

Novel Bonding of Tertiary Diphosphines to Metal Ring Carbonyl Complexes

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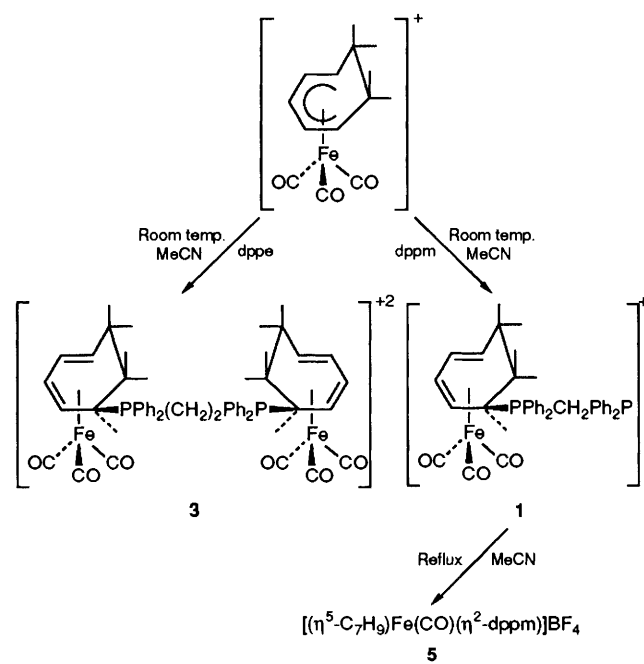
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Tertiary diphosphines form complexes with various metal ring carbonyl cations of new and novel structural types including ring adducts, e.g. $[(\eta^4\text{-C}_7\text{H}_9\text{-5-}exo\text{-}\eta^1\text{-PPh}_2\text{CH}_2\text{PPh}_2)\text{Fe}(\text{CO})_3]\text{BF}_4$ diphosphine bridged ring dimers, e.g. $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2[(\eta^4\text{-C}_7\text{H}_9)\text{Fe}(\text{CO})_3]_2[\text{BF}_4]_2$ and diphosphine bridged ring-metal dimers, e.g. $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{PPh}_2(\text{CH}_2)_3\text{PPh}_2(exo\text{-}\eta^6\text{-C}_7\text{H}_7)\text{Cr}(\text{CO})_3][\text{BF}_4]_2$.

Tertiary diphosphines such as bis(diphenylphosphino)-methane $\{\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2$, $n = 1, 2$, 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 $[(\eta^4\text{-C}_7\text{H}_9\text{-5-}exo\text{-}\eta^1\text{-PPh}_2\text{CH}_2\text{PPh}_2)\text{Fe}(\text{CO})_3]\text{BF}_4$, **1**, and $[(\eta^6\text{-C}_7\text{H}_7\text{-}exo\text{-}dppm)\text{Cr}(\text{CO})_3]\text{BF}_4$, **2**. Secondly, diphosphine linked ring dimers as in $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2[(\eta^4\text{-C}_7\text{H}_9)\text{Fe}(\text{CO})_3]_2[\text{BF}_4]_2$, **3** and, lastly, diphosphine bridged ring-metal dimers as in $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{PPh}_2(\text{CH}_2)_3\text{PPh}_2(exo\text{-}\eta^6\text{-C}_7\text{H}_7)\text{Cr}(\text{CO})_3][\text{BF}_4]_2$, **4**.

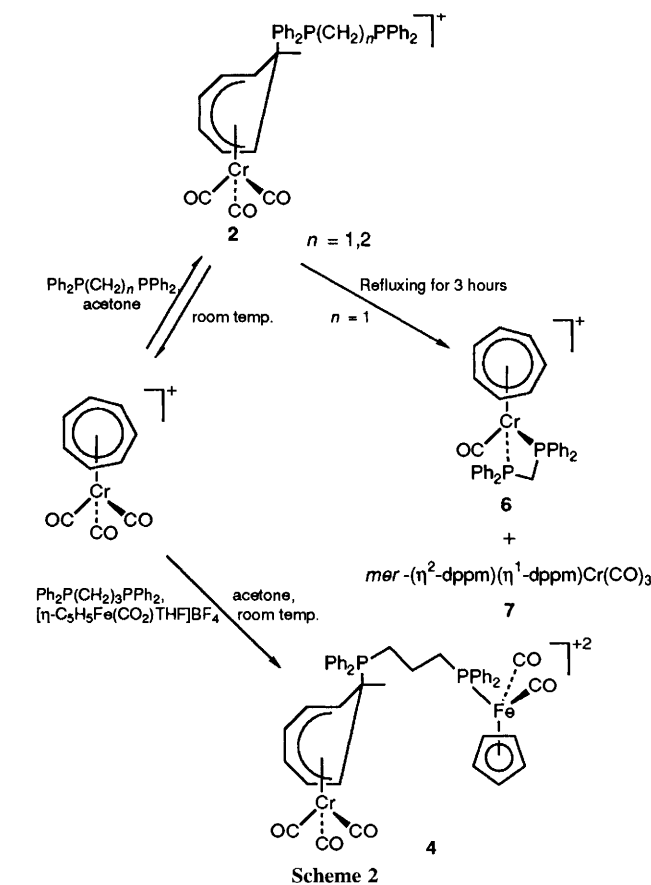
Complex **1**‡ was obtained by reaction of dppm with $[(\eta^5\text{-C}_7\text{H}_9)\text{Fe}(\text{CO})_3]\text{BF}_4$ in MeCN at room temperature.



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

‡ *Crystal data* for **1**: Crystal of $\text{C}_{35}\text{H}_{31}\text{BF}_4\text{FeO}_3\text{P}_2 \cdot (\text{CHCl}_3)_2$, $M = 942.98$, triclinic space group $P\bar{1}$, $a = 12.727(1)$, $b = 13.457(2)$, $c = 14.767(2)$, Å, $\alpha = 97.75(2)$, $\beta = 114.26(2)$, $\gamma = 108.67(2)$, $U = 2077.98$ Å³, $Z = 2$, $\lambda = 0.7093$ Å, $\mu(\text{Mo-K}\alpha) = 14.36$ 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 ($2 < 2\theta < 52^\circ$) used in the refinement and 320 parameters in the model (SHELX76). Final $R = 0.0840$ and $R_w = 0.0963$ with minimization of $[\sum W(|F_o| - |F_c|)^2 / \sum W|F_o|^2]^{1/2}$ 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.

Based on ¹H, ¹³C and ³¹P 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, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{PPh}_2(\text{CH}_2)_3\text{PPh}_2(exo\text{-}\eta^6\text{-C}_7\text{H}_7)\text{Cr}(\text{CO})_3][\text{BF}_4]_2$.



§ *Selected spectroscopic data* for compounds **1–4** and **6**. ¹H, ¹³C and ³¹P NMR data (270 MHz; J values in Hz). Spectra run in $[\text{D}_6]\text{acetone}$ solvent unless otherwise stated. ³¹P 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(CH₂)], 3.36 (t, HB(CH₂)). ¹³C, δ 46.9 (d, C4) ($J_{\text{C-P}} 7.6$), 34.3 (d, C5) ($J_{\text{C-P}} 37.6$), 22.5 (s, C6), 19.5 (t, CH₂) ($J_{\text{C-P}} 46.2$). ³¹P, δ +31.9 (d, P-C5), -29.2 (d, P pendant) ($J_{\text{P-P}} 61.1$).

For **2** ¹H NMR, δ 5.78 (dd, H7), 3.83 (t, H1,6). ¹³C, δ 36.7 (d, C7) ($J_{\text{C-P}} 33.3$), 55.5 (s, C1,6), 16.89 (m, CH₂). ³¹P, δ +20.8 (d, P-C7) ($J_{\text{P-P}} 58$), -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}), ¹³C, δ 46.6 (dd, C4) ($J_{\text{C-P}} 3.2$ Hz), 35.5 (d, C5) ($J_{\text{C-P}} 37.4$), 22.4 (s, C6). ³¹P, δ +31.8.

For **4** ¹H NMR, δ 5.49 [s, 5H(C₅H₅)], 5.76 (dd, H7), 3.79 (t, H1,6). ¹³C, δ 89.5 (s, C₅H₅), 36.5 (d, C7) ($J_{\text{C-P}} 30.09$), 55.3 (s, C1,6), 210.7 (d, CO-Fe) ($J_{\text{C-P}} 24.7$), 221.8 (s, CO-Cr). ³¹P, δ +22.3 (d, P-C7), δ +59.5 (P-Fe).

For **6** ¹H NMR ($[\text{D}_3]\text{acetonitrile}$), δ 5.79 (s, 7H), 4.75 [m, HA(CH₂)], 3.56 [m, HB(CH₂)]. ¹³C, δ 97.8 (s, C₇ ring), 42.3 (m, CH₂), ³¹P, δ +36.5.

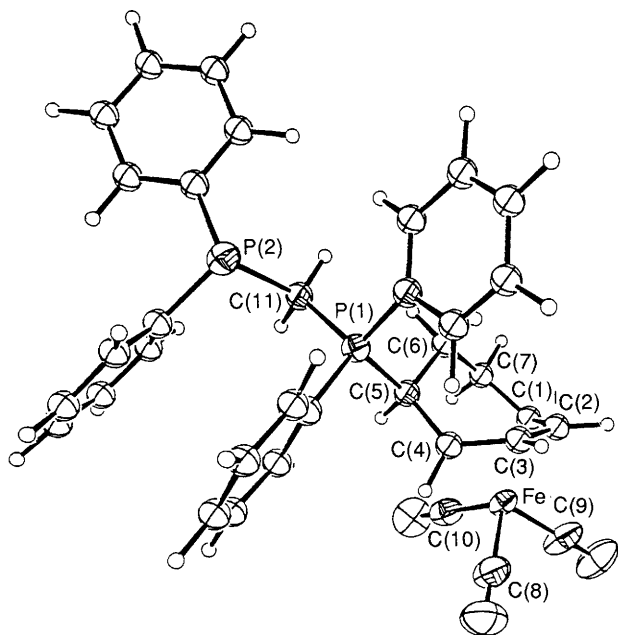


Fig. 1 Molecular structure of $[(\eta^4\text{-C}_7\text{H}_9\text{-5-exo-}\eta^1\text{-dppm})\text{Fe}(\text{CO})_3]\text{BF}_4$, **1**. Selected bond distances (Å): Fe–C(4) 2.110(6), Fe–C(3) 2.035(8), Fe–C(2) 2.040(8), Fe–C(1) 2.134(7), P(1)–C(5) 1.856(6), P(1)–C(11) 1.796(7), C(4)–C(5) 1.550(1), C(5)–C(6) 1.510(9), C(6)–C(7) 1.534(9). Bond angles ($^\circ$) 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).

$\text{C}_7\text{H}_9\text{Fe}(\text{CO})(\eta^2\text{-dppm})\text{BF}_4$, **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 $[(\eta^7\text{-C}_7\text{H}_7)\text{Cr}(\text{CO})_3]\text{BF}_4$ reacts with dppm (and dppe) in acetone at room temperature to give $[(\eta^6\text{-C}_7\text{H}_7\text{-exo-dppm})\text{Cr}(\text{CO})_3]\text{BF}_4$, **2**. Again the ^1H NMR§ spectra are similar to those of the analogous monophosphine ring adducts³ and the ^{31}P NMR§ data confirm the presence of a ring-bonded phosphorus ($\delta_{\text{P}} + 20.8$) and a pendant phosphorus ($\delta_{\text{P}} - 27.8$). In contrast to the iron complex, **1**, the chromium series, **2**, readily form on reflux the metal chelate, $[(\eta^7\text{-C}_7\text{H}_7)\text{Cr}(\text{CO})(\eta^2\text{-dppm})]\text{BF}_4$, **6**, and $[\text{mer}-(\eta^1\text{-dppm})(\eta^2\text{-dppm})\text{Cr}(\text{CO})_3]$, **7**.⁴ Complex **6** is the first example of carbonyl substitution by tertiary phosphines of the tropylium tricarbonylchromium cation. Finally, reaction of $[(\eta^7\text{-C}_7\text{H}_7)\text{Cr}(\text{CO})_3]\text{BF}_4$, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{THF})]\text{BF}_4$ ⁵ and $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ in acetone at room temperature gave salmon-pink crystals of the novel diphosphine bridged ring-metal dimer, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{PPh}_2(\text{CH}_2)_3\text{PPh}_2(\text{exo-}\eta^6\text{-C}_7\text{H}_7)\text{Cr}(\text{CO})_3][\text{BF}_4]_2$, **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 $\eta^6\text{-C}_7\text{H}_7$ ring very close to those of the ring adduct, **2**. The ^{31}P NMR§ shows one phosphorus atom bonded to a ring carbon atom ($\delta_{\text{P}} + 22.3$) as in **2** and the other phosphorus coordinated to the iron atom ($\delta_{\text{P}} + 59.5$) similar to that reported for $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-dppp})]\text{BF}_4$.⁵

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

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