

The CO-substitution reactions of analogues of $[\text{Fe}_2\{\eta\text{-C}_5\text{H}_5\}_2(\text{CO})_2(\mu\text{-CO})_2]$ in which the two cyclopentadienyl ligands are linked by a two-carbon chain

M. Gary Cox and A.R. Manning

Department of Chemistry, University College, Belfield, Dublin 4 (Ireland)

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Abstract

The CO ligands in various complexes $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ have been substituted by PR_3 (1 CO ligand replaced), P(OR)_3 (1 CO ligand replaced), and $\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2$ where $n = 1, 2$, or 3 (1 or 2 CO ligands replaced). When $\text{A-B} = R, S\text{-CH(NMe}_2\text{)CH(NMe}_2\text{)}$ or $\text{CH}_2\text{C(O)}$ the substitution may be brought about thermally in refluxing di-*n*-butyl ether, but when $\text{A-B} = R, R/S, S, S\text{-CH(NMe}_2\text{)CH(NMe}_2\text{)}$ this fails, and UV photolysis is required. The thermal reaction between $R, S\text{-[Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CH(NMe}_2\text{)CH(NMe}_2\text{)C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ and $\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2$ gives two products, $R, S\text{-[Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CH(NMe}_2\text{)CH(NMe}_2\text{)C}_5\text{H}_4\}(\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2)(\mu\text{-CO})_2]$ and $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CHC(NMe}_2\text{)C}_5\text{H}_4\}(\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2)(\mu\text{-CO})_2]$. The latter species were isolated as $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CH}_2\text{C(O)C}_5\text{H}_4\}(\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2)(\mu\text{-CO})_2]$, and their proportion found to increase with increasing n . The IR spectra of the $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4\}(\text{CO})(\text{L})(\mu\text{-CO})_2]$ complexes where $\text{L} = \text{PMePh}_2$ show a doubling of the absorption band of the terminal CO ($\nu\text{-CO}$) which is attributed to isomerism arising from restricted rotation about the Fe–P bond, whilst comparison of the $\nu\text{(CO)}$ frequencies where $\text{L} = \text{P(OR)}_3$ and $\text{L} = \text{PR}_3$ suggests that the variation of electron density on one Fe atom is largely experienced by the remaining $\nu\text{-CO}$ ligand coordinated to the other Fe atom and not by the two shared $\mu\text{-CO}$ ligands. Dynamic NMR studies show that when $\text{A-B} = R, S\text{-CH(NMe}_2\text{)CH(NMe}_2\text{)}$ there is a slowable restricted rotation about the ring-linking C–C bond but not for other A–B, and that for the various diphosphine complexes, it is possible to slow conformational changes within the $\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2$ ligand when $n = 2$ or 3 , as it is in their $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2)(\mu\text{-CO})_2]$ counterparts.

Key words: Iron; Cyclopentadienyl; Phosphine; Substitution; Fluxionality

1. Introduction

Although the CO-substitution reactions of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})_2]$ with mono- and bidentate P^{III} ligands have been studied extensively [1], much less effort has been devoted to related complexes in which the two cyclopentadienyl ligands are linked and the $\text{Fe}_2(\text{CO})_4$ moiety is constrained to a *cis* conformation. Cotton *et al.* [2] have prepared $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CH(NMe}_2\text{)CH(NMe}_2\text{)C}_5\text{H}_4\}(\text{CO})(\text{P(OPh)}_3)(\mu\text{-CO})_2]$ and $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CMe}_2\text{CMe}_2\text{C}_5\text{H}_4\}(\text{CO})(\text{P(OPh)}_3)(\mu\text{-CO})_2]$ from tetracarbonyl precursors and P(OPh)_3 . Nelson and Wright obtained $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{SiMe}_2\text{-C}_5\text{H}_4\}(\text{CO})(\text{PPh}_3)(\mu\text{-CO})_2]$ and $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{SiMe}_2\text{-C}_5\text{H}_4\}(\text{P(OPh)}_3)_2(\mu\text{-CO})_2]$ by reaction of $[\text{Me}_2\text{Si(C}_5\text{H}_4\text{Fe(CO)(L))}_2]$ ($\text{L} = \text{PPh}_3$ or P(OPh)_3) with $n\text{-BuLi}$ at -78°C [3], and $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_5\text{H}_4\}(\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2)(\mu\text{-CO})_2]$ by the UV-initiated reaction of $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ with $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ [4].

$[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{SiMe}_2\text{-C}_5\text{H}_4\}(\text{P(OPh)}_3)_2(\mu\text{-CO})_2]$ by reaction of $[\text{Me}_2\text{Si(C}_5\text{H}_4\text{Fe(CO)(L))}_2]$ ($\text{L} = \text{PPh}_3$ or P(OPh)_3) with $n\text{-BuLi}$ at -78°C [3], and $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_5\text{H}_4\}(\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2)(\mu\text{-CO})_2]$ by the UV-initiated reaction of $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ with $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ [4].

2. Experimental details

Published methods were used to prepare $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ [$\text{A-B} = R, S\text{-CH(NMe}_2\text{)CH(NMe}_2\text{)}$ [5], $R, R/S, S, S\text{-CH(NMe}_2\text{)CH(NMe}_2\text{)}$ [5], $\text{CH}_2\text{C(O)}$ [6], $\text{CHC(NMe}_2\text{)}$ [6]] and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2)(\mu\text{-CO})_2]$ ($n = 2$ or 3) [1]. Other chemicals were purchased.

Correspondence to: Professor A.R. Manning.

All reactions were carried out under nitrogen in solvents which had been dried and deoxygenated by refluxing over calcium hydride, and were monitored by IR spectroscopy.

2.1. The reactions of $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ with P^{III} ligands

A solution of equimolar amounts of $R, S\text{-}[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2)\text{C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ and $\text{L} = \text{PMePh}_2$, PR_3 or P(OR)_3 ($\text{R} = \text{Me}$ or Et) in di-n-butyl ether (150 cm^3) was refluxed for 30 min. The solvent was removed under reduced pressure, the residue chromatographed (alumina/dichloromethane), and the products recrystallized from dichloromethane/pentane mixtures to give green crystals of $R, S\text{-}[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2)\text{C}_5\text{H}_4\}(\text{CO})(\text{L})(\mu\text{-CO})_2]$ in ca. 80% yield.

Under the same conditions $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CH}_2\text{C}(\text{O})\text{C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ and P(OEt)_3 gave $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CH}_2\text{C}(\text{O})\text{C}_5\text{H}_4\}(\text{CO})(\text{P(OEt)}_3)(\mu\text{-CO})_2]$.

The bidentate ligands $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1, 2$ or 3) and $R, S\text{-}[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2)\text{C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ gave, after ca. 5 h, a mixture of green $R, S\text{-}[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2)\text{C}_5\text{H}_4\}(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-CO})_2]$ and green $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CH}_2\text{C}(\text{O})\text{C}_5\text{H}_4\}(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-CO})_2]$ in a ratio which depended on n . $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CH}_2\text{C}(\text{O})\text{C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ gave $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CH}_2\text{C}(\text{O})\text{C}_5\text{H}_4\}(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-CO})_2]$ only, and $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CHC}(\text{NMe}_2)\text{C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ gives $[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CHC}(\text{NMe}_2)\text{C}_5\text{H}_4\}(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-CO})_2]$. In the last case chromatography was not used. The total product yields from all the reactions were 75–80%.

The related reactions of $R, R/S, S\text{-}[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2)\text{C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ took place only when the reaction mixtures were also irradiated with a Philips HPR 125 W UV lamp for 10–24 h, and gave $R, R/S, S\text{-}[\text{Fe}_2\{\eta, \eta\text{-C}_5\text{H}_4\text{CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2)\text{C}_5\text{H}_4\}(\text{CO})(\text{L})(\mu\text{-CO})_2]$ ($\text{L} = \text{PMe}_3$, PEt_3 , PMePh_2 or

TABLE 1. Melting points and analyses of complexes described in the text

Ligand, L ^a	Melting point (°C) ^b	Analyses ^c				
		%C	%H	%N	%Fe	%P
<i>R,S</i> -[Fe ₂ {η,η- <i>C</i> ₅ H ₄ CH(NMe ₂)CH(NMe ₂) <i>C</i> ₅ H ₄ }(CO) ₃ (L)]						
P(OMe) ₃	142–145	46.8 (47.0)	5.5 (5.0)			
P(OEt) ₃	131–132	49.5 (49.7)	6.1 (6.1)	4.4 (4.6)	18.7 (18.5)	5.0 (5.1)
PMe ₃	dec. 174	51.4 (51.6)	6.1 (5.5)	5.3 (5.5)	21.3 (21.9)	6.3 (6.1)
PEt ₃	dec. 189	53.5 (53.9)	6.6 (6.6)	4.8 (5.0)		5.7 (5.6)
PMePh ₂	212–214	60.7 (60.2)	5.7 (5.5)	3.9 (4.4)	17.2 (17.5)	5.0 (4.9)
<i>R,R/S,S</i> -[Fe ₂ {η,η- <i>C</i> ₅ H ₄ CH(NMe ₂)CH(NMe ₂) <i>C</i> ₅ H ₄ }(CO) ₃ (L)]						
P(OMe) ₃	194–196	46.2 (46.9)	5.5 (5.0)	4.5 (5.0)		5.7 (5.5)
PMe ₃	dec. 223	52.3 (51.7)	6.2 (5.5)	5.4 (5.5)	22.4 (21.9)	
PEt ₃	dec. 210	53.9 (53.9)	6.6 (6.6)	4.7 (5.0)		
PMePh ₂	dec. 230	60.2 (60.2)	5.6 (5.5)	4.0 (4.4)	17.7 (17.6)	5.1 (4.9)
[Fe ₂ {η,η- <i>C</i> ₅ H ₄ CH ₂ C(O) <i>C</i> ₅ H ₄ }(CO) ₃ (L)]						
P(OEt) ₃	202–204	46.8 (47.4)	4.7 (4.7)		20.8 (21.0)	6.0 (5.8)
<i>R,S</i> [Fe ₂ {η,η- <i>C</i> ₅ H ₄ CH(NMe ₂)CH(NMe ₂) <i>C</i> ₅ H ₄ }(CO) ₂ (L)]						
DPPM	dec. 201	64.5 (65.0)	5.5 (5.5)	3.3 (3.5)	13.9 (14.1)	7.6 (7.8)
DPPE	dec. 172	65.8 (65.3)	6.0 (5.7)	2.8 (3.2)	13.2 (13.8)	7.5 (7.6)
<i>R,R/S,S</i> -[Fe ₂ {η,η- <i>C</i> ₅ H ₄ CH(NMe) ₂ CH(NMe ₂) <i>C</i> ₅ H ₄ }(CO) ₂ (L)]						
DPPM	192–194	65.3 (65.0)	5.7 (5.5)	3.3 (3.5)		
DPPE ^e	dec. 256	64.0 (64.2)	5.8 (5.3)	3.3 (3.4)	13.6 (13.6)	7.5 (7.5)
DPPP ^f	172–174	62.3 (62.3)	5.6 (6.1)	3.3 (3.2)		6.8 (7.0)
[Fe ₂ {η,η- <i>C</i> ₅ H ₄ CH ₂ C(O) <i>C</i> ₅ H ₄ }(CO) ₂ (L)]						
DPPE ^g	181–184	65.6 (65.2)	5.3 (4.6)	0 (0)		
DPPE	181–183	64.2 (65.2)	5.1 (4.6)	0 (0)		8.3 (8.4)
DPPP ^h	dec. 210	70.1 (70.6)	5.7 (5.8)	0 (0)	12.2 (12.0)	6.5 (6.3)

^a DPPM = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$; DPPE = $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$; and DPPP = $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$. ^b Melting points determined in sealed tubes; dec. denotes decomposition. ^c Calculated values in parentheses. ^d $1/3 \text{ C}_6\text{H}_{14}$ of crystallization. ^e H_2O of crystallization. ^f $2.5 \text{ H}_2\text{O}$ of crystallization. ^g From direct reaction of $[\text{Fe}_2\{\eta^5, \eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{COC}_5\text{H}_4\}(\mu\text{-CO})_2(\text{CO})_2]$ with DPPE. ^h $2 \text{ C}_6\text{H}_5\text{CH}_3$ of crystallization confirmed by ^1H NMR spectroscopy.

P(OMe)_3 or $R,R/S,S\text{-}[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{CH(NMe}_2\text{)CH(NMe}_2\text{)C}_5\text{H}_4\}\{\text{Ph}_2\text{P(CH}_2\text{)}_n\text{PPh}_2\}(\mu\text{-CO})_2]$. In all cases the reaction yields were *ca.* 80%.

Elemental analyses (Table 1) were carried out by the Analytical Laboratory of University College, Dublin. IR spectra (Table 2) were recorded on Perkin Elmer 1710 and 1720 FTIR spectrometers, and NMR spectra (Table 3) on a JEOL JNM-GX270 spectrometer.

3. Results and discussion

The complex $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})_2]$ undergoes CO substitution by phosphines under relatively mild thermal conditions [1]. The corresponding reactions of various $[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ derivatives occur much less readily. This implies that *trans*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})_2]$ is more labile than the *cis* isomer, but this is not the whole answer as the nature of A-B is important. When it is $\text{CH}_2\text{C(O)}$, $\text{CH}=\text{C(NMe}_2\text{)}$ or $R,S\text{-CH(NMe}_2\text{)CH(NMe}_2\text{)}$, substitution may be brought about thermally, but not when

it is $R,R/S,S\text{-CH(NMe}_2\text{)CH(NMe}_2\text{)}$, $\text{CH}_2\text{CH(NMe}_2\text{)}$, $\text{CH}_2\text{CH(OH)}$ or CH_2CH_2 . However, when $\text{A-B} = R,R/S,S\text{-CH(NMe}_2\text{)CH(NMe}_2\text{)}$, substitution has been effected photolytically.

The ring-linking group A-B was unaffected in all substitution reactions except those involving $R,S\text{-}[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{CH(NMe}_2\text{)CH(NMe}_2\text{)C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ with $\text{Ph}_2\text{P(CH}_2\text{)}_n\text{PPh}_2$ when $n = 2$ or 3 (see below).

In refluxing di-n-butyl ether, the complexes $[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ where $\text{A-B} = \text{CH}_2\text{C(O)}$ or $R,S\text{-CH(NMe}_2\text{)CH(NMe}_2\text{)}$ react with less bulky phosphines and phosphites, L ($= \text{P(OMe)}_3$, P(OEt)_3 , PMe_3 , PET_3 or PMePh_2 but not PPh_3), to give $[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4\}(\text{CO})(\text{L})(\mu\text{-CO})_2]$. When $\text{A-B} = R,R/S,S\text{-CH(NMe}_2\text{)CH(NMe}_2\text{)}$ similar substitution reactions take place only on simultaneous UV irradiation. A related complex where $\text{L} = \text{P(OPh)}_3$ and $\text{A-B} = \text{CMe}_2\text{CMe}_2$ was also obtained photolytically [2]. More than one CO ligand could not be replaced by L. In contrast, it is possible to prepare $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3\{\text{PPh}_3\}]$ [1] and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2\{\text{P(OMe)}_3\}_2(\mu\text{-CO})_2]$, but the latter is very unstable [7].

TABLE 2. Infrared spectra ($1550\text{--}2200\text{ cm}^{-1}$) of compounds containing P^{III} ligands

Ligand (L)	Absorption bands ^a			
	$\nu(\text{CO})$	$\nu(\text{CO})$	$\nu(\mu\text{-CO})$	$\nu(\mu\text{-CO})$
$R,S\text{-}[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{CH(NMe}_2\text{)CH(NMe}_2\text{)C}_5\text{H}_4\}(\text{CO})(\text{L})(\mu\text{-CO})_2]$				
P(OMe)_3	1966 (9.4)		1780 (0.9)	1747 (10)
P(OEt)_3	1965 (9.8)		1779 (1.1)	1746 (10)
PMe_3	1941 (9.7)		1775 (0.9)	1744 (10)
PET_3	1936 (8.3)		1775 (0.8)	1743 (10)*
PMePh_2	1962 (3.6)	1944 (9.3)	1771 (0.8)	1742 (10)
$R,R/S,S\text{-}[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{CH(NMe}_2\text{)CH(NMe}_2\text{)C}_5\text{H}_4\}(\text{CO})(\text{L})(\mu\text{-CO})_2]$				
P(OMe)_3	1967 (9.4)			1748 (10)
PMe_3	1938 (8.2)			1748 (10)
PET_3	1936 (9)			1744 (10)
PMePh_2	1962 (3)	1945 (10)		1742 (10)
$[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{CH}_2\text{C(O)C}_5\text{H}_4\}(\text{CO})(\text{L})(\mu\text{-CO})_2]$				
P(OEt)_3	1972 (10)			1758 (10)
$R,S\text{-}[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{CH(NMe}_2\text{)CH(NMe}_2\text{)C}_5\text{H}_4\}(\text{L})(\mu\text{-CO})_2]$				
DPPM			1729 (1.2)	1692 (10)
DPPE			1728 (1.2)	1688 (10)
$R,R/S,S\text{-}[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{CH(NMe}_2\text{)CH(NMe}_2\text{)C}_5\text{H}_4\}(\text{L})(\mu\text{-CO})_2]$				
DPPM			1732 (0.8)	1691 (10)
DPPE			1727 (0.9)	1690 (10)
DPPP			1722 (1.1)	1685 (10)
$[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{CH}_2\text{C(O)C}_5\text{H}_4\}(\text{L})(\mu\text{-CO})_2]$				
DPPE			1740 (2)	1701 (10)
DPPP			1737 (1)	1698 (10)
$[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{CHC(NMe}_2\text{)C}_5\text{H}_4\}(\text{L})(\mu\text{-CO})_2]$				
DPPE			1737 (0.7)	1699 (10)

^a Peak positions in cm^{-1} with relative peak heights in parentheses. All spectra were run in hexane solution.

TABLE 3. ^1H NMR spectra of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_4\text{-A-B-C}_5\text{H}_4(\text{CO})_3(\text{L})]$ (L = tertiary phosphine), $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_4\text{-A-B-C}_5\text{H}_4(\text{CO})_2(\text{L})]$ (L = $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$), and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{L})]$ complexes (L = $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$) measured in CDCl_3 solution at 293 K

L	Resonances ^a				P ^{III} ligand
	C ₅ H ₄ ^b	H-CNMe ₂	NMe ₂		
A-B = R,S-CH(NMe ₂)CH(NMe ₂)					
P(OMe) ₃	5.14 (1), 5.10 (1), 4.98 (2), 4.79 (3), 4.70 (1)	3.16 (2)	2.23 (12)	3.57 (d, 9, J(PMe) = 11.2)	
P(OEt) ₃	5.12 (1), 5.09 (1), 4.98 (1), 4.92 (1), 4.86 (1), 4.77 (2), 4.64 (1)	3.16 (2)	2.23 (12)	CH ₂ 3.98 (m, 6); CH ₃ 1.19 (t, 9, J(HH) = 7.1)	
PMe ₃ ^c	5.08 (1), 5.05 (1), 4.99 (1), 4.92 (2), 4.73 (1), 4.7 (1), 4.54 (1)	3.13 (d, 1), 3.16 (d, 1) (J(HH) = 3.1)	2.23 (6) 2.23 (6)	1.0 (d, 9, J(PMe) = 9.16)	
PMe ₃ ^d	5.23 (1), 5.15 (1), 5.10 (1), 5.00 (1), 4.90 (1), 4.81 (1), 4.70 (1), 4.55 (1)	3.18 (0.5, br), 3.07 (br, 1) 2.98 (br, 0.5)	2.19 (6, br) 2.22 (6)	1.02 (d, 9, J(PMe) = 9.17)	
PEt ₃	5.10 (2), 5.03 (1), 4.97 (1), 4.89 (1), 4.80 (1), 4.77 (1), 4.63 (1)	3.13 (d, 1), 3.15 (d, 1) (J(HH) = 2.9)	2.22 (12)	CH ₂ 1.28 (m, 6); Me 1.03 (m, 9, J(PMe) = 14.3, J(HH) = 7.5)	
PMePh ₂	5.09 (2), 4.99 (1), 4.92 (2), 4.45 (1), 3.90 (1)	3.23 (2)	2.22 (6)	Ph 7.3-7.6 (m, 10)	
Ph ₂ PCH ₂ PPh ₂	5.06 (2), 4.70 (2), 4.64 (2), 3.86 (2)	3.35 (2)	2.23 (6)	CH ₃ 1.46 (d, 3, J(PMe) = 9)	
Ph ₂ P(CH ₂) ₂ PPh ₂	4.94 (2), 4.63 (2), 4.12 (br, 2), 3.88 (br, 2)	3.37 (2)	2.28 (12)	Ph 7.21-7.36 (m, 20); CH ₂ 1.88 (m, 1) 1.68 (m, 1)	
A-B = R,R / S,S-CH(NMe ₂)CH(NMe ₂)				(J(PH) = 9.9, J(HH) 14.5)	
P(OMe) ₃	5.13 (1), 5.10 (1), 4.92 (1), 4.80 (1), 4.70 (2), 4.63 (1), 4.52 (1)	2.98 (d, 1), 3.03 (d, 1) (J(HH) = 11.6 Hz)	2.22 (12)	Ph 7.65 (8), 7.39 (12); CH ₂ 1.40 (m, br, 4)	
P(Me) ₃	5.09 (1), 5.07 (1), 4.75 (1), 4.71 (1), 4.67 (1), 4.65 (1), 4.60 (1), 4.50 (1)	2.99 (2)	1.99 (6)		
P(Et) ₃	5.10 (1), 5.07 (1), 4.76 (1), 4.70 (2), 4.66 (1), 4.64 (1), 4.51 (1)	2.96 (2)	1.96 (6) 1.98 (6)		
PMePh ₂ ^c	5.00 (2), 4.83 (2), 4.72 (9), 4.54 (1), 4.52 (1), 4.39 (1)	2.95 (d, 1), 3.11 (d, 1) (J(HH) = 11.7)	1.95 (6) 1.90 (6)	CH ₂ 1.27 (m, 6) Me 1.04 (m, 9, J(PMe) = 14.5, J(HH) = 7.7) Ph 7.20-7.62 (m, 10)	

PMePh_2^d	5.07 (1), 5.03 (1), 4.99 (1), 4.91 (1), 4.80 (1), 4.63 (1), 4.42 (1), 3.86 (1)	2.97 (d, 1), 3.18 (d, 1) ($J(\text{HH}) = 11.8$)	2.14 (br, 3) 1.58 (br, 3) 1.91 (br, 6) 2.03 (12)	Ph 7.38–7.43 (br, 10) Me 1.59 (d, 3, $J(\text{PMe}) = 8.6$)
$\text{Ph}_2\text{PCH}_2\text{PPh}_2$	4.62 (2), 4.53 (2), 4.46 (2), 4.10 (2)	3.17 (2)		7.20–7.68 (m, 20); CH_2 1.72 (t, 2, $J(\text{PH}) = 9.9$)
$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2^e$	4.88 (2), 4.56 (2), 4.51 (2), 3.20 (2)	3.04 (2)	1.90 (12)	Ph 6.91 (6), 7.20 (2), 7.34 (8), 8.13 (4); CH_2 1.34 (m, br, 4)
$\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$	3.01 (2), 4.43 (2), 4.50 (2), 4.90 (2)	3.01 (2)	1.89 (12)	Ph 7.06–7.25 (m, 20); CH_2 1.33 (br, 4), 0.70 (br, 2)
$\text{A-B} = \text{CH}_2\text{C}(\text{O})\text{P}(\text{OEt})_3$	5.24 (2), 5.10 (2), 5.04 (2), 4.94 (2)	CH_2 2.94 (2)		CH_2 3.97 (m, 6)
$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$	5.22 (2), 4.85 (2), 4.14 (2), 3.84 (2)	CH_2 2.87 (2)		CH_3 1.20 (t, 9, $J(\text{HH}) = 7.1$) Ph 7.63 (br, 8), 7.43 (br, 12)
$\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2^e$	4.82 (2), 4.63 (2), 4.47 (br, 2), 3.71 (br, 2)	CH_2 2.81 (2)		CH_2 1.40 (m, 4) Ph 7.66 (br, 8), 7.41 (br, 12); CH_2 1.43 (m, 4), 0.8 (m, 2)
$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{L})]$ $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2^f$	$\text{C}_5\text{H}_5 = 4.11$ (10)			Ph 7.65 (br, 8), 7.39 (br, 12); CH_2 1.31 (d, 4, $J(\text{PH}) = 11.9$) Ph 8.03 (br, 4), 7.57 (br, 6) 7.29 (br, 6), 7.17 (br, 4)
$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2^g$	$\text{C}_5\text{H}_5 = 4.11$ (10)			CH_2 1.67 (m, br, 2), 0.92 (m, br, 2) Ph 7.62 (br, 8), 7.36 (br, 12);
$\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2^f$	$\text{C}_5\text{H}_5 = 4.10$ (10)			CH_2 1.35 (m, 4), 0.71 (m, 2)
$\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2^h$	$\text{C}_5\text{H}_5 = 4.10$ (10)			Ph 8.96 (t, 2), 7.91 (t, 2), 7.79 (t, 2), 7.50 (q, 4), 7.26 (t, 4), 7.08 (t, 2), 6.96 (t, 2), 6.54 (t, 2); CH_2 1.35 (m, 4), 0.81 and 0.68 (br, 2)

^a Chemical shifts measured as ppm downfield from Me_4Si as an internal standard with integrations in parentheses. All resonances are singlets unless it is stated otherwise. d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants J quoted in Hz. ^b All C_5H_5 resonances are multiplets and C_5H_5 are singlets. ^c Spectrum run in CD_2Cl_2 solution at 298 K. ^d Spectrum run in CD_2Cl_2 solution at 188 K. ^e Spectrum run in $\text{CD}_3\text{C}_6\text{D}_5$ solution at 273 K. ^f Spectrum run in $\text{CD}_2\text{Cl}_2/\text{CS}_2$ (1:1) solution at 303 K. ^g Spectrum run in $\text{CD}_2\text{Cl}_2/\text{CS}_2$ (1:1) solution at 183 K.

The photolytic reactions of $R,R/S,S\text{-}[\text{Fe}_2(\eta,\eta\text{-C}_5\text{H}_4\text{CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2)\text{C}_5\text{H}_4)(\text{CO})_2(\mu\text{-CO})_2]$ with $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1, 2$ or 3) were shown by IR spectroscopy to proceed via $[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4\}(\text{CO})(\text{L})(\mu\text{-CO})_2]$ intermediates, presumably containing η^1 -diphosphine ligands. The concentration of these species is never high, and they disappear before the end of the reaction to leave $R,R/S,S\text{-}[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2)\text{C}_5\text{H}_4\}(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-CO})_2]$ as the sole products. In contrast, the thermal reactions of $R,S\text{-}[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2)\text{C}_5\text{H}_5\}(\text{CO})_2(\mu\text{-CO})_2]$ with $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ are more complicated. They also proceed via $[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4\}(\text{CO})(\text{L})(\mu\text{-CO})_2]$ intermediates but the final products depend on n . When $n = 1$, only $R,S\text{-}[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2)\text{C}_5\text{H}_4\}(\text{Ph}_2\text{P}(\text{CH}_2)_1\text{PPh}_2)(\mu\text{-CO})_2]$ was obtained. However, when $n = 2$ a second product was also formed, $[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{CH}(\text{NMe}_2)\text{C}_5\text{H}_4\}(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)(\mu\text{-CO})_2]$, which is the more important of the two when $n = 3$. Their ratio goes from 100:0 when $n = 1$, to *ca.* 60:40 when $n = 2$ and *ca.* <5: >95 when $n = 3$. As these compounds had to be separated by chromatography, the second products were not isolated as such but as $[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{CH}_2\text{C}(\text{O})\text{-C}_5\text{H}_4\}(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-CO})_2]$ (*cf.* ref. 6). However, they were identified by comparison of their spectra with those of authentic samples.

The conversion of $\text{A-B} = R,S\text{-CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2)$ to $\text{CH}=\text{C}(\text{NMe}_2)$ is a Me_2NH elimination reaction which has been achieved more formally by methylation followed by treatment of the salt with base, *i.e.* $\text{A-B} = R,S\text{-CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2) \rightarrow R,S\text{-CH}(\text{NMe}_2)\text{CH}(\text{NMe}_3)^+ + \text{OH}^- \rightarrow \text{CH}=\text{C}(\text{NMe}_2)$ [6]. However, in the present case there are no obvious electrophiles or strong bases, and the reaction appears to have no counterpart in conventional organic chemistry. It does not take place when solutions of $R,S\text{-}[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2)\text{C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ or $R,S\text{-}[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2)\text{C}_5\text{H}_4\}(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)(\mu\text{-CO})_2]$ in di-*n*-butyl ether are with refluxed with or without UV irradiation in the presence or absence of added water and, in the latter case, added $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$. The product dependence on the length of the $(\text{CH}_2)_n$ chain is puzzling, but it may indicate that the $\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ intermediate is the reactive species and that the uncoordinated P atom plays a role.

Both $[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ where $\text{A-B} = \text{CHC}(\text{NMe}_2)$ and $\text{CH}_2\text{C}(\text{O})$ react with $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ in refluxing di-*n*-butyl ether to give $[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4\}(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)(\mu\text{-CO})_2]$.

3.1. Infrared spectra

The positions of the absorption bands due to $\nu(\text{CO})$ vibrations of the metal carbonyl ligands are summarized in Table 2. In general their relative intensities and frequencies are what would be expected by comparison with their counterparts derived from *cis*- $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$. The spectra of complexes where $\text{A-B} = \text{CH}_2\text{C}(\text{O})$ all show an absorption band of medium intensity at *ca.* 1680 cm^{-1} due to the ketone $\nu(\text{CO})$ vibration.

In solution, the spectra of $[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4\}(\text{CO})(\text{L})(\mu\text{-CO})_2]$ where $\text{A-B} = R,S$ and $R,R/S,S\text{-CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2)$ and $\text{L} = \text{PR}_3$ ($\text{R} = \text{Me, Et, OMe or OEt}$) show a single $\nu(\text{t-CO})$ absorption band, and two bands, one weak and one strong, due to their symmetric and antisymmetric $\nu(\mu\text{-CO})$ vibrations, respectively. In the solids the spectra are similar but often more complex due to solid state effects. In contrast, when $\text{L} = \text{PMePh}_2$ the solution spectra show two unequal $\nu(\text{t-CO})$ bands, and the more intense $\nu(\mu\text{-CO})$ band is very asymmetric. This behaviour may be due to the presence of isomers arising from restricted rotation about the Fe-P bond, similar to that observed for $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{L})\text{I}]$, $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{L}]$ and related mononuclear compounds [8]. It is the first time that it has been reported for dinuclear complexes, and it is surprising that the effect on the $\mu\text{-CO}$ ligands is much less than that on the t-CO ligand coordinated to the other Fe atom (but see below).

In general terms the replacement of one and then both t-CO groups in the $[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ complexes by P^{III} ligands results in greater back-bonding to the remaining CO ligands and $\nu(\text{CO})$ frequencies which all decrease on each substitution. However, the true situation may not be so simple. Comparison of the spectra of $[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4\}(\text{CO})(\text{L})(\mu\text{-CO})_2]$ for $\text{L} = \text{P}(\text{OMe})_3$ with those for $\text{L} = \text{PET}_3$ show that whereas the $\nu(\text{t-CO})$ frequencies decrease by *ca.* 30 cm^{-1} , the $\nu(\mu\text{-CO})$ decrease by only *ca.* 5 cm^{-1} (Table 2). This strongly implies that the increased electron density on one Fe atom on going from $\text{L} = \text{P}(\text{OMe})_3$ to $\text{L} = \text{PET}_3$ is removed largely by the t-CO group coordinated to the other metal atom rather than the two shared $\mu\text{-CO}$ ligands.

3.2. ^1H NMR spectra and fluxionality

The spectra are summarized in Table 3. They are readily assigned by comparison with those of related systems. The cyclopentadienyl resonances have not been assigned to specific protons. There is no evidence of coupling of ^{31}P to the protons of A-B, although

there may be such coupling to some of the cyclopentadienyl protons. This was not investigated further.

Many of the spectra are temperature-dependent owing to various fluxional processes within the $\text{C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4$ and $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ligands. The first of these are similar to those observed in the $[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4\}(\text{CO})_4]$ precursors [6]. Thus, the C-C(O)-C_5 moiety is planar in $[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{-CH}_2\text{C(O)C}_5\text{H}_4\}(\text{CO})_4]$ and the two CH_2 protons are inequivalent, but they interchange rapidly on the NMR time scale even at low temperatures. When $\text{A-B} = \text{R,S-CH(NMe}_2\text{)CH(NMe}_2\text{)}$, the two $\text{CH(NMe}_2\text{)-C}_5\text{H}_4$ moieties are inequivalent, and appear so in solution at low temperature, but on warming, a partial rotation about the ring-linking C-C bond results in rapid exchanges; furthermore the two different NMe_2 groups undergo rapid rotation-inversion processes, which render their methyl groups equivalent at room temperature, but in some instances these may be slowed on cooling. In contrast, when $\text{A-B} = \text{R,R/S,S-CH(NMe}_2\text{)CH(NMe}_2\text{)}$, the two $\text{CH(NMe}_2\text{)C}_5\text{H}_4$ moieties are equivalent, and there is no partial rotation about the C-C bond which could result in interchange H and NMe_2 groups; the rotation-inversion of the NMe_2 groups may be slowed in some cases. Where activation energies ΔG_{T_c} for these processes have been calculated from coalescence temperatures T_c [9], they are close to the values obtained for the $[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4\}(\text{CO})_2(\mu\text{-CO})_2]$ precursors [6]. ($\Delta G_{T_c} = \text{ca. } 10.6 \text{ kcal mol}^{-1}$ for the restricted rotation about the ring-linking C-C bond when A-B is $\text{R,S-CH(NMe}_2\text{)CH(NMe}_2\text{)}$ and $\text{ca. } 9 \text{ kcal mol}^{-1}$ for rotation-inversion of the NMe_2 groups in both this and its R,R/S,S isomer.)

Another effect of A-B may be the lowering of the overall molecular symmetry compared with that for $\text{cis-}[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})_2]$. Thus when $\text{A-B} = \text{CH}_2\text{C(O)}$ the two terminal sites are always inequivalent but the bridging sites are equivalent even at low temperatures (two isomers of $[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{-CH}_2\text{C(O)C}_5\text{H}_4\}(\text{CO})\{\text{P(OEt)}_3\}(\mu\text{-CO})_2]$ are possible, but only one appears to be formed (Table 3)); when $\text{A-B} = \text{R,S-CH(NMe}_2\text{)CH(NMe}_2\text{)}$, the two bridging sites are always inequivalent but the terminal sites are equivalent until the partial rotation about the C-C bond slows, when they become inequivalent; and when $\text{A-B} = \text{R,R/S,S-CH(NMe}_2\text{)CH(NMe}_2\text{)}$, both terminal and bridging sites are equivalent but the molecule does not possess a plane of symmetry. The ^1H NMR signals from the phosphine ligands are also affected in more subtle ways, as the presence of chiral carbon atoms in A-B leads to inequivalent protons of the CH_2 groups of P(OEt)_3 and $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ligands. It was to by-pass these problems that we studied first the ^1H

NMR spectra of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-CO})_2]$ ($n = 2$ or 3), which are easier to interpret. Both of these complexes show a single C_5H_5 resonance at all temperatures down to 183 K, indicating that the two $\text{Fe}(\text{C}_5\text{H}_5)\text{PPh}_2$ moieties remain indistinguishable. When $n = 2$, the CH_2 doublet splits on cooling into two multiplets, as do each of the two broad Ph resonances. This appears to be due to a slowing of a conformational change in the Fe-P-C-C-P-Fe ring, which interchanges and renders equivalent, the CH_2 protons and the two Ph groups on each of the equivalent Ph_2PCH_2 moieties. However, there are two possible arrangements of the P-C-C-P chain with respect to the Fe-Fe bond. In one, both of the CH_2 groups lie on the same side of the Fe_2P_2 plane, and in the other, these groups lie on opposite sides. The available evidence suggests that only one arrangement is present in the case under consideration, but does not define which, although we favour the second since this would have a cisoid staggered arrangement of the two CH_2P moieties. When $n = 3$, similar processes appear to take place. The changes in the CH_2 resonances are not so clear. Although the broad resonance due to the central group splits into a broad doublet on cooling, the broad multiplet due to the terminal methylenes becomes broader and less well-defined. On the other hand, the two broad Ph resonances change to a total of eight well-defined resonances showing detailed $^1\text{H-}^1\text{H}$ coupling. Perhaps the rotation of the Ph groups is slowed also, but it is not clear why this does not happen when $n = 2$. The values obtained for ΔG_{T_c} (Table 4) are similar ($\text{ca. } 11.5 \text{ kcal mol}^{-1}$) in both compounds. This suggests that their most important components are due to the barriers to restricted rotation about the Fe-P bond arising from the relatively bulky phenyl groups rather than to restricted rotations within the $\text{P}(\text{CH}_2)_n\text{P}$ chains.

The ^1H NMR spectra of the $[\text{Fe}_2\{\eta,\eta\text{-C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4\}(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-CO})_2]$ derivatives ($n = 2$ or 3) also vary with temperature, indicating that conformational changes within the $\text{Fe-Fe-P}(\text{CH}_2)_n\text{P}$ ring and, perhaps, rotation of the phenyl groups can be slowed. However, these spectra are not amenable to

TABLE 4. Energies of activation ΔG_{T_c} and coalescence temperatures T_c for fluxional processes within the $\text{Fe-P-(CH}_2\text{)}_n\text{-P-Fe}$ moieties of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-CO})_2]$ complexes

n	Resonance	T_c (K)	ΔG_{T_c} (kcal mol^{-1})
1	CH_2	237	11.9
1	Ph	253	11.3
2	CH_2	245	11.3
2	Ph	240	11.5
2	Ph	248	11.4

detailed interpretation owing to the lowered molecular symmetry and fluxional processes within the $\text{C}_5\text{H}_4\text{-A-B-C}_5\text{H}_4$ ligands, as mentioned above. At lower temperatures there are often a plethora of weak, overlapping resonances, and the problem is further complicated by sample solubility.

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