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Preliminary communication

$[Fe(CO)_2\{P(OPh)_3\}_2(CS)]$. THE FIRST STABLE THIOCARBONYL DERIVATIVE OF IRON(0) PENTACARBONYL

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Summary

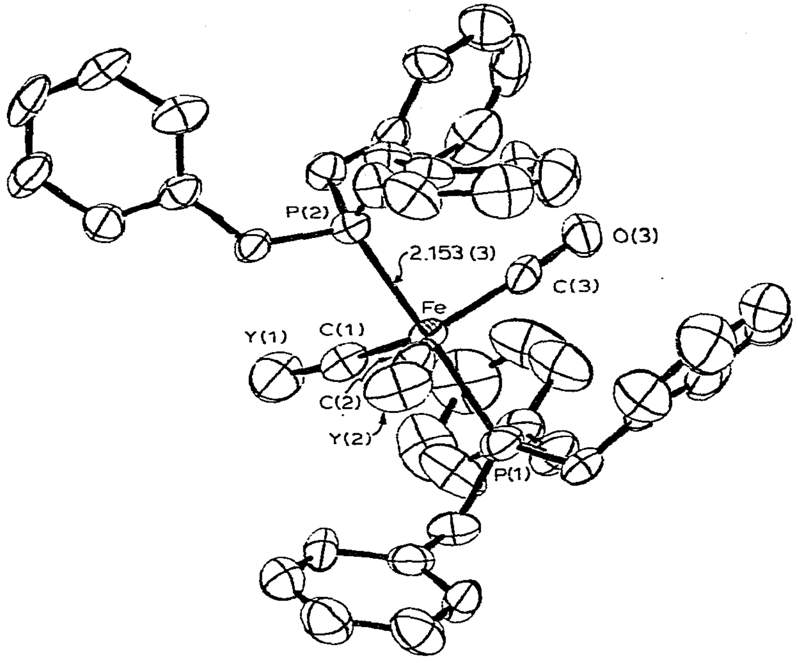
In some circumstances, $P\text{-}nBu_3$ pr $P\text{-}nBu_3/CCl_4$ desulphurises $[Fe(CO)_2\{P(OPh)_3\}_2(CS_2)]$ to give $[Fe(CO)_2\{P(OPh)_3\}_2(CS)]$ which has trigonal bipyramidal coordination about the iron atom with the phosphite ligands in axial positions.

Although the desulphurisation of η^2-CS_2 complexes of the transition metals is often straight-forward [1], the conversion of the readily accessible $[Fe(CO)_2(PR_3)_2(CS_2)]$ [2] to $[Fe(CO)_2(PR_3)_2(CS)]$ has proved to be difficult. An alternative route to compounds of this type, the reaction of $[Fe(CO)_4]^{2-}$ with Cl_2CS has been used by Petz to prepare a very unstable compound which was thought to be $[Fe(CO)_4(CS)]$ [3].

The normal reaction of $[Fe(CO)_2\{P(OPh)_3\}_2(CS_2)]$ with $P\text{-}nBu_3$ in benzene or chloroform solution is the replacement of one and then both phosphite ligands by the phosphine [4]. However, we occasionally observed the formation of another product in variable amounts. This proved to be the title compound, $[Fe(CO)_2\{P(OPh)_3\}_2(CS)]$. Attempts to improve the yield of this reaction met with little success, but we have found that a $P\text{-}nBu_3/CCl_4$ reagent consistently gives 10—15% yields of the desired compound.

The yellow complex is the first stable derivative of Fe^0 to have been prepared which contains a thiocarbonyl ligand. Its IR spectrum ($\nu(CO)$ 1983 and 1921 cm^{-1}; $\nu(CS)$ 1222 cm^{-1}) is consistent with the molecular structure as determined by an X-ray diffraction study (Fig.1). This reveals a trigonal bipyramidal coordination about the iron atom with triphenylphosphite ligands occupying axial coordination positions and also with disorder between the equatorial CS ligand and one of the CO groups.

Crystal data: $C_{39}H_{30}O_8P_2SFe$, M = 776.5, Triclinic, a 11.040 (6), b 9.915 (5),



Angles (underlined) in °
Distances in Å
Y = S or O (disorder)

Fe-C(1) = 1.80 (1)
Fe-C(2) = 1.77 (1)
Fe-C(3) = 1.82 (1)
C(1)-Y(1) = 1.42 (1)
C(2)-Y(2) = 1.36 (1)
C(3)-O(3) = 1.16 (1)

P(1)-Fe-P(2)	177.3 (1)
P(1)-Fe-C(1)	91.9 (3)
P(1)-Fe-C(2)	90.4 (3)
P(1)-Fe-C(3)	90.6 (3)
P(2)-Fe-C(1)	85.7 (3)
P(2)-Fe-C(2)	91.7 (3)
P(2)-Fe-C(3)	89.9 (3)
C(1)-Fe-C(2)	118.8 (5)
C(2)-Fe-C(3)	118.8 (5)
C(3)-Fe-C(1)	122.3 (5)
Fe-C(3)-O(3)	176.9 (9)
Fe-C(1)-Y(1)	175.0 (7)
Fe-C(2)-Y(2)	176.5 (8)

Fig. 1. The structure of $[Fe(CO)_2\{P(OPh)_3\}_2(CS)]$.

c 17.247 (10) Å, α 92.4 (1), β 98.0 (1), γ 100.0 (1)°, *U* 1836.7 Å^3, D_M 1.38 g cm^{-3} (by flotation), $Z = 2$, D_C 1.403 g cm^{-3}, $F(000) = 800$, μ(Mo—K_α) 6.2 cm^{-1}; space group = $P1$ or $P\bar{1}$, solved and refined in $P\bar{1}$ to $R = 0.068$, $R' = 0.089$ from 2645 independent non-zero reflexions from precession photographs for layers 0−3*kl*, *h*0−3*l* and (110)0−4.

A remarkable feature of the desulphurisation using P-nBu$_3$ is that it was carried out in the presence of a large excess of this ligand. Under such circumstances the starting complex is usually converted entirely to $[Fe(CO)_2(P\text{-}nBu_3)_2(CS_2)]$ [4] but the only thiocarbonyl product detected, and in yields of up to 60% on one unrepeatable occasion, was $[Fe(CO)_2\{P(OPh)_3\}_2(CS)]$. Furthermore, we have not been able to convert $[Fe(CO)_2(PR_3)_2(CS_2)]$ (R = alkyl or phenyl) to their corresponding thiocarbonyls.

We have suggested previously that the bonding between a η^2-CS$_2$ ligand and Fe in the $[Fe(CO)_2(PR_3)_2(CS_2)]$ derivatives results in a considerable amount of metal to carbon disulphide electron transfer which is enhanced by an electron-rich metal centre resulting from the use of more basic PR$_3$ ligands [4]. Perhaps a corollary of this is that with the less basic ligands [PR$_3$ = P(OPh)$_3$ as opposed to P-nBu$_3$], the conversion of η^2-CS$_2$ to CS takes place more readily. This effect has also been observed in the conversion of various [Cr(η^6-Arene)(CO)$_2$(CS$_2$)] to [Cr(η^6-Arene)(CO)$_2$(CS)] [5].

Studies of the chemistry of [Fe(CO)$_2${P(OPh)$_3$}$_2$(CS)] have been limited by our inability to find a consistent mode of preparation. However, we have found that halogens will convert it to air-stable salts such as [Fe(CO)$_2${P(OPh)$_3$}$_2$(CS)(I)]$^+$[I$_3$]$^-$. Complexes of this type are intermediates in the oxidation of [Fe(CO)$_5$] to [Fe(CO)$_4$X$_2$], but the [Fe(CO)$_5$X]X salts are not stable at room temperature (X = halogen) [6].

References

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