Novel Bonding of Tertiary Diphosphines to Metal Ring Carbonyl Complexes

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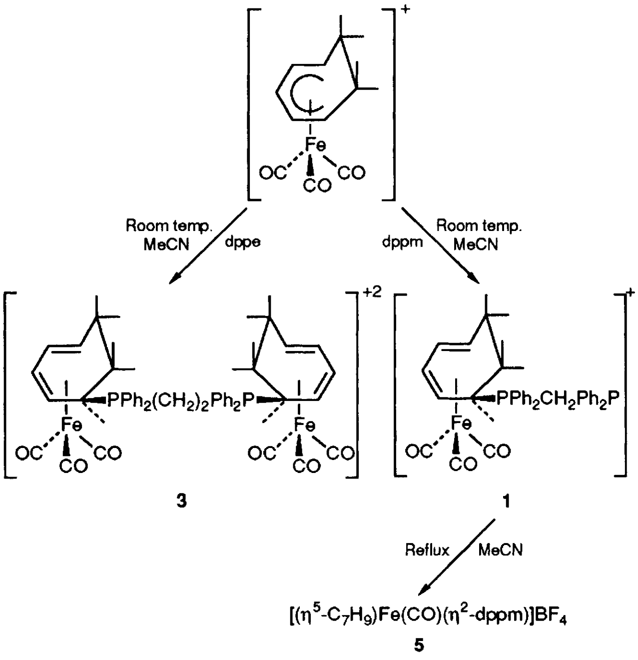
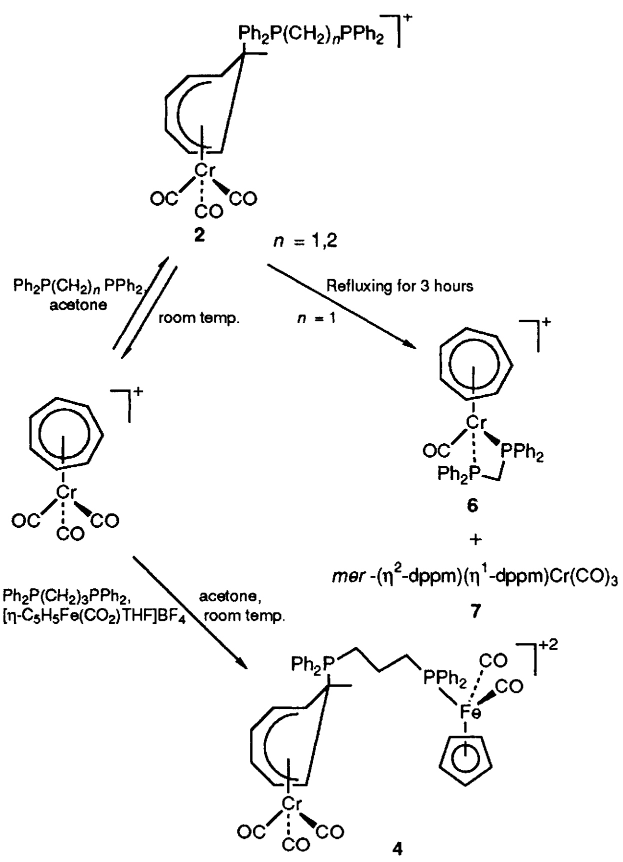
Tertiary diphosphines form complexes with various metal ring carbonyl cations of new and novel structural types including ring adducts, *e.g.* $[(\eta^4\text{-}C_7H_9\text{-}5\text{-}exo\text{-}\eta^1\text{-}PPh_2CH_2PPh_2)Fe(CO)_3]BF_4$ diphosphine bridged ring dimers, *e.g.* $Ph_2P(CH_2)_2PPh_2[(\eta^4\text{-}C_7H_9)Fe(CO)_3]_2[BF_4]_2$ and diphosphine bridged ring-metal dimers, *e.g.* $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_2(CH_2)_3PPh_2(exo\text{-}\eta^6\text{-}C_7H_7)Cr(CO)_3][BF_4]_2$.

Tertiary diphosphines such as bis(diphenylphosphino)methane $\{PPh_2(CH_2)_nPPh_2$, n = 1, dppm$\}$ are ubiquitous ligands in organometallic chemistry. Invariably, they bond to a particular metal centre in either an η^1 or η^2 mode or bridge two metal centres in polynuclear complexes.[1] In this note we report a number of new complexes† with hitherto unobserved structures illustrating first, the bonding of a diphosphine to a ring carbon atom in a mononuclear metal ring carbonyl complex as in $[(\eta^4\text{-}C_7H_9\text{-}5\text{-}exo\text{-}\eta^1\text{-}PPh_2CH_2PPh_2)Fe(CO)_3]BF_4$, **1**, and $[(\eta^6\text{-}C_7H_7\text{-}exo\text{-dppm})Cr(CO)_3]BF_4$, **2**. Secondly, diphosphine linked ring dimers as in $Ph_2P(CH_2)_2PPh_2[(\eta^4\text{-}C_7H_9)Fe(CO)_3]_2[BF_4]_2$, **3** and, lastly, diphosphine bridged ring-metal dimers as in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_2(CH_2)_3PPh_2(exo\text{-}\eta^6\text{-}C_7H_7)Cr(CO)_3][BF_4]_2$, **4**.

Complex **1**‡ was obtained by reaction of dppm with $[(\eta^5\text{-}C_7H_9)Fe(CO)_3]BF_4$ in MeCN at room temperature. Based on ^1H, ^{13}C and ^{31}P NMR§ data and confirmed by the X-ray structure determination (Fig. 1), we have identified **1** as the 5-*exo*-ring adduct of the starting cation with dppm. Prolonged reflux (3 days) gives the metal chelate, $[(\eta^5\text{-}$



Scheme 1



Scheme 2

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† Satisfactory elemental analyses were obtained for all the new compounds.

‡ *Crystal data* for **1**: Crystal of $C_{35}H_{31}BF_4FeO_3P_2\cdot(CHCl_3)_2$, M = 942.98, triclinic space group $P\bar{1}$, a = 12.727(1), b = 13.457(2), c = 14.767(2), Å, α = 97.75(2), β = 114.26(2), γ = 108.67(2), U = 2077.98 Å^3, Z = 2, λ = 0.7093 Å, μ(Mo-K$_\alpha$) = 14.36 cm^{-1}, F(000) = 956. Data were corrected for Lorentz and polarization effects but not for absorption. Direct methods (SHELX-86), 4368, with $I > 3\sigma(I)$ unique data ($2 < 2\theta < 52°$) used in the refinement and 320 parameters in the model (SHELX76). Final R = 0.0840 and R_w = 0.0963 with minimization of $[\Sigma W(|F_o| - |F_c|)^2/\Sigma W|F_o|^2]^{1/2}$ with $W = 1/[\sigma^2(F_o) - 0.00023\, F_o^2]$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ *Selected spectroscopic data* for compounds **1**–**4** and **6**. ^1H, ^{13}C and ^{31}P NMR data (270 MHz; J values in Hz). Spectra run in [$^2H_6$]acetone solvent unless otherwise stated. ^{31}P δ values quoted relative to H_3PO_4.

For **1** ^1H NMR ($CDCl_3$), δ 2.67 (dd, H4), 3.53 (dt, H5), 1.72 (br, H6$_{endo}$), 0.92 (m, H6$_{exo}$), 3.73 [t, HA(CH_2)], 3.36 (t, HB(CH_2)). ^{13}C, δ 46.9 (d, C4) ($J_{C\text{-}P}$ 7.6), 34.3 (d, C5) ($J_{C\text{-}P}$ 37.6), 22.5 (s, C6), 19.5 (t, CH_2) ($J_{C\text{-}P}$ 46.2). ^{31}P, δ +31.9 (d, P–C5), −29.2 (d, P pendant) ($J_{P\text{-}P}$ 61.1).

For **2** ^1H NMR, δ 5.78 (dd, H7), 3.83 (t, H1,6). ^{13}C, δ 36.7 (d, C7) ($J_{C\text{-}P}$ 33.3), 55.5 (s, C1,6), 16.89 (m, CH_2). ^{31}P, δ + 20.8 (d, P–C7) ($J_{P\text{-}P}$ 58), −27.8 (d, P pendant).

For **3** ^1H NMR ($CDCl_3$), δ 2.73 (dd, H4), 3.48 (dt, H5), 1.64 (br, H6$_{endo}$), 0.89 (m, H6$_{exo}$), ^{13}C, δ 46.6 (dd, C4) ($J_{C\text{-}P}$ 3.2 Hz), 35.5 (d, C5) ($J_{C\text{-}P}$ 37.4), 22.4 (s, C6). ^{31}P, δ +31.8.

For **4** ^1H NMR, δ 5.49 [S, 5H(C_5H_5)], 5.76 (dd, H7), 3.79 (t, H1,6). ^{13}C, δ 89.5 (s, C_5H_5), 36.5 (d, C7) ($J_{C\text{-}P}$ 30.09), 55.3 (s, C1,6), 210.7 (d, CO–Fe) ($J_{C\text{-}P}$ 24.7), 221.8 (s, CO–Cr). ^{31}P, δ +22.3 (d, P–C7), δ +59.5 (P–Fe].

For **6** ^1H NMR ([$^2H_3$]acetonitrile), δ 5.79 (s, 7H), 4.75 [m, HA (CH_2)], 3.56 [m, HB(CH_2)]. ^{13}C, δ 97.8 (s, C_7 ring), 42.3 (m, CH_2), ^{31}P, δ +36.5.

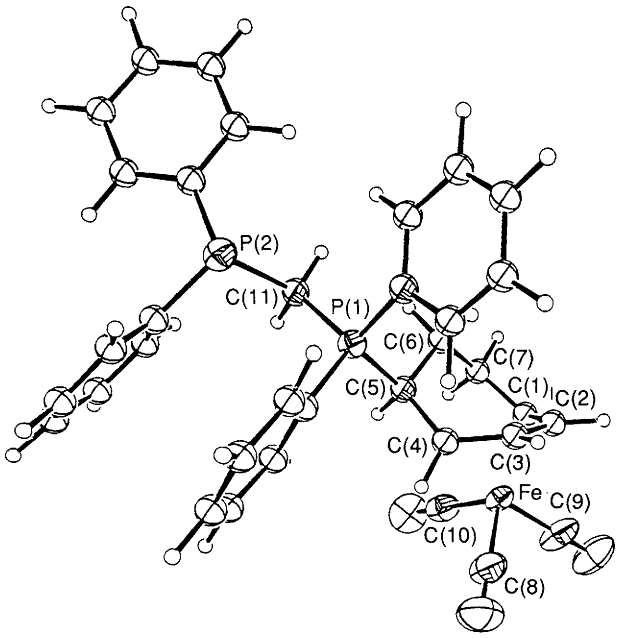

Fig. 1 Molecular structure of [(η^4-C_7H_9-5-*exo*-η^1-dppm)Fe(CO)$_3$)] BF_4, **1**. Selected bond distances (Å): Fe–C(4) 2.110(6), Fe–C(3) 2.035(8), Fe–C(2) 2.040(8), Fe–C(1) 2.134(7), P(1)–C(5) 1.856(6), P(1)–C(11) 1.796(7), C(4)–C(5) 1.550(1), C(5)–C(6) 1.510(9), C(6)–C(7) 1.534(9). Bond angles (°) C(6)–C(5)–P(1) 107.2(4), C(3)–Fe–C(10) 134.8(3), C(6)–C(5)–C(4) 114.3(6), C(2)–Fe–C(10) 132.1(4), C(4)–C(5)–P(1) 106.8(5), C(1)–Fe–C(9) 90.4(3), C(6)–C(7)–C(1) 114.3(7), C(4)–Fe–C(8) 89.8(3), C(4)–Fe–C(10) 96.8(3), C(3)–Fe–C(8) 94.6(4), C(1)–Fe–C(10) 93.5(4), C(2)–Fe–C(9) 93.0(4), C(4)–Fe–C(3) 40.8(3), P(1)–C(11)–P(2) 109.6(4), C(1)–Fe–C(2) 40.0(3), C(2)–Fe–C(3) 39.4(3).

C_7H_9)Fe(CO)(η^2-dppm)]BF_4, **5**. In contrast, dppe ($n = 2$) and higher homologues do not form ring adducts but give instead diphosphine ring-bridged dimers as in **3** (Scheme 1). The ^1H and ^{13}C NMR§ data for **3** confirmed 5-*exo*-ring addition and the ^{31}P NMR§ data showed the presence of only ring linked phosphorus atoms. The ^1H and ^{13}C NMR§ spectra of **1** and **3** are very similar to those of the analogous monophosphine 5-*exo*-ring adducts.[2] Similar ring addition also occurs when [(η^7-C_7H_7)Cr(CO)$_3$]BF_4 reacts with dppm (and dppe) in acetone at room temperature to give [(η^6-C_7H_7-*exo*-dppm)Cr(CO)$_3$]BF_4, **2**. Again the ^1H NMR§ spectra are similar to those of the analogous monophosphine ring adducts[3] and the ^{31}P NMR§ data confirm the presence of a ring-bonded phosphorus (δ_P +20.8) and a pendant phosphorus (δ_P −27.8). In contrast to the iron complex, **1**, the chromium series, **2**, readily form on reflux the metal chelate, [(η^7-C_7H_7)Cr(CO)(η^2-dppm)]BF_4, **6**, and [*mer*-(η^1-dppm)(η^2-dppm)Cr(CO)$_3$], **7**.[4] Complex **6** is the first example of carbonyl substitution by tertiary phosphines of the tropylium tricarbonylchromium cation. Finally, reaction of [(η^7-C_7H_7)Cr(CO)$_3$]BF_4, [(η^5-C_5H_5)Fe(CO)$_2$(THF)]BF_4[5] and $Ph_2P(CH_2)_3PPh_2$ in acetone at room temperature gave salmon-pink crystals of the novel diphosphine bridged ring-metal dimer, [(η^5-C_5H_5)Fe(CO)$_2$PPh$_2$(CH$_2$)$_3$PPh$_2$(*exo*-η^6-C_7H_7)Cr(CO)$_3$][BF_4]$_2$, **4**, (Scheme 2). The ^1H and ^{13}C NMR§ data for **4** show clearly the single C_5H_5 resonance and four resonances for the η^6-C_7H_7 ring very close to those of the ring adduct, **2**. The ^{31}P NMR§ shows one phosphorus atom bonded to a ring carbon atom (δ_P + 22.3) as in **2** and the other phosphorus coordinated to the iron atom (δ_P + 59.5) similar to that reported for [(η^5-C_5H_5)Fe(CO)$_2$(η^1-dppp)]BF_4.[5]

Further studies of the stabilities and reactivity of these diphosphine complexes are in progress.

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References

1 R. J. Puddephatt, *Chem. Soc. Rev.*, 1983, **12** (2), 99.
2 D. A. Brown, S. Chawla, W. Glass and F. Hussein, *Inorg. Chem.*, 1982, **21**, 2726.
3 P. Hackett and G. Jaouen, *Inorg. Chim. Acta*, 1975, **12**, 19.
4 A. Blagg, G. R. Cooper, P. G. Pringle, R. Robson and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1984, 933.
5 D. L. Reyer and C. Coleman, *J. Organomet. Chem.*, 1977, **131**, 153.