Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

A MIXED MERCAPTIDE HALIDE COMPLEX OF IRON: $Fe_2(CO)_5(S\text{-iso-}Pr)_3I$

K. FARMERY AND M. KILNER
Chemistry Department, The University of Durham, Durham City (Great Britain)

(Received February 5th, 1969)

SUMMARY

Mass spectral evidence is presented for the complex $Fe_2(CO)_5(S\text{-iso-}Pr)_3I$, which is assigned a structure having terminal iodine and bridging mercaptide groups.

INTRODUCTION

Attempts to prepare mixed mercaptide halide derivatives of the metal carbonyls have been made by various workers, but none have been characterised. Complete elimination of carbon monoxide occurs when the mercaptide complexes $[Fe(CO)_3SR]_2$ (R = Ph, Et) are treated with hydrogen chloride or with iodine in pyridine solution[1], but with iodine and bromine in dichloromethane, brown and orange solids were obtained[2]. The materials are carbonyl-, halide- and mercaptide-containing complexes which could not be identified. More recently, unidentified complexes were obtained from the reactions of $Fe(CO)_4I_2$ with organotin thiolates $(R_3Sn{-}SR')$[3].

RESULTS AND DISCUSSION

As part of a study of the reactions of the iron carbonyl halides with mercaptans we have worked on the reactions of $Fe(CO)_4I_2$ with isopropyl mercaptan and thiophenol. Rigorous exclusion of air was necessary at all stages and the reactions were performed in the presence of magnesium carbonate to remove any hydrogen iodide formed. Evolution of carbon dioxide, observed for each reaction, indicated substitution of $-I$ by $-SR$. Using iso-PrSH, a red solid was obtained in low yield (15%) which was separated from the small amounts of $[Fe(CO)_3S\text{-iso-}Pr]_2$ by recrystallisation from hexane at −78°, and identified by mass spectrometry as $Fe_2(CO)_5(S\text{-iso-}Pr)_3I$.

The complex decomposes over several hours in the solid state at room temperature and much more rapidly in solution even in the dark. When exposed to daylight or air total decomposition occurs in a few minutes, producing free iodine and a residue containing S-iso-Pr groups. Attempted sublimation causes extensive decomposition at 70° but a little of the complex does sublime.

The complex had to be recrystallised several times before a mass spectrum was obtained free from $[Fe(CO)_3\ S\text{-iso-}Pr]_2$. The parent ion at *m/e* 604 and the break-

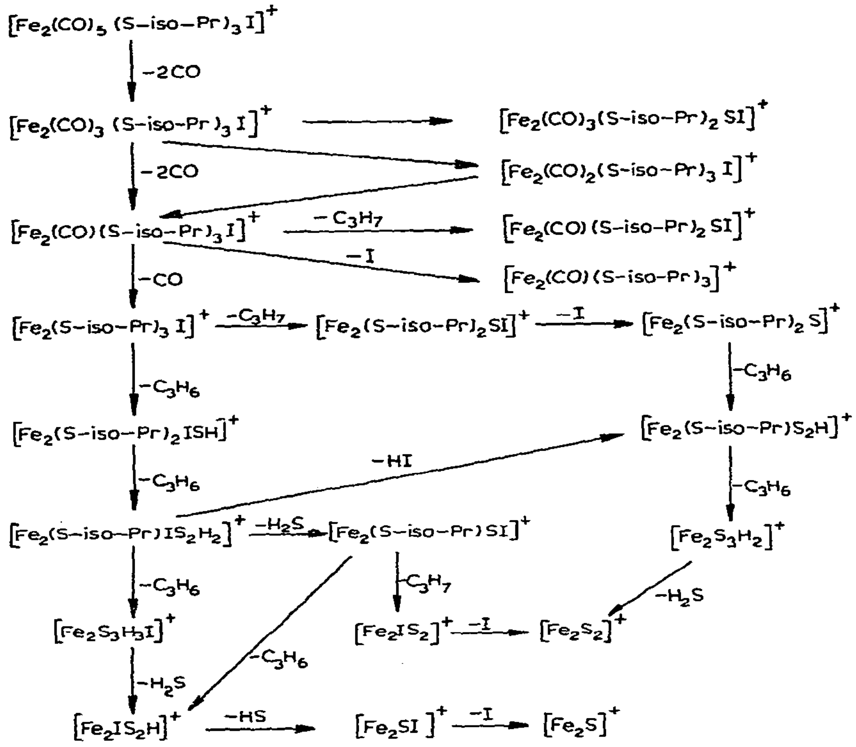
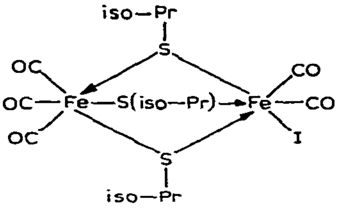


Fig. 1. Breakdown scheme for $[Fe_2(CO)_5(S\text{-iso-Pr})_3I]^+$ (metastable transitions are indicated by insertion of the neutral fragment against the arrow).

down pattern (Fig. 1) correspond to the formulation $Fe_2(CO)_5(S\text{-iso-Pr})_3I$. A notable feature of the spectrum is the loss of the isopropyl radical as well as carbon monoxide from the ions $[Fe_2(CO)_3(S\text{-iso-Pr})_3I]^+$ and $[Fe_2(CO)(S\text{-iso-Pr})_3I]^+$. In general fragmentation of ions obtained from metal carbonyl complexes occurs by successive loss of the carbonyl groups[4], but several similar instances are known of daughter ions (usually of low intensity) formed by an alternative breakdown involving loss of peripheral groups. $Et_3GeMo(CO)_3(\pi\text{-}C_5H_5)$, for example, fragments in part by loss of ethyl radicals[5], and for $(Me_2N)_3PM(CO)_5$ ($M = Cr$, Mo), weak ions produced by elimination of Me_2N fragments have been observed[6]. The absence of an ion corresponding to $(P\text{–}CO)^+$ is not unusual and many carbonyl complexes, especially when they contain organic groups tend to lose two CO groups simultaneously[4,6]. The isopropyl groups fragment by loss of propene, a process which has been observed for both main group metal and transition metal compounds[4,5]. Dinuclear ions persist throughout the fragmentation processes (Fig. 1), mononuclear ions being completely absent.

In the study of the manganese and rhenium carbonyl halides, $M(CO)_5X$ and $M_2(CO)_8X_2$, an appreciable difference was observed between the ease of elimination of terminal and bridging ligands[7]. Loss of halogen and carbonyl are comparable for the mononuclear species although MX^+ ions are of considerable abundance, but in the halogen bridged dimers, the M_2X_2 units persist unfragmented until all the CO groups are lost. Since in $Fe_2(CO)_5(S\text{-iso-Pr})_3I$ iodine is lost early in the fragmentation process (Fig. 1), iodine is possibly terminally bound to a metal and the sulphur groups, because of their strong attachment to the iron atoms, are possibly bridging between the two metals. The complex is assigned structure (I) which satisfies the inert gas rule for each iron atom, and is consistent with the known bridging tendencies of the mercaptide[8] and iodide groups. The iodide group has a low bridging tendency as illustrated by $Fe_2(CO)_8I_2$ (ref. 9), in which the $Fe(CO)_4I$ units are held together solely by a Fe–Fe bond, whereas for mercaptide groups the tendency is for bridges to form *i.e.* $Fe_2(CO)_6(SEt)_2$ (ref. 10).



(I)

For a complex with this structure four strong and one weak carbonyl absorptions in the stretching region of the IR spectrum are expected. In cyclohexane solution the four strong bands are observed (Table 1) but no weak absorption could be detected. Two of the strong bands are unresolved in chloroform solution and again no weak absorption could be assigned to a carbonyl stretching frequency. Additional shoulders occur in the solid state spectrum due possibly to the arrangement of the carbonyl complexes in the unit cell of the crystal. Attempts to measure molecular weights by osmometry and cryoscopy were unsuccessful because of the instability of the complex in solution and low solubility in solvents. ^1H NMR spectra were also unsatisfactory for the same reasons, but two unresolved peaks (τ 6.8–7.0 and 8.6–8.7) were observed in the positions and relative intensities expected for isopropyl groups.

TABLE 1

C–O STRETCHING FREQUENCIES FOR $Fe_2(CO)_5(S\text{-iso-Pr})_3I$

Form	ν(C–O) (cm^{-1})						
Nujol mull	2088 s	2082 (sh)	2045 (sh)	2037 s	2025 s	2010 vw	1993 s
$CHCl_3$ soln.	2085 s			2032 s (br)			1998 m
C_6H_{12} soln.	2081 s			2035 s	2028 s		2000 s

Thermal instability at room temperature precluded the identification of the material by elemental analysis because of the time involved in handling the material at room temperature in a glove box. During the process the complex was shown to lose carbon monoxide. Indeed the data for CO content after the samples had been handled in the glove box indicates that on average, from one to two CO groups are lost from the complex, and in addition, data for carbon, hydrogen and iron content correspond to the formulation $Fe_2(CO)_{3-4}(S\text{-iso-Pr})_3I$.

Neutral ligands such as phosphines and arsines normally stabilise metal carbonyl systems[11], and an attempt to stabilise $Fe_2(CO)_5(S\text{-iso-Pr})_3I$ with triphenylarsine in cyclohexane at room temperature led to complete loss of carbon monoxide. The progress of the reaction was followed by recording the IR spectrum at intervals as the arsine was added, but only the steady disappearance of the absorptions due to the initial complex was observed. The carbonyl groups appeared to be too labile for the complex to be made thermally stable at room temperature.

Thiophenol reacts with $Fe(CO)_4I_2$ in the presence of magnesium carbonate in ether solution but not in chloroform. The products, which contain iodine, carbon monoxide and the mercaptide group, vary depending on the stoichiometries of the reactants and the molar quantity of magnesium carbonate used. The products are all unstable in light, and at room temperature, and it was not possible to separate, purify and handle the materials for identification although many attempts were made. Attempts to produce more thermally stable complexes by substituting chelating ligands for carbonyl groups again led to a complete loss of carbon monoxide. With 2,2′-bipyridine, for example, one reaction product was $[FeBipy_3]I_2$. The use of derivatives of $Fe(CO)_4I_2$, such as a diphosphine derivative, as the starting material, were again unsuccessful.

Thus the reactions of mercaptans with $Fe(CO)_4I_2$ lead to thermally unstable, air reactive and light sensitive complexes which can be detected in solution by IR spectroscopy, but which in the main eluded identification. An isopropyl mercaptide complex which appears to be marginally more thermally stable than others detected, was characterised because it was sufficiently thermally stable to allow the mass spectrum to be measured at low source temperatures.

EXPERIMENTAL

$Fe(CO)_4I_2$, obtained from $Fe(CO)_5$ and I_2 in ether, was recrystallised from chloroform/hexane mixtures, magnesium carbonate dried at 120° and isopropyl mercaptan vacuum distilled before use. Solvents were dried over sodium.

The reactions were performed as far as possible in the dark or subdued light, and oxygen was rigorously excluded at all times. Mass spectra were obtained using an A.E.I. MS9 spectrometer at 70 eV with a source temperature at insertion of 80°, and IR spectra obtained using a Grubb–Parsons Spectromaster.

Reaction of $Fe(CO)_4I_2$ with isopropyl mercaptan

A double Schlenk tube containing in one arm, $Fe(CO)_4I_2$ (10 g, 24 mmoles), magnesium carbonate (10 g) and diethyl ether (50 ml) was degassed and isopropyl mercaptan (7 ml) condensed onto the reaction mixture *in vacuo* at $-196°$. After warming to room temperature gas evolution occurred and the solution darkened in colour from red-brown to black. The solvent was removed *in vacuo* after ~3 h and pumped until the small amount of free iodine had sublimed out. Solvent extraction of the residue with hexane (3 × 50 ml) and cooling the solution to $-78°$ yielded a red solid which contained about 10% $Fe_2(CO)_6(SR)_2$. Further recrystallisations from hexane solutions at $-78°$ gave the pure red product $Fe_2(CO)_5(S\text{-iso-Pr})_3I$. Yield 1.1 g(15%). (Found: C, 26.6, 27.0; H, 3.77, 3.83; CO, 17.4, 16.1; Fe, 19.9, 20.1. $Fe_2(CO)_5(S\text{-iso-Pr})_3I$ calcd.: C, 27.8; H, 3.48; CO, 23.2; Fe, 18.6. $Fe_2(CO)_4(S\text{-iso-Pr})_3I$ calcd.: C, 27.1; H, 3.65; CO, 19.4; Fe, 19.5. $Fe_2(CO)_3(S\text{-iso-Pr})_3I$ calcd.: C, 26.2; H, 3.83; CO, 15.3; Fe, 20.4%.)

ACKNOWLEDGEMENTS

The authors wish to thank the S.R.C. for a studentship (to K.F.) and Mond International for their generous gift of iron carbonyl.

REFERENCES

1 W. Hieber and P. Spacu, *Z. Anorg. Allg. Chem.*, 233 (1937) 353.
2 R. B. King and M. B. Bisnette, *Inorg. Chem.*, 4 (1965) 1663.
3 E. W. Abel, B. C. Crosse and T. J. Leedham, unpublished work quoted in ref. 8.
4 D. B. Chambers, F. Glockling and J. R. C. Light, *Quart. Rev. (London)*, 22 (1968) 317 and references therein.
5 A. Carrick and F. Glockling, *J. Chem. Soc., A*, (1968) 913.
6 R. B. King, *J. Amer. Chem. Soc.*, 90 (1968) 1412.
7 B. F. G. Johnson, R. D. Johnston, J. Lewis and B. H. Robinson, *J. Organometal. Chem.*, 10 (1967) 105.
8 E. W. Abel and B. C. Crosse, *Organometal. Chem. Rev.*, 2 (1967) 443.
9 F. A. Cotton, T. G. Dunne, B. F. G. Johnson and J. S. Wood, *Proc. Chem. Soc.*, (1964) 175.
10 L. F. Dahl and C.-H. Wei, *Inorg. Chem.*, 2 (1963) 328.
11 T. A. Manuel, *Advan. in Organometal. Chem.*, Academic Press, London, Vol. 3, p. 181.