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# Synthesis and spectroscopic characterisation of compounds with formula $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\{\text{Fe}(\text{CO})_4\}]$ and $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}_2\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]$ ( $n = 3, 4$ and $6$ )

Rosamund Hourihane <sup>a,\*</sup>, Geraldine Gray <sup>a</sup>, Trevor Spalding <sup>b</sup>, Tony Deeney <sup>c</sup>

<sup>a</sup> Chemistry Department, Cork Institute of Technology, Rossa Avenue, Bishopstown, Cork, Ireland

<sup>b</sup> Chemistry Department, University College Cork, College Road, Cork, Ireland

<sup>c</sup> Physics Department, University College Cork, College Road, Cork, Ireland

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## Abstract

The work described herein concerns the synthesis and characterisation of compounds with formula  $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\{\text{Fe}(\text{CO})_4\}]$  and  $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}_2\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]$  ( $n = 3, 4, 6$ ). The iron bis-phosphine cluster compounds with formula  $[\{\text{Fe}_3(\text{CO})_{11}\}_2\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]$  and  $[\{\text{Fe}_3(\text{CO})_{11}\}\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\{\text{Fe}(\text{CO})_4\}]$  ( $n = 3, 4, 6$ ) were reacted with stoichiometric amounts of cyclohexene episulfide  $[\text{SC}_6\text{H}_{10}]$  in toluene at  $70^\circ\text{C}$  for 30–60 min. Optimum yields of 42.1–78.2%, were obtained for  $\{\text{Fe}_2\text{S}_2\text{--Fe}\}$  type species when a 1:4 cluster–ligand mole ratio was used, while the  $\{\text{Fe}_2\text{S}_2\}_2$  type species were prepared in yields of 30–38% when a 1:8 cluster–ligand mole ratio was used. The volume of reaction solvent was kept to a minimum. For the latter cluster compounds, three isomeric products were isolated from each reaction; a justification for their presence is offered. All of these reactions afford clusters with fewer iron atoms but with S atoms incorporated. In these reactions the  $\text{Fe}_3$ -unit is ‘degraded’ but at the same time the cluster is expanded from three atoms  $\{\text{Fe}_3\}$  to four  $\{\text{Fe}_2\text{S}_2\}$ . © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Iron; Diphosphine; Sulfur; Bridging ligand; Mössbauer; Isomer

## 1. Introduction

Iron and sulfur have an affinity for one another [1]. Quite often complexes are formed by the reactions between metal carbonyls, or their derivatives, and elemental sulfur [2]. However, iron also shows a tendency to abstract sulfur atoms from a wide variety of compounds including episulfides [3], disulfanes [4], or more usually thiocyanate ion [5]. The cluster size can be expanded [6–8] or expanded and degraded simultaneously [9,10] with the incorporation of sulfur into the cluster unit. The cluster compounds discussed here follow the trends described, however they also contain phosphine ligands.

The results will be discussed in two sections as follows, (i) compounds with formula  $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}\text{Ph}_2\text{P}$

$(\text{CH}_2)_n\text{PPh}_2\{\text{Fe}(\text{CO})_4\}]$   $n = 3$  (1),  $n = 4$  (2) and  $n = 6$  (3), obtained from the reaction of the  $\{\text{Fe}_3\text{--Fe}\}$ , clusters with cyclohexene episulfide and (ii) compounds with formula  $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}_2\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]$   $n = 3$  (4–6),  $n = 4$  (7–9) and  $n = 6$  (10–12) formed from the reaction of the  $\{\text{Fe}_3\text{--Fe}_3\}$  double clusters with cyclohexene episulfide. The products were characterised using IR and Mössbauer spectroscopies as well as C, H, Fe, S analysis.

## 2. Experimental

### 2.1. General

All reactions were carried out under an inert atmosphere. Subsequent work was carried out in air. All purified products were stored in the refrigerator, or under vacuum. Tetrahydrofuran (THF) was freshly dis-

\* Corresponding author. Fax: +353-21-345-191.

E-mail address: rhourihane@cit.ie (R. Hourihane).

titled from potassium diphenylketyl. Toluene was freshly distilled from sodium diphenylketyl. Hexane and dichloromethane were dried over  $P_2O_5$  and distilled prior to use. All other solvents were reagent grade and used as received. Bisphosphine ligands and cyclohexene episulfide were commercial products obtained from Aldrich. Iron cluster compounds  $[\{Fe_3(CO)_{11}\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$  and  $[\{Fe_3(CO)_{11}\}_2Ph_2P(CH_2)_nPPh_2]$   $n = 3–6$ , were prepared as described in the literature [11].

IR spectra were recorded on Perkin–Elmer 682 or Mattson Polaris FTIR 10410, spectrophotometers. Solution spectra were obtained in sodium chloride cells. Relative intensities were designated as vs, very strong; s, strong; m, medium; w, weak; vw, very weak; other descriptions were sh, shoulder; shp, sharp; br, broad.

Mössbauer spectra of the iron-containing compounds were recorded at liquid-nitrogen temperatures (80 K) using a commercial constant acceleration drive unit and transducer (Harwell Instruments) in conjunction with a Canberra System 40 multichannel analyser as previously described [12]. The source was  $^{57}Co$  in Rh and was of 20 mCi nominal strength. Data was processed on a Vax 11/780 computer and all data were referred to the spectrum of sodium nitroprusside as standard. When sufficient quantities of material were available,

samples were prepared for Mössbauer experiments, by wrapping (0.05–0.1 g) of the compound in paper, which was then wrapped in adhesive tape, forming a pouch and placed in the gamma ray beam. For small samples ( $< 0.03$  g) the material was dissolved in the least amount of dichloromethane needed to transfer the compound to the prepared pouch. The solvent was allowed to evaporate, before the sample was frozen in liquid nitrogen. Recording times varied between 24 h and 4 days.

All C and H analyses were carried out on a PE 240 analyser. Sulfur content was determined by the oxygen flask method. Iron content was determined by atomic absorption spectroscopy using a Pye Unicam SP 191 atomic absorption spectrophotometer.

## 2.2. Standard reaction procedure for the reaction between compounds $[\{Fe_3(CO)_{11}\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$ , and $[\{Fe_3(CO)_{11}\}_2Ph_2P(CH_2)_nPPh_2]$ ( $n = 3–6$ ) with cyclohexene episulfide

Each of the title compounds was reacted with a stoichiometric amount of cyclohexene episulfide in toluene under an inert atmosphere at 65–70°C for 30–60 min. Specific reaction details are outlined in Tables 1 and 2. The extent of the reaction was moni-

Table 1  
Reaction of  $[\{Fe_3(CO)_{11}\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$  (A) with cyclohexene episulfide (B) <sup>a</sup>

| <i>n</i> | Reagent A, g (mmol) | Reagent B volume, ml (mmol) | Solvent volume (ml) | Time (min) | Product formula                                         | g (% yield)  |
|----------|---------------------|-----------------------------|---------------------|------------|---------------------------------------------------------|--------------|
| 6        | 0.29 (0.263)        | 0.11 (0.98)                 | 75                  | 60         | $[\{Fe_2S_2(CO)_5\}Ph_2P(CH_2)_6PPh_2\{Fe(CO)_4\}]$ (3) | 0.193 (78.2) |
| 4        | 0.115 (0.11)        | 0.049 (0.43)                | 20                  | 30         | $[\{Fe_2S_2(CO)_5\}PPh_2(CH_2)_4PPh_2\{Fe(CO)_4\}]$ (2) | 0.06 (60.3)  |
| 3        | 0.088 (0.082)       | 0.037 (0.3)                 | 20                  | 30         | $[\{Fe_2S_2(CO)_5\}Ph_2P(CH_2)_3PPh_2\{Fe(CO)_4\}]$ (1) | 0.031 (42.1) |

<sup>a</sup> Mole ratio, 1:4 A–B; reaction temperature, 70°C; reaction solvent, toluene.

Table 2  
Reaction of  $[\{Fe_3(CO)_{11}\}_2Ph_2P(CH_2)_nPPh_2]$  (A) with cyclohexene episulfide (B) <sup>a</sup>

| <i>n</i> | Reagent A, g (mmol) | Reagent B volume, ml (mmol) | Solvent volume (ml) | Time (min) | Product formula                                | g (% yield)  |
|----------|---------------------|-----------------------------|---------------------|------------|------------------------------------------------|--------------|
| 6        | 0.10 (0.071)        | 0.064 (0.57)                | 75                  | 50         | $[\{Fe_2S_2(CO)_5\}_2Ph_2P(CH_2)_6PPh_2]$ (10) | 0.026 (32.7) |
|          |                     |                             |                     |            | $[\{Fe_2S_2(CO)_5\}_2Ph_2P(CH_2)_6PPh_2]$ (11) | 0.025 (31.7) |
|          |                     |                             |                     |            | $[\{Fe_2S_2(CO)_5\}_2Ph_2P(CH_2)_6PPh_2]$ (12) | 0.029 (37.4) |
| 4        | 0.069 (0.05)        | 0.045 (0.40)                | 20                  | 30         | $[\{Fe_2S_2(CO)_5\}_2Ph_2P(CH_2)_4PPh_2]$ (7)  | 0.017 (32.5) |
|          |                     |                             |                     |            | $[\{Fe_2S_2(CO)_5\}_2Ph_2P(CH_2)_4PPh_2]$ (8)  | 0.016 (29.3) |
|          |                     |                             |                     |            | $[\{Fe_2S_2(CO)_5\}_2Ph_2P(CH_2)_4PPh_2]$ (9)  | 0.006 (11.2) |
| 3        | 0.133 (0.097)       | 0.088 (0.77)                | 20                  | 30         | $[\{Fe_2S_2(CO)_5\}_2Ph_2P(CH_2)_3PPh_2]$ (4)  | 0.034 (33.2) |
|          |                     |                             |                     |            | $[\{Fe_2S_2(CO)_5\}_2Ph_2P(CH_2)_3PPh_2]$ (5)  | 0.03 (29.1)  |
|          |                     |                             |                     |            | $[\{Fe_2S_2(CO)_5\}_2Ph_2P(CH_2)_3PPh_2]$ (6)  | 0.016 (15.5) |

<sup>a</sup> Mole ratio 1:8 A–B; reaction temperature, 70°C; reaction solvent, toluene.

tored by thin-layer chromatography using silica gel 60 as the stationary phase and dichloromethane–hexane as eluant. The reaction mixture was filtered and the toluene removed under reduced pressure. The residue was dissolved in dichloromethane and chromatographed using preparative thin-layer chromatography, with silica gel (PF<sub>254</sub>) on glass plates and a mixture of 3:2 dichloromethane–hexane as eluant.

### 2.2.1. Reaction of $[\{Fe_3(CO)_{11}\}_2Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$ ( $n = 3–6$ ) with cyclohexene episulfide

The solvent was removed under reduced pressure yielding a red–brown residue. Chromatographic separation afforded one main product (red–brown) and trace amounts of others. Only the main product was extracted into dichloromethane. The dichloromethane was removed under reduced pressure and the residue was redissolved in hexane. The volume of hexane was reduced to 10 ml and stored for 2–3 days at 0°C. A microcrystalline red–brown solid was recovered and was characterised by IR and Mössbauer spectroscopies, as well as chemical analyses (Table 3, Section 3), as  $[\{Fe_2S_2(CO)_5\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$  ( $n = 3–6$ ).

### 2.2.2. Reaction of $[\{Fe_3(CO)_{11}\}_2Ph_2P(CH_2)_nPPh_2]$ ( $n = 3–6$ ) with cyclohexene episulfide

The solvent was removed under reduced pressure yielding a red–brown residue. Chromatographic separation afforded three red–brown products. These were extracted into dichloromethane. The solvent was removed under reduced pressure and the residues were redissolved in hexane. The volume of hexane was reduced to 5 ml in each case and was stored for up to 2 weeks at 0°C. Microcrystalline red–brown solids were recovered for all three compounds, which were characterised by IR and Mössbauer spectroscopies, two of the three compounds in each case were further characterised by chemical analyses (Table 4, Section 3), as  $[\{Fe_2S_2(CO)_5\}_2Ph_2P(CH_2)_nPPh_2]$  ( $n = 3–6$ ).

## 3. Results and discussion

### 3.1. Compounds with formula $[\{Fe_2S_2(CO)_5\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$ ( $n = 3$ (**1**), $n = 4$ (**2**), $n = 6$ (**3**))

#### 3.1.1. Syntheses

Compounds **1**, **2** and **3** were the only products isolated from the reaction between the appropriate dark green compound  $[\{Fe_3(CO)_{11}\}_2Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$  ( $n = 3, 4, 6$ ), and stoichiometric amounts of cyclohexene episulfide in toluene at 70°C for 30–60 min (Scheme 1). Optimum yields of **1**, 42.1%, **2**, 60.3% and **3**, 78.2%, were obtained when a 1:4 cluster–ligand mole ratio was used and the volume of reaction solvent kept to a minimum. In all cases the products were separated

by preparative thin-layer chromatography. The C, H, and Fe analyses were consistent with the proposed  $[\{Fe_2S_2(CO)_5\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$  formulation. Further support for the proposed structures comes from the IR and Mössbauer spectra of the products (Table 3).

#### 3.1.2. Spectroscopic characterisation

**3.1.2.1. IR spectra.** A summary of the energies of band maxima of the IR absorptions in the carbonyl region for compounds **1–3** is given in Table 3, together with related data for  $[Fe_2S_2(CO)_6]$  [13],  $[\{Fe(CO)_4\}_2PhP(CH_2)_nPPh_2]$   $n = 3, 4$  [14],  $n = 6$  [15], and  $[Fe_2CoS_2(CO)_6(\eta^5-C_5H_5)]$  [16]. From Table 3 it can be seen that the absorptions in the spectra of compounds **1–3** are a ‘combination’ of those due to two distinguishable units, i.e.  $[Fe(CO)_4]$  and  $[Fe_2(CO)_5]$ . However, as both units have overlapping CO absorption band maxima, unambiguous assignment of particular absorptions to a specific individual unit is difficult.

For example, considering compound **3** ( $n = 6$ ), the carbonyl absorptions occur at 2060 m, shp, 2040 shp, 2020 m, shp, 2005 m, shp, 1990 s, br, 1955w, br and 1920 vs, br  $cm^{-1}$ . The absorptions at 2040, 1990, 1955 and 1920  $cm^{-1}$  may be assigned to the  $[Fe(CO)_4]$  unit. However the absorptions at 2040 and 1990/5  $cm^{-1}$  may also arise from the  $[Fe(CO)_3]$  fragment, Table 3.

The remaining absorptions at 2005, 2020 and 2060  $cm^{-1}$  can be assigned to the  $[Fe_2S_2(CO)_5]$  species which may contain an  $[Fe(CO)_3]$  unit by comparison with values reported by Havlin and Knox for  $[Fe_2S_2(CO)_6]$  [13] and Cowie et al. for  $[Fe_2CoS_2(CO)_6(\eta^5-C_5H_5)]$  [16] (Table 3, see also Table 4). Similar assignments can be made for compounds **1** and **2**.

**3.1.2.2. Mössbauer spectra.** Further support for the  $[\{Fe_2S_2(CO)_5\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$  ( $n = 3, 4, 6$ ) formulation for compounds **1**, **2** and **3** comes from the Mössbauer spectroscopic studies. The values ( $mm\ s^{-1}$ ) of isomer shift ( $\delta$ ) and quadrupole splitting ( $\Delta$ ), together with the line assignment, numbered 1–6 from left to right, are given in Table 3. The Mössbauer spectra of compounds **2** and **3** are illustrated in Fig. 1. The Mössbauer parameters can be assigned to specific units within each compound as follows. Taking as an example compound **3**, the pair of absorptions with  $\Delta = 2.44\ mm\ s^{-1}$ , is assigned to the  $Fe(CO)_4$  unit by comparison with values of  $\Delta = 2.44, 2.58$  and  $2.41\ mm\ s^{-1}$  for equivalent sites in  $[Fe(CO)_4PPh_3]$  [17,18],  $[Fe(CO)_4PMe_2]$  [19] and  $[\{Fe(CO)_4\}_2Ph_2P(CH_2)_6PPh_2]$  [15], respectively. Because of the similarity of the  $\Delta$  values reported here to those in previous compounds, where apical substitution of the  $[Fe(CO)_4]$  unit was

justified, apical substitution is also proposed here. Now considering the  $[\text{Fe}_2\text{S}_2(\text{CO})_5]$  species, it can be seen from Table 2 that it is more difficult to assign Mössbauer parameters as compound **3** gives an unresolved doublet for two possible sites. However, if either compound **1** or **2** is considered, two resolved doublets are discernible (Fig. 1). The assignments ( $\delta$ ) and ( $\Delta$ ) values

for the substituted and unsubstituted sites are made in accordance with literature suggestions for compounds with thiolate ligands [20,21]. The unsubstituted  $\text{Fe}(\text{CO})_3$  site is assigned to the higher  $\Delta$  value while the substituted  $\text{Fe}(\text{CO})_2\text{P}$  site is assigned to the lower  $\Delta$  value. The substituted atom shows a decrease in  $\Delta$  attributable to a decrease in electron back donation of

Table 3

Characteristics of substituted iron carbonyl compounds with  $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\{\text{Fe}(\text{CO})_4\}]$  formulation

| Compound                                                                                                                                                       | Anal. Calc. (Found) |                |                  | IR                                                                                                      | Mössbauer                                                                                 |                       |                  |                          |                  |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------|----------------|------------------|---------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|-----------------------|------------------|--------------------------|------------------|
|                                                                                                                                                                | C                   | H              | Fe               | $\nu_{\text{max}}$ CO (cm <sup>−1</sup> )                                                               | Site                                                                                      | $\chi^{\text{g}}$     | $\delta$         | $\Delta$                 | $\Gamma$         |
| [{Fe <sub>2</sub> S <sub>2</sub> (CO) <sub>5</sub> }Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>6</sub> PPh <sub>2</sub> {Fe(CO) <sub>4</sub> }] (3) <sup>a</sup> | 49.91<br>(50.03)    | 3.44<br>(3.73) | 17.84<br>(17.98) | 2040 m, shp,<br>1955 m, br<br>1920 vs, br<br>2060 m, shp,<br>2020 m, shp,<br>2005 m, shp,<br>1990 s br  | Fe(CO) <sub>4</sub> <sup>t</sup> P<br><br>Fe(CO) <sub>3</sub> S<br>Fe(CO) <sub>2</sub> PS | 1,6<br><br>2,5        | 0.20<br><br>0.32 | 2.44<br><br>0.60         | 0.20<br><br>0.35 |
| [{Fe <sub>2</sub> S <sub>2</sub> (CO) <sub>5</sub> }Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>4</sub> PPh <sub>2</sub> {Fe(CO) <sub>4</sub> }] (2) <sup>a</sup> | 48.82<br>(48.00)    | 3.10<br>(3.07) | 18.41<br>(18.18) | 2040 s, shp,<br>1955 m, br,<br>1920 vs, br<br>2065 m, shp,<br>2020 m, shp<br>2010 m, shp,<br>1995 s, br | Fe(CO) <sub>4</sub> <sup>t</sup> P<br><br>Fe(CO) <sub>3</sub> S<br>Fe(CO) <sub>2</sub> PS | 1,6<br><br>2,5<br>3,4 | 0.20<br><br>0.35 | 2.44<br><br>0.85<br>0.45 | 0.35<br><br>0.60 |
| [{Fe <sub>2</sub> S <sub>2</sub> (CO) <sub>5</sub> }Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> PPh <sub>2</sub> {Fe(CO) <sub>4</sub> }] (1) <sup>a</sup> | 48.04<br>(47.52)    | 2.93<br>(3.22) | 18.68<br>(18.91) | 2040 s, shp,<br>1955 m, br,<br>1920 vs, br<br>2065 m<br>2020 m, shp,<br>1990 s, br                      | Fe(CO) <sub>4</sub> <sup>t</sup> P<br><br>Fe(CO) <sub>3</sub> S<br>Fe(CO) <sub>2</sub> PS | 1,6<br><br>2,5<br>3,4 | 0.19<br><br>0.34 | 2.39<br><br>0.85<br>0.50 | 0.35<br><br>0.60 |
| [{Fe(CO) <sub>4</sub> }Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> <sup>a,c</sup>                                                          |                     |                |                  | 2040 vs, shp,<br>1992 vw, sh,<br>1955, s,<br>1920 vs, br<br>1992 vw, sh,<br>1955, s,<br>1929 vs, br     | Fe(CO) <sub>4</sub> <sup>t</sup> P                                                        |                       | 0.19             | 2.41                     | 0.25             |
| [{Fe(CO) <sub>4</sub> }] <sub>2</sub> Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> PPh <sub>2</sub> ] <sup>a,c</sup>                                       |                     |                |                  | 2040 vs, shp,<br>2010 vw,<br>1955 vw,<br>1960 s,<br>1920 vs br                                          | Fe(CO) <sub>4</sub>                                                                       |                       | 0.19             | 2.46                     |                  |
| [Fe <sub>2</sub> S <sub>2</sub> (CO) <sub>6</sub> ] <sup>b</sup>                                                                                               |                     |                |                  | 2083 s,<br>2042 s,<br>2005 m                                                                            | Fe(CO) <sub>3</sub> S                                                                     |                       | 0.29             | 0.59                     | 0.45             |
| [Fe <sub>2</sub> CoS <sub>2</sub> (CO) <sub>6</sub> (η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )] <sup>d</sup>                                             |                     |                |                  | 2068 s,<br>2042 vs,<br>1993 vs                                                                          | Fe(CO) <sub>3</sub>                                                                       |                       |                  |                          |                  |
| [Fe(CO) <sub>5</sub> ] <sup>e</sup>                                                                                                                            |                     |                |                  |                                                                                                         | Fe(CO) <sub>5</sub> <sup>t</sup>                                                          |                       |                  |                          | 2.60             |
| [Fe(CO) <sub>4</sub> PPh <sub>3</sub> ] <sup>f</sup>                                                                                                           |                     |                |                  |                                                                                                         | Fe(CO) <sub>4</sub> <sup>t</sup> P                                                        |                       | 0.20             | 2.44                     |                  |

<sup>a</sup> IR solvent  $\text{CH}_2\text{Cl}_2$ .

<sup>b</sup> IR solvent  $\text{CCl}_4$ .

<sup>c</sup> Ref. [15].

<sup>d</sup> Ref. [16].

<sup>e</sup> Ref. [17].

<sup>f</sup> Ref. [18].

<sup>g</sup>  $\chi$ , line assignment;  $\delta$ , isomer shift;  $\Delta$ , quadrupole splitting;  $\Gamma$ , peak-width at half-height.

Table 4

Characteristics of substituted iron carbonyl compounds with proposed  $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}_2\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]$  formulation

| Compound                                                                                                 | Anal. Calc. (Found) |                |                  | IR<br>$\nu_{\text{max}}$ CO ( $\text{cm}^{-1}$ )                                                       | Mössbauer                                                                 |                |                  |                  |          |
|----------------------------------------------------------------------------------------------------------|---------------------|----------------|------------------|--------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|----------------|------------------|------------------|----------|
|                                                                                                          | C                   | H              | Fe               |                                                                                                        | Site                                                                      | $\chi^d$       | $\delta$         | $\Delta$         | $\Gamma$ |
| $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}_2\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2]$ ( <b>10</b> ) | 44.23<br>(44.65)    | 2.97<br>(3.47) | 20.55<br>(20.50) | 2063m, shp,<br>2038 w, shp,<br>2020 m, shp,<br>2010 m, shp<br>1990 s, br,<br>1970 sh,<br>1920 w, br    | $\text{Fe}(\text{CO})_3\text{S}$<br><br>$\text{Fe}(\text{CO})_2\text{SP}$ | 1,4<br><br>2,3 | 0.33             | 0.80<br><br>0.48 | 0.45     |
| $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}_2\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2]$ ( <b>11</b> ) | 44.23<br>(43.90)    | 2.97<br>(3.52) | 20.55<br>(20.49) | 2063 s, shp,<br>2040 vw, sh,<br>2020 vw,<br>2010 w,<br>1990 vs, br                                     | $\text{Fe}(\text{CO})_3\text{S}$<br><br>$\text{Fe}(\text{CO})_2\text{SP}$ | 1,4<br><br>2,3 | 0.33             | 0.80<br><br>0.50 | 0.50     |
| $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}_2\text{Ph}_2\text{P}(\text{CH}_2)_2]$ ( <b>12</b> )             |                     |                |                  | 2063 s, shp,<br>2040 m, shp,<br>2025 s, shp,<br>2010 s, shp,<br>1990 vs, br                            | $\text{Fe}(\text{CO})_3\text{S}$<br><br>$\text{Fe}(\text{CO})_2\text{SP}$ | 1,4<br><br>2,3 | 0.33             | 0.88<br><br>0.63 | 0.55     |
| $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}_2\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2]$ ( <b>7</b> )  | 43.13<br>(42.16)    | 2.67<br>(2.60) | 21.09<br>(21.10) | 2070 m, shp,<br>2040 m, shp,<br>2025 m, shp,<br>2010 m, shp,<br>1995 vs, br                            | $\text{Fe}(\text{CO})_3\text{S}$<br><br>$\text{Fe}(\text{CO})_2\text{SP}$ | 1,4<br><br>2,3 | 0.31             | 0.90<br><br>0.68 | 0.60     |
| $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}_2\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2]$ ( <b>8</b> )  | 43.13<br>(44.60)    | 2.67<br>(2.96) | 21.09<br>(21.53) | 2065 s, shp,<br>2040 vw, sh,<br>2020 w, sh<br>2010 m, shp,<br>1995 vs, br                              | $\text{Fe}(\text{CO})_3\text{S}$<br><br>$\text{Fe}(\text{CO})_2\text{SP}$ | 1,4<br><br>2,3 | 0.33             | 0.90<br><br>0.68 | 0.60     |
| $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}_2\text{Ph}_2\text{P}(\text{CH}_2)_2]$ ( <b>9</b> )              |                     |                |                  | 2065 m, shp,<br>2040 m,<br>2025 m,<br>2010 m,<br>1995 vs, br                                           | $\text{Fe}(\text{CO})_3\text{S}$<br><br>$\text{Fe}(\text{CO})_2\text{SP}$ | 1,4<br><br>2,3 | 0.36             | 0.90<br><br>0.58 | 0.60     |
| $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}_2\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2]$ ( <b>4</b> )  | 42.60<br>(43.08)    | 2.59<br>(2.37) | 21.37<br>(21.50) | 2060 m, shp,<br>2040 w, shp,<br>2020 m, shp,<br>2005 m, shp,<br>1990 vs, br,<br>1960 sh,<br>1920 w, br | $\text{Fe}(\text{CO})_3\text{S}$<br><br>$\text{Fe}(\text{CO})_2\text{SP}$ |                | 0.35             | 0.63             | 0.55     |
| $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}_2\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2]$ ( <b>5</b> )  | 42.60<br>(41.70)    | 2.59<br>(2.67) | 21.37<br>(21.55) | 2060 m, shp,<br>2040 vw, sh,<br>2020 vw, sh,<br>2005 m, shp,<br>1995 vs br                             | $\text{Fe}(\text{CO})_3\text{S}$<br><br>$\text{Fe}(\text{CO})_2\text{SP}$ | 1,4<br><br>2,3 | 0.35             | 0.85<br><br>0.45 | 0.68     |
| $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}_2\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2]$ ( <b>6</b> )  |                     |                |                  | 2065 m, shp,<br>2040 w, shp,<br>2020 m, shp,<br>2010 m, shp,<br>1990 s, br                             | $\text{Fe}(\text{CO})_3\text{S}$<br><br>$\text{Fe}(\text{CO})_2\text{SP}$ | 1,4<br><br>2,3 | 0.35<br><br>0.39 | 0.80<br><br>0.44 | 0.60     |
| $[\text{Fe}_2\text{S}_2(\text{CO})_6]$ <sup>a,b</sup>                                                    |                     |                |                  | 2083 s,<br>2042 s,<br>2005 m                                                                           | $\text{Fe}(\text{CO})_3\text{S}$                                          |                | 0.29             | 0.59             | 0.45     |
| $[\text{Fe}_2\text{CoS}_2(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)]$ <sup>a,b,c</sup>                   |                     |                |                  | 2068 s,<br>2042 s,<br>1993 vs                                                                          |                                                                           |                |                  |                  |          |

<sup>a</sup> IR solvent  $\text{CCl}_4$ .<sup>b</sup> Ref. [13].<sup>c</sup> Ref. [16]<sup>d</sup>  $\chi$ , line assignment;  $\delta$ , isomer shift;  $\Delta$ , quadrupole splitting;  $\Gamma$ , peak-width at half-height.

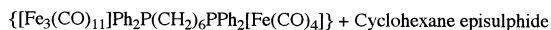
the phosphine ligand compared with a CO ligand [20]. Interestingly, the  $\Delta$  value for the unsubstituted atom ( $0.85 \text{ mm s}^{-1}$ ) shows an increase, which may indicate a slight change in geometry of the CO ligands at this iron atom. de Beer et al. reported similarly for compounds with thiolate ligands [21]. Similar assignments may be made for compound **1**.

The isomer shift values for the  $\text{Fe}(\text{CO})_4\text{P}$  unit are  $0.20 \text{ mm s}^{-1}$  for **3** and **2** and  $0.19 \text{ mm s}^{-1}$  for **1**, which are very close to the value for this site in  $[\text{Fe}(\text{CO})_4\text{PPh}_3]$  [18],  $\delta = 0.20 \text{ mm s}^{-1}$  or in compound  $[\{\text{Fe}(\text{CO})_4\}_2\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2]$  [15]  $\delta = 0.19 \text{ mm s}^{-1}$ . The  $\delta$  value assigned to each iron atom in the 'Fe<sub>2</sub>' unit in each of the three compounds (**1–3**) are 0.34, 0.35 and  $0.32 \text{ mm s}^{-1}$ , respectively. These show a marked increase from that of the unsubstituted system  $\text{Fe}_2\text{S}_2(\text{CO})_6$ ,  $\delta = 0.29 \text{ mm s}^{-1}$ . An increase in isomer shift may be expected with substitution of a CO by a phosphine ligand for the reason discussed above [20].

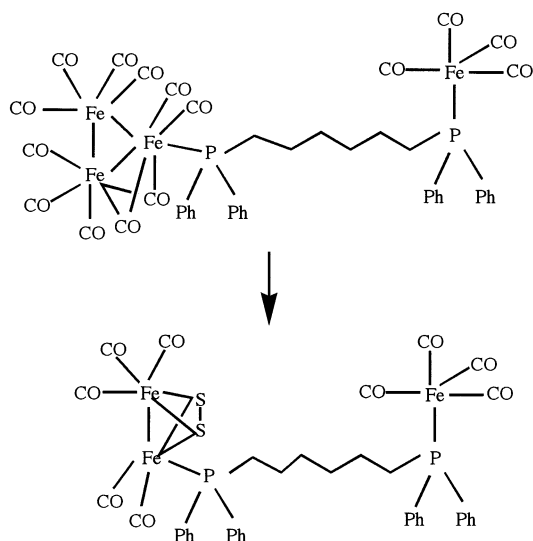
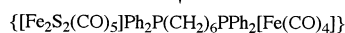
### 3.2. Compounds with formula $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}_2\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]$ $\{n = 3 \text{ (4–6)}, n = 4 \text{ (7–9)}, n = 6 \text{ (10–12)}\}$

#### 3.2.1. Syntheses

The title compounds were isolated from the reaction between the dark green compound  $[\{\text{Fe}_3(\text{CO})_{11}\}_2\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]$  ( $n = 3–6$ ) and stoichiometric amounts of cyclohexene episulfide in toluene at  $70^\circ\text{C}$  for 30–85 min. From each reaction three products were separated



Toluene  $70^\circ\text{C}$ , 30–60 mins.



Scheme 1. Proposed reaction scheme for the formation of compounds with formulae  $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}_2\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2[\text{Fe}(\text{CO})_4]]$ .

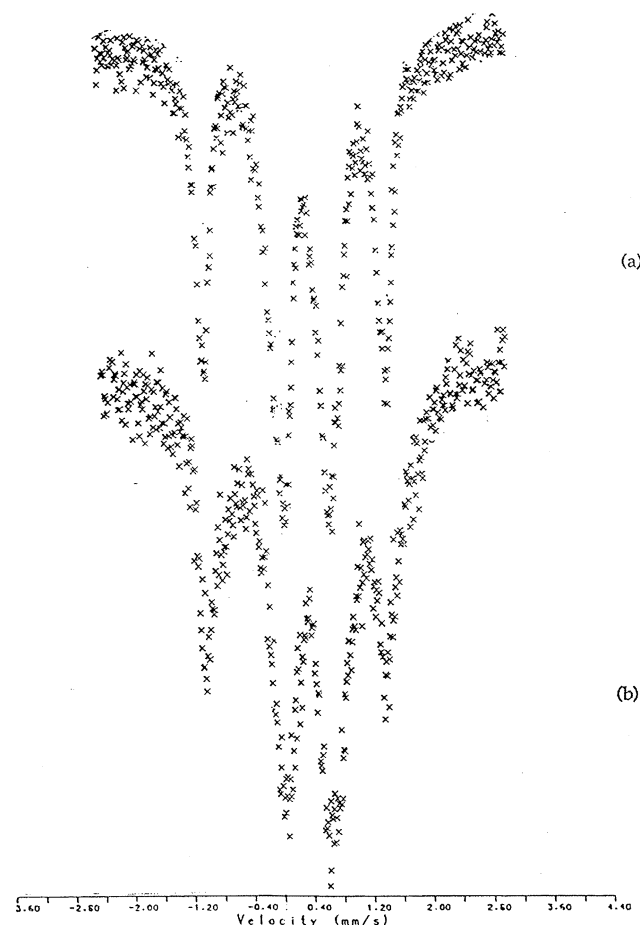


Fig. 1. Mössbauer spectra of compounds with formula  $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}_2\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2[\text{Fe}(\text{CO})_4]]$  (a)  $n = 4$  (**2**) and (b)  $n = 6$  (**3**).

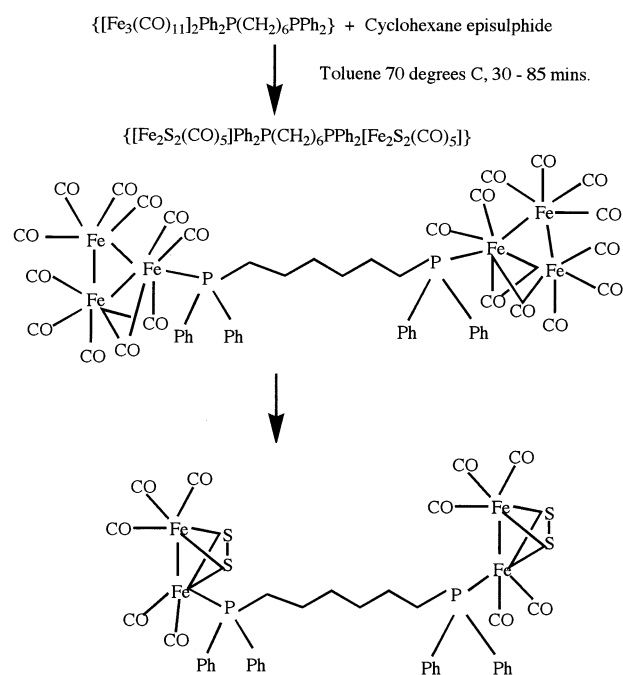
by preparative thin-layer chromatography (Scheme 2, for  $n = 6$ , i.e. compounds **10–12**). Generally optimum yields of 30–38% were obtained when a 1:8 cluster–ligand mole ratio was used but in two cases, compounds **6** and **9**, the isolated yields were 15.5 and 11.2%, respectively. For the six compounds that were obtained sufficiently pure, the C, H, and Fe analyses were consistent with the proposed  $[\{\text{Fe}_2\text{S}_2(\text{CO})_5\}_2\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]$  formulation, Table 4. All nine compounds were characterised by IR and Mössbauer spectroscopies. This data also supported the above formulation.

#### 3.2.2. Spectroscopic characterisation

**3.2.2.1. IR spectra.** A summary of the IR absorptions in the carbonyl region for compounds **4–12** is given in Table 4. From this table it can be seen that the positions of the carbonyl absorptions for each set of three compounds (**4–6**, **7–9** and **10–12**) are very similar. Comparison of these values with those reported in the

literature for compounds with  $[\text{Fe}_2\text{S}_2(\text{CO})_x]$  units shows remarkable similarities. For example, compound **11**,  $n = 6$ , with carbonyl absorptions, 2063 m, shp, 2040 w, shp, 2020 w, 2010 w, 1990 vs, br  $\text{cm}^{-1}$ , and  $[\text{Fe}_2\text{CoS}_2(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)]$  [16] with absorptions 2068, 2042 and 1995  $\text{cm}^{-1}$  are very similar. Other comparable values are provided by  $[\text{Fe}_2\text{PdS}_2(\text{CO})_6(\mu\text{-PPh}_3)_2]$  [22] with carbonyl absorptions 2050, 2008, 1971  $\text{cm}^{-1}$ , or the compounds already discussed (Section 3.2.1, Table 3). However, it is impossible to assign individual absorptions to particular sites.

**3.2.2.2. Mössbauer spectra.** The values ( $\text{mm s}^{-1}$ ) of isomer shift ( $\delta$ ) and quadrupole splitting ( $\Delta$ ) for compounds **4–12** are summarised in Table 4, together with the line assignment numbered 1–4 from left to right. The Mössbauer spectra of compounds **4** and **10** are illustrated in Fig. 2. From the table it can be seen that all  $\text{Fe}(\text{CO})_3\text{S}$  sites of the  $\text{Fe}_2\text{S}_2(\text{CO})_5\text{P}$  unit are assigned a quadrupole splitting value of  $0.85 \pm 0.05 \text{ mm s}^{-1}$ , while the  $\text{Fe}(\text{CO})_2\text{PS}$  sites have  $\Delta = 0.56 \pm 0.12 \text{ mm s}^{-1}$ . The only exception is compound **4**,  $n = 3$ , which gave an unresolved doublet from which both sites were assigned a value of  $\Delta 0.63 \text{ mm s}^{-1}$ . If these values are compared with those in Table 3, it can be seen that there is a remarkable similarity in the quadrupole splitting values for the substituted and unsubstituted iron sites within the  $\text{Fe}_2\text{S}_2(\text{CO})_5\text{L}$  moiety, which endorses the proposed formulation for these compounds.



Scheme 2. Proposed reaction scheme for the formation of compounds with formulae  $\{[\text{Fe}_2\text{S}_2(\text{CO})_5]_2\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}$ .

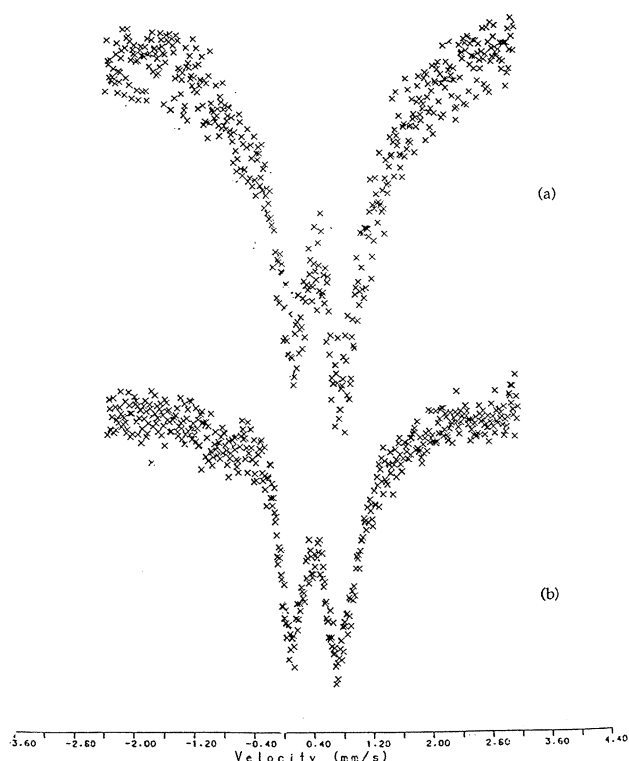


Fig. 2. Mössbauer spectra of compounds with formula  $\{[\text{Fe}_2\text{S}_2(\text{CO})_5]_2\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}$  (a)  $n = 6$  (**10**) and  $n = 3$  (**4**).

The isomer shift value for all sites is  $0.39 \pm 0.05 \text{ mm s}^{-1}$ , which is very similar to that ( $\delta = 0.34 \pm 0.05$ ) for similar species in Table 1.

The peak-width at half-height values  $\Gamma$  increase with decreasing  $n$ ,  $\Gamma = 0.50 \text{ mm s}^{-1}$  ( $n = 6$ ) and  $0.68 \text{ mm s}^{-1}$  ( $n = 3$ ).

#### 4. Presence of isomers

The three compounds formed in each reaction were found to have remarkably similar IR and Mössbauer spectra. For each set of three compounds, it was found that if any single purified material was allowed to stand

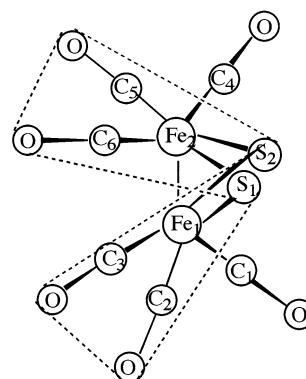


Fig. 3. Geometrical representation of  $[\text{Fe}_2\text{S}_2(\text{CO})_6]$ .

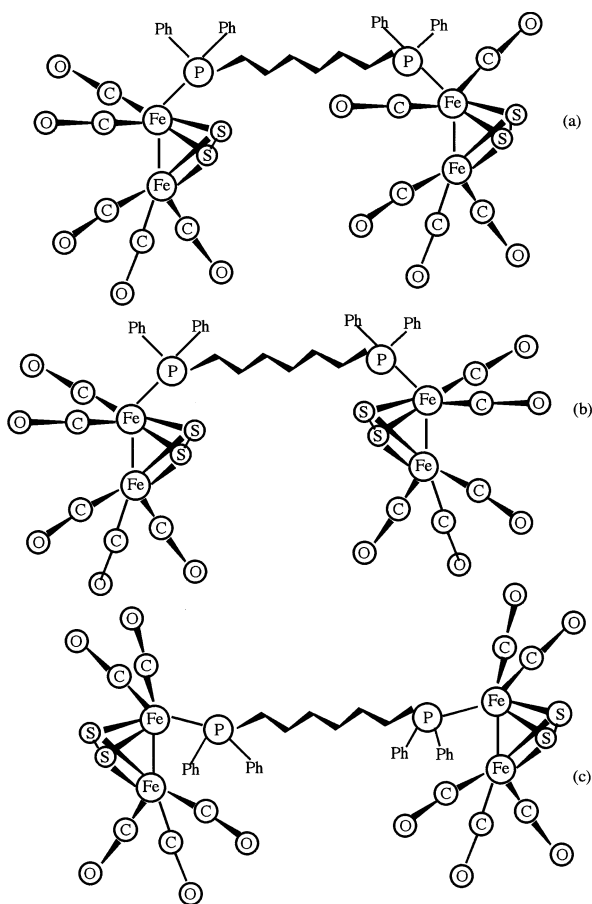


Fig. 4. Possible combinations of two  $[\text{Fe}_2\text{S}_2(\text{CO})_6]$  units; (a) apical to basal, (b) apical to apical and (c) basal to basal.

in dichloromethane solution for 30–60 min, mixtures of all three compounds resulted. This clearly suggested the presence of reactions leading to isomer formation or, possibly, cluster-rearrangement. However, the latter possibility was ruled out by the closely similar spectra of the products and the chemical analyses.

From the examination of the structure of  $[\text{Fe}_2\text{S}_2(\text{CO})_6]$ , a number of possible isomers formed by linking two such clusters through a diphenylphosphine ligand may be predicted. The crystal structure of  $[\text{Fe}_2\text{S}_2(\text{CO})_6]$  was determined by Wei and Dahl, in 1965 [23] (Fig. 3). Assuming that the probability of substitution of any of the four 'pseudo basal' carbonyls C(2), (3), (5), (6) or either of the two 'pseudo apical' carbonyls C(1), (4) by a phosphine ligand will be the same, there are three possible ways in which the ligand can link two  $[\text{Fe}_2\text{S}_2(\text{CO})_x]$  units. These are via apical to apical, apical to basal or basal to basal positions, (Fig. 4). It is difficult to predict a theoretical ratio in which these isomers might be formed without knowing how steric and environmental factors effect CO substitution.

Three isomers are predicted in theory and realised in practice, in an experimental ratio of 1:1:1. It might not have been expected that the isomers would be formed in equal amounts for the reasons outlined above. However, the rate of formation of one isomer over another as well as the thermodynamic stability of certain isomers over others must also have an influence. Unfortunately, because the isomers interconvert so rapidly in solution, the isolation of crystals of a single isomer could not be achieved.

### Acknowledgements

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