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# PREPARATION AND SPECTRAL INVESTIGATIONS OF DERIVATIVES OF $Fe_3S_2(CO)_9$ FORMED BY REPLACEMENT OF CARBONYL GROUPS

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## Summary

Some derivatives of enneacarbonyldithiotriiron have been prepared by replacing one, two or three carbonyls by triphenylphosphine or nitrogen-containing ligands. The infrared spectra of the new compounds in the carbonyl region are described and discussed in terms of the $\pi$-acceptor properties of the respective ligands. The mass spectra of the triphenylphosphine and acetonitrile derivatives support the concept of unusually strong bonding in the $Fe_3S_2$ grouping

## Introduction

A novel method for the preparation of enneacarbonyldithiotriiron was recently reported [1], and removes the difficulty [2] of obtaining this compound in a pure state. The structure of the compound has been shown, by X-ray diffraction studies [3], to have the iron and sulfur atoms arranged in a distorted tetragonal pyramid with an unusual heptacoordinated iron atom at the apex. In the reaction between $Fe_3X_2(CO)_9$ ($X = S, Se$) and some phosphine and arsine type ligands [4] it was found that only one carbonyl could be replaced at moderate temperatures and low ligand concentrations. Even at higher temperatures and greater ligand concentrations only two carbonyls could be replaced. Similarly, in the binuclear complexes $Fe_2X_2(CO)_6$ ($X = S, Se$), only one or, under more drastic conditions, two carbonyls could be replaced by other ligands [5].

In view of the above results it was of interest to find out whether more basic ligands would replace more than one or two carbonyls. An additional aim was to evaluate the influence, if any, of the substituent ligands on the structure of the $Fe_3S_2$ core. We describe below the investigations of the reactions

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TABLE 1

EXPERIMENTAL DETAILS

| Compound | Reactant (g, mmol) | Solvent | Conditions | | Crystallization solvent | Yield (g, %) |
|---|---|---|---|---|---|---|
| | | | time (h) | temp (°C) | (temp)(°C) | |
| $Fe_3S_2(CO)_8[P(C_6H_5)_3]$ | $P(C_6H_5)_3$, (0.108, 0.41) | pentane/dichloromethane, 9/1 | 7 | 75-78 | pentane | 0.18, 60.6 |
| $Fe_3S_2(CO)_7[P(C_6H_5)_3]_2$ | $P(C_6H_5)_3$, (0.215, 0.82) | pentane/dichloromethane 9/1 | 11 | 75-78 | pentane | 0.22, 55.8 |
| $Fe_3S_2(CO)_7(C_{12}H_8N_2)$ | $C_{12}H_8N_2$, (0.074 g 0.41) | pentane/dichloromethane 9/1 | 4 | 53-55 | pentane/dichloromethane, 1/1 | 0.18, 71.6 |
| $Fe_3S_2(CO)_7(C_{10}H_8N_2)$ | $C_{10}H_8N_2$, (0.064, 0.41) | cyclohexane/dichloromethane, 1/1 | 8 | 68 | cyclohexane/dichloromethane, 1/1 (−80) | 0.16, 65.9 |
| $Fe_3S_2(CO)_8(CH_3CN)$ | $CH_3CN$, (8.0, 195.2) | cyclohexane/dichloromethane 1/1 | 5 | 60-62 | petrol. ether 30-50° | 0.18, 87.6 |
| $Fe_3S_2(CO)_7[N(C_2H_5)_3]_2$ | $N(C_2H_5)_3$, (4.5, 44.47) | cyclohexane/dichloromethane 1/1 | 1.5 | 43-45 | pentane/dichloromethane, 1/1 | 0.12, 46.1 |
| $Fe_3S_2(CO)_6(C_5H_5N)_3$ | $C_5H_5N$, (5.0, 63.21) | cyclohexane/dichloromethane 1/1 | 4 | 80-82 | pentane | 0.16, 60.7 |
| $Fe_3S_2(CO)_6(C_5H_{10}N)_3$ | $C_5H_{10}N$, (4.0, 46.97) | cyclohexane/dichloromethane 1/1 | 6 | 75-78 | petrol. ether 30-50° | 0.14, 51.7 |

of enneacarbonyldithiotriiron with triphenylphosphine and some nitrogen-containing ligands. The results mostly confirm the earlier [4] findings, but some complexes of formula $Fe_3S_2(CO)_6L_3$ were prepared.

## Experimental

All operations were carried out under oxygen-free nitrogen or pure argon. The materials used were of high purity, and the solvents were dried and distilled before use. Enneacarbonyldithiotriiron was prepared as previously described [1]. Infrared spectra were recorded in carbon tetrachloride solutions on a Perkin—Elmer Model 125 Grating Spectrophotometer. Mass spectrometric measurements were carried out on a CH-5 Varian MAT Mass Spectrometer at 70 eV with an emission current of 100 A and an HTE 150° inlet system.

### *Preparation of derivatives*

The derivatives were prepared by refluxing a mixture of 0.2 g (0.41 mmol) $Fe_3S_2(CO)_9$ and the respective ligand in 20 ml of solvent at a carefully controlled temperature. The course of the reaction was monitored by noting any colour changes or by removing small samples by syringe at appropriate times and recording the IR spectra. Changes in the CO absorption bands or the appearance of characteristic bands of the coordinated ligands provided indications of the progress of the reaction. The experimental conditions, the solvent used for crystallization and the yields, are shown in Table 1. The analytical data appear in Table 2.

TABLE 2

ANALYTICAL DATA FOR THE DERIVATIVES

| Compound | Colour | Analysis found (calcd.) (%) | | | | |
|---|---|---|---|---|---|---|
| | | C | H | N | S | Fe |
| $Fe_3S_2(CO)_6(C_5H_5N)_3$ | Brown | 39.51<br>(39.59) | 2.32<br>(2.38) | 6.58<br>(6.60) | 10.12<br>(10.07) | 26.32<br>(26.31) |
| $Fe_3S_2(CO)_6(C_5H_{10}N)_3$ | Brown | 38.43<br>(38.50) | 4.58<br>(4.63) | 6.35<br>(6.41) | 9.88<br>(9.79) | 25.63<br>(25.59) |
| $Fe_3S_2(CO)_7[N(C_2H_5)_3]_2$ | Reddish brown | 36.19<br>(36.22) | 4.87<br>(4.81) | 4.53<br>(4.45) | 10.21<br>(10.18) | 26.50<br>(26.60) |
| $Fe_3S_2(CO)_8(CH_3CN)$ | Red | 24.21<br>(24.17) | 0.68<br>(0.61) | 2.88<br>(2.82) | 13.11<br>(12.91) | 33.72<br>(33.74) |
| $Fe_3S_2(CO)_7(C_{12}H_8N_2)$ | Red | 37.61<br>(37.54) | 1.38<br>(1.33) | 4.57<br>(4.61) | 10.61<br>(10.54) | (27.57) |
| $Fe_3S_2(CO)_7(C_{10}H_8N_2)$ | Red | 34.92<br>(34.96) | 1.41<br>(1.38) | 4.83<br>(4.80) | 10.95<br>(10.98) | 28.74<br>(28.70) |
| $Fe_3S_2(CO)_8[P(C_6H_5)_3]$ | Red-brown | 43.53<br>(43.39) | 2.18<br>(2.11) | | 9.02<br>(8.93) | 23.38<br>(23.34) |
| $Fe_3S_2(CO)_7[P(C_6H_5)_3]_2$ | Red-brown | 54.31<br>(54.22) | 3.22<br>(3.18) | | 6.92<br>(6.73) | 17.82<br>(17.61) |

## Results and discussion

Only in the cases of pyridine and piperidine was it possible to replace three carbonyls of enneacarbonyldithiotriiron. The other ligands, namely triphenylphosphine and the nitrogen-containing compounds, acetonitrile, triethylamine, *ortho*-phenanthroline and $\alpha,\alpha'$-dipyridyl, behaved like the phosphine and arsine type ligands previously studied [4], i.e. they replaced only one or two carbonyls. All attempts to prepare more highly substituted derivatives were unsuccessful and led to the decomposition of the initial iron complex.

The new substituted derivatives are not very stable towards air or moisture. The $\alpha,\alpha'$-dipyridyl and *ortho*-phenanthroline derivatives are exceptions, possibly due to a chelating effect. Except for the pyridine and piperidine derivatives all the products are fairly soluble in common organic solvents.

It has been shown [6] that aliphatic amines have no ability to accept $d_\pi$ electrons except by a hyperconjugation mechanism, which is rather ineffective. In contrast, heterocyclic amines, like pyridine or dipyridyl, are capable of accepting $d_\pi$ electrons from a metal [6], while acetonitrile has a small, but definite ability to accept $\pi$ electrons in competition with carbonyl groups [7]. However, pyridine is also able to act as a simple donor in metal complexes, in contrast to carbonyls, in which the CO—metal bond must be synergic [6]. It follows that pyridine and piperidine are able to displace three carbonyls, because they can compete effectively for the available $d_\pi$ electrons with the CO groups. This is also true to some extent for the triphenylphosphine [8] ligand, which can form both mono- and di-substituted derivatives. The bidentate ligands, *ortho*-phenanthroline and dipyridyl form complexes of the type $Fe_3S_2(CO)_7L$.

The CO stretching frequencies of the derivatives and of the parent compound are listed in Table 3. Features of the CO stretching frequencies confirm the suggestions above concerning the nature of the metal—ligand bonding. Since the nitrogen atoms have little or practically no acceptor ability, they impart a slightly negative charge to the metal atom, which in turn increases its back-donation to the carbonyl groups. This leads to the observed

TABLE 3

INFRARED SPECTRA

| Compound | $\nu$CO region (in $CCl_4$) ($cm^{-1}$) |
|---|---|
| $Fe_3S_2(CO)_9$ | 2086 w, 2067 vs, 2051 vs, 2032 s, 2014 m |
| $Fe_3S_2(CO)_8[P(C_6H_5)_3]$ | 2063 vs, 2044 vs, 2023 s, 2001 w, 1981 vw |
| $Fe_3S_2(CO)_7[P(C_6H_5)_3]_2$ | 2060 vs, 2040 vs, 2021 s, 1998 w, 1982 vw |
| $Fe_3S_2(CO)_8(NCCH_3)$ | 2062 vs, 2042 vs, 2021 s, 2004 m, 1982 w(br) |
| $Fe_3S_2(CO)_7[N(C_2H_5)_3]_2$ | 2061 vs, 2040 vs, 2022 s, 1998 m(sh), 1985 w(br) |
| $Fe_3S_2(CO)_7(N_2H_8C_{12})$ | 2061 vs, 2043 vs, 2022 s, 2005 m, 1995 w, 1984 w(br) |
| $Fe_3S_2(CO)_7(N_2H_8C_{10})$ | 2062 vs, 2042 vs, 2021 s, 2004 m, 1995 w, 1985 vw |
| $Fe_3S_2(CO)_6(NC_5H_5)_3$ | 2058 s, 2040 vs, 2020 s, 2002 m(sh), 1995 w, 1979 vw |
| $Fe_3S_2(CO)_6(NC_5H_{10})_3$ | 2059 s, 2041 vs, 2022 s, 2001 m, 1982 w(br) |

lowering of the C—O stretching frequencies in all nitrogen derivatives. A decrease in the carbonyl frequencies is observed for the triphenylphosphine complexes also, but to a smaller degree. This can be attributed to $\pi$-character in the metal—ligand bond, the *3d* orbitals of the phosphorus serving as acceptor orbitals. The same phenomenon has been observed in carbonyl complexes of other metals with triphenyl-phosphine, -arsine and -stibine ligands [8].

From the available evidence it is difficult to state with certainty, whether the carbonyl substitution takes place at the seven-coordinated apical iron atom or one of the two basal iron atoms. Moreover, there is no evidence that the carbonyls of only one iron atom are replaced. However, since no more than three carbonyl groups can be replaced, and some of them by bidentate ligands, it can be assumed that all the replacements take place at one iron atom. The bridging sulfur atoms have a larger electron withdrawing influence on the apical, seven-coordinated, iron atom and hence there is some reason for believing that this particular iron atom is the one involved in the substitution reactions.

Mass spectrometric studies have been carried out for enneacarbonyldithiotriiron [1] and two of the monosubstituted derivatives, $Fe_3S_2(CO)_8[P(C_6H_5)_3]$ and $Fe_3S_2(CO)_8(CH_3CN)$. The fragmentation patterns show that the substituted ligands are split off before the loss of all the carbonyls, but in all the three compounds the $Fe_3S_2$ core appears with maximum intensity. These results confirm the view [1] that stability is imparted to the iron cluster by the bridging sulfur atoms.

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