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Substitution and Addition Reactions of Tricarbonyl(η-1,5-cyclohexadienylium)- and Tricarbonyl(η-1,5-cycloheptadienylium)iron Cations with Tertiary Diphosphines

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A new series of metal diphosphine complexes formed by the reaction of the diphosphines, $PPh_2(CH_2)_nPPh_2$, n = 2–6, with the tricarbonyl(η-1,5-cyclohexadienylium)- and tricarbonyl(η-1,5-cycloheptadienylium)iron cations are described. The first series, formed by dppm (n = 1) only, comprise 5-*exo* ring adducts involving the bonding of only one phosphorus atom of the diphosphine to ring carbon atom 5 of the tricarbonylcyclodienyliron cation. The second series are diphosphine ring linked dimers, e.g. [5,5′-*exo*-$PPh_2(CH_2)_3PPh_2\{(\eta^4\text{-}C_6H_7)Fe(CO)_3\}_2](BF_4)_2$. The structures of the members of both series are fully consistent with their spectroscopic properties, and in one case, the ring adduct $[(\eta^4\text{-}C_7H_9\text{-}5\text{-}exo\text{-}\eta^1\text{-dppm})Fe(CO)_3]BF_4$, the structure was confirmed by X-ray crystallography.

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]

The reactions between nucleophiles and metal carbonyl complexes of π-acids such as the title compounds may proceed by a number of pathways to give a variety of products including (a) addition of the nucleophile to a carbon atom of one of the carbonyl groups,[5] (b) ring addition,[6] and (c) carbonyl substitution.[7] The prediction of which of these routes is taken by a particular combination of metal carbonyl complex and nucleophile is still difficult. Kinetic products may be observed under one set of conditions (e.g. low temperatures) and thermodynamic products under other conditions (e.g. higher temperatures). In the case of both the tricarbonyl(η-1,5-cyclohexadienylium)iron cation (I) and the tricarbonyl(η-1,5-cycloheptadienylium)iron cation (II), soft nucleophiles such as monophosphines generally give 5-*exo* adducts, e.g. $[(5\text{-}exo\text{-}C_7H_9PPh_3)Fe(CO)_3]^+$, as the stable thermodynamic product[8] with endo adducts occurring less commonly.[9] In contrast, hard nucleophiles such as methoxide and hydroxide give initial attack at low temperatures at a carbonyl carbon atom with formation of the kinetic product, e.g. $C_7H_9Fe(CO)_2(COOMe)$, which rearranges intermolecularly on raising the temperature to the thermodynamically stable product, $[(5\text{-}exo\text{-}C_7H_9OMe)Fe(CO)_3]$.[5] To date, diphosphines, which are some of the most ubiquitous ligands in organometallic chemistry, have been found to bond directly only to the metal atoms of complexes and frequently to form strongly bonded metal dimers.[10] In the case of metal carbonyl complexes of π-acids, e.g. the tropyllium complexes, $[(\eta^7\text{-}C_7H_7)M(CO_3)]BF_4$, M = Mo and W, three main types of products have been identified: (a) monosubstituted complexes, $[(\eta^7\text{-}C_7H_7)Mo(CO)_2(\eta_1\text{-diphosphine})]^+$, (b) chelated complexes, $[(\eta^7\text{-}C_7H_7)Mo(CO)(\eta_2\text{-diphosphine})]^+$, and (c) binuclear complexes in which the diphosphine bridges two metal atoms, e.g. $[\{(\eta^7\text{-}C_7H_7)Mo(CO)_2\}_2\text{-}\mu\text{-}PPh_2(CH_2)PPh_2](PF_6)_2$.[11]

In this paper, we report that the title ring metal carbonyl complexes I and II react quite differently from the above well-established pattern to form two new structural types of complexes: firstly, 5-*exo* ring adducts involving the bonding of only one phosphorus atom of the diphosphine to ring carbon 5 and, secondly, diphosphine ring linked dimers, e.g. [5,5′-*exo*-$PPh_2(CH_2)_3PPh_2\{(\eta^4\text{-}C_6H_7)Fe(CO)_3\}_2](BF_4)_2$, as well as, in some cases, the normal chelates and metal–metal diphosphine linked dimers.

Experimental Section

Solvents were freshly dried by standard methods. All reactions and workup were carried out under high purity nitrogen. Tertiary diphosphines (dppm, dppe, dppp, dppb, dppn, and dpph) (n = 1, 2, 3, 4, 5, and 6, respectively) were obtained commercially and used without further purification. Infrared spectra were measured using a 0.1-mm CaF_2 cell on a Perkin-Elmer 1720 FT spectrometer linked to a 3700 data station. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a JEOL GX 270 spectrometer. FAB

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Table I. Analytical Data and Infrared Carbonyl Stretching Frequencies for Diphosphine Complexes of $[C_6H_7Fe(CO)_3]BF_4$ and $[C_7H_9Fe(CO)_3]BF_4$

complex	calculated				found				IR ν(CO), cm^{-1}
	C	H	P	F	C	H	P	F	
Ring Adducts									
[(η^4-C_6H_7-5-*exo*-dppm)Fe$(CO)_3$]BF_4 (III)	59.2	4.23	8.98		58.7	3.94	7.94		2058, 1986
[(η^4-C_7H_9-5-*exo*-dppm)Fe$(CO)_3$]BF_4 (IV)	59.7	4.43	8.80		60.1	4.87	8.57		2056, 1986
Diphosphine Ring Linked Dimers									
[(5,5′-*exo*-dppe){(η^4-C_6H_7)Fe$(CO)_3$}$_2$][BF_4]$_2$ (V)	52.3	3.79	6.14		53.1	4.07	7.06		2061, 1989
[(5,5′-*exo*-dppe){(η^4-C_7H_9)Fe$(CO)_3$}$_2$][BF_4]$_2$ (VI)	53.2	4.08	5.97		53.3	4.36	6.75		2056, 1987
[(5,5′-*exo*-dppp){(η^4-C_6H_7)Fe$(CO)_3$}$_2$][BF_4]$_2$ (VII)	52.8	3.90	6.05		53.5	4.42	7.14		2060, 1988
[(5,5′-*exo*-dppp){(η^4-C_7H_9)Fe$(CO)_3$}$_2$][BF_4]$_2$ (VIII)	53.7	4.21	5.89		53.0	4.38	6.64		2056, 1987
[(5,5′-*exo*-dppb){(η^4-C_6H_7)Fe$(CO)_3$}$_2$][BF_4]$_2$ (IX)	53.2	4.08	5.97		53.0	3.98	5.52		2060, 1989
[(5,5′-*exo*-dppb){(η^4-C_7H_9)Fe$(CO)_3$}$_2$][BF_4]$_2$ (X)	54.1	4.35	5.81		53.3	4.28	6.09		2056, 1986
[(5,5′-*exo*-dppn){(η^4-C_6H_7)Fe$(CO)_3$}$_2$][BF_4]$_2$ (XI)	53.7	4.21	5.89		53.4	4.03	5.52		2060, 1988
[(5,5′-*exo*-dppn){(η^4-C_7H_9)Fe$(CO)_3$}$_2$][BF_4]$_2$ (XII)	54.5	4.48	5.74		55.2	5.06	6.02		2056, 1986
[(5,5′-*exo*-dpph){(η^4-C_6H_7)Fe$(CO)_3$}$_2$][BF_4]$_2$ (XIII)	54.1	4.35	5.81		54.1	4.08	5.07		2060, 1987
[(5,5′-*exo*-dpph){(η^4-C_7H_9)Fe$(CO)_3$}$_2$][BF_4]$_2$ (XIV)	54.9	4.61	5.67		53.1	4.60	5.42		2056, 1985
Diphosphine Mixed Ring Linked Dimer									
[(5,5′-*exo*-dppp){(η^4-C_6H_7)Fe$(CO)_3$(η^4-C_7H_9)Fe$(CO)_3$}][BF_4]$_2$ (XV)	53.2	4.08	5.97		54.3	4.51	6.12		2057, 1988
Diphosphine Metal Linked Dimers									
[{(η^5-C_6H_7)Fe$(CO)_2$}$_2$(μ-dppe)][BF_4]$_2$ (XVI)	52.9	4.01	6.50		52.7	4.11	7.74		1982, 1927
[{(η^5-C_7H_9)Fe$(CO)_2$}$_2$(μ-dppe)][BF_4]$_2$ (XVII)	53.8	4.31	6.31		55.5	4.72	7.25		1983, 1925
[{(η^5-C_6H_7)Fe$(CO)_2$}$_2$(μ-dppp)][BF_4}$_2$ (XVIII)	53.4	4.16	6.40		53.0	4.22	7.53		1982, 1927
[{(η^5-C_7H_9)Fe$(CO)_2$}$_2$(μ-dppp)][BF_4]$_2$ (XIX)	54.3	4.45	6.22		55.7	4.82	7.30		1983, 1925
Diphosphine Metal Chelates									
[(η^5-C_6H_7)Fe(CO)(η^2-dppm)][BF_4] (XX)	60.6	4.61	9.77		59.1	4.49	8.59		1982
[(η^5-C_7H_9)Fe(CO)(η^2-dppm)][BF_4] (XXI)	61.1	4.82	9.56		61.4	4.82	9.16		1981
Diphosphonium Salt									
[(C_7H_9)$PPh_2(CH_2)_3PPh_2$(C_7H_9)][BF_4]$_2$·$^1/_2CH_2Cl_2$ (XXII)	61.1	5.52	7.61	18.6	61.5	6.11	7.72	18.2	18.2

mass spectra were run in a glycerol matrix on a VG 70E mass spectrometer with argon as bombardment gas at 8 kV. Analyses were performed by the Microanalytical Laboratory of the Chemical Services Unit of University College Dublin and are given in Table I together with the infrared carbonyl stretching frequencies of compounds III–XXI. The starting complexes, [(η^5-C_6H_7)Fe$(CO)_3$]BF_4 (I) and [(η^5-C_7H_9)Fe$(CO)_3$]BF_4 (II), were prepared by published methods.[7]

Preparation of Phosphonium Ring Adducts III and IV. Bis(diphenylphosphino)methane (dppm) (0.628 g, 1.63 mmol) was added to a stirred solution of [(η^5-C_6H_7)Fe$(CO)_3$]BF_4 (I) (0.5 g, 1.63 mmol) in acetonitrile (50 mL) at room temperature and reacted for 10 min. Solvent was removed under reduced pressure and the product chromatographed on alumina and eluted with $CHCl_3$. On reduction of the volume to *ca.* 10 mL and addition of hexane, pale yellow crystals of [(η^4-C_6H_7-5-*exo*-dppm)Fe$(CO)_3$]-BF_4 (III) (0.45 g 89%) formed. Complex IV, [(η^4-C_7H_9-5-*exo*-dppm)Fe$(CO)_3$]BF_4, was prepared similarly.

Preparation of the Diphosphine Ring Linked Dimers [(5,5′-*exo*-$PPh_2(CH_2)_nPPh_2$){η^4-C_xH_yFe$(CO)_3$}$_2$][BF_4]$_2$ (n = 2–6; x, y = 6, 7; x, y = 7, 9) (V–XIV). A typical procedure is as follows: 1,2-Bis(diphenylphosphino)ethane (dppe) (0.325 g, 0.816 mmol) was added to a stirred solution of I (0.50 g, 1.63 mmol) in acetonitrile (50 mL) at room temperature in a 1:2 molar ratio, and the mixture was allowed to react for 10 min. The workup was identical with that described above for III and gave yellow crystals of V ($n = 2$; $x, y = 6, 7$) (0.39 g, 78%). Compounds VI–XIV were prepared similarly from the appropriate starter and diphosphine.

Preparation of the Diphosphine Mixed Ring Linked Dimer [(5,5′-*exo*-$PPh_2(CH_2)_3PPh_2$){(η^4-C_6H_7)Fe$(CO)_3$(η^4-C_7H_9)-Fe$(CO)_3$}][BF_4]$_2$ (XV). The diphosphine mixed ring linked dimer (XV) was prepared via the above procedure by addition of dppp to a mixture of I and II in a molar ratio of 1:1:1 in acetonitrile as solvent (yield 79%).

Preparation of the Diphosphine Metal Linked Dimers [{(η^5-C_xH_y)Fe$(CO)_2$}$_2$(μ-$PPh_2(CH_2)_nPPh_2$)][BF_4]$_2$ (n = 2, 3; x, y = 6, 7; x, y = 7, 9) (XVI–XIX). A typical preparation is as follows: I (0.5 g, 1.63 mmol) and dppe (0.325 g, 0.816 mmol) were refluxed in acetonitrile (50 mL) for 3 days. Solvent was removed under vacuum and the product chromatographed on alumina and eluted with $CHCl_3$. On concentration of solvent to *ca.* 10 mL, addition of hexane gave a dark yellow product. Recrystallization from CH_2Cl_2/hexane gave dark yellow crystals of XVI (0.29 g, 58%). Compounds XVII–XIX were prepared similarly from the appropriate starter and diphosphine.

Preparation of Diphosphine Metal Chelates [(η^5-C_xH_y)-Fe(CO)(η^2-dppm)]BF_4 (x, y = 6, 7; x, y = 7, 9) (XX and XXI). I (0.5 g, 1.63 mmol) and trimethylamine *N*-oxide (TMNO) (0.18 g, 1.56 mmol) were stirred in acetonitrile (50 mL) for 10 min at room temperature when a red color developed. The solution was filtered, dppm (0.628 g, 1.63 mmol) was added, and stirring was continued for another 30 min. Solvent was removed under reduced pressure, and the product was chromatographed on alumina and eluted first with benzene and then with CH_2Cl_2. The red eluate was concentrated to *ca.* 10 mL, and addition of hexane gave orange crystals of XX (0.38 g, 76%). XXI was prepared similarly from II and dppm.

Decomplexation and Hydride Abstraction Reactions of IV and VIII Hydride Abstraction. To a solution of VIII (0.5 g, 0.48 mmol) in dried THF (50 mL) was added a solution of triphenylmethyl fluoroborate (0.16 g, 0.48 mmol) in 10 mL of THF. No reaction ensued as monitored by IR spectroscopy, even on raising the temperature.

Oxidation by Iodine. Iodine (0.54 g) was added to a solution of VIII (0.5 g, 0.48 mmol) in dichloromethane at room temperature, and the reaction continued for 48 h. The crude mixture was filtered, the volume was reduced to 10 mL, and then the mixture was washed sequentially with a 10-mL portion of saturated aqueous sodium bisulfite solution, three 10-mL portions of 1 M hydrochloric acid, and one 10-mL portion of saturated aqueous sodium chloride solution. The dichloromethane layer was separated, dried over magnesium sulfate, and filtered, and on reduction of the volume, pale yellow crystals formed. These were recrystallized from a dichloromethane ether mixture, redissolved in the minimum volume of dichloromethane, and treated with a solution of $AgBF_4$ in the same solvent to effect anion exchange of iodide by tetrafluoroborate. After filtration and concentration white crystals formed which, on recrystallization from CH_2Cl_2/ether, gave white needle crystals of the

Table II. ^{1}H and (^{13}C) NMR Spectral Data for Selected Complexes

complex	chemical shift	assignments
III	2.94 (t), 2.83 (q), J_{45} = 3.2 Hz	H_1, H_4
	(58.3), J_{P-C} = 7.6 Hz	C_1
	(50.6), J_{P-C} = 8.6 Hz	C_4
	4.68 (t), 5.24 (t)	H_2, H_3
	(85.1), (85.1)	C_2, C_3
	3.44 (t), J_{45} = 3.2 Hz	H_5
	(31.7), J_{P-C} = 37.6 Hz	C_5
	2.31 (m), $J_{5-6_{endo}}$ = 3.3 Hz	$H_{6_{endo}}$
	1.84 (m), $J_{5-6_{exo}}$ = 11.5 Hz	$H_{6_{exo}}$
	(26.4)	C_6
IV	3.01 (t), 2.67 (dd), J_{45} = 0	H_1, H_4
	(58.1), (46.9), J_{P-C} = 7.6	C_1, C_4
	5.07 (t), 4.99 (t)	H_2, H_3
	(90.4), (86.2)	C_2, C_3
	3.53 (t), J_{45} = 0	H_5
	(34.3), J_{P-C} = 37.6 Hz	C_5
	1.72 (br), $J_{5-6_{endo}}$ = 3.2 Hz	$H_{6_{endo}}$
	0.92 (m), $J_{5-6_{exo}}$ = 10.2 Hz	$H_{6_{exo}}$
	(22.5)	C_6
	1.85 (br)	$H_{7_{endo}}$
	2.03 (br)	$H_{7_{exo}}$
	(26.7), J_{P-C} = 13.9 Hz	C_7
V	3.10 (t), 2.95 (dd)	H_1, H_4
	(60.6), J_{P-C} = 7.5 Hz	C_1
	(51.6), J_{P-C} = 8.6 Hz	C_4
	4.80 (t), 5.12 (t)	H_2, H_3
	(86.2), (86.7)	C_2, C_3
	3.65 (t)	H_5
	(31.7), J_{P-C} = 37.6 Hz	C_5
	2.40 (m)	$H_{6_{endo}}$
	1.70 (m)	$H_{6_{exo}}$
	(26.9)	C_6
VIII	3.13 (t), 2.73 (dd)	H_1, H_4
	(57.9)	C_1
	(46.6), J_{P-C} = 6.5 Hz	C_4
	5.15 (t), 4.98 (t)	H_2, H_3
	(90.4), (85.9)	C_2, C_3
	3.48 (dt)	H_5
	(35.5), J_{P-C} = 37.5 Hz	C_5
	1.64 (br)	$H_{6_{endo}}$
	0.89 (m)	$H_{6_{exo}}$
	(22.4)	C_6
	2.05 (br)	$H_{7_{endo}}$
	2.08 (br)	$H_{7_{exo}}$
	(26.7), J_{P-C} = 14.0 Hz	C_7
	Metal Chelate	
XVI	3.97 (br)	H_1, H_5
	(81.2)	C_1, C_5
	5.26 (m)	H_2, H_4
	(99.5)	C_2, C_4
	7.10 (t)	H_3
	(96.0)	C_3
	1.33 (m)	$H_{6_{endo}}$, $H_{7_{endo}}$
	2.40 (m)	$H_{6_{exo}}$, $H_{7_{exo}}$
	(32.3)	C_6, C_7
	Diphosphine Bridged Metal Dimers XVI–XIX (^{13}C NMR Data Only)	
XVIII	(82.2)	C_1, C_5
	(97.1)	C_2, C_4
	(95.2)	C_3
	(31.5)	C_6, C_7
	Diphosphonium Dication XXII	
XXII	5.64 (t), 5.53 (dd)	H_1, H_4
	(65.9)	C_1
	(53.5)	C_4
	5.96 (t), 5.84 (t)	H_2, H_3
	(124.0), (122.4)	C_2, C_3
	4.30 (br)	H_5
	(37.1), J_{P-C} = 47.2 Hz	C_5
	1.75 (br)	$H_{6_{endo}}$
	1.59 (br)	$H_{6_{exo}}$
	(26.7)	C_6
	2.40 (br)	$H_{7_{endo}}$, $H_{7_{exo}}$
	(29.7)	C_7

diphosphonium salt $[C_7H_9PPh_2(CH_2)_3PPh_2C_7H_9][BF_4]_2$. Analyses together with ^{1}H, ^{13}C, and ^{31}P NMR spectral data are given in Tables I–III.

Hydride Abstraction from IV. This was attempted as described above for VIII, and again no reaction ensued.

Oxidation of IV by Iodine. Attempts to decomplex IV using iodine as oxidant as described above for VIII were only partially successful. In some cases with prolonged reaction times (72 h) the infrared carbonyl peaks of IV were replaced by those of II, indicating loss of the *exo* dppm group, whereas for shorter reaction times, although the ν(CO) peaks of IV disappeared, workup of the reaction mixture as described for VIII gave white crystals with varying analyses, although the ^{31}P NMR spectra gave peaks at δ 33.7 and 26.4 ppm consistent with formation of a phosphonium cation.

Results and Discussion

5-*Exo* Ring Adducts III and IV. Reaction of both I and II with equimolar quantities of $PPh_2CH_2PPh_2$ (dppm) in acetonitrile at room temperature proceeded rapidly to completion (~10 min) and formation of the 5-*exo* ring adducts III and IV, respectively (Scheme I). The structures of III and IV are fully consistent with their ^{1}H, ^{13}C, and ^{31}P NMR spectral data (Tables II and III) discussed below, and in particular, the ^{31}P results show clearly the presence of pendant phosphorus atoms at δ −28.82 and −29.16 ppm and phosphorus bonded to C_5 at δ 31.67 and 31.89 ppm in III and IV, respectively. Similarly, in the ^{13}C spectra, the C_5 peaks occur at δ 32 ppm (J_{P-C} = 37 Hz) and δ 34 ppm (J_{P-C} = 37 Hz), respectively. The solid-state structure of IV has also been confirmed by an X-ray structure determination.[8]

Attempts at hydride abstraction from IV by triphenylmethyl fluoroborate were unsuccessful even with prolonged heating. As discussed in the Experimental Section, attempts at decomplexation of IV with iodine were only partly successful. Prolonged reaction resulted in loss of the *exo* dppm group and re-formation of the cation II. Shorter reaction times gave products whose ^{31}P NMR spectra (δ 33.7 and 26.4 ppm) indicated formation of a phosphonium cation, but the analytical results were unsatisfactory.

Diphosphine Ring Linked Dimers V–XIV. In contrast to dppm, the higher diphosphines, $PPh_2(CH_2)_nPPh_2$; n = 2, dppe; n = 3, dppp; n = 4, dppb; n = 5, dppn; n = 6, dpph, do not form ring adducts when reacted at room temperature with I and II in 1:1 molar ratios; however, on increasing the cation/ligand molar ratio to 2:1, rapid reaction ensued in acetonitrile at room temperature to form a new series of diphosphine ring dimers V–XIV: $[5,5'\text{-}exo\text{-}PPh_2(CH_2)_nPPh_2\{(\eta^4\text{-}C_xH_y)Fe(CO)_3\}_2][BF_4]_2$; n = 2–6; x, y = 6, 7; x, y = 7, 9 (Scheme II). The infrared carbonyl stretching frequencies of this series are virtually identical with and are very close to those of the monomeric dppm ring adducts III and IV (Table I). Again the ^{1}H, ^{13}C, and ^{31}P NMR spectra are fully consistent with the proposed structures as discussed below, and the ^{31}P NMR spectra clearly differentiate the ring-linked dimers V–XIV from the ring adducts III and IV with the former series exhibiting only one phosphorus peak in the range δ 31.56–33.90 ppm assigned to phosphorus atoms bonded to the ring carbon atoms 5 and 5′ and no absorptions due to pendant phosphorus atoms as observed for III and IV. Again the ^{13}C spectra confirmed phosphorus splitting of the C_5 ($C_{5'}$) signals. In the case of the diphosphine ring linked dimers containing the longer chain alkanes, i.e. compounds IX–XIV, inclusive, the FAB mass spectra all showed a parent ion peak with loss of one BF_4 group with the correct m/e value giving further support to the dimeric structure.

Table III. ^{31}P NMR Spectral Data of Diphosphonium Complexes[a] (85% H_3PO_4 as Internal Standard)

complex	δ(P_a)	δ(P_b)	δ(P_c)	δ(P_m)	$J(P_1,P_2)$
Ring Adduct					
[(η^4-C_6H_7-5-*exo*-dppm)Fe(CO)$_3$]BF_4 (III)	−28.82	31.67			61.10
[(η^4-C_7H_9-5-*exo*-dppm)Fe(CO)$_3$]BF_4 (IV)	−29.16	31.89			61.10
Ring-Linked Dimers					
[(5,5′-*exo*-dppe){(η^4-C_6H_7)Fe(CO)$_3$}$_2$][BF_4]$_2$ (V)		33.73			
[(5,5′-*exo*-dppe){(η^4-C_7H_9)Fe(CO)$_3$}$_2$][BF_4]$_2$ (VI)		33.90			
[(5,5′-*exo*-dppp){(η^4-C_6H_7)Fe(CO)$_3$}$_2$][BF_4]$_2$ (VII)		31.56			
[(5,5′-*exo*-dppp){(η^4-C_7H_9)Fe(CO)$_3$}$_2$][BF_4]$_2$ (VIII)		31.84			
[(5,5′-*exo*-dppb){(η^4-C_6H_7)Fe(CO)$_3$}$_2$][BF_4]$_2$ (IX)		32.73			
[(5,5′-*exo*-dppb){(η^4-C_7H_9)Fe(CO)$_3$}$_2$][BF_4]$_2$ (X)		32.90			
[(5,5′-*exo*-dppn){(η^4-C_6H_7)Fe(CO)$_3$}$_2$][BF_4]$_2$ (XI)		32.78			
[(5,5′-*exo*-dppn){(η^4-C_7H_9)Fe(CO)$_3$}$_2$][BF_4]$_2$ (XII)		32.98			
[(5,5′-*exo*-dpph){(η^4-C_6H_7)Fe(CO)$_3$}$_2$][BF_4]$_2$ (XIII)		32.76			
[(5,5′-*exo*-dpph){(η^4-C_7H_9)Fe(CO)$_3$}$_2$][BF_4]$_2$ (XIV)		32.95			
Mixed Ring Diphosphine Linked Dimer					
[(η^4-C_6H_7-5,5′-*exo*-dppp-η^4-C_7H_9)Fe_2(CO)$_6$][BF_4]$_2$ (XV)		31.33			
Metal-Linked Dimers					
[{(η^5-C_6H_7)Fe(CO)$_2$}$_2$(μ-dppe)][BF_4]$_2$ (XVI)				83.46	
[{(η^5-C_7H_9)Fe(CO)$_2$}$_2$(μ-dppe)][BF_4]$_2$ (XVII)				81.23	
[{(η^5-C_6H_7)Fe(CO)$_2$}$_2$(μ-dppp)][BF_4]$_2$ (XVIII)				43.58	
[{(η^5-C_7H_9)Fe(CO)$_2$}$_2$(μ-dppp)][BF_4]$_2$ (XIX)				38.31	
Metal Chelate					
[(η^5-C_6H_7)Fe(CO)(η^2-dppm)][BF_4] (XX)			10.21		
[(η^5-C_7H_9)Fe(CO)(η^2-dppm)][BF_4] (XXI)			9.15		
diphosphonium dication (XXII)	29.7				6.10

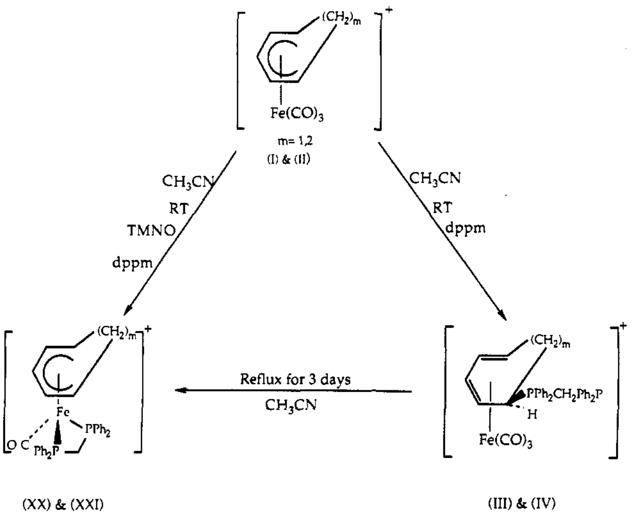
[a] P_a = unbonded phosphorus atom, P_b = phosphorus atom bonded to C_5 of the ring, P_c = chelated phosphorus atom, P_m = phosphorus atom bonded to metal, $J(P_1,P_2)$ = coupling constant between two phosphorus atoms in hertz.

Again attempts at hydride abstraction from VIII by triphenylmethyl fluoroborate were unsuccessful; however, oxidation by iodine resulted in decomplexation and isolation of the diphosphonium salt, [$C_7H_9PPh_2(CH_2)_3$-$PPh_2C_7H_9$][BF_4]$_2$, of reasonable purity. The ^{13}C NMR spectrum showed a resonance at δ 37.12 ppm (J_{P-C} = 47.2 Hz), confirming retention of the bonding of the C_7H_9 ring to the diphosphine at C_5 as in VIII. The ^{31}P spectrum showed a single resonance at δ 29.27 ppm (J_{P-P} = 6.10 Hz).

It is interesting to note that in the case of the C_6 and C_7 cyclodienyliumtricarbonyliron cations (I and II) involved in these studies, only dppm forms the monomeric ring adducts (III and IV) whereas the longer chain diphosphines $PPh_2(CH_2)_nPPh_2$, n = 2, 3, 4, ..., form only the ring-linked dimers (V–XV). The reasons for the contrasting behavior between dppm and the longer chain members are not clear; however, the decomplexation studies show clearly that the dppm monoadduct ligand is less stable than the ring-linked dimer ligands formed by the longer chain diphosphines since only for VIII was it possible to obtain the free diphosphonium dimer ligand as a stable compound. Parallel studies with the tricarbonyltropylliumchromium cation led to monomeric ring adducts for n = 1 and 2, a mixture of the ring adduct and ring-linked dimer for n = 3, and only the ring-linked dimer for n = 4.[13] It is possible that the puckering of the cyclodiene rings in I and II and subsequent bonding of the diphosphine of C_5 may, for longer chain diphosphines, lead to steric interaction between the pendant PPh_2 group and the metal/ring moiety. Such interaction would be less likely in the ring adducts formed from the planar [(η^7-C_7H_7)M(CO)$_3$]$^+$ system.

Mixed Ring Diphosphine Linked Dimer (XV). Reaction of equimolar quantities of I and II with dppp (molar ratio 1:1:1) in acetonitrile at room temperature gave the corresponding mixed complex [(5,5′-*exo*-dppp)-{(η^4-C_6H_7)Fe(CO)$_3$(η^4-C_7H_9)Fe(CO)$_3$}][BF_4]$_2$ (XV), as confirmed by its spectroscopic properties (Tables II and III); however, complete verification of the structure of XV requires an X-ray structure determination for which suitable crystals were not obtained.

Scheme I. Formation of Ring Adducts and Chelates



Diphosphine Metal Linked Dimers XVI–XIX. In contrast to the formation of ring-linked dimers (V–XIV) observed at room temperature, prolonged refluxing of I and II with dppe and dppp in a 2:1 molar ratio in acetonitrile led to the formation of the diphosphine metal linked dimers: [{(η^5-(C_xH_y)Fe(CO)$_2$}$_2$(μ-$PPh_2(CH_2)_nPPh_2$)]-[BF_4]$_2$ (n = 2, 3; x, y = 6, 7; x, y = 7, 9) (XVI–XIX). This series is analogous to the above tropyllium series previously reported.[7] The infrared carbonyl stretching frequencies of this series are virtually identical within the range 1982–3 cm^{-1} and 1925–7 cm^{-1}, about 70 cm^{-1} lower than those for either the ring adducts III and IV or the ring-linked dimers V–XIV as expected on replacement of a metal carbonyl

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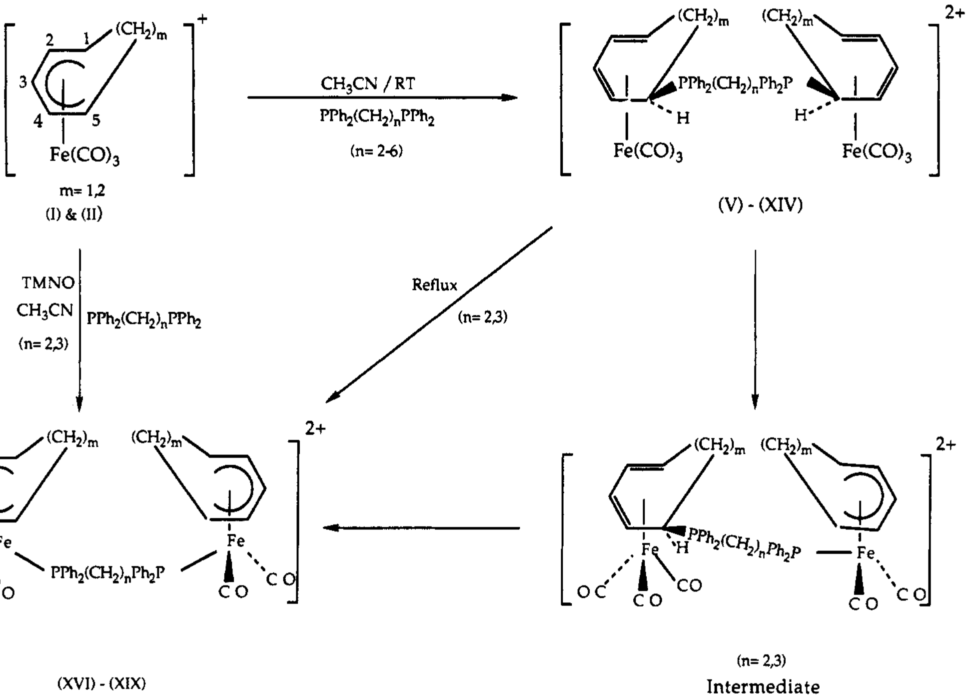
[13] Burns, J. Private communication.

Scheme II. Formation of Ring- and Metal-Linked Dimers



group by the poorer π-accepting diphosphine ligands. Again the ^1H, ^{13}C, and especially ^{31}P NMR spectra clearly distinguish this series from the ring adducts and ring-linked dimers with the metal-bonded phosphorus atoms exhibiting resonances at δ 83.46 and 81.23 ppm for XVI and XVII, respectively (i.e. $n = 2$; $x, y = 6, 7$; $x, y = 7, 9$), and at δ 43.58 and 38.31 ppm for XVIII and XIX, respectively ($n = 3$; $x, y = 6, 7$; $x, y = 7, 9$). Monitoring the above reactions between the title cations I and II and dppe and dppp by infrared spectroscopy showed initial formation of the corresponding diphosphine ring linked dimers [i.e., V and VI, VII and VIII; ν(CO) at *ca.* 2056 and 1986 cm^{-1}] followed by the metal-linked dimers (XVI–XIX). It is tempting to speculate that the reactions proceed via the phosphine ring linked dimers with subsequent rupture of a phosphorus–ring carbon bond and formation of a phosphorus metal bond giving as an intermediate a diphosphine metal–ring bridged species, e.g. $[(\eta^5\text{-}C_7H_9)Fe(CO)_2PPh_2(CH_2)_2PPh_2(5\text{-}exo\text{-}\eta^4\text{-}C_7H_9)Fe(CO)_3][BF_4]_2$. We have recently prepared a number of stable complexes of this type involving ring–metal diphosphine bridging between different ring systems and different metals, e.g. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_2(CH_2)_3PPh_2(exo\text{-}\eta^6\text{-}C_7H_7)Cr(CO)_3][BF_4]_2$.[8] However, it appears that compounds of the above type involving identical rings and metals are less stable than the closely related carbonyl-substituted diphosphine linked metal dimers, e.g. XVI–XIX which occur widely.[6] XVI–XIX may also be prepared from I and II by carbonyl activation with TMNO (Scheme II).

Metal Chelates. As expected, dppm, alone of the diphosphines employed in this work, shows a strong tendency to form the simple monomeric chelates $[(\eta^5\text{-}C_xH_y)Fe(CO)(\eta^2\text{-dppm})]BF_4$ (XX and XXI) ($x, y = 6, 7$; $x, y = 7, 9$) either by prolonged reflux of I and II with dppm or, preferably, by carbonyl activation of I and II with TMNO and reaction with dppm at room temperature (Scheme I). The infrared and ^1H, ^{13}C, and ^{31}P NMR spectra are fully consistent with chelate formation.

NMR Spectra of Ring Adducts III and IV. The NMR spectra of a variety of 5-*exo*-substituted cyclohexadiene- and cycloheptadieneiron tricarbonyl complexes have been assigned previously.[2]

In the case of the cyclohexadiene complexes, it was assumed that C_1, C_2, C_3 and C_4 formed one plane while C_1, C_4, C_5, and C_6 formed another plane, but for the cycloheptadiene system, puckering occurred with these atoms (see Scheme II for numbering of the rings). In the present work, single-frequency ^1H decoupling experiments, ^1H–^{13}C correlated spectroscopy, and ^1H–^1H correlated spectroscopy were used in making assignments. The shape and analysis of the H_5 signal is of major importance. In the previously studied 5-*exo* adducts, $[(\eta^4\text{-}C_7H_9\text{-}5\text{-}exo\text{-}X)Fe(CO)_3]BF_4$; X = NCS, SCN, etc.,[2] in which the 5-*exo* substituent (X) does not couple with $H_{5_{endo}}$, H_5 formed a double doublet whereas 5-*endo* substitution would form a narrow triplet. In $[(\eta^4\text{-}C_7H_9\text{-}5\text{-}exo\text{-dppm})Fe(CO)_3]BF_4$, however, H_5 occurs as a triplet due to coupling with the bonded phosphorus atom of dppm. The *exo* conformation is confirmed by the ^1H–^1H COSY spectrum which shows the multiplet H_5 correlated with $H_{6_{exo}}$ and $H_{6_{endo}}$ with $J_{5,6_{exo}} > J_{5,6_{endo}}$ (Table II). In addition, the H_5 multiplet does not show any cross-peaks to H_4, $H_{7_{exo}}$, or $H_{7_{endo}}$. These results are in excellent agreement with those obtained previously for a series of 5-*exo* complexes $[C_7H_9RFe(CO)_3]BF_4$ (R = amines).[5] The experimental pattern was also successfully simulated using coupling constants in good agreement with previous work[2] with, in addition for this case, $J_{5\text{-}P} = 11.0$ Hz. However, the $J_{5,6_{exo}}$ and $J_{5,6_{endo}}$ assignments given in ref 2 (Table II) should be reversed. It is noteworthy that in IV $H_{6_{exo}}$ is considerably shielded, occurring at δ 0.92 ppm. The X-ray crystal structure shows one of the phenyl groups of dppm to be located above C_6, whereas $H_{6_{endo}}$, on the other side of the diene ring, is unaffected. A ^1H–^{13}C correlated 2D spectrum enabled the ^{13}C spectrum to be interpreted unambiguously (Table II) with coupling due to ^{31}P occurring. The largest $J_{P\text{-}C}$ splittings occur with C_5 (37.6 Hz), C_4 (7.6 Hz), and C_7 (13.9 Hz). No coupling with phosphorus was shown by C_6. In the case of $[(\eta^4\text{-}C_6H_7\text{-}5\text{-}exo\text{-dppm})Fe(CO)_3]BF_4$ (III), the same techniques were used in making assignments and the results (Table II) are in good agreement with previous studies;[2] in this case no extra shielding of $H_{6_{exo}}$ was observed, presumably because a phenyl group of dppm was not so close to C_6 as in IV. Unfortunately, we were not able to obtain suitable crystals of III for X-ray analysis.

NMR Spectra of Ring Dimers V–XIV. As discussed above, the ^{31}P NMR spectra provided good evidence for the dimeric nature of this series. The ^1H (and ^{13}C) NMR spectra also support *exo* attachment of both of the phosphorus atoms of dppe to the C_5 ($C_{5'}$) carbon atoms of the two diene rings. Thus for $[(5,5'\text{-}exo\text{-dppe})\{(\eta^4\text{-}C_7H_9\text{-}Fe(CO)_3\}_2][BF_4]_2$ (VI), the coupling constants about $H_{5(5')}$ were calculated as $J_{4,5} = 0$; $J_{5,6_{exo}} = 11.0$ Hz, and $J_{5,6_{endo}} = 3.2$ Hz, in good agreement with those for IV, confirming the *exo* arrangement about C_5 and $C_{5'}$. Similar results were obtained for the other members of the series based on the C_7 ring. Those based on the C_6 ring again gave assignments close to those of III (Table II).

Diphosphine Metal Linked Dimers XVI–XIX. In general the ^1H NMR spectra of this series were generally broad, possibly due to fluxionality; however, the ^{13}C and ^{31}P NMR spectral data (Tables II and III) are in full accord with the metal centers bridged by the diphosphine. Thus the ^{13}C NMR spectral data (Table II) are very similar to those of the starter cations I and II with no phosphorus splitting of the C_5 or C_4 peaks observed in contrast to the above series of diphosphine ring dimers V–XV. Similarly, the ^{31}P spectral data (Table III) show only one resonance typical of a phosphorus bonded to an iron atom.[7]

Metal Chelates. For both XX and XXI, the ^1H and ^{13}C NMR spectra are similar to those of the parent tricarbonylmetal cations I and II with small upfield shifts indicating preservation of the η_5 bonding mode of the C_6H_7 and C_7H_9 rings (Table II). The ^{31}P NMR spectral data (Table III) show only one resonance in the low-field region at δ 10.21 and 9.15 for XX and XXI, respectively, confirming the chelate structure.

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