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Synthesis of dibridged diphosphine metal carbonyl complexes and related phosphine transfer reactions

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Abstract

A series of dibridged diphosphine metal complexes of general formula $[5,5'\text{-dppx}^1\text{-}\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}(\mu\text{-dppx}^2)][BF_4]_2$ (x^1, $x^2 = $ p, p (IX); x^1, $x^2 = $ b, b (X); x^1, $x^2 = $ n, n (XI); x^1, $x^2 = $ h, h (XII); $x^1 = $ p, $x^2 = $ b (XIII); $x^1 = $ b, $x^2 = $ n (XIV); $x^1 = $ n, $x^2 = $ h (XV)) containing both metal–metal and ring–ring diphosphine bridges are reported. In the course of the synthetic studies, phosphine transfer reactions (both mono and diphosphine) were observed between a metal bonded phosphine and a sufficiently electrophilic metal carbonyl cation. Phosphine transfer also occurs when normal hydride abstraction reactions are attempted with only stoichiometric amounts of $[Ph_3C][BF_4]$. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carbonyl; Dibridged; Dinuclear; Diphosphine; Iron; Oligomer; Phosphine transfer

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1. Introduction

The coordination of cyclic π-hydrocarbons to transition metals generally results in activation of the ring to nucleophilic addition to produce a monofunctionalized π-hydrocarbon [1–3]. In the case of addition of phosphines, both mechanistic and synthetic studies have been reviewed [4]. For example, the tricarbonyl(η-1,5-cyclohexadienylium) iron cation reacts with monophosphines, PR_3 (R = *n*-Bu, Ph), to form the 5-*exo* ring adduct $[(\eta^4\text{-}C_6H_7\text{-}5\text{-}exo\text{-}PR_3)Fe(CO)_3]BF_4$ via a bimolecular process [4]. In contrast, diphosphines such as $PPh_2(CH_2)_iPPh_2$ (dppx; x = p, *i* = 3; x = b, *i* = 4; x = n, *i* = 5; x = h, *i* = 6) generally bond to the metal atoms of metal carbonyl complexes forming three main types of substituted complexes: (a) monosubstituted e.g. $[(\eta^7\text{-}C_7H_7)Mo(CO)_2(\eta^1\text{-diphosphine})]^+$; (b) chelated complexes, e.g. $[(\eta^7\text{-}C_7H_7)Mo(CO)(\eta^2\text{-diphosphine})]^+$ and (c) binuclear complexes in which the diphosphine bridges the metal atoms, e.g. $[\{(\eta^7\text{-}C_7H_7)Mo(CO)_2\}_2\text{-}(\mu\text{-diphosphine})][PF_6]_2$ [5,6].

However, in the past few years, we have shown that diphosphines can form a series of complexes with a variety of different bridging modes, ring–ring, metal–ring as well as metal–metal [7–9]. Thus the diphosphine ring–ring bridged dimers, $[5,5'\text{-}exo\text{-}PPh_2(CH_2)_iPPh_2\text{-}\{(\eta^4\text{-}C_xH_y)Fe(CO)_3\}_2][BF_4]_2$ ($i = 2$–6; $x = 6$, $y = 7$; $x = 7$, $y = 9$) have been reported [7], and the presence of the ring–ring bridge was confirmed in a crystal structure determination of the analogous $[5,5'\text{-}exo\text{-}PPh_2(CH_2)_3PPh_2\text{-}\{(\eta^6\text{-}C_7H_7)Cr(CO)_3\}_2][BF_4]_2$ [8]. A series of binuclear complexes containing metal–ring diphosphine bridges have also been reported, with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}\{PPh_2(CH_2)_3PPh_2\text{-}(\eta^6\text{-}C_7H_7)Cr(CO)_3\}][BF_4]_2$ as a typical example [9]. In view of the above proven ability of diphosphines to form various types of bridges (metal–metal, metal–ring, ring–ring), it was of interest to attempt the synthesis of polynuclear complexes containing two diphosphine bridges of different types, e.g. metal–metal and ring–ring and to investigate their properties.

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A series of complexes of general formula [5,5′-dppx^1-{(η^4-C_6H_7)Fe(CO)$_2$}$_2$-(μ-dppx^2)][BF$_4$]$_2$ (x^1, x^2 = p, p (IX); x^1, x^2 = b, b (X); x^1, x^2 = n, n (XI); x^1, x^2 = h, h (XII); x^1 = p, x^2 = b (XIII); x^1 = b, x^2 = n (XIV); x^1 = n, x^2 = h (XV)), containing both metal–metal and ring–ring diphosphine bridges, have been obtained as described below. However, during these studies it was noted that organometallic cations such as [(η^5-C_6H_7)Fe(CO)$_2$L]BF$_4$ (L = CO, PPh$_3$, P(OPh)$_3$, PPh$_2$Me, PMe$_3$) not only react with free monophosphines, PR$_3$, to give the well established ring adducts [(η^4-C_6H_7-5-*exo*-PR$_3$)Fe(CO)$_2$L]BF$_4$, but are sufficiently electrophilic to react with metal bonded monophosphines to give the same products as those formed with free monophosphines, albeit at a much slower rate. In other words, a phosphine transfer reaction occurs from the metal bonded phosphine complex to the electrophilic cation. Similar transfer reactions also occur with diphosphines as discussed below. Interestingly, phosphine transfer reaction also occurs with sufficiently electrophilic cations, containing metal–phosphine entities, when normal hydride abstraction reactions are attempted with the customary hydride abstraction reagent [Ph$_3$C][BF$_4$] present in only stoichiometric amounts.

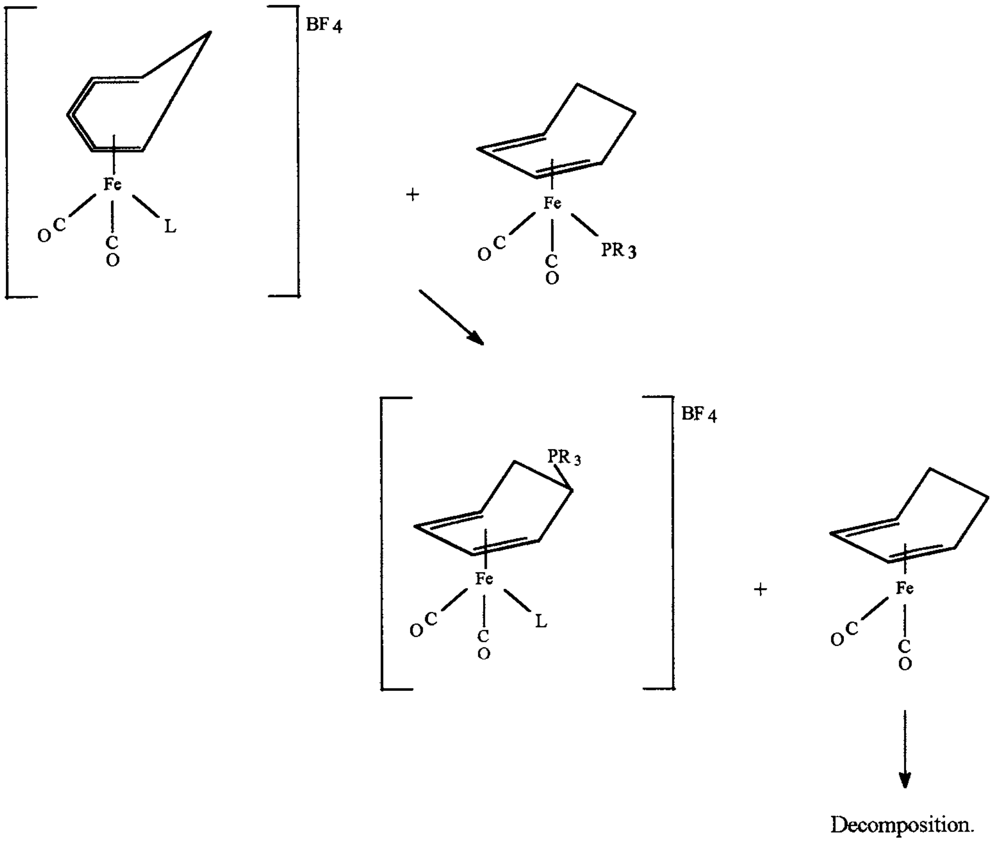
2. Results and discussion

2.1. Phosphine transfer reactions induced by [Ph$_3$C][BF$_4$]

Hydride abstraction from a diene metal carbonyl complex by [Ph$_3$C][BF$_4$] is a ubiquitous reaction, dating from the early observation of the formation of tropylium metal complexes from the corresponding cycloheptatriene complexes [10]. Similarly, the complexes (η^4-C_6H_8)Fe(CO)$_2$L (L = CO, PPh$_3$, PPh$_2$Me, PPhMe$_2$, PMe$_3$) react with excess [Ph$_3$C][BF$_4$] to form [(η^5-C_6H_7)Fe(CO)$_2$L][BF$_4$] [11]. However, when (η^4-C_6H_8)Fe(CO)$_2$PPh$_2$Me, for example, was reacted with only a stoichiometric amount of [Ph$_3$C][BF$_4$], in dichloromethane at room temperature, after about 30 min not only were the IR carbonyl stretching frequencies of the above complex observed—at 1964 and 1904 cm^{-1}, together with bands at 2042 and 2000 cm^{-1} due to the expected hydride abstraction product [(η^5-C_6H_7)Fe(CO)$_2$PPh$_2$Me][BF$_4$]—but in addition new bands occurred at 1986 and 1930 cm^{-1} which were assigned to the ring adduct [(η-C_6H_7-5-*exo*-PPh$_2$Me)Fe(CO)$_2$PPh$_2$Me][BF$_4$], although the reaction mixture contained no free PPh$_2$Me. Overnight reaction resulted in a mixture of the expected hydride abstraction product, [(η^5-C_6H_7)Fe(CO)$_2$PPh$_2$Me][BF$_4$] together with the ring adduct [(η^4-C_6H_7-5-*exo*-PPh$_2$Me)Fe(CO)$_2$-PPh$_2$Me][BF$_4$], with IR carbonyl stretching frequencies at 2042, 2000, 1986 and 1930 cm^{-1}. We suggest that, although there is no free phosphine present, formation of the above phosphine ring adduct occurs by initial formation of the 'normal' hydride abstraction product, [(η^5-C_6H_7)Fe(CO)$_2$PPh$_2$Me][BF$_4$], in which the ring is sufficiently electrophilic to attack the Fe–P bond of unreacted substrate (η^4-C_6H_8)Fe(CO)$_2$PPh$_2$Me with formation of the ring adduct, Scheme 1. This mechanism was confirmed by direct reaction between [(η^5-C_6H_7)Fe(CO)$_2$PPh$_2$Me][BF$_4$] and (η^4-C_6H_8)Fe(CO)$_2$-PPh$_2$Me in acetonitrile at room temperature, which gave the ring adduct [(η^4-C_6H_7-5-*exo*-PPh$_2$Me)Fe(CO)$_2$PPh$_2$Me][BF$_4$] (see below and Table 1).

2.2. Phosphine transfer reactions in the absence of [Ph$_3$C][BF$_4$]

The above reaction in which monophosphine transfer occurs from a metal bonded monophosphine to a sufficiently electropositive metal carbonyl cation, is a general reaction. This was confirmed by reacting a series of cations [(η^5-C_6H_7)Fe(CO)$_2$L][BF$_4$] (L = CO, PPh$_3$, PPh$_2$Me, P(OPh$_3$), PMe$_3$) with a series of neutral ring hydride adducts, (η^4-C_6H_8)Fe(CO)$_2$L′ (L′ = PPh$_3$, PPh$_2$Me, PMe$_3$) in the absence of [Ph$_3$C][BF$_4$]. In all cases, [(η^4-C_6H_7-5-*exo*-L)Fe(CO)$_2$L′][BF$_4$] was obtained and characterised by analytical, infrared and ^{31}P-NMR spectroscopy (see supplementary material). The rate of the above phosphine transfer reaction was always much slower than the corresponding direct reaction between [(η^5-C_6H_7)Fe(CO)$_2$L][BF$_4$] and L′ (see Table 1) although, of course, the final ring adducts are confirmed as identical by analytical and spectroscopic data (see supplementary material and experimental section for a typical pair of reactions). Although kinetic studies of the phosphine transfer reactions were not possible because of accompanying decomposition, an approximate estimate of comparative rates of reaction was obtained by noting the time at which the infrared carbonyl stretching frequencies of both reagents had been replaced by those of the phosphonium ring adduct (see Table 1). A number of general conclusions emerge. As expected, the reactions with free ligand L′ are much faster than with the corresponding Fe–L′ complex, so clearly the strength of the Fe–L′ bond is a factor. Also, the ring electrophilicity of the cation is involved since reactions between weaker electrophiles e.g. [(η^5-C_6H_7)Fe(CO)$_2$PMe$_3$][BF$_4$] and the neutral series are measurably slower than those with stronger electrophiles e.g. [(η-C_6H_7)Fe(CO)$_2$PPh$_3$][BF$_4$] (see Table 1). These qualitative comparisons suggest an associative transition state for the phosphine transfer reaction involving both C–P bond formation and Fe–P bond breaking.



Scheme 1. Monophosphine transfer.

2.3. Diphosphine transfer reactions induced by [Ph$_3$C][BF$_4$]

In a reaction similar to that in Section 2.1 above, it was found that treatment of the neutral metal–metal diphosphine mono-bridged complexes $\{(\eta^4\text{-C}_6\text{H}_8)\text{Fe(CO)}_2\}_2$-($\mu$-dppx) (dppx = PPh$_2$(CH$_2$)$_iPPh_2$; x = p, $i = 3$ (I); x = b, $i = 4$ (II); x = n, $i = 5$ (III); x = h, $i = 6$ (IV)) with stoichiometric amounts of [Ph$_3$C][BF$_4$] gave a series of dibridged diphosphine complexes [5,5′-dppx^1-$\{(\eta^4\text{-C}_6\text{H}_8)\text{Fe(CO)}_2\}_2$-($\mu$-dppx^2)][BF$_4$]$_2$ (x^1, x^2 = p, p (IX); x^1, x^2 = b, b (X); x^1, x^2 = n, n (XI); x^1, x^2 = h, h (XII); x^1, x^2 = p, b (XIII); x^1, x^2 = b, n (XIV); x^1, x^2 = n, h (XV)), which were identical with the same series prepared by the synthetic route described below (Section 2.4). As in the case of the analogous monophosphine complexes (Section 2.1), formation of the dibridged diphosphine series occurs by initial formation of the normal hydride abstraction product, [$\{(\eta^5\text{-C}_6\text{H}_7)\text{Fe(CO)}_2\}_2$-($\mu$-dppx)][BF$_4$]$_2$, which is sufficiently electrophilic to attack the Fe–P bonds of unreacted neutral $\{(\eta^4\text{-C}_6\text{H}_8)\text{Fe(CO)}_2\}_2$-($\mu$-dppx), with formation of the dibridged complex, [5,5′-dppx^1-$\{(\eta^4\text{-C}_6\text{H}_8)\text{Fe(CO)}_2\}_2$-($\mu$-dppx^2)][BF$_4$]$_2$. This mechanism was confirmed by monitoring these reactions using infrared spectroscopy in acetonitrile. For example, after 5 min of reaction between $\{(\eta^4\text{-C}_6\text{H}_8)\text{Fe(CO)}_2\}_2$-($\mu$-dppn) (III) and [$\{(\eta^5\text{-C}_6\text{H}_7)\text{Fe(CO)}_2\}_2$-($\mu$-dppn)][BF$_4$]$_2$ (VII), ν(CO) bands of the neutral (III) and cationic (VII) metal–metal dimers, at 1963, 1903, 2044 and 2004 cm^{-1}, respectively, were observed; however, after 10 min, new bands at 1983 and 1923 cm^{-1}, assigned to [5,5′-dppn-$\{(\eta^4\text{-C}_6\text{H}_8)\text{Fe(CO)}_2\}_2$-($\mu$-dppn)][BF$_4$]$_2$ (XI), appeared and after 2 h were the only bands present.

As in the analogous monophosphine transfer reaction (Section 2.2), this mechanism was confirmed by direct reaction between the neutral ((I)–(IV)) and cationic metal–metal dimers ((V)–(VIII)), in the absence of [Ph$_3$C][BF$_4$] and in a 1:1 ratio in dichloromethane, yielding the dibridged series [5,5′-dppx^1-$\{(\eta^4\text{-C}_6\text{H}_7)\text{Fe(CO)}_2\}_2$-($\mu$-dppx^2)][BF$_4$]$_2$ (x^1, x^2 = p, p (IX); x^1, x^2 = b, b (X); x^1, x^2 = n, n (XI); x^1, x^2 = h, h (XII); x^1, x^2 = p, b (XIII); x^1, x^2 = b, n (XIV); x^1, x^2 = n, h (XV)), Scheme 2. The analytical and spectroscopic properties of the complexes prepared by this method were identical with those prepared by the more efficient route described below (see Section 2.4 and Table 2).

2.4. Synthesis of the dibridged diphosphine complexes [5,5′-dppx^1-{(η^4-C_6H_7)Fe(CO)$_2$}$_2$-(μ-dppx^2)][BF$_4$]$_2$ (x^1, x^2 = p, p (IX); x^1, x^2 = b, b (X); x^1, x^2 = n, n (XI);x^1, x^2 = h, h (XII); x^1, x^2 = p, b (XIII); x^1, x^2 = b, n (XIV); x^1, x^2 = n, h (XV))

The synthetic route shown in Scheme 3, involving Steps (a), (b) and (c), was used to prepare the above series of dibridged diphosphine complexes.

Firstly in Step (a), the neutral metal–metal diphosphine linked dimers, {(η^4-C_6H_8)Fe(CO)$_2$}$_2$-(μ-dppx) (x = p, (I); x = b, (II); x = n, (III); x = h, (IV)), were prepared by refluxing (η^4-C_6H_8)Fe(CO)$_3$ and the appropriate diphosphine in a 2:1 ratio in cyclohexanol for ≈ 48 h. The reaction was monitored by infrared spectroscopy and considered complete when the initial ν(CO) carbonyl frequencies at 2042 and 1969 cm^{-1} were replaced by bands at ≈ 1963 and 1903 cm^{-1}, due to {(η^4-C_6H_8)Fe(CO)$_2$}$_2$-(μ-dppx) (x = p, (I); x = b, (II); x = n, (III); x = h, (IV)) which were characterised by microanalysis, ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy. The latter was especially useful with only one region of absorption, at ≈ δ 63.3 ppm, assigned to the metal bonded P atoms, with no high field resonances characteristic of a pendant P atom, thereby excluding any mononuclear products such as (η^4-C_6H_8)Fe(CO)$_2$-(η^1-dppx) (Table 2 and supplementary material).

In step (b), reaction of the above neutral metal–metal diphosphine dimers (I–IV) with excess [Ph$_3$C][BF$_4$] (ratio 1:3), in dichloromethane as solvent, gave good yields of the dicationic metal–metal diphosphine linked dimers [{(η^5-C_6H_7)Fe(CO)$_2$}$_2$-(μ-dppx)][BF$_4$]$_2$ (x = p^1 (V); x = b (VI); x = n (VII); x = h (VIII)) by normal hydride abstraction, in contrast to the diphosphine transfer reaction which occurs when only 1:1 ratios of {(η^4-C_6H_8)Fe(CO)$_2$}$_2$-(μ-dppx) and [Ph$_3$C][BF$_4$] are used (Section 2.3). Again, the reaction can be monitored conveniently by infrared spectroscopy. For example, when the neutral dimer {(η^4-C_6H_8)Fe(CO)$_2$}$_2$-(μ-dppn) (III) was reacted with a 3 M excess of [Ph$_3$C][BF$_4$] in dichloromethane, the ν(CO) stretching frequencies of (III) at 1963 and 1903 cm^{-1} were quickly replaced by bands at 2044 and 1998 cm^{-1} assigned to the dicationic metal–metal dimer [{(η^5-C_6H_7)Fe(CO)$_2$}$_2$-(μ-dppn)][BF$_4$]$_2$ (VII). The dicationic complexes (V)–(VIII) were characterised by microanalysis and ^{1}H, ^{13}C and ^{31}P-NMR spectroscopy (see Table 2).

Table 1
Comparison of relative rates of phosphine transfer to electrophiles from metal bonded and free phosphines, reactions A and B, respectively

L	L′	Reaction Time	
		A[a]	B[b]
CO	PPh$_3$	72 h	5 min
CO	PPh$_2$Me	48 h	5 min
CO	PMe$_3$	48 h	15 min
P(OPh)$_3$	PPh$_3$	48 h	30 min
PPh$_3$	PPh$_3$	48 h	30 min
PPh$_3$	PPh$_2$Me	24 h	5 min
PPh$_3$	PMe$_3$	72 h	5 min
PPh$_2$Me	PPh$_3$	no reaction	90 min
PPh$_2$Me	PPh$_2$Me	48 h	5 min
PPh$_2$Me	Pme$_3$	48 h	5 min
PMe$_3$	PPh$_3$	96 h	[c]
PMe$_3$	PPh$_2$Me	96 h	5 min
PMe$_3$	Pme$_3$	96 h	15 min

[a] Reaction A [(η^5-C_6H_7)Fe(CO)$_2$L]BF$_4$ + (η^4-C_6H_8)Fe(CO)$_2$L′ → [(η^4-C_6H_7-5-L′)Fe(CO)$_2$L]BF$_4$ [b] Reaction B [(η^5-C_6H_7)Fe(CO)$_2$L]BF$_4$ + L′ → [(η^4-C_6H_7-5-L′)Fe(CO)$_2$L]BF$_4$ [c] Does not go to completion.

In the final step, Step (c), the synthesis of the dibridged diphosphine complexes consists of forming the 5-5′ ring–ring diphosphine bridge by reacting [{(η^5-C_6H_7)Fe(CO)$_2$}$_2$-(μ-dppx^2)][BF$_4$]$_2$ (V)–(VIII) in a 1:1 ratio with a free diphosphine ligand, dppx^1. For example, reaction between [{(η^5-C_6H_7)Fe(CO)$_2$}$_2$-(μ-dppb)][BF$_4$]$_2$ (VI) and free dppb, in dichloromethane as solvent, was complete in ≈ 10 min, indicated by the rapid replacement of the ν(CO) stretching frequencies of (VI), at 2043 and 1998 cm^{-1}, by two new bands at 1980 and 1922 cm^{-1}, due to [5,5′-dppb-{(η^4-C_6H_7)Fe(CO)$_2$}$_2$-(μ-dppb)][BF$_4$]$_2$ (X). The rapid formation of the second diphosphine bridge under such mild conditions supports the formation of a ring–ring bridge rather than metal–ring bridges which would involve breaking of the strong metal–metal diphosphine bridge. A series of new dibridged complexes [5,5′-dppx^1-{(η^4-C_6H_7)Fe(CO)$_2$}$_2$-(μ-dppx^2)][BF$_4$]$_2$ (IX–XV) were isolated as yellow solids and characterised by analysis, ^{13}C and ^{31}P spectroscopy (Table 2). In general, the ^{1}H-NMR spectra were broad and featureless (see supplementary material), but there was no evidence for paramagnetic impurities and variable temperature ^{1}H-NMR measurements gave no improvement. The ^{31}P-NMR spectra (Table 2) showed two groups of absorptions, one group around δ 60 ppm and the second around δ 30 ppm; the former group was assigned to metal-bonded P atoms and the latter to ring–carbon bonded P atoms. For example, for [5,5′-dppn-{(η^4-C_6H_7)Fe(CO)$_2$}$_2$-(μ-dppn)][BF$_4$]$_2$ (XI), the ^{31}P-NMR resonances occurred at δ 61.7, 60.4, 60.3, and at δ 30.3, 30.2, 29.6 ppm. The reasons for these multiple peaks are not clear. Coupling between the phosphorus atoms is ruled out by the long chain lengths of the diphosphine bridges. It is possible that the complex spectra may arise from the presence of isomers with different types of bridging modes, e.g. an isomer containing two metal–ring bridges or conformers within the diphosphine ring–ring bridge may be present. However the presence of oligomers cannot be excluded.

In the absence of suitable crystals for X-ray crystal structure determinations, the Electrospray Mass Spec-

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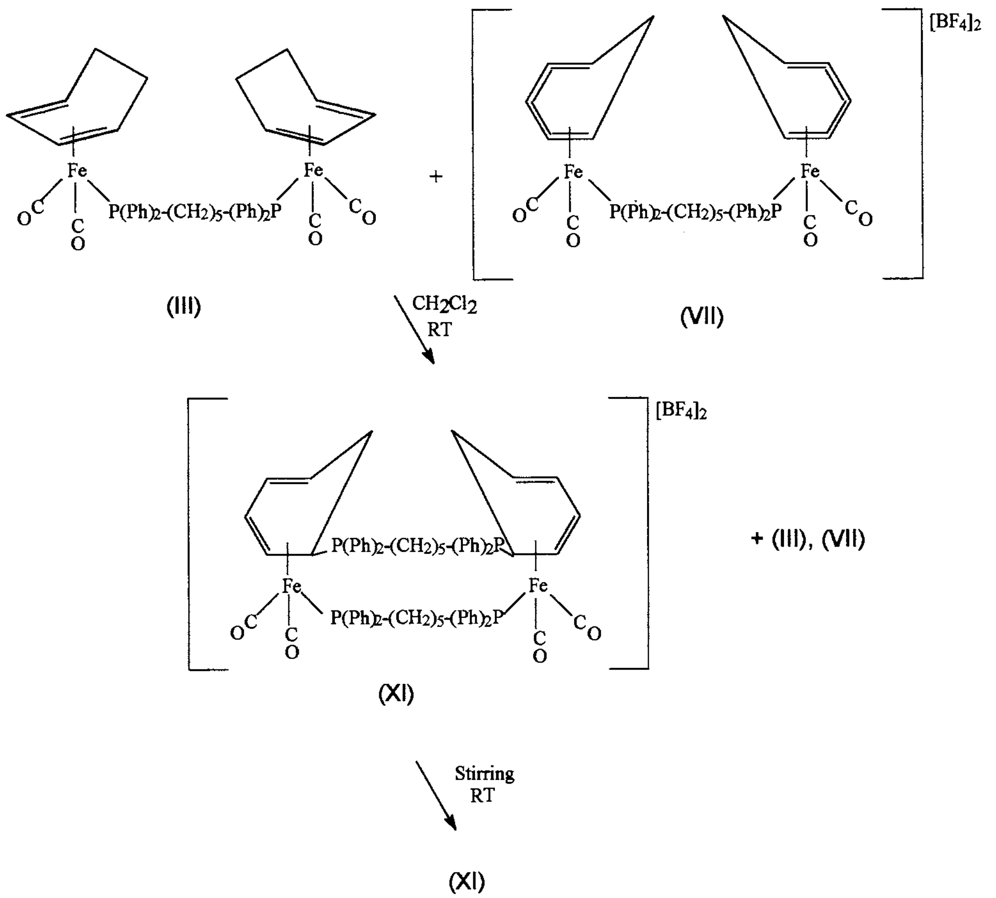
[1] This complex has been prepared before [7].



Scheme 2. Diphosphine transfer.

tra of complexes (X), (XII), (XIII) and (XV) were measured, and confirmed the presence of the dibridged dimer for [5,5′-dppn-{(η^4-C_6H_7)Fe(CO)$_2$}$_2$-(μ-dpph)][BF$_4$]$_2$ (XV), [5,5′-dppb-{(η^4-C_6H_7)Fe(CO)$_2$}$_2$-(μ-dppb)][BF$_4$]$_2$ (X) and [5,5′-dppp-{(η^4-C_6H_7)Fe(CO)$_2$}$_2$-(μ-dppb)][BF$_4$]$_2$ (XIII), with major molecular ion peaks at 1363, 1321 and 1307 Da e^{-1} (*m*/*z*), respectively (Table 3). No peaks of mass higher than the molecular ion were observed, although fragmentation peaks occurred. For example, loss of BF$_4$ and the ring bonded diphosphine ligand from [5,5′-dppp-{(η^4-C_6H_7)Fe(CO)$_2$}$_2$-(μ-dppb)][BF$_4$]$_2$ (X) yielded the fragment [{(η^4-C_6H_7)Fe(CO)$_2$}$_2$-(μ-dppb)]BF$_4$ at 895 Da e^{-1}; loss of (η^4-C_6H_7)Fe(CO)$_2$ and BF$_4$ yielded [{(η^4-C_6H_7)Fe(CO)$_2$}-(η^1-dppb)] at 617 Da e^{-1}; further loss of CO and the cyclohexadienyl ring yielded the fragments [{(η^4-C_6H_7)Fe}-(η^1-dppb)] and [Fe–dppb] at 561 and 482 Da e^{-1}, respectively; whilst the dppb ligand was observed at 426 Da e^{-1}. [5,5′-dppn-{(η^4-C_6H_7)Fe(CO)$_2$}$_2$-(μ-dpph)][BF$_4$]$_2$ (XV) yielded the fragment [{(η^4-C_6H_7)-Fe(CO)$_2$}$_2$-(μ-dpph)]BF$_4$ at 923 Da e^{-1}. The formation of these fragments in which the metal–metal diphosphine bridge is retained and the weaker ring–ring bridge is cleaved provides support for the formulation of this series as dibridged diphosphine complexes containing metal–metal and ring–ring bridges. As outlined in Table 3, a similar fragmentation pattern was observed for (XIII).

However, in contrast, for [5,5′-dpph-{(η^4-C_6H_7)Fe(CO)$_2$}$_2$-(μ-dpph)][BF $_4$]$_2$ (XII), peaks of mass between 1500–3000 Da e^{-1} were obtained. In addition to a molecular ion peak at 1377 Da e^{-1}, assigned to [5,5′-dpph-{(η^4-C_6H_7)Fe(CO)$_2$}$_2$-(μ-dpph)]BF$_4$, and a fragmentation pattern similar to that obtained for the above complexes (X), (XIII), and (XV) (Table 3). The high mass peak at 2840 Da e^{-1} is tentatively assigned to the molecular ion of the tetramer [5,5′-(dpph)$_2$-{(η^4-C_6H_7)Fe(CO)$_2$}$_4$-(μ-dpph)$_2$][BF$_4$]$_4$ (XIIa). The fragmentation pattern of such a tetrameric structure can be described in terms of sequential loss of BF$_4$, (η^4-C_6H_7)Fe(CO)$_2$ or a diphosphine ligand, Table 3. Thus the peak at 2475 Da e^{-1} represents [5-dpph-{(η^4-C_6H_7)Fe(CO)$_2$}$_4$-(μ-dpph)$_2$][BF$_4$]$_4$ (loss of dpph); [5-dpph-{(η^4-C_6H_7)Fe(CO)$_2$}$_4$-(μ-dpph)$_2$][BF$_4$]$_3$ (loss of dpph and BF$_4$) is observed at 2386 Da e^{-1}; a peak at 2108 Da e^{-1} is assigned to [5-dpph-{(η^4-C_6H_7)Fe-(CO)$_2$}$_3$-(μ-dpph)$_2$][BF$_4$]$_2$ (loss of (η^4-C_6H_7)Fe(CO)$_2$ and BF$_4$); [5-dpph-{(η^4-C_6H_7)Fe(CO)$_2$}$_4$-(μ-dpph)]-[BF$_4$]$_2$ (loss of two BF$_4$ and dpph ligands) is observed at

Table 2
Analytical data, IR carbonyl stretching frequencies and ^{31}P-NMR data for the diphosphine complexes

Complex	Anal. found (Calcd.)%			IR ν(CO)	δ Pa	δ Pb
	C	H	P	(cm^{-1})	(ppm)	(ppm)
Neutral diphosphine linked metal–metal dimers						
$\{(\eta^4\text{-}C_6H_8)Fe(CO)_2\}_2\text{-}\mu$-dppp (I)[a]	64.5 (64.8)	5.39 (5.28)	7.37 (7.79)	1963, 1903	—	63.1
$\{(\eta^4\text{-}C_6H_8)Fe(CO)_2\}_2\text{-}\mu$-dppb (II)	65.0 (65.1)	5.51 (5.43)	7.49 (7.65)	1963, 1903	—	63.2
$\{(\eta^4\text{-}C_6H_8)Fe(CO)_2\}_2\text{-}\mu$-dppn (III)	65.4 (65.5)	5.61 (5.58)	7.44 (7.52)	1962, 1903	—	63.3
$\{(\eta^4\text{-}C_6H_8)Fe(CO)_2\}_2\text{-}\mu$-dpph (IV)	65.5 (65.8)	5.77 (5.73)	7.37 (7.40)	1962, 1902	—	63.3
Cationic diphosphine linked metal–metal dimers						
$[(\eta^5\text{-}C_6H_7)Fe(CO)_2]_2\text{-}\mu$-dppp][BF$_4$]$_2$ (V)	52.9 (53.0)	4.27 (4.12)	6.47 (6.38)	2041, 1998	—	58.3
$[\{(\eta^5\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}\mu$-dppb][BF$_4$]$_2$ (VI)	53.5 (53.5)	4.56 (4.26)	6.37 (6.29)	2043, 1998	—	61.5
$[\{(\eta^5\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}\mu$-dppn][BF$_4$]$_2$ (VII)	54.3 (54.2)	4.75 (4.42)	6.97 (6.23)	2044, 1998	—	59.5
$[\{(\eta^5\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}\mu$-dpph][BF$_4$]$_2$(VIII)	54.4 (54.4)	4.67 (4.54)	6.08 (6.11)	2044, 1998	—	59.2
Diphosphine linked dibridged dimers						
[5,5′-dppp-$\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}\mu$-dppp] [BF$_4$]$_2$ (IX)	60.5 (60.8)	4.98 (4.78)	8.78 (8.98)	1983, 1929	31.3, 32.1, 33.0	59.8, 61.8, 62.3
[5,5′-dppb-$\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}\mu$-dppb] [BF$_4$]$_2$(X)	59.9 (61.3)	5.68 (4.97)	8.45 (8.81)	1980, 1922	32.0, 32.8, 33.9	59.2, 60.6, 60.3
[5,5′-dppn-$\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}\mu$-dppn] [BF$_4$]$_2$ (XI)	61.8 (61.8)	5.36 (5.15)	8.99 (8.64)	1983, 1923	29.1, 29.8, 31.0	61.0, 62.4, 63.0
[5,5′-dpph-$\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}\mu$-dpph] [BF$_4$]$_2$ (XII)	61.2 (62.2)	5.54 (5.32)	8.43 (8.46)	1983, 1923	28.3, 29.9, 30.5	61.3, 61.7, 63.0
[5,5′-dppp-$\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}\mu$-dppb] [BF$_4$]$_2$(X III)	60.0 (61.1)	4.91 (4.88)	7.90 (8.89)	1980, 1923	30.0, 30.6, 31.4	61.9, 62.1, 62.8
[5,5′-dppb-$\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}\mu$-dppn] [BF$_4$]$_2$(X IV)	59.9 (61.6)	5.25 (5.06)	8.87 (8.72)	1981, 1924	29.0, 30.3, 30.9	61.0, 62.6, 63.8
[5,5′-dppn-$\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}\mu$-dpph] [BF$_4$]$_2$ (XV)	62.2 (62.0)	5.24 (5.24)	7.93 (8.55)	1979, 1922	29.0, 29.8, 31.2	60.9, 62.0, 62.9

Pa = ring bonded phosphorous atom and Pb = metal bonded phosphorus atom, relative to 85% H_3PO_4.

[a] Ref. 7.

1933 Da e^{-1} and a peak at 1655 Da e^{-1} is assigned to [5-dpph-$\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_3\text{-}(\mu$-dpph)][BF$_4$]$_2$ (loss of $(\eta^4\text{-}C_6H_7)Fe(CO)_2$).

3. Conclusions

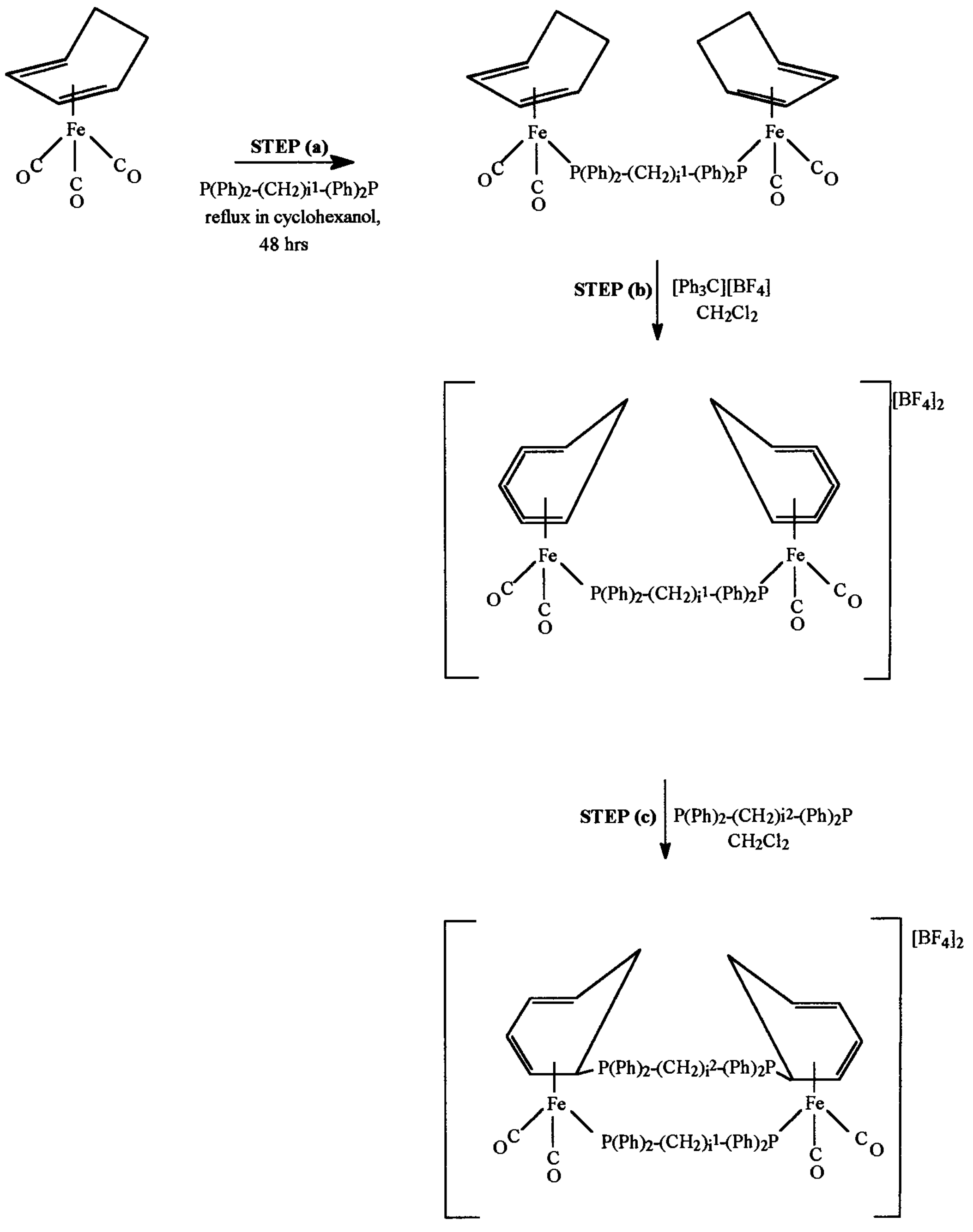
The ^{31}P-NMR spectra taken in conjunction with the ESMS studies confirm that complexes (IX–XV) are dibridged dimers containing metal–metal and ring–ring bridges with the possible presence of isomers containing metal–ring bridges. In the case of (XII), the ESMS provides evidence for both the above type of dibridged dimer (XII) and a tetramer (XIIa), which may contain ring–ring bridges between the rings of separate metal–metal bridged moieties.

4. Experimental details

Solvents were freshly dried prior to use, according to standard methods. All reactions were carried out under high purity nitrogen. The tertiary monophosphine and diphosphine ligands were obtained commercially and used without further purification. The neutral compounds $(\eta^4\text{-}C_6H_8)Fe(CO)_2L$ (L = CO, PPh$_3$, PPh$_2$Me, P(OPh)$_3$, PMe$_3$) and the corresponding dienyl cations $[(\eta^5\text{-}C_6H_7)Fe(CO)_2L]BF_4$ were prepared following published methods [12,13].

Infrared spectra were recorded on a Mattson Galaxy FT3000 Spectrometer, using CaF$_2$ plates with 0.1 mm spacings. ^{1}H, ^{13}C, and ^{31}P-NMR spectra were recorded using a JEOL GX270 FT spectrometer. Analyses were performed by the Microanalytical laboratory of the Chemical Services Unit of this department.

The electrospray experiments were carried out in the University of Warwick, using a Fisons' 'Quattro II' triple quadrupole mass spectrometer equipped with an atmospheric pressure ionisation (API) source operated in the nebulizer-assisted electrospray mode. The potential on the electrospray needle was set at 3.6 kV, and the extraction cone voltage was normally set at 40 V. Mass spectra were acquired over the range m/z 3500–500 m/z.



Scheme 3. Preparation of the dibridged linked dimers via a three step process.

4.1. Preparation of the monophosphine ring adducts $[(\eta^4\text{-}C_6H_7\text{-}5\text{-}PR_3)Fe(CO)_2L]BF_4$ ($PR_3 = PPh_3$, PPh_2Me, PMe_3; $L = CO$, $P(OPh)_3$, PPh_3, PPh_2Me, PMe_3)

The preparation of $[(\eta^4\text{-}C_6H_7\text{-}5\text{-}PPh_2Me)Fe(CO)_2PPh_2Me]BF_4$ is given as a general example, although reaction times vary and are summarised in Table 1.

$[(\eta^5\text{-}C_6H_7)Fe(CO)_2PPh_2Me]BF_4$ (0.5 g; 1.05 mmol) and PPh_2Me (0.21 g; 1.05 mmol) were mixed in 50 ml of dry acetonitrile. The reaction was monitored by infrared spectroscopy and was complete after 5 min.

Removal of solvent under reduced pressure and recrystallisation from CH_2Cl_2/diethyl ether; gave $[(\eta^4\text{-}C_6H_7\text{-}5\text{-}PPh_2Me)Fe(CO)_2PPh_2Me]BF_4$ as a yellow solid (0.56 g; 79%). Analytical and spectroscopic details are given in the supplementary material.

Table 3
ES mass spectral data (m/z) for the dibridged complexes (X), (XII), (XIII), (VX)

Fragment (m/z)	Complex	(XIII)	(X)	(XV)	(XII)	(XIIa)
	dppx^1 dppx^2	dppp dppb	dppb dppb	dppn dpph	dpph dpph	dpph dpph
$[5,5'\text{-dppx}^1\text{-}\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}(\mu\text{-dppx}^2)][BF_4]_2$		1394	1408	1450	1464	—
$[5,5'\text{-dppx}^1\text{-}\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}(\mu\text{-dppx}^2)]BF_4^+$		1307	1321	1363	1377	—
$[5,5'\text{-dppx}^1\text{-}\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}(\mu\text{-dppx}^2)]^+$		1029	1043	—	—	—
$[\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}\text{-}\mu\text{-dppx}^2)]BF_4^+$		895	895	923	923	—
$[5,5'\text{-dppx}^1\text{-}\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}]BF_4^+$		887	—	—	—	—
$[(\eta^4\text{-}C_6H_7)Fe(CO)_2\text{-}(\mu\text{-dppx}^2)]^+$		617	617	645	645	—
$[(\eta^4\text{-}C_6H_7)Fe(CO)\text{-}(\eta\text{-dppx}^2)]^+$		—	—	617	617	—
$[(\eta^4\text{-}C_6H_7)Fe\text{-}(\eta\text{-dppx}^2)]^+$		561	561	538	538	—
$[Fe\text{-}(\eta\text{-dppx}^2)]^+$		481	482	510	510	—
$[\text{dppx}^2]^+$		429	427	454	454	—
$[5,5'\text{-}(\text{dppx}^1)_2\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_4\text{-}(\mu\text{-dppx}^2)_2][BF_4]_4$		—	—	—	—	2928
$[5,5'\text{-}(\text{dppx}^1)_2\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_4\text{-}(\mu\text{-dppx}^2)_2][BF_4]_3^+$		—	—	—	—	2867
$[5,5'\text{-dppx}^1\text{-}\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_4\text{-}(\mu\text{-dppx}^2)_2][BF_4]_4^+$		—	—	—	—	2475
$[5,5'\text{-dppx}^1\text{-}\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_4\text{-}(\mu\text{-dppx}^2)_2][BF_4]_3^+$		—	—	—	—	2386
$[5,5'\text{-dppx}^1\text{-}\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_4\text{-}(\mu\text{-dppx}^2)_2]^+$		—	—	—	—	2126
$[5,5'\text{-dppx}^1\text{-}\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_4\text{-}(\mu\text{-dppx}^2)_2][BF_4]_2^+$		—	—	—	—	2108
$[5,5'\text{-dppx}^1\text{-}\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_4\text{-}(\mu\text{-dppx}^2)][BF_4]_2^+$		—	—	—	—	1933
$[5,5'\text{-dppx}^1\text{-}\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_4\text{-}(\mu\text{-dppx}^2)][BF_4]_2^+$		—	—	—	—	1655
$[5\text{-dppx}^1\text{-}\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}(\mu\text{-dppx}^2)][BF_4]_2^+$		—	—	—	—	1464
$[5\text{-dppx}^1\text{-}\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}(\mu\text{-dppx}^2)]BF_4^+$		—	—	—	—	1377
$[\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}(\mu\text{-dppx}^2)]BF_4^+$		—	—	—	—	923
$[\{(\eta\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}(\mu\text{-dppx}^2)]^+$		—	—	—	—	645
$[\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}(\mu\text{-dppx}^2)]^+$		—	—	—	—	617
$[Fe(CO)\text{-}(\eta\text{-dppx}^2)]^+$		—	—	—	—	538
$[Fe\text{-}(\eta\text{-dppx}^2)]^+$		—	—	—	—	510
$[\text{dppx}^2]^+$		—	—	—	—	454

4.2. Formation of phosphonium ring adducts $[(\eta^4\text{-}C_6H_7\text{-}5\text{-}PR_3\text{-})Fe(CO)_2L]BF_4$ by electrophilic attack of $[(\eta^5\text{-}C_6H_7)Fe(CO)_2L]BF_4$ on the metal–phosphorus bond of $(\eta^4\text{-}C_6H_8)Fe(CO)_2PR_3$ ($PR_3 = PPh_3$, PPh_2Me, PMe_3; $L = CO$, $P(OPh)_3$, PPh_3, PPh_2Me, PMe_3)

The reaction between $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ and $(\eta^4\text{-}C_6H_8)Fe(CO)_2PPh_2Me$ is given as an example, although all of the reactions were carried out following the same procedure. The results are summarised in Table 1.

$[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ (0.5 g; 1.63 mmol) and $(\eta^4\text{-}C_6H_8)Fe(CO)_2PPh_2Me$ (0.64 g; 1.63 mmol) were reacted in 50 ml of dry acetonitrile, at room temperature. The ν(CO) frequencies at 2114 and 2068 cm^{-1} for the cations and 1964 and 1904 cm^{-1} for the neutral complex, were replaced by those of the product (XVI)–(XXV), at 2056 and 1982 cm^{-1} after 48 h.

The solution was filtered, solvent removed under reduced pressure and the product recrystallised form CH_2Cl_2/diethyl ether, and characterised by analysis, IR and ^{31}P-NMR spectroscopy (0.20 g; 30%). (See supplementary material.)

4.3. Preparation of the neutral metal–metal diphosphine linked dimers $\{(\eta^4\text{-}C_6H_8)Fe(CO)_2\}_2\text{-}(\mu\text{-dppx})$ ($x = p$ (I); $x = b$ (II); $x = n$ (III); $x = h$ (IV))

(I)–(IV) were prepared by reacting $(\eta^4\text{-}C_6H_8)Fe(CO)_3$ with dppx (x = p, b, n, h) in a 2:1 ratio. For example, (2.0 g; 9.0 mmol) of $(\eta^4\text{-}C_6H_8)Fe(CO)_3$ and (2.0 g; 4.5 mmol) of dppn were dissolved in 100 ml of cyclohexanol and refluxed for 48 h. The reaction mixture was cooled and 50 ml of petroleum ether (40/60) added, precipitating black decomposition products. The solution was filtered and cyclohexanol removed by vacuum distillation. The yellow residue was purified by chromatography on a short column of alumina and eluted with 1:3 CH_2Cl_2/petroleum ether (40/60). Removal of solvent under reduced pressure gave the product as a yellow solid (2.6 g; 64%). Analytical and spectroscopic details are given in Table 2.

4.4. Preparation of the metal–metal diphosphine linked dimers $[\{(\eta^5\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}(\mu\text{-dppx})][BF_4]_2$ *(x = p, (V); x = b, (VI); x = n, (VII); x = h, (VIII))*

$\{(\eta^4\text{-}C_6H_8)Fe(CO)_2\}_2\text{-}\mu$-dppn (0.5 g; 0.56 mmol) was dissolved in 50 ml of CH_2Cl_2. $[Ph_3C][BF_4]$ (0.63 g; 1.9 mmol) was added to the solution. After 15 min, diethyl ether was added to the reaction mixture, precipitating the product $[\{(\eta^5\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}(\mu\text{-dppp})][BF_4]_2$. Filtration and recrystallisation from CH_2Cl_2/diethyl ether gave a yellow solid (0.48 g; 80%). Analytical and spectroscopic details are given in Table 2.

4.5. Preparation of the dibridged series $[5,5'\text{-dppx}^1\text{-}\{(\eta^4\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}(\mu\text{-dppx}^2)][BF_4]_2$ *(x^1, x^2 = p, p (IX); x^1, x^2 = b, b (X); x^1, x^2 = n, n (XI); x^1, x^2 = h, h (XII); x^1, x^2 = p, b (XIII); x^1, x^2 = b, n (XIV); x^1, x^2 = n, h (XV))*

Two types of these complexes were prepared by similar procedures: (i) $\text{dppx}^1 = \text{dppx}^2$, with the same type of diphosphine ligand at both linkages; (ii) $\text{dppx}^1 \neq \text{dppx}^2$, with different diphosphine ligands at the two linkages.

$[\{(\eta^5\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}(\mu\text{-dppn})][BF_4]_2$ (VII) (0.5 g; 0.52 mmol) in 50 ml of CH_2Cl_2. (0.22 g; 0.54 mmol) of dppn was added. After 30 min, the solvent was removed under reduced pressure and recrystallisation from CH_2Cl_2/diethyl ether gave a dark yellow solid (0.43 g; 60%). Analytical and spectroscopic details are given in Tables 2 and 3.

4.6. Reaction of $(\eta^4\text{-}C_6H_8)Fe(CO)_2PR_3$ *($PR_3 = PPh_3$, PPh_2Me, PMe_3) with a deficiency of* $[Ph_3C][BF_4]$

To $(\eta^4\text{-}C_6H_8)Fe(CO)_2PPh_2Me$ (0.5 g; 1.28 mmol) in 50 ml of dry CH_2Cl_2, at room temperature, $[Ph_3C][BF_4]$ (0.4 g; 1.20 mmol) was added. After 30 min, ν(CO) stretching frequencies of the neutral complex $(\eta^4\text{-}C_6H_8)Fe(CO)_2PPh_2Me$ at 1964 and 1904 cm^{-1}, were accompanied by bands at 2042 and 2000 cm^{-1} assigned to $[(\eta^5\text{-}C_6H_7)Fe(CO)_2PPh_2Me]BF_4$ as well as bands at 1986 and 1930 cm^{-1} assigned to the ring adduct $[(\eta^4\text{-}C_6H_7\text{-}5\text{-}PPh_2Me)Fe(CO)_2PPh_2Me]BF_4$.

Stirring overnight gave a mixture of $[(\eta^5\text{-}C_6H_7)Fe(CO)_2PPh_2Me]BF_4$ and the phosphonium ring adduct $[(\eta^4\text{-}C_6H_7\text{-}5\text{-}PPh_2Me)Fe(CO)_2PPh_2Me]B\ F_4$, confirmed from the ν(CO) stretching frequencies at 2042, 2000, 1986 and 1930 cm^{-1}.

4.7. Reaction of $\{(\eta^4\text{-}C_6H_8)Fe(CO)_2\}_2\text{-}(\mu\text{-dppx})$ *(x = p, b, n, h) with a deficiency of* $[Ph_3C][BF_4]$

To $\{(\eta^4\text{-}C_6H_8)Fe(CO)_2\}_2\text{-}(\mu\text{-dppb})$ (II) (0.5 g; 0.56 mmol) in 50 ml of CH_2Cl_2, at room temperature, $[Ph_3C][BF_4]$ (0.20 g; 0.58 mmol) was added. After 30 min, ν(CO) stretching frequencies of the neutral complex $\{(\eta^4\text{-}C_6H_8)Fe(CO)_2\}_2\text{-}(\mu\text{-dppb})$ (II) at 1965 and 1903 cm^{-1}, were accompanied by peaks at 2044 and 1998 cm^{-1} assigned to $[\{(\eta^5\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}(\mu\text{-dppb})][BF_4]_2$ (VI) as well as peaks at 1982 and 1928 cm^{-1} assigned to $[5,5'\text{-dppb-}\{(\eta^5\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}(\mu\text{-dppb})][BF_4]_2$ (X).

Stirring overnight resulted in a mixture of $[\{(\eta^5\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}(\mu\text{-dppb})][BF_4]_2$ (VI) and $[5,5'\text{-dppp-}\{(\eta^5\text{-}C_6H_7)Fe(CO)_2\}_2\text{-}(\mu\text{-dppp})][BF_4]_2$ (X), confirmed from the ν(CO) stretching frequencies at 2044, 1998, 1982 and 1928 cm^{-1}.

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