv}CPh)_2$ [9] in which the alkyne triple bond is coordinated in the trigonal plane and a phosphorus atom axially to a trigonally bipyramidal iron atom. Finally, the Fe—P(1) (2.279(2) Å) and Fe—P(2) (2.256(2) Å) bond lengths are significantly different, with the shorter bond to the stronger σ-donor, less bulky ligand.

The availability of these η^2-CS_2 complexes opens up a route to low valent thiocarbonyl complexes of iron as well as organometallic complexes via electrophilic additions to the CS_2 ligand. Preliminary experiments indicate an extensive chemistry for these η^2-CS_2 complexes, which will be described in future publications.

Acknowledgement

H.L.B. thanks the French D.G.R.S.T. for the award of a studentship and A.J.C. is grateful to the National Research Council of Canada for financial support of this work.

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