Journal of Organometallic Chemistry, 482 (1994) 301–308

Synthesis of diphosphine-linked binuclear metal–ring carbonyl complexes

David A. Brown, Ibrahim El-Gamati, William K. Glass and Khaled Kreddan

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

(Received March 9, 1994)

Abstract

Three series (A, B and C) of homobinuclear and heterobinuclear diphosphine-bridged metal–ring carbonyl complexes containing in series A a diphosphine metal–metal bridge $[(\eta^x\text{-ring}_A)(CO)_2M_A\text{–}\mu\text{-}P_2\text{–}M_B(CO)_2(\eta^y\text{-ring}_B)]^{2+}$ ($\text{ring}_A = C_6H_6$, $C_6H_5CH_3$ or C_9H_7; $\text{ring}_B = C_5H_5$ or C_9H_7; M_A = Mn or Fe; M_B = Fe; $-P_2- = Ph_2P(CH_2)_nPPh_2$, n = 1(1, 2, 3, 4), in series B a diphosphine metal–ring bridge $[(\eta^x\text{-ring}_A)(CO)_2M_A\text{–}P_2\text{-}exo\text{-}(\eta^{y-1}\text{-ring}_B)M_B(CO)_3]^{2+}$ ($\text{ring}_A = C_5H_5$, C_9H_7, C_6H_6 or $C_6H_5CH_3$; $\text{ring}_B = C_6H_7$, C_7H_9 or C_7H_7; M_A = Mn or Fe; M_B = Fe or Cr) and in series C a diphosphine ring–ring bridge $[\{-P_2-\}\{(5\text{-}exo\text{-}\eta 4\text{-}(C_xH_y)Fe(CO)_3\}\{(7\text{-}exo\text{-}\eta^6\text{-}C_7H_7)Cr(CO)_3\}]^{2+}$ (x, y = 6,7;7,9) have been made by the facile reaction of suitably activated or substituted ring–metal carbonyl cations with various diphosphines.

Key words: Manganese; Iron; Chromium; Diphosphine; Carbonyl; Binuclear complexes

1. Introduction

Tertiary diphosphines such as the diphenyldiphosphinoalkanes $PPh_2(CH_2)_nPPh_2$ (n = 1, dppm; n = 2, dppe; n = 3, dppp; n = 4, dppb) normally bond directly via the phosphorus atoms to the metal atoms of organometallic molecules and frequently form strongly bonded metal dimers whose reactions with small molecules have been extensively investigated [1]. However, we have shown recently that the above diphosphines may react quite differently under mild conditions with a variety of metal carbonyl complexes of π acids to give new structural types of diphosphine metal complexes [2–4] which include, firstly, *exo* ring adducts involving the bonding of only one phosphorus atom of the *diphosphine* to a ring carbon atom of the π-acid ligand, *e.g.* $[(\eta^4\text{-}C_7H_9\text{-}5\text{-}exo\text{-dppm})Fe(CO)_3][BF_4]$ and, secondly, diphosphine-linked ring–ring dimers, *e.g.* $[(7,7'\text{-}exo\text{-dppb})\{(\eta^6\text{-}C_7H_7)Cr(CO)_3\}_2][BF_4]_2$. The structures of both complexes have been confirmed by X-ray crystallography [2,4].

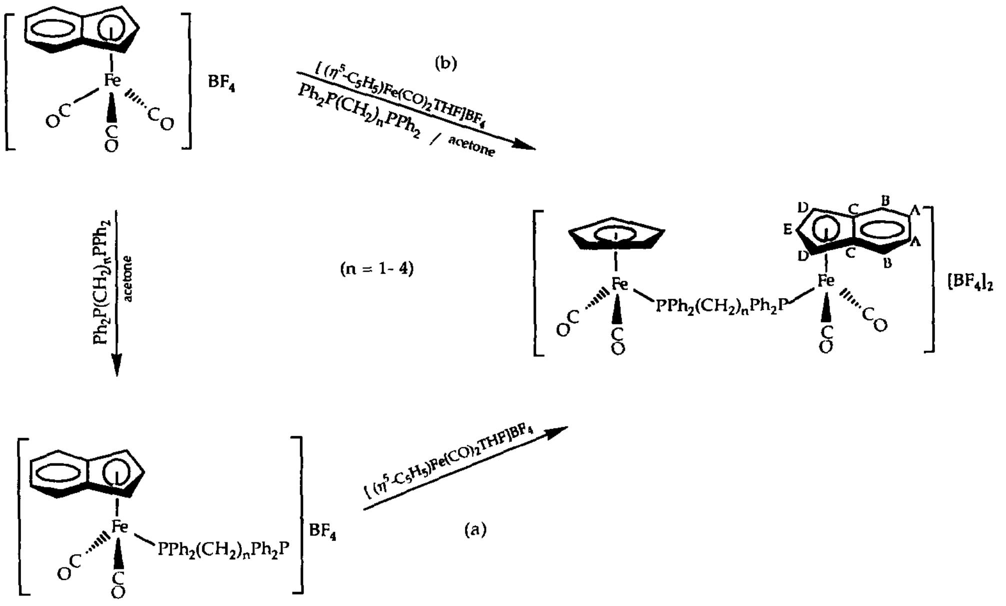
We report here the synthesis of a wide range of homobinuclear and heterobinuclear metal–ring carbonyl complexes (**I–XXIX**) in three series which contain the following series A, the well-established diphosphine bridged metal–metal structure [1]; series B, diphosphine-linked metal–ring bridges; series C, diphosphine-linked ring–ring bridges.

2. Results and discussion

In general, direct reaction between two different ring–metal carbonyl cations $[(\eta^x\text{-ring}_A)M_A(CO)_3]^+$ and $[\eta^y\text{-ring}_B)M_B(CO)_3]^+$ and a diphosphine $(-P_2-)\{-P_2- = PPh_2(CH_2)_nPPh_2$ (n = 1, dppm; n = 2, dppe; n = 3, dppp; n = 4, dppb)}, which is essentially a self-assembly type procedure, was unsuccessful in the absence of some activating procedure. In order to promote reaction under mild conditions, it was found necessary first to replace one carbonyl group of one cation by a monodentate bonded diphosphine to form $[(\eta^x\text{-ring}_A)M_A(CO)_2(\eta^1\text{-}P_2\text{-})]^+$ and then to replace one carbonyl group of the second cation by a labile group such as tetrahydrofuran (THF) to form $[(\eta^y\text{-ring}_B)M_B(CO)_2(THF)]^+$. Reaction of these substituted ring–metal carbonyl complexes then proceeded rapidly at room temperature to give binuclear diphosphine metal–metal bridged cations $[(\eta^x\text{-ring}_A)(CO)_2M_A\text{–}\mu\text{-}P_2\text{-}M_B(CO)_2\text{-}$

Correspondence to: Professor D.A. Brown.

0022-328X/94/$7.00
SSDI 0022-328X(94)24654-2

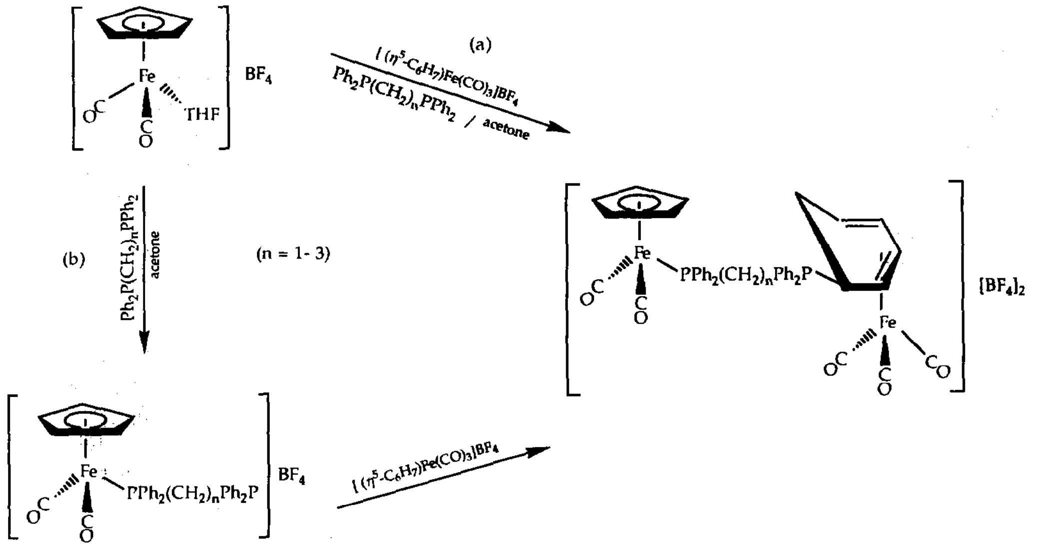


Scheme 1.

$(\eta^y$-$ring_B)]^{2+}$ (Scheme 1(a)), both homonuclear and heteronuclear, depending on the nature of M_A and M_B (method 1).

In some cases, the metal–metal bridged complexes may be prepared by activation of only one of the starter cations, *e.g.* by the synthesis of $[(\eta^5$-C_5H_5-$Fe(CO)_2(THF)]^+$, and allowing it to react by a self-assembly route, with another ring–metal carbonyl cation, *e.g.* $[(\eta^5$-$C_9H_7)Fe(CO)_3]^+$ in the presence of a diphosphine (method 2 and Scheme 1(b)). Similarly, direct reaction of $[(\eta^x$-$ring_A)M_A(CO)_2(\eta^1$-$P_2)]^+$ with $[(\eta^y$-$ring_B)M_B(CO)_3]^+$ can also be used in some cases (method 3). By these various routes, a range of binuclear diphosphine metal–metal bridged complexes (**I–XI**) was prepared (Table 1).

The ring–metal diphosphine-bridged complexes (series B) (**XII–XXV** may be prepared by a modified self-assembly-type reaction between a ring–metal carbonyl complex containing a labile ligand $[(\eta^x$-$ring_A)M_A(CO)_2(THF)]^+$, the cyclodienyl iron tricarbonyl cations $[(\eta^5$-$C_xH_y)Fe(CO)_3]^+$ (x, $y = 6, 7; 7, 9$), and a diphosphine (method 4 and Scheme 2(a)). Alter-



Scheme 2.

TABLE 1. Analytical data, IR carbonyl stretching frequencies and ^{31}P NMR data for binuclear diphosphine ligand complexes

Complex	Anal. Found (calc.) (%)			IR ν (CO) (cm^{-1})	δ (ppm)	δ (ppm)
	H	C	P			
Series A: diphosphine metal–metal bridged dimers (I–IX)					δ(PM_A)	δ(PM_B)
$[(C_6H_6)Mn(CO)_2(\mu\text{-dppc})(CO)_2Fe(C_5H_5)][PF_6][BF_4]$ (**I**)[a]	49.2 (49.6)	3.8 (3.1)	8.5 (9.4)	2055, 2004, 1956	72.1	62.9
$[(C_6H_6)Mn(CO)_2(\mu\text{-dppp})(CO)_2Fe(C_5H_5)][PF_6][BF_4]$ (**II**)[a]	49.4 (50.0)	4.2 (3.7)	8.0 (9.1)	2054, 2005, 1956	66.3	57.9
$[(C_6H_5CH_3)Mn(CO)_2(\mu\text{-dppe})(CO)_2Fe(C_5H_5)][PF_6][BF_4]$ (**III**)[a]	49.8 (49.9)	3.8 (3.7)	10.6 (9.2)	2054, 1988, 1952	72.9	62.8
$[(C_6H_5CH_3)Mn(CO)_2(\mu\text{-dppp})(CO)_2Fe(C_5H_5)][PF_6][BF_4]$ (**IV**)[a]	50.2 (50.4)	4.1 (3.9)	9.1 (9.1)	2054, 1997, 1951	66.9	57.9
$[(C_9H_7)Fe(CO)_2(\mu\text{-dppm})(CO)_2Fe(C_5H_5)][BF_4]_2$ (**V**)[a]	53.1 (53.6)	3.6 (3.6)	6.2 (6.5)	2050, 2008	67.9	63.8
$[(C_9H_7)Fe(CO)_2(\mu\text{-dppe})(CO)_2Fe(C_5H_5)][BF_4]_2$ (**VI**)[a]	54.1 (54.2)	4.1 (3.7)	7.5 (6.4)	2052, 2008	66.7	63.1
$[(C_9H_7)Fe(CO)_2(\mu\text{-dppp})(CO)_2Fe(C_5H_5)][BF_4]_2$ (**VII**)[a]	53.7 (54.6)	3.9 (3.8)	7.2 (6.3)	2052, 2008	62.6	58.0
$[(C_9H_7)Fe(CO)_2(\mu\text{-dppb})(CO)_2Fe(C_5H_5)][BF_4]_2$ (**VIII**)[a]	54.9 (55.0)	4.2 (4.0)	7.3 (6.2)	2050, 2006	63.3	58.4
$[(C_6H_6)Mn(CO)_2(\mu\text{-dppe})(CO)_2Fe(C_9H_7)][PF_6][BF_4]$ (**IX**)[a]	48.1 (51.7)	3.6 (3.6)	9.2 (8.9)	2048, 2004, 1956	71.9	65.4
$[(C_6H_5CH_3)Mn(CO)_2(\mu\text{-dppe})(CO)_2Fe(C_9H_7)][PF_6][BF_4]$ (**X**)[a]	51.1 (52.1)	3.9 (3.8)	8.7 (8.8)	2048, 2000, 1952	72.7	65.1
$[(C_6H_6)Mn(CO)_2(\mu\text{-dppp})(CO)_2Fe(C_9H_7)][PF_6][BF_4]$ (**XI**)[a]	50.2 (52.1)	3.8 (3.7)	10.1 (8.8)	2048, 2002, 1955	66.0	62.3
Series B: diphosphine-bridged metal–ring complexes (XII–XXV)					δ(PM)	δ(PR)
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(dppe)(exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3][BF_4]_2$ (**XII**)[a]	51.8 (52.1)	3.9 (3.7)	6.1 (6.4)	2046, 2011, 1985	58.4	31.3
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(dppp)(exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3][BF_4]_2$ (**XIII**)[a]	53.1 (52.5)	4.5 (3.9)	5.8 (6.3)	2056, 2008, 1984	63.8	33.8
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(dppe)(exo\text{-}\eta^4\text{-}C_7H_9)Fe(CO)_3][BF_4]_2$ (**XIV**)[a]	51.2 (52.6)	4.9 (3.9)	5.8 (6.3)	2054, 2010, 1983	58.4	31.6
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(dppp)(exo\text{-}\eta^4\text{-}C_7H_9)Fe(CO)_3][BF_4]_2$ (**XV**)[a]	52.7 (53.1)	4.1 (4.1)	6.3 (6.2)	2054, 2008, 1982	63.7	33.6
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(dppp)(exo\text{-}\eta^6\text{-}C_7H_7)Cr(CO)_3][BF_4]_2$ (**XVI**)[a]	52.4 (53.4)	4.0 (3.9)	6.2 (6.3)	2054, 2009, 1992, 1931, 1901	59.5	22.3
$[(\eta^5\text{-}C_9H_7)Fe(CO)_2(dppm)(exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3][BF_4]_2$ (**XVII**)[a]	52.9 (53.8)	4.0 (3.6)	5.1 (6.2)	2057, 2010, 1988	65.9	27.2
$[(\eta^5\text{-}C_9H_7)Fe(CO)_2(dppe)(exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3][BF_4]_2$ (**XVIII**)[a]	52.9 (54.2)	3.9 (3.8)	6.1 (6.1)	2056, 2004, 1986	68.7	33.8
$[(\eta^5\text{-}C_9H_7)Fe(CO)_2(dppp)(exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3][BF_4]_2$ (**XIX**)[a]	53.6 (54.6)	3.9 (3.9)	6.2 (6.0)	2056, 1999, 1987	62.8	31.3
$[(\eta^5\text{-}C_9H_7)Fe(CO)_2(dppe)(exo\text{-}\eta^4\text{-}C_7H_9)Fe(CO)_3][BF_4]_2$ (**XX**)[a]	54.3 (54.6)	4.0 (3.9)	5.8 (6.0)	2053, 2004, 1983	62.8	31.5
$[(\eta^5\text{-}C_9H_7)Fe(CO)_2(dppp)(exo\text{-}\eta^4\text{-}C_7H_9)Fe(CO)_3][BF_4]_2$ (**XXI**)[a]	54.3 (55.1)	4.2 (4.1)	6.0 (5.9)	2053, 2001, 1983	68.4	33.5
$[(\eta^6\text{-}C_6H_6)Mn(CO)_2(dppp)(exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3][PF_6][BF_4]$ (**XXII**)[a]	49.4 (50.3)	3.9 (3.6)	9.3 (8.8)	2056, 1988, 1956	66.5	31.1
$[(\eta^6\text{-}C_6H_6)Mn(CO)_2(dppp)(exo\text{-}\eta^4\text{-}C_7H_9)Fe(CO)_3][PF_6][BF_4]$ (**XXIII**)[a]	49.6 (50.6)	3.9 (3.9)	8.8 (8.7)	2053, 1983, 1957	66.5	31.3
$[(\eta^6\text{-}C_6H_5CH_3)Mn(CO)_2(dppm)(exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3][PF_6][BF_4]$ (**XXIV**)[a]	49.2 (49.7)	3.6 (3.6)	9.3 (8.9)	2057, 1988, 1959	74.1	27.1
$[(\eta^6\text{-}C_6H_5CH_3)Mn(CO)_2(dppb)(exo\text{-}\eta^4\text{-}C_7H_9)Fe(CO)_3][PF_6][BF_4]$ (**XXV**)[a]	49.2 (48.1)	4.2 (3.9)	7.9 (7.9)	2056, 1988, 1951	76.1	31.8
Series C: diphosphine bridged ring–ring complexes (XXVI–XXIX)					δ(PR_1)	δ(PR_2)
$[\{PPh_2(CH_2)_3PPh_2\}\{(5\text{-}exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3\}\{(7\text{-}exo\text{-}\eta^6C_7H_7)Cr(CO)_3\}][BF_4]_2$ (**XXV**)[b]	52.6 (53.3)	3.9 (3.9)	6.2 (6.0)	2060, 1966, 1941, 1908	31.8	21.6
$[\{PPh_2(CH_2)_4PPh_2\}\{(5\text{-}exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3\}\{(7\text{-}exo\text{-}\eta^6\text{-}C_7H_7)Cr(CO)_3\}][BF_4]_2$ (**XXVII**)[b]	53.1 (53.9)	3.9 (4.1)	6.1 (5.9)	2060, 1997, 1941, 1905	31.8	21.0
$[\{PPh_2(CH_2)_3PPh_2\}\{(5\text{-}exo\text{-}\eta^4\text{-}C_7H_9)Fe(CO)_3\}\{(7\text{-}exo\text{-}\eta^6\text{-}C_7H_7)Cr(CO)_3\}][BF_4]_2$ (**XXVIII**)[b]	53.2 (53.9)	4.3 (4.1)	6.1 (5.9)	2056, 1995, 1941, 1908	31.5	20.2
$[\{PPh_2(CH_2)_4PPh_2\}\{(5\text{-}exo\text{-}\eta^4\text{-}C_7H_9)Fe(CO)_3\}\{(7\text{-}exo\text{-}\eta^6\text{-}C_7H_7)Cr(CO)_3\}][BF_4]_2$ (**XXIX**)[b]	53.9 (54.4)	4.6 (4.2)	6.1 (5.8)	2056, 1996, 1941, 1905	33.8	22.7

M_A, metal one; M_B, metal two; M = metal; R = ring. PM_A = phosphorus atom bonded to M_A; P_M = phosphorus atom bonded to M. PM_B = phosphorus atom bonded to M_B; P_R = phosphorus atom bonded to R. $R_1 = (C_6H_7)$ or (C_7H_9); $R_2 = (C_7H_7)$. P_{R_1} = phosphorus atom bonded to R_1. P_{R_2} = phosphorus atom bonded to R_2. [a] Solvent acetonitrile. [b] Solvent dichloromethane. 85% H_3PO_4 as internal standard.

natively, reaction between $[(\eta^x\text{-ring}_A)M_A(CO)_2(\eta^1\text{-}P_2)]^+$ and the cyclodienyl iron tricarbonyl cation may be used (method 5 and Scheme 2(b)).

Finally, the ring–ring diphosphine-bridged dimers (series C) **XXVI–XXIX** may be prepared simply by direct assembly between $[(\eta^7\text{-}C_7H_7)Cr(CO)_3]^+$, the cyclodienyl cations $[(\eta^5\text{-}C_xH_y)Fe(CO)_3]^+$ (x, y = 6, 7; 7, 9) and the appropriate diphosphine, $PPh_2(CH_2)_nPPh_2$ (n = 3, dppp; n = 4, dppb) (method 6 and Scheme 3). We now consider each series in turn.

2.1. Series A: diphosphine metal–metal bridged dimers (I–IX)

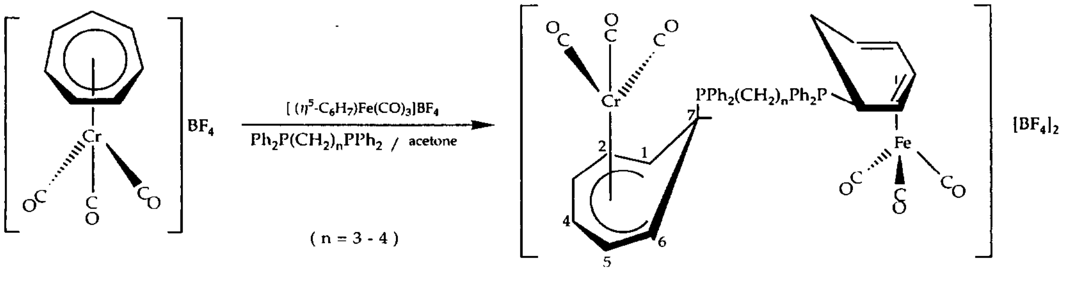
A series of the complexes $[(\eta^x\text{-ring}_A(CO)_2M_A\text{-}\mu\text{-}P_2\text{-}M_B(CO)_2(\eta^y\text{-ring}_B)]^{2+}$ containing cyclopentadienyl, indenyl and benzene rings with M_A, M_B = Mn or Fe in various combinations were prepared by the general routes discussed above (see Section 3 for details). Analytical and spectroscopic data given in Tables 1 and 2 support their formulation as diphosphine-linked metal–metal dimers. For example, two of the IR carbonyl stretching frequencies of $[(\eta^6\text{-}C_6H_5CH_3)(CO)_2Mn(\mu\text{-dppp})Fe(CO)_2(\eta^5\text{-}C_5H_5)][PF_6][BF_4]$ (**IV**) which appear at 2054 and 2004 cm^{-1}, are close to those for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-dppp})][BF_4]$ [5]; another two, at 2004 and 1956 cm^{-1}, are close to those for $[(\eta^6\text{-}C_6H_5CH_3)Mn(CO)_2(\eta^1\text{-dppp})][PF_6]$ [6].

The ^1H NMR spectrum gives clear support for retention of the hapticities of both ring$_A$ and ring$_B$ in **IV** (Table 2). Thus the cyclopentadienyl ring shows a double doublet at δ = 5.15 ppm and the toluene protons appear as a doublet of doublets for H(2,6) at δ = 5.36 ppm, a doublet of triplets for H(3,5) at δ = 5.9 ppm and a doublet of triplets for H(4) at δ = 5.5 ppm. Similarly, the ^{13}C spectrum is consistent with retention of hapticity by both rings, with the absence of any ^{13}C resonance due to a carbon atom to which phosphorus is bonded which would result in a typical splitting with $J(C\text{–}P) \approx 30\text{–}40$ Hz.

The ^{31}P NMR spectrum (Table 1) provides the most conclusive evidence, showing a resonance at δ = 66.9 ppm due to the phosphorus bonded to the manganese atom, a value very close to that of δ = 67.2 ppm found for $[(\eta^6\text{-}C_6H_5CH_3)Mn(CO)_2(\eta^1\text{-dppp})][PF_6]$ [6], and a second resonance at δ = 57.9 ppm due to phosphorus bonded to the iron atom, a value close to that of δ = 60.3 ppm for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-dppp})][BF_4]$ [5]. Resonances due to a phosphorus atom bonded to a ring carbon atom that appear around the region of $\delta \approx 20\text{–}30$ ppm and exhibit a clear splitting due to P–C coupling ($J_{P\text{–}C} \approx 30\text{–}40$ Hz) and those due to a pendant P which occur around $\delta \approx -30$ ppm are clearly absent in the case of **IV** and other members of series A (**I–XI**), whereas they are present in the case of compounds of the series B (**XII–XXV**) and series C (**XXVI–XXIX**).

2.2. Series B: Diphosphine bridged metal–ring complexes (XII–XXV)

As for series A, NMR spectroscopy is the most informative spectroscopic technique for elucidating the structures of series B. Thus, in general, the ^1H NMR spectra of the cations of series B complexes $[(\eta^x\text{-ring}_A)M_A(CO)_2(PPh_2(CH_2)_nPPh_2)\text{-}exo\text{-}(\eta^{y-1}\text{-ring}_B)M_B(CO)_3]^{2+}$ (ring$_A$ = C_6H_6, C_6H_5 CH_3 or C_9H_7; ring$_B$ = C_6H_7, C_7H_9 or C_7H_7; M_A = Fe or Mn; M_B = Fe or Cr; n = 1, 2, 3, 4) (**XII–XXV**) are similar to those of their constituent mononuclear parts. For example, the ^1H NMR spectrum of $[(\eta^6\text{-}C_6H_5CH_3)Mn(CO)_2(\text{dppm})(exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3][PF_6][BF_4]$ (**XXIV**) (Table 2) is very similar to that of $[(\eta^6\text{-}C_6H_5CH_3)Mn(CO)_2(\eta^1\text{-dppm})][PF_6]$ [6] and $[(\eta^4\text{-}C_6H_7\text{-}5\text{-}exo\text{-dppm})Fe(CO)_3][BF_4]$ [3]. In particular, H(5) (C_6H_7 ring) appears as a double triplet at δ = 3.9 ppm ($J_{P\text{–}H}$ = 7.2 Hz) close to the values for the dppm ring adduct of $[(C_6H_7)Fe(CO)_3]^+$ [3]. Similarly, C(5) appears at δ = 33.7 ppm with $J_{P\text{–}C}$ = 33.3 Hz. Finally the ^{31}P spectrum (Table 1) provides clear evidence for a metal–ring diphosphine bridge, with resonances at δ = 74.1 and δ = 27.1 ppm due to phosphorus bonded to the manganese centre and phosphorus bonded to C(5) of the C_6H_7 ring respectively. These values are very close to, but not identical with those for the parent mononuclear compounds. The differences in δ values



Scheme 3.

TABLE 2. ^1H and ^{13}C NMR spectra data for selected binuclear diphosphine ligand complexes

Complex	Chemical shift δ (ppm)	Assignment	
Series A: diphosphine metal–metal bridged dimers (***IV***)			
$[(C_6H_5CH_3)Mn(CO)_2(\mu\text{-dppp})(CO)_2Fe(C_5H_5)][PF_6][BF_4]$ [a]	7.45 (m)	$-C_6H_5$ (phenyls)	
	5.90 (dt)	H (3,5)	
	5.36 (dt)	H (2,6)	
	5.52 (dt)	H (4)	
	5.15 (dt)	C_5H_5	
	2.80 (s)	CH_3	
	2.69 (dq)	CH_2-(α)	
	2.53 (dq)	CH_2-(γ)	
	1.14 (m)	CH_2-(β)	
	223.00 (d)	Mn–CO	
	210.73 (d)	Fe–CO	
	131.97 (m)	$-C_6H_5$ (phenyls)	
	116.09 (s)	$C(1)-CH_3$	
	101.60 (d)	C(2,6)	
	97.80 (d)	C(3,5)	
	97.20 (d)	C(4)	
	89.40 (d)	C_5H_5	
	33.80 (m)	$-CH_2$(α,γ)	
	20.74 (d)	CH_2(β)	
	20.27 (s)	CH_3	
Series B: diphosphine bridged metal–ring complexes (***XXIV***)			
$[(\eta^6\text{-}C_6H_5CH_3)Mn(CO)_2(dppm)(exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3][PF_6][BF_4]$ [a]	7.50 (br)	$-C_6H_5$ (phenyls)	
	5.45 (br)	H(4)	$(C_6H_5CH_3)$
	5.61 (br)	H(3,5)	$(C_6H_5CH_3)$
	5.96 (br)	H(2,6)	$(C_6H_5CH_3)$
	2.75 (br)	H(1)	(C_6H_7)
	4.65 (br)	H(2)	(C_6H_7)
	5.10 (t)	H(3)	(C_6H_7)
	2.50 (br)	H(4)	(C_6H_7)
	3.90 (dt)	H(5)	(C_6H_7)
	1.51 (br)	$H(6)_{exo}$	(C_6H_7)
	2.24 (br)	$H(6)_{endo}$	(C_6H_7)
	Not clear	CH_2	
	2.32 (br)	CH_3	
	223.00 (d)	Mn(CO)	
	211.00 (s)	Fe(CO)	
	131.00 (m)	$-C_6H_5$ (phenyls)	
	118.00 (s)	$C(1)CH_3$	$(C_6H_5CH_3)$
	102.00 (s)	C(2,6)	$(C_6H_5CH_3)$
	97.00 (s)	C(3,5)	$(C_6H_5CH_3)$
	94.00 (s)	C(4)	$(C_6H_5CH_3)$
	59.65 (s)	C(1)	(C_6H_7)
	85.50 (s)	C(2)	(C_6H_7)
	86.20 (s)	C(3)	(C_6H_7)
	50.60 (d)	C(4)	(C_6H_7)
	33.70 (d)	C(5)	(C_6H_7)
	26.50 (s)	C(6)	(C_6H_7)
	24.15 (br)	CH_2	
	19.60 (s)	CH_3	
Series C: diphosphine bridged ring–ring complexes (***XXVII***)			
$[\{PPh_2(CH_2)_4PPh_2\}\{(5\text{-}exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3\}\{(7\text{-}exo\text{-}\eta^6\text{-}C_7H_7)Cr(CO)_3\}][BF_4]_2$ [b]	7.65 (m)	Phenyls	
	3.07 (br)	H(1)	(C_6H_7) ring
	4.96 (br)	H(2)	(C_6H_7) ring
	5.30 (br)	H(3)	(C_6H_7) ring
	2.89 (br)	H(4)	(C_6H_7) ring
	3.61 (br)	H(5)	(C_6H_7) ring
	1.82 (br)	H(6)*exo*	(C_6H_7) ring
	2.62 (br)	H(6)*endo*	(C_6H_7) ring

TABLE 2 (continued)

Complex	Chemical shift δ (ppm)	Assignment
	3.12 (br)	H(1,6) (C_7H_7) ring
	4.84 (br)	H(2,5) (C_7H_7) ring
	5.58 (br)	H(3,4) (C_7H_7) ring
	5.54 (br)	H(7) (C_7H_7) ring
	2.65 (br)	$-CH_2$ (α, δ)
	1.46 (br)	$-CH_2$ (β, γ)
	54.28 (s)	C(1) (C_6H_7) ring
	85.43 (s)	C(2) (C_6H_7) ring
	85.91 (s)	C(3) (C_6H_7) ring
	51.37 (s)	C(4) (C_6H_7) ring
	31.49 (d)	C(5) (C_6H_7) ring
	26.87 (s)	C(6) (C_6H_7) ring
	59.05 (s)	C(1,6) (C_7H_7) ring
	97.13 (s)	C(2,5) (C_7H_7) ring
	103.59 (s)	C(3,4) (C_7H_7) ring
	35.59 (d)	C(7) (C_7H_7) ring
	22.41 (m)	$-CH_2$ (α,δ)
	16.99 (m)	$-CH_2$ (β,γ)

[a] Solvent acetonitrile. [b] Solvent dichloromethane.

for **XXIV** ($\delta = 74.1$ ppm) and the parent ($\delta = 70.4$ ppm) for P bonded to Mn when compared with those for P bonded to a ring carbon atom (**XXIV** $\delta = 27.1$ ppm; parent, $\delta = 31.7$ ppm) suggest that there is more donation from P to Mn in the metal–ring dimer than in the parent cation and slightly less donation from P to C(5); however, this is not a general trend, and in the case of dppe, dppp and dppb, which do not form mono-ring adducts with the parent cyclodienylium iron tricarbonyl cations [3], comparison must be made with the corresponding symmetric diphosphine-bridged ring–ring dimers [3]. In these cases, the differences between values of δ_P for P–C(5) in series B and those for corresponding ring–ring dimers depend on the chain length of the diphosphine, sometimes being positive (dppp) and sometimes negative (dppe).

2.3. *Series C: Diphosphine bridged ring–ring complexes (XXVI–XXIX)*

Four of these complexes (**XXVI–XXIX**) were obtained by a self-assembly route based on reaction of the $[(\eta^7\text{-}C_7H_7)Cr(CO)_3]^+$ cation with one of the cyclodienyl iron tricarbonyl cations $[(\eta^5\text{-}(C_xH_y)Fe(CO)_3]^+$ (x, y = 6, 7; 7, 9) and either dppp or dppb. Analytical and spectroscopic data are given in Tables 1 and 2. Again, as with series B, the spectroscopic properties are very similar to, but not identical with, those of the corresponding symmetric homonuclear diphosphine-bridged ring–ring complexes of iron [3] and chromium [4]. For example, $[\{dppb\}\{5\text{-}exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3\}\{7\text{-}exo\text{-}\eta^6\text{-}C_7H_7)Cr(CO)_3\}][BF_4]_2$ (**XXVII**) shows ν(CO) stretching frequencies at 2057, 1991, 1931 and 1900 cm^{-1}, which are close to those for the $Fe(CO)_3$ moiety in $[(5,5'\text{-}exo\text{-}dppb)\{\eta^4\text{-}C_6H_7)Fe(CO)_3\}_2][BF_4]_2$ (ν_{CO} = 2056 and 1986 cm^{-1}) [3] and the $Cr(CO)_3$ moiety in $[(7,7'\text{-}exo\text{-}dppb)\{(\eta^6\text{-}C_7H_7)Cr(CO)_3\}_2][BF_4]_2$ [4]. Similarly, the ^1H and ^{13}C NMR spectra are very similar to those of the analogous symmetric ring–ring dimers. For example, C(5) (C_6H_7 ring) in **XXVII** appears as a doublet at $\delta = 31.5$ ppm with $J_{P-C} = 39.7$ Hz compared with $\delta = 31.2$ ppm with $J_{P-C} = 37.1$ Hz in $[(5,5'\text{-}exo\text{-}dppb)\{(\eta^4\text{-}C_6H_7)Fe(CO)_3\}_2][BF_4]_2$ [3] and C(7)(C_7H_7 ring) at $\delta = 35.6$ ppm (doublet) with $J_{P-C} = 30.1$ Hz compared with $\delta = 34.1$ ppm (doublet) with $J_{P-C} = 30$ Hz in $[(7,7'\text{-}exo\text{-}dppb)\{(\eta^6\text{-}C_7H_7)Cr(CO)_3\}_2][BF_4]_2$ [4]. Finally, the ^{31}P NMR spectra again provide the most convincing evidence for diphosphine-linked ring–ring dimers in series C, with in each case two distinct resonances, one in the region 20–22 ppm due to a phosphorus atom bonded *exo* to the C(7) atom of the C_7H_7 ring [4] and one in the region 30–32 ppm due to a phosphorus atom bonded *exo* to the C(5) atom of the C(6) and C(7) cyclodienyl rings [3]. No ^{31}P resonances due to phosphorus atoms bonded to a metal centre were observed, in contrast with series A and B.

Finally, it should be noted that in a number of the above diphosphine-linked dimers the ^{31}P signals are split within the range 10–40 Hz. In some cases the splittings are unequal at the two phosphorus atoms; clearly the splittings are not due to mutual phosphorus coupling as in a typical mononuclear cation such as $[(\eta^5\text{-}C_9H_7)Fe(CO)_2(\eta^1\text{-}dppe)][BF_4]$ where $J_{PP} = 39.7$ Hz [7]. We consider that the ^{31}P splittings observed in a number of these complexes arise from conformational isomerism. Further studies are in progress to elucidate the nature of this isomerism.

3. Experimental details

Solvents were freshly dried by standard methods. All reactions and work-up were carried out under high purity nitrogen. Tertiary diphosphines (dppm, dppe, dppp and dppb) ($n = 1$, 2, 3 and 4, respectively) were purchased from suppliers and used without further purification. IR 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 GX270 spectrometer. Analyses were performed by the Microanalytical Laboratory of the Chemical Services Unit of University College Dublin and are given in Table 1 together with the IR carbonyl stretching frequencies of the new compounds. Published methods were used for the preparation of the starter cations [6–11].

Typical preparations are as follows.

3.1. Series A

3.1.1. (Preparation of $[(\eta^6\text{-}C_6H_5CH_3)Mn(CO)_2(\mu\text{-}dppp)(CO)_2Fe(\eta^5\text{-}C_5H_5)][PF_6][BF_4]$ (IV): method 1

(Toluene)manganese bis(diphenylphosphino)propane dicarbonyl hexafluorophosphate (0.3 g, 0.29 mmol) was treated with cyclopentadienyl iron dicarbonyl tetrahydrofuran tetrafluoroborate (0.2 g, 0.59 mmol) in acetone (50 ml) at room temperature under nitrogen. The reaction was monitored by IR spectroscopy until the carbonyl stretching peaks of the starting cation $[\eta^5\text{-}(C_5H_5)Fe(CO)_2THF]BF_4$ had disappeared (9 h). The addition of ether led to precipitation of the product as yellow crystals (68% yield). The product is stable under nitrogen at 0°C.

3.1.2. Preparation of $[(\eta^5\text{-}C_9H_7)Fe(CO)_2(\mu\text{-}dppb)(CO)_2Fe(\eta^5\text{-}C_5H_5)][BF_4]_2$ (VIII): method 2

Reaction of a 1 : 1 : 1 molar ratio of $[(\eta^5\text{-}C_9H_7)Fe(CO)_3]BF_4$ (0.3 g, 0.87 mmol) with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2THF]BF_4$ (0.34 g, 0.88 mmol) and bis(diphenyl phosphino)butane (0.29 g, 0.86 mmol) in acetone (50 ml) at room temperature under nitrogen gave the metal–metal dimer $[(\eta^5\text{-}C_9H_7)Fe(CO)_2(\mu\text{-}dppb)(CO)_2Fe(\eta^5\text{-}C_5H_5)][BF_4]_2$. The reaction was monitored by IR spectroscopy until conversion into the desired complex was complete (4 h). The solution was then filtered, and addition of ether precipitated the final product as yellow crystals (70% yield). The product is stable at room temperature.

3.1.3. Preparation of $[(\eta^6\text{-}C_6H_6)Mn(CO)_2(\mu\text{-}dppe)(CO)_2Fe(\eta^5\text{-}C_9H_7)][PF_6][BF_4]$(IX): method 3

A mixture of benzene manganese bis(diphenylphosphino)ethane tetrafluoroborate (0.4 g, 0.4 mmol) and indenyl iron tricarbonyl trafluoroborate (0.14 g, 0.41 mmol) in acetone (50 ml) was stirred at room temperature under nitrogen until conversion was complete, as shown by IR spectroscopy (12 h). Filtration of the solution and addition of ether precipitated the product as yellow crystals (67% yield).

3.2. Series B

3.2.1. Preparation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(dppp)(exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3][BF_4]_2$ (XIII): method 4

A mixture of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2THF]BF_4$ (0.3 g, 0.89 mmol), $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ (0.273 g, 0.89 mmol) and bis(diphenylphosphino)propane (0.37 g, 0.89 mmol) in a 1 : 1 : 1 molar ratio in acetone (50 ml) was kept at room temperature under nitrogen until conversion into the desired complex was complete, as shown by IR spectroscopy (6 h). The solution was filtered, and addition of ether precipitated the product as yellow crystals of the diphosphine-bridged ring–metal dimer $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(dppp)(exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3][BF_4]_2$ (74% yield). The product was stable for several months under nitrogen at 0°C.

3.2.2. Preparation of $[(\eta^6\text{-}C_6H_5CH_3)Mn(CO)_2(dppm)(exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3][PF_6][BF_4]$ (XXIV): method 5

A mixture of $[(\eta^6\text{-}C_6H_5CH_3)Mn(CO)_3]PF_6$ (0.3 g, 0.79 mmol) and bis(diphenylphosphino)methane (0.31 g, 0.80 mmol) in acetone (50 ml) was kept at room temperature under nitrogen until conversion into $[(\eta^6\text{-}C_6H_5CH_3)Mn(CO)_2(\eta^1\text{-}dppm)][PF_6]$ was complete, as confirmed by IR spectroscopy. The salt $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ (0.24 g, 0.79 mmol) was then added and the reaction monitored by IR spectroscopy until the carbonyl stretching peaks of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ had disappeared (30 min). The addition of ether then precipitated yellow crystals of the diphosphine-bridged ring–metal dimer $[(\eta^6\text{-}C_6H_5)Mn(CO)_2(dppm)(exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3][PF_6][BF_4]$ (68% yield).

3.3. Series C

3.3.1. Preparation of $[(dppb)\{(5\text{-}exo\text{-}\eta^4\text{-}C_6H_7)Fe(CO)_3\}\{(7\text{-}exo\text{-}\eta^6\text{-}C_7H_7)Cr(CO)_3\}][BF_4]_2$ (XXVII): method 6

A mixture of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ (0.5 g, 1.6 mmol), $[(\eta^7\text{-}C_7H_7)Cr(CO)_3]BF_4$ (0.5 g, 1.6 mmol) and bis(diphenylphosphino)butane (0.69 g, 1.6 mmol) (in acetonitrile (50 ml) was kept at room temperature under nitrogen until complete conversion had occurred, as shown by IR spectroscopy. The solution was filtered, and addition of ether precipitated the product as salmon-pink crystals. These were filtered off and recrystallized from dichloromethane–hexane to give a 78% yield of the ring–ring dimer [(dppb){(5-*exo*-η^4-C_6H_7)Fe$(CO)_3$}{(7-*exo*-η^6-C_7H_7)Cr$(CO)_3$}]$[BF_4]_2$.

Acknowledgments

We thank Mrs. Geraldine Fitzpatrick for her expert help with recording the NMR spectra.

References

1 R.J. Puddephatt, *Chem. Soc. Rev.*, (1983) 99.

2 D.A. Brown, J. Burns, I. El-Gamati, W.K. Glass, K. Kreddan, M. Salama, D. Cunningham, T. Higgins and P. McArdle, *J. Chem. Soc., Chem. Commun.* (1992) 701.

3 D.A. Brown, W.K. Glass and M.M. Salama, *Organometallics, 12* (1993) 2515.

4 D.A. Brown, J. Burns, W.K. Glass, D. Cunningham, P.A. McArdle, T. Higgins and M. Salama, *Organometallics*, in press.

5 E.E. Isaacs and W.A.G. Graham, *J. Organomet. Chem. 120* (1976) 407.

6 D.A. Brown, W.K. Glass, K.M. Kreddan, D. Cunningham, P.A. McArdle and T. Higgins, *J. Organomet. Chem. 418* (1991) 91.

7 D.A. Brown, N.J. Fitzpatrick, W.K. Glass, H. Ahmed, D. Cunningham and P.A. McArdle, *J. Organomet. Chem.*, *455* (1993) 157.

8 D.L. Reger and C. Coleman, *J. Organomet. Chem.*, *131* (1977) 153.

9 H.H. Hammud and G.M. Moran, *J. Organomet. Chem.*, *307* (1986) 255.

10 H.R. Jr. Dauben and D.J. Bertelli, *J. Am. Chem. Soc.*, *83* (1961) 479.

11 J.D. Munro and P.L. Pauson, *J. Chem. Soc.*, (1961) 3475.