ELSEVIER

Journal of Organometallic Chemistry 642 (2002) 40–47

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis and spectroscopic characterisation of compounds with formula $[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$ and $[\{Fe_2(SPh)_2(CO)_5\}_2Ph_2P(CH_2)_nPPh_2]$ ($n = 3$, 4 and 6)

Rosamund Hourihane [a,*], Geraldine Gray [a], Trevor Spalding [b], Tony Deeney [c]

[a] *Chemistry Department, Cork Institute of Technology, Rossa Avenue, Bishopstown, Cork, Ireland*
[b] *Chemistry Department, University College Cork, College Road, Cork, Ireland*
[c] *Physics Department, University College Cork, College Road, Cork, Ireland*

Received 18 April 2001; received in revised form 19 September 2001

Abstract

This work describes the synthesis and characterisation of the title compounds. This is the second in a series of reactions involving iron bis-phosphine cluster compounds $[\{Fe_3(CO)_{11}\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$ and $[\{Fe_3(CO)_{11}\}_2Ph_2P(CH_2)_nPPh_2]$ ($n = 3$, 4 and 6). Here, the iron bis-phosphine cluster compounds are reacted with stoichiometric amounts of diphenyldisulphide (Ph_2S_2) in toluene at 65–70 °C for 30 min. The reactions afforded three products regardless of the *n*-value. Irrespective of the iron-containing reagent, one product is common to all reactions. A total of seven different compounds were isolated, six of which are new. The product formulations are:

(i) the known compound $[Fe_2(SPh)_2(CO)_6]$ (common product);
(ii) $[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$; and
(iii) $[\{Fe_2(SPh)_2(CO)_5\}_2Ph_2P(CH_2)_nPPh_2]$, ($n = 3$, 4 and 6).

Yields ranged 2–37% depending on the particular reactions. Reactions involving the $\{Fe_3–Fe\}$ type species with $[Ph_2S_2]$ (1:1 or 1:2 mole ratio) afforded predominantly phosphine sulphur compounds type (ii) above, whereas, when the $\{Fe_3–Fe_3\}$ type species were reacted (1:2 or 1:4 mole ratio), the major products were of type (iii) above. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Iron; Diphosphine; Disulphide; Bridging ligand; Mössbauer

1. Introduction

We report here the second in a series of reactions involving iron bis-phosphine cluster compounds $[\{Fe_3(CO)_{11}\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$ and $[\{Fe_3(CO)_{11}\}_2Ph_2P(CH_2)_nPPh_2]$ ($n = 3$, 4 and 6) with sulphur and selenium ligands. In the first of the series, these iron bis-phosphine cluster compounds were reacted with cyclohexene episulphide $[SC_6H_{10}]$ [1]. Reactions afford clusters with fewer iron atoms but with S-atoms incorporated. Compounds with two di iron di sulphur units linked by a bis-phosphine ligand were reported, formulation $[\{Fe_2S_2(CO)_5\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$ and $[\{Fe_2S_2(CO)_5\}_2Ph_2P(CH_2)_nPPh_2]$ ($n = 3$, 4 and 6). In these reactions, the Fe_3-unit is 'degraded', but at the same time the cluster is expanded from three atoms $\{Fe_3\}$ to four $\{Fe_2S_2\}$.

The series of reactions described in this work add thiolate sulphur, diphenyl disulphide (Ph_2S_2). Compounds with general formula $[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$ and $[\{Fe_2(SPh)_2(CO)_5\}_2Ph_2P(CH_2)_nPPh_2]$ ($n = 6$, bis(diphenylphosphino)hexane (dpph); $n = 4$, bis(diphenylphosphino)butane (dppb); and $n = 3$, bis(diphenylphosphino)propane (dppp)) are the new products formed in the reaction between $\{Fe_3–Fe\}$ and $\{Fe_3–Fe_3\}$ bis-phosphine double clusters with diphenyldisulphide (Ph_2S_2). $[Fe_2(SPh)_2(CO)_6]$ is a common product formed in all reactions. Products reported here maintain the bis-phosphine link, reduce the iron content of the cluster and add thiolate. This is

---

* Corresponding author. Fax: + 353-21-545343.
E-mail address: rhourihane@cit.ie (R. Hourihane).

0022-328X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(01)01277-3

similar to what was observed and reported by us previously in the first series, when sulphur was added. The compounds presented here were characterised by IR and Mössbauer spectroscopies as well as C, H, S and Fe analyses (Table 3).

Simple phosphine compounds of the type $[Fe_2(SPh)_2(CO)_{6-n}(PR_3)_n]$ (R = Me, Ph, OMe) [2–8], and ditertiary phosphine compounds where the bis-phosphine ligand used was dppm and dppe, have been reported previously [3,4,7,8]. De Beer and Haines found that the bis-phosphine ligand attached either

1. monodentate at one iron atom as in $[Fe(SR)_2(CO)_3Fe(CO)_2L]$ (R = Me, Et; L = $Ph_2PCH_2PPh_2$, dppm, $Ph_2P(CH_2)_2PPh_2$, dppe; benzene, room temperature);
2. symmetrically, bridging the two iron atoms of the 'Fe_2' unit $[Fe(SR)(CO)_2]_2L$ (L = (dppm), $Ph_2PNEtPPh_2$; toluene or xylene); or
3. when L = dppe, a trisubstituted product $[Fe(CO)_2(SR)_2LFe(CO)L]$ was the product formed where one bisphosphine ligand was bidentate and the other was monodentate, to the 'Fe_2' unit [3]. The latter species described is also the product formed when $[Fe_2(SR)_2(CO)_6]$ is irradiated with UV light in benzene solution (R = Me, Et; L = dppm, dppe or *cis*-$Ph_2PC_2H_2PPh_2$).

Cluster compounds where two 'Fe_2' units are bridged by two diphosphine ligands $[Fe_2(SR)_2(CO)_4L]_2$ (L = dppe) have also been reported [9].

All of the aforementioned cluster compounds, however, resulted from the reaction of an $Fe_2(SR)_2$ system with simple phosphines, yielding cluster compounds which have undergone substitution without expansion, i.e. the number of iron atoms in the cluster remains constant.

The literature also shows that when 'Fe_3' clusters are reacted with thiolate the products are thiolate substituted di iron carbonyl clusters [10–14]. However, when an 'Fe_3' system is reacted with S and then P, the Fe_3 cluster is not degraded [15–17].

The compounds described in this work illustrate that when an Fe_3 bisphosphine-substituted unit is further reacted with a thiolate ligand simultaneous reduction of the Fe_3 cluster to an Fe_2 cluster and expansion from a three-atom cluster to a four-atom bisphosphine-substituted unit incorporating thiolate occurs. Thus, reactions involving iron bis-phosphine 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, 4 and 6) with sulphur (cyclohexene episulphide) or thiolate sulphur (Ph_2S_2) give similar type of compounds. These products might be expected for the latter type of ligand, since they conform to literature reports, however, the products, resulting when the former ligand is reacted, are unexpected.

2. Experimental

2.1. Materials

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 distilled freshly from potassium diphenylketyl. Toluene was distilled freshly from sodium diphenylketyl. Hexane and CH_2Cl_2 were dried over P_2O_5 and distilled prior to use. All other solvents were of reagent grade and used as received. Bisphosphine ligands and Ph_2S_2 were commercial products obtained from Aldrich Chemicals, UK. 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, 4 and 6) were prepared as described by us in the literature [18,21].

2.2. Apparatus

Infrared spectra were recorded on Perkin–Elmer 682 or Mattson Polaris FTIR 10410 spectrophotometers. Solution spectra were obtained in NaCl 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 (Marwell Instruments) in conjunction with a Canberra System 40 multichannel analyser as previously described [19]. The source was ^{57}Co in Rh and was of 20-mCi nominal strength. Data were 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 γ-ray beam. For small samples (less than 0.03 g), the material was dissolved in the least amount of CH_2Cl_2 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. Sulphur 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.

2.3. Standard reaction procedure for the reaction between either of the following iron-containing compounds $[\{Fe_3(CO)_{11}\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$*, and* $[\{Fe_3(CO)_{11}\}_2Ph_2P(CH_2)_nPPh_2]$*,* $n = 3–6$ *and diphenyldisulphide*

Each of the title compounds were reacted with a stoichiometric amount of Ph_2S_2 in toluene under an inert atmosphere at 65–70 °C for 30 min. Specific reaction details are outlined in Tables 1 and 2. The extent of the reaction was monitored by TLC using silica gel 60 as the stationary phase and CH_2Cl_2–hexane as eluant. The reaction mixture was filtered and the toluene removed under reduced pressure yielding a orange-red residue. The residue was dissolved in CH_2Cl_2 and chromatographed using preparative TLC, with silica gel (PF_{254}) on glass plates and a mixture of CH_2Cl_2–hexane (3:2) as eluant.

Chromatographic separation afforded four products one of which had a red–orange colour and three were orange in colour. Only three products were produced in sufficient quantities to be isolated. These were extracted into CH_2Cl_2. The solvent was removed under reduced pressure and the residue was redissolved in hexane. The volume of hexane was reduced to 5 ml in each case and the solutions were stored at −20 °C for times ranging from 2 days to 2 weeks. The products in the form of microcrystalline solids were recovered and characterised by IR and Mössbauer spectroscopies as well as chemical analysis (Table 3), as

$[Fe_2(SPh)_2(CO)_6]$ (**1**);
$[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$ ($n =$ 3, (**2**); $n = 4$, (**3**); $n = 6$, (**4**);
$[\{Fe_2(SPh)_2(CO)_5\}_2Ph_2P(CH_2)_nPPh_2$ ($n = 3$, (**5**); $n =$ 4, (**6**); $n = 6$, (**7**).

3. Results and discussion

3.1. The reaction between $[\{Fe_3(CO)_{11}\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}$ *or* $[\{Fe_3(CO)_{11}\}_2Ph_2P(CH_2)_nPPh_2]$ *(n = 3, 4, 6) and diphenyldisulphide* $[(C_6H_5)_2S_2]$

3.1.1. Syntheses

The title reactions were carried out in toluene at 65–70 °C for 30 min. Three products were isolated for each reaction (Scheme 1). One product **1** was common to all reactions. Thus in total, seven different compounds, six of which are new, were isolated and characterised. The products were separated by preparative TLC. These were characterised by IR and Mössbauer

Table 1
Reaction of $[\{Fe_3(CO)_{11}\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$ (A) with diphenyldisulphide (B)

n	Reagent A (g (mmol))	Reagent B (g (mmol))	Product formula	g (% Yield)
6	0.095 (0.086)	0.038 (0.172)	$[Fe_2(SPh)_2(CO)_6]$	0.23 (53.7)
			$[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_6PPh_2\{Fe(CO)_4\}]$	0.024 (25.4)
			$[\{Fe_2(SPh)_2(CO)_5\}_2Ph_2P(CH_2)_6PPh_2]$	0.009 (7.2)
4	0.128 (0.119)	0.026 (0.119)	$[Fe_2(SPh)_2(CO)_6]$	0.015 (25.2)
			$[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_4PPh_2\{Fe(CO)_4\}]$	0.05 (38.9)
			$[\{Fe_2(SPh)_2(CO)_5\}_2Ph_2P(CH_2)_4PPh_2]$	0.014 (8.5)
3	0.086 (0.079)	0.017 (0.079)	$[Fe_2(SPh)_2(CO)_6]$	0.02 (50.9)
			$[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_3PPh_2\{Fe(CO)_4\}]$	0.015 (18.2)
			$[\{Fe_2(SPh)_2(CO)_5\}_2Ph_2P(CH_2)_3PPh_2]$	0.003 (2.1)

Mole ratio A:B, 1:1; reaction temperature, 65–70 °C; reaction solvent toluene, 30 ml; reaction time, 30 min. Yields calculated as in Ref. [1].

Table 2
Reaction of $[\{Fe_3(CO)_{11}\}_2Ph_2P(CH_2)_nPPh_2]$ (A) with diphenyldisulphide (B)

n	Reagent A (g (mmol))	Reagent B (g (mmol))	Product formula	g (% yield)
6	0.082 (0.058)	0.025 (0.116)	$[Fe_2(SPh)_2(CO)_6]$	0.018 (63.8)
			$[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_6PPh_2\{Fe(CO)_4\}]$	0.002 (3.3)
			$[\{Fe_2(SPh)_2(CO)_5\}_2Ph_2P(CH_2)_6PPh_2]$	0.005 (5.6)
4	0.097 (0.071)	0.02 (0.091)	$[Fe_2(SPh)_2(CO)_6]$	0.016 (44.5)
			$[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_4PPh_2\{Fe(CO)_4\}]$	0.013 (18.2)
			$[\{Fe_2(SPh)_2(CO)_5\}_2Ph_2P(CH_2)_4PPh_2]$	0.036 (36.6)
3	0.153 (0.118)	0.024 (0.118)	$[Fe_2(SPh)_2(CO)_6]$	0.029 (52.1)
			$[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_3PPh_2\{Fe(CO)_4\}]$	0.017 (14.1)
			$[\{Fe_2(SPh)_2(CO)_5\}_2Ph_2P(CH_2)_3PPh_2]$	0.020 (13.5)

Mole ratio A:B, 1:2 or 1:2; reaction temperature, 65–70 °C; reaction solvent toluene, 30 ml; reaction time, 30 min. Yields calculated as in Ref. [1].

Table 3
Characteristics of substituted iron carbonyl compounds with proposed $[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$ and $[\{Fe_2(SPh)_2(CO)_5\}_2Ph_2P(CH_2)_nPPh_2]$ formulations

Compound	Anal. Calc. (Found)				IR	Mössbauer				
	C	H	S	Fe	ν_{max} CO (cm^{-1})	Site	χ	δ	Δ	Γ
$[Fe_2(SPh)_2(CO)_6]$ (**1**) [a,b]					2070, 2036, 2003, 1995	$Fe(CO)_3SPh$		0.32	1.01	
$[Fe_2(SPh)_2(CO)_6]$ (**1**) [c]	43.41 (43.58)	2.03 (2.16)	12.89 (13.15)	22.40 (21.25)	2065 m, shp, 2028 vs,shp, 2000 w, shp, 1985 vs, br	$Fe(CO)_3SPh$		0.35	1.01	0.25
$[\{Fe_2(SMe)_2(CO)_5\}PEt_3]$ [d]					2041 s, 1981 s, 1967 s, 1923 m					
$[\{Fe(CO_4)_2\}Ph_2P(CH_2)_3PPh_2]$ [e]					2040 vs, shp, 2010 vw, 1955 vw, 1960 s, 1920 vs br					
$[\{Fe(CO)_4\}Ph_2P(CH_2)_2]_2$ [e]					2040 vs, shp, 1992 vw, sh 1955, s, 1929 vs, br					
$[\{Fe_2(SEt)_2(CO)_5\}Ph_2P(CH_2)_2PPh_2]$ [d]					2036 s, 1980 s, 1922 m					
$[\{Fe_2(SEt)_2(CO)_5\}Ph_2PCH_2PPh_2]$ [d]						$Fe(CO)_3(SEt)_2$ $Fe(CO)_3(SEt)_2P$		0.29 0.31	1.24 0.76	0.23 0.25
$[\{Fe(SMe)(CO)_2\}Ph_2PCH_2PPh_2]_2$ [d]						$Fe(CO)_3(SMe)_2P$		0.31	0.84	0.30
$[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_6PPh_2\{Fe(CO)_4\}]$ (**4**) [c]	56.07 (55.95)	3.88 (3.80)	5.88 (5.55)	15.33 (15.45)	2038 s, shp, 1990 sh, 1986 sh, 1970 s, br, 1955 sh, 1920 s, br, 1915 s, br	$Fe(CO)_4P$ $Fe(CO)_3(SPh)_2$	1.6 2.5	0.19 0.39	2.42 1.23	0.22 0.40

Table 3 (*Continued*)

Compound	Anal. Calc. (Found)				IR	Mössbauer				
	C	H	S	Fe	ν_{max} CO (cm^{-1})	Site	χ	δ	Δ	Γ
[{$Fe_2(SPh)_2(CO)_5$}$Ph_2P(CH_2)_4PPh_2${$Fe(CO)_4$}] (**3**) [c]	55.29	3.60	6.03	15.73	2040 s, shp,	$Fe(CO)_4$ ′P	1.6	0.20	2.40	0.23
	(55.63)	(3.91)	(6.11)	(15.07)	1970 s, br,	$Fe(CO)_3(SPh)_2$	2.5	0.37	1.25	0.40
					1960 sh,	$Fe(CO)_2(SPh)_2P$	3.4		0.90	
					1950 sh,					
					1920 s, br					
[{$Fe_2(SPh)_2(CO)_5$}$Ph_2P(CH_2)_3PPh_2${$Fe(CO)_4$}] (**2**) [c]	54.89	3.45	6.11	15.94	2038 vs, shp,	$Fe(CO)_4$ ′P	1.6	0.20	2.41	0.25
	(54.46)	(3.91)	(5.47)	(16.19)	1969 vs, br,	$Fe(CO)_3(SPh)_2$	2.5	0.38	1.23	0.40
					1915 vs, br	$Fe(CO)_2(SPh)_2P$	3.4		0.85	
[{$Fe_2(SPh)_2(CO)_5$}$_2Ph_2P(CH_2)_6PPh_2$] (**7**) [c]	55.12	3.75	9.21	16.00	2038 vs, shp,	$Fe(CO)_3(SPh)_2$		0.39	1.01	0.40
	(55.00)	(4.08)	(9.50)	(16.05)	1970 vs, br,	$Fe(CO)_2(SPh)_2P$				
					1950 sh,					
					1919 w, br					
					1910 w, br					
[{$Fe_2(SPh)_2(CO)_5$}$_2Ph_2P(CH_2)_4PPh_2$] (**6**) [c]	54.49	3.60	9.39	16.33	2040 s, shp,	$Fe(CO)_3(SPh)_2$	1.4	0.36	1.20	0.65
	(54.62)	(4.28)	(9.44)	(16.65)	1970 vs, br,	$Fe(CO)_2(SPh)_2P$	2.3		0.88	
					1955 sh,					
					1960 sh,					
					1950 sh,					
					1915 m, br					
[{$Fe_2(SPh)_2(CO)_5$}$_2Ph_2P(CH_2)_3PPh_2$] (**5**) [c]	54.17 (54.34)	3.46 (4.08)	9.47 (9.66)	16.52 (16.78)	2040 vs, shp,	$Fe(CO)_3(SPh)_2$	1.4	0.37	1.20	0.65
					1970 vs, br,	$Fe(CO)_2(SPh)_2P$	2.3		0.88	
					1955 sh,					
					1915 w, br					

χ, line assignment; δ, isomer shift; Δ, quadrupole splitting; Γ, peakwidth at half height. All isomer shift data are referenced to sodium nitroprusside, to reference to iron subtract 0.257 from values in the table.

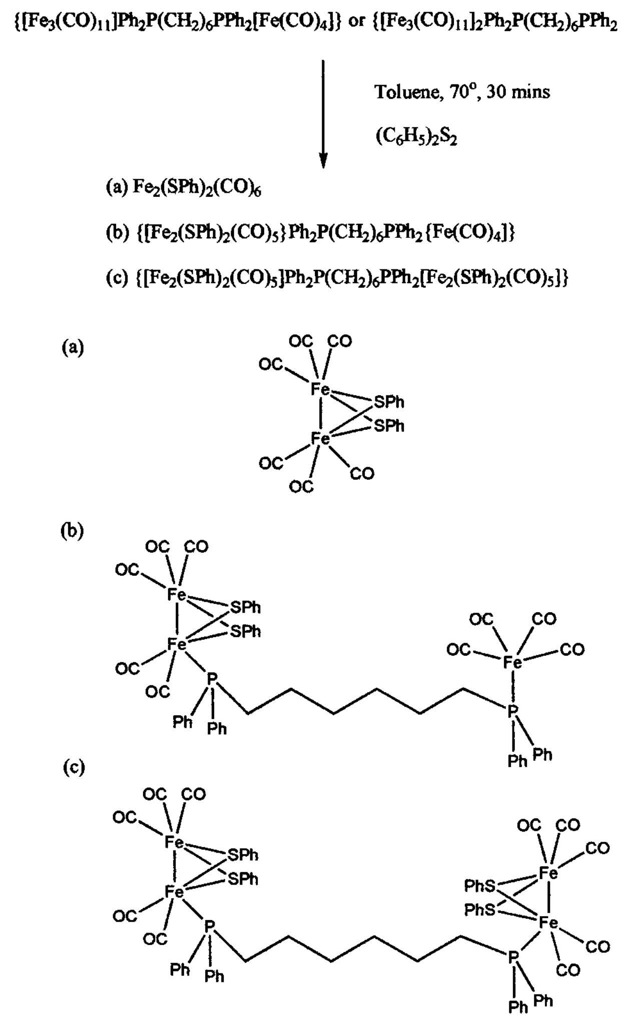
[a] IR solvent CS_2.

[b] Refs. [20,22].

[c] IR Solvent CH_2Cl_2 (Ref.: this work).

[d] Ref. [3].

[e] Refs. [1,21].



Scheme 1. Proposed reaction scheme for the formation of compounds with formulae: (a) $Fe_2(SPh)_2(CO)_6$ (1); $\{[Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_6PPh_2\{Fe(CO)_4]\}$ (4); $\{[Fe_2(SPh)_2(CO)_5]Ph_2P(CH_2)_6PPh_2[Fe_2(SPh)_2(CO)_5]\}$ (7).

spectroscopies and C, H, S and Fe analyses (Table 3). The product formulations are:

(i) the single common product $[Fe_2(SPh)_2(CO)_6]$ (**1**);
(ii) $[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$ $n = 3$, (**2**); $n = 4$, (**3**); $n = 6$, (**4**);
(iii) $[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_nPPh_2]$ $n = 3$, (**5**); $n = 4$, (**6**); $n = 6$, (**7**).

Tables 1 and 2 illustrate how the choice of starting material influences product yield. For example, reactions involving $[\{Fe_3(CO)_{11}\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$ afforded the phosphine-containing compounds, which were predominantly of the type $[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$ $n = 3$, (**2**); $n = 4$, (**3**); $n = 6$, (**4**).

However, when the compounds $[\{Fe_3(CO)_{11}\}_2Ph_2P(CH_2)_nPPh_2]$ were the starting materials the products with $[\{Fe_2(SPh)_2(CO)_5\}_2Ph_2P(CH_2)_nPPh_2]$ ($n = 3$, (**5**); $n = 4$, (**6**); $n = 6$, (**7**)) formulation were produced in higher yields. An exception to this is when $n = 3$, here both product formulations have similar % yields.

3.1.2. Spectroscopic characterisation

3.1.2.1. Infrared spectra. A summary of the energies of the band maxima of the IR absorptions in the carbonyl region for compounds **1**–**7** is given in Table 3 along with data previously reported for **1** [20].

Considering compounds of the type $[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$ $n = 3$, (**2**); $n = 4$, (**3**); $n = 6$, (**4**), it can be seen that all three have very similar CO absorption patterns. For the proposed formulation, a combination of absorptions due to two distinct units, i.e. $Fe(CO)_4$ and $Fe_2(SPh)_2(CO)_5$ would be expected. Characteristic absorptions for the $Fe(CO)_4$ unit occur at 2040 vs, 1990 sh, 1955 s, and 1920 vs cm^{-1} in CH_2Cl_2, for example, compounds $[\{Fe(CO)_4\}Ph_2P(CH_2)_3]_2)$ and $[\{Fe(CO)_4\}Ph_2P(CH_2)_2]_2)$, [21] (Table 3). While those of the $Fe_2(SR)_2(CO)_5$ unit occur at 2036 s, 1980 s, and 1922 m cm^{-1} in CH_2Cl_2, for example, compound $[Fe_2(SEt)_2(CO)_5Ph_2P(CH_2)_2PPh_2]$ [3] (Table 3). Since these absorptions overlap largely, it would be difficult to distinguish these units by IR spectroscopy alone. To take a specific example, the spectrum of compound **4**, $n = 6$, has absorptions at 2038 s, shp, 1990 sh, 1970 s, br, 1960 sh, 1955 sh, 1920 s, br and 1915 s, br cm^{-1} in CH_2Cl_2, and clearly, they cannot unambiguously be assigned to specific units.

The possibility of chelating phosphine ligands or bidentate ligands being attached to one iron atom in the 'Fe_2' species can apparently be ignored, since the absorptions due to these types of compounds are clearly different from those reported in this work. For example, $[Fe(SMe)_2(CO)_3Fe(CO)$ (dppe)] has CO absorptions at 2017, 1946, and 1900 cm^{-1}, where the phosphine is chelating to the iron [3] and $[\{Fe(SEt)_2(CO)_2\}_2$ (dppm)] has CO absorptions at 1900, 1946 and 1927 cm^{-1}, where the phosphine is bidentate to the iron [3].

If the IR spectra of compounds of the type $[\{Fe_2(SPh)_2(CO)_5\}_2Ph_2P(CH_2)_nPPh_2]$ $n = 3$, (**5**); $n = 4$, (**6**); $n = 6$, (**7**) are examined, it can be seen that all three compounds have very similar CO absorptions. Their spectra can be analysed more successfully than those for **2**–**4** since there is only the $Fe_2(SPh)_2(CO)_5$ unit to consider and a number of similar compounds are reported in the literature [1,3]. For example, compound **7** shows carbonyl absorptions at 2038 vs, shp, 1970 vs, br, 1950 sh, 1919 w, br, 1910 w, br cm^{-1} in CH_2Cl_2. The compound $[\{Fe_2(SEt)_2(CO)_5\}Ph_2P(CH_2)_nPPh_2]$ with carbonyl absorptions at 2036 s, 1980 s, and 1922 m in CH_2Cl_2 or $[Fe_2(SMe)_2(CO)_5PEt_3]$ with CO absorptions at 2041 s, 1981 s, 1967 s, 1923 m in hexane [3] compare well with those obtained for compound **7**.

Similar assignments can be made for compounds **5** and **6**.

3.1.2.2. Mössbauer spectra. The values (mm s^{-1}) of isomer shift (δ), quadrupole splitting (Δ) together with the line assignment, numbered 1–6 from left to right, for compounds **1**–**7** are given in Table 3. The Mössbauer spectra for compounds **2**, **6** and **7** are illustrated in Fig. 1. The quadrupole splitting value of 1.01 mm s^{-1} for compound **1** is the same as that reported in the literature, but the isomer shift value of 0.35 mm s^{-1} is shifted slightly from the value of 0.32 mm s^{-1} reported previously [20,22]. However, since all values are ± 0.02 mm s^{-1}, both values overlap within allowed experimental error.

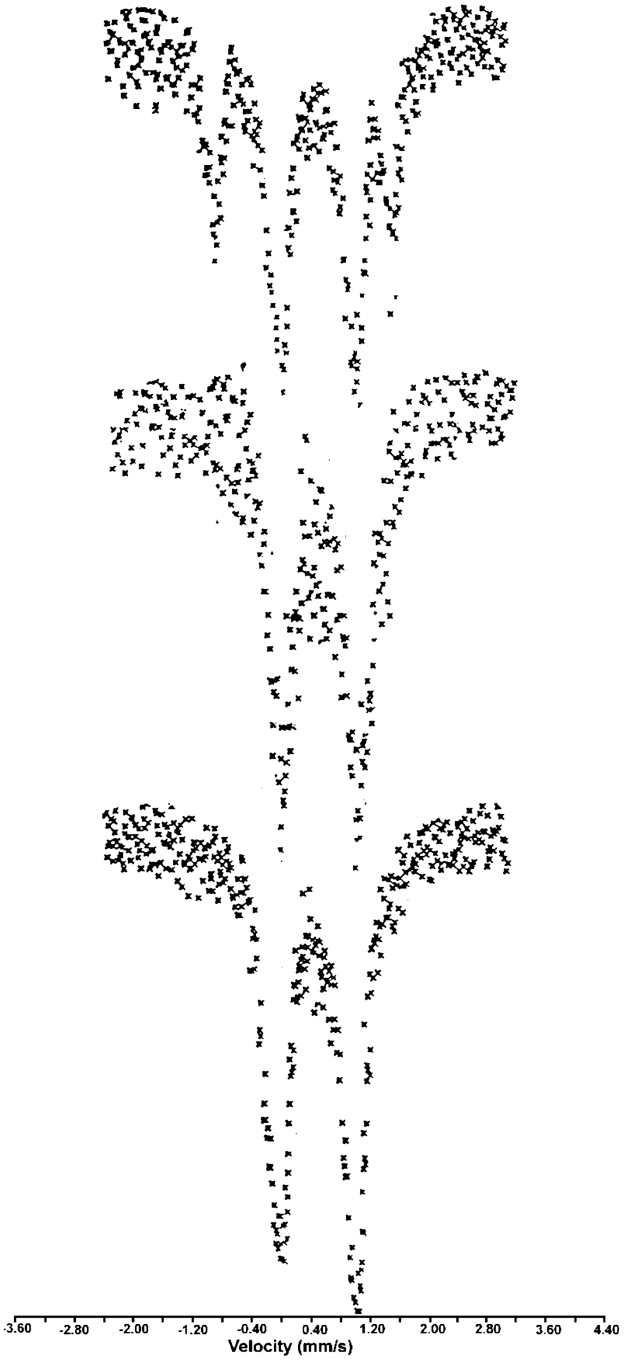
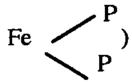


Fig. 1. Mössbauer spectra of compounds with formulae (a) $[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_3PPh_2\{Fe(CO)_4\}]$ (**2**); $[\{Fe_2(SPh)_2(CO)_5\}_2Ph_2P(CH_2)_nPPh_2$ (b) $n = 4$, (**6**); (c) $n = 6$, (**7**).

The Mössbauer spectra of compounds $[\{Fe_2(SPh)_2(CO)_5\}Ph_2P(CH_2)_nPPh_2\{Fe(CO)_4\}]$ (**2**–**4**) all show three resolved doublets, which distinguish the three different iron sites within these compounds. Fig. 1 contains the spectrum of **2**. The site with the largest Δ-value (ca. 2.41 mm s^{-1}) is assigned to the $Fe(CO)_4$ unit with a monodentate phosphine ligand attached in an apical position. This assignment is justified by comparison with literature values [1]. The second largest quadrupole splitting value ca. 1.24 mm s^{-1} is assigned to the unsubstituted iron site of the $Fe_2(SPh)_2(CO)_5$ unit, since it is most like that of the 'parent molecule' $[Fe_2(SPh)_2(CO)_6]$ (**1**) (1.01 mm s^{-1}). Lastly, the quadrupole splitting of ca. 0.87 mm s^{-1} is assigned to the substituted iron atom of the 'Fe_2' unit, i.e. the $Fe(SPh)_2(CO)_2P$ site. These assignments are justified by comparison with literature data [3,20,22,23]. For example, the compounds $[\{Fe_2(SR)_2(CO)_5\}Ph_2P(CH_2)PPh_2]$ $\{R = Et,\ R = Me\}$ have $\Delta = 1.24$ and 1.13 mm s^{-1}, respectively, for the unsubstituted site, and $\Delta = 0.76$ and 0.74 mms^{-1}, respectively, for the substituted site [3]. Further support for the correctness of the assignment for the substituted site comes from comparison of the quadrupole splitting value with that for the iron atoms in $[Fe(SMe)(CO)_2\ dppm]_2$ $\Delta = 0.84$ mm s^{-1}, where both irons are substituted by phosphine ligands in a monodentate fashion [3]. The possibility of chelating phosphine ligands may be ruled out by comparison with the Δ-value for the phosphine substituted site (CO Fe ) in $[Fe(SPh)_2(CO)_3Fe(CO)\ dppe]$, which has a Δ of 0.61 mm s^{-1}, clearly different to the lowest Δ-value of ca. 0.87 mm s^{-1} in compounds **2**–**4**.

Support for the unsubstituted site assignment comes from examination of the isomer shift values. There is very little difference between that of the parent molecule $[Fe_2(SPh)_2(CO)_6]$ (**1**) with $\delta = 0.35$, and values for compounds **2**–**4** with $\delta = 0.38$, 0.37, and 0.39 mm s^{-1}, respectively. This suggests that the site is essentially unchanged.

The three compounds $[\{Fe_2(SPh)_2(CO)_5\}_2Ph_2P(CH_2)_nPPh_2]$ (**5**–**7**) contain two iron sites in the $Fe_2(SPh)_2(CO)_5$ units. Each has one $Fe(SPh)_2(CO)_2P$– and one $Fe(SPh)_2(CO)_3$–. The two iron sites are distinguished clearly in compounds **5** and **6**, and have similar Mössbauer parameters to those for the $Fe_2(SPh)_2(CO)_5$ unit in compounds **2**–**4** above, discussed previously. However, in the spectra of compound **7** these sites are unresolved and are assigned values of $\delta = 0.39$ and $\Delta = 1.01$ mm s^{-1} for both sites.

Thus the arrangement of ligands proposed for compounds of the type [{$Fe_2(SPh)_2(CO)_5$}$Ph_2P(CH_2)_n$-PPh_2{$Fe(CO)_4$}] (**2**–**4**) consists of an $Fe(CO)_4$ unit with the phosphine ligand attached in an apical position and an $Fe_2(SPh)_2(CO)_5$ unit with the phosphine ligand attached either to an apical or basal position, ((b) Scheme 1). The proposed structure for compounds of type [{$Fe_2(SPh)_2(CO)_5$}$_2Ph_2P(CH_2)_nPPh_2$] (**5**–**7**) consists of two $Fe_2(SPh)_2(CO)_5$ units linked by the diphosphine ligand via combinations of apical or basal positions (Scheme 1(c)).

Acknowledgements

We wish to thank Cork Institute of Technology for scholarship support for a student.

References

[1] R. Hourihane, G. Gray, T.R. Spalding, T. Deeney, J. Organomet. Chem. 595 (2000) 191.

[2] G. Natile, L. Maresca, G. Bor, Inorg. Chim. Acta 23 (1977) 37.

[3] J.A. de Beer, R.J. Haines, R. Greatrex, N.N. Greenwood, J. Chem. Soc. A (1971) 3271.

[4] A. Darchen, H. Mousser, H. Patin, J. Chem. Soc. Chem. Commun. (1988) 968.

[5] (a) R.E. Dessy, R. Kornmann, C. Smith, R. Haytor, J. Am. Chem. Soc. 90 (1968) 2001;
(b) G. Zotti, R.D. Rieke, J.S. McKennis, J. Organomet. Chem. 228 (1982) 281.

[6] P.M. Treichel, R.A. Crane, R. Mathews, K.R. Bonnin, D. Powell, J. Organomet. Chem. 402 (1991) 233.

[7] M.S. Arabi, R. Mathieu, R. Pailblanc, J. Organomet. Chem. 177 (1979) 199.

[8] G. Le Borgne, D. Grandjean, R. Mathieu, R. Pailblanc, J. Organomet. Chem. 131 (1977) 429.

[9] J.A. DeBeer, R.J. Haines, J. Organomet. Chem. 36 (1972) 297.

[10] J.A. DeBeer, R.J. Haines, J. Chem. Soc. Chem. Commun. (1970) 288.

[11] R.B. King, J. Am. Chem. Soc. 84 (1962) 2460.

[12] L.F. Dahl, C. Martell, D.L. Wampler, J. Am. Chem. Soc. 83 (1961) 1761.

[13] (a) W. Heiber, Z. Anorg. Allg. Chem. 233 (1937) 353;
(b) W. Heiber, Z. Anorg. Allg. Chem. 305 (1964) 265.

[14] J.A. Adelcke, Y.W. Chen, L.K. Lui, Organometals 11 (1992) 2543.

[15] P. Mathur, I.J. Mavunkal, V. Rugmini, J. Organomet. Chem. 367 (1989) 243.

[16] S. Jy Wang, R.J. Angelici, Inorg. Chem. 27 (1988) 3233.

[17] A. Darchen, C. Mahé, H. Patin, J. Chem. Soc. Chem. Commun. (1982) 243.

[18] G. Ferguson, R. Houihane, T.R. Spalding, Acta Crystallogr., Sect. C C47 (1991) 544.

[19] W.E. Carroll, F.A. Deeney, F.J. Lalor, J. Organomet. Chem. 198 (1980) 189.

[20] E. Kostiner, M.L.N. Reddy, D.S. Urch, A.G. Massey, J. Organomet. Chem. 15 (1968) 383.

[21] R. Hourihane, Ph.D. Thesis, U.C.C., Ireland, 1992.

[22] E. Kostiner, A.G. Massey, J. Organomet. Chem. 19 (1969) 233.

[23] R.V. Parish, The Organic Chemistry of Iron, vol. 1, Academic Press, New York, 1978.