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Substitution and Addition Reactions of the $(CO)_3(\eta^7\text{-tropylium})M$ Cations (M = Cr, Mo, W) with Tertiary Diphosphines

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The reactions of the title compounds I–III, $[(\eta^7\text{-}C_7H_7)M(CO)_3]BF_4$ (M = Cr, Mo, and W, respectively), with the diphosphines $PPh_2(CH_2)_nPPh_2$ (n = 1–4) at low temperatures (–40 to –60 °C) form two new series of complexes which are quite different from previous carbonyl substitution products. The first series (IV–VI) formed by the diphosphines (n = 1–3) comprise 7-*exo* ring adducts involving the bonding of only one phosphorus atom of the diphosphine to ring carbon atom 7 of I. The second series (VII and VIII) are diphosphine ring linked dimers, e.g. $[(7,7'\text{-}exo\text{-dppb})\{\eta^6\text{-}C_7H_7)Cr(CO)_3\}_2][BF_4]_2$, for which X-ray crystallography confirms a diphosphine linked ring–ring structure with the $Cr(CO)_3$ moieties situated on opposite sides of the ring systems. The ring C–phosphorus bond length of 1.852 Å indicates a relatively weak bond, consistent with facile cleavage of these adducts on reaction with nucleophiles such as hydride.

Introduction

Tertiary diphosphines such as the bis(diphenylphosphino)alkanes $PPh_2(CH_2)_nPPh_2$ (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.[2,3] These include, first, exo ring adducts involving the bonding of only one phosphorus atom of the diphosphine to a ring carbon of the π-acid ligand, e.g. $[(\eta^4\text{-}C_7H_9\text{-}5\text{-}exo\text{-dppm})Fe(CO)_3][BF_4]$, the structure of which was confirmed by X-ray crystallography.[2] A second type is the diphosphine ring–ring linked dimers, e.g. $[(5,5'\text{-}exo\text{-dppe})\{(\eta^4\text{-}C_6H_7)Fe(CO)_3\}_2][BF_4]_2$,[3] and the last type is a series of metal–ring linked dimers, both homonuclear and heterobinuclear, e.g. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2dppp(exo\text{-}\eta^6\text{-}C_7H_7)Cr(CO)_3][BF_4]_2$.[2] No X-ray crystallographic studies have yet been reported for any member of the last two series.

In the present paper, we report an extension of these studies to the reactions of the above diphosphines with the title compounds $[(\eta^7\text{-}C_7H_7)M(CO)_3][BF_4]$ (I, M = Cr; II, M = Mo; III, M = W). Complexes of the first of the above series have been prepared from I, e.g. $[(\eta^6\text{-}C_7H_7\text{-}exo\text{-dppm})Cr(CO)_3][BF_4]$ (IV), and complexes of the second series have been prepared as well involving ring–ring diphosphine linked dimers, e.g. $[(7,7'\text{-}exo\text{-dppb})\{(\eta^6\text{-}C_7H_7)Cr(CO)_3\}_2]\{BF_4\}_2$ (VIII), for which a full structure determination by X-ray crystallography is now reported. No stable complexes of these types were obtained from II or III; however, low-temperature spectroscopic studies gave clear evidence for initial formation of ring adducts with dppm (first series) and also with PPh_3 as discussed below.

Previous studies of the reactions of monophosphines PR_3 with the title compounds I–III present a somewhat checkered history, which is not surprising in view of the fact that the reaction between a nucleophile and a ring metal carbonyl cation may proceed by a number of pathways to give a variety of products, including ring adducts, carbonyl substitution and addition products, and substituted metal carbonyls, following metal–ring bond fission. We have recently examined in detail, using ab initio MO methods, the relative stabilities of various possible intermediates formed by hydride attack on $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]BF_4$.[4] In this case the intermediates corresponding to both direct metal and carbonyl attack lie close in energy, in accord with low-temperature ^1H NMR studies,[5,6] and so it is not surprising that reactions of ring metal carbonyl complexes such as I–III with nucleophiles may give various products depending on solvent, reaction conditions, and the nature of the central metal. Thus, thermal reaction of monophosphines, e.g. PPh_3 with II, showed exclusively carbonyl substitution[7,8] but subsequent kinetic studies with $P(n\text{-}Bu)_3$ were interpreted in terms of initial ring addition for all members of the series, I–III.[9] Finally, by using low temperatures for the reaction, Salzer was able to isolate the monophosphine ring adduct $[(\eta^6\text{-}$

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C_7H_7-*exo*-$P(iPr)_3)Mo(CO)_3][BF_4]$ as a stable product.[10] In contrast, reaction of the chromium compound I with strongly nucleophilic phosphines such as $P(nBu)_3$ even at room temperature give the corresponding ring adduct as the only stable product, whereas with the less nucleophilic PPh_3 an equilibrium is set up between the cation I and ring adduct.[11] In the case of the reactions of the bis(diphenylphosphino)alkanes with the title compounds II and III three main types of carbonyl substitution products were reported: (a) the monosubstituted complex $[(\eta^7\text{-}C_7H_7)Mo(CO)_2(\eta^1\text{-diphosphine})]PF_6$, (b) chelated complexes $[(\eta^7\text{-}C_7H_7)Mo(CO)(\eta^2\text{-diphosphine})]PF_6$, and (c) binuclear complexes containing a diphosphine bridge between two metal atoms, e.g. $[\{(\eta^7\text{-}C_7H_7)Mo(CO)_2\}_2\text{-}\mu\text{-dppm}][PF_6]_2$.[12] To the best of our knowledge, there have been no previous reports of the reactions of diphosphines with I.

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, and dppb) 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. Low-temperature spectra were obtained with a Specac variable-temperature cell (P/N 21.500). ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a JEOL GX 270 spectrometer. Analyses were performed by the Microanalytical Laboratory of the Chemical Services Unit of University College Dublin. The starting complexes $[(\eta^7\text{-}C_7H_7)M(CO)_3][BF_4]$ (I, M = Cr; II, M = Mo; III, M = W) were prepared by published methods.[13]

Preparation of Phosphonium Ring Adducts IV and V. Bis(diphenylphosphino)methane (dppm) (0.5 g, 1.3 mmol) was added to a stirred solution of I (0.41 g, 1.3 mmol) in CH_2Cl_2 at −40 °C and reacted for 30 min. Solvent was removed under reduced pressure. Recrystallization from CH_2Cl_2 gave red crystals of $[(\eta^6\text{-}C_7H_7\text{-}exo\text{-dppm})Cr(CO)_3]BF_4$ (IV; 0.7 g, 76%). Anal. Calcd for $C_{35}H_{29}CrO_3P_2BF_4$: C, 60.2; H, 4.1; P, 8.8. Found: C, 60.0; H, 4.6; P, 8.9. ^1H NMR (CD_2Cl_2): δ 5.78 (dt, H_7, $J_{6,7}$ = 9 Hz), 5.67 (dt, $H_{3,4}$), 5.13 (dt, $H_{2,5}$), 3.827 (dt, $H_{1,6}$), 3.77 (t, CH_2). ^{13}C NMR (CD_2Cl_2): δ 104.74 ($C_{3,4}$), 98.39 ($C_{2,5}$), 55.47 ($C_{1,6}$), 36.92 (d, C_7, J_{CP} = 33.3 Hz), 16.89 (CH_2). IR (CH_2Cl_2): 1998, 1942, 1905 cm^{-1}. Complex V $[(\eta^6\text{-}C_7H_7\text{-}exo\text{-dppe})Cr(CO)_3]BF_4$ was prepared similarly (0.69 g, 74.3%). Anal. Calcd for $C_{36}H_{31}CrO_3P_2BF_4$: C, 60.7; H, 4.4, P, 8.7. Found: C, 60.7; H, 4.7; P, 8.8. ^1H NMR (CD_2Cl_2): δ 5.95 (dt, H_7, $J_{6,7}$ = 8.9 Hz), 5.81 (dt, $H_{3,4}$), 5.13 (dt, $H_{2,5}$), 3.84 (dt, $H_{1,6}$), 3.55 (m, CH_2 (α)), 3.22 (m, CH_2 (β)). ^{13}C NMR (CD_2Cl_2): δ 106.62 ($C_{3,4}$), 98.61 ($C_{2,5}$), 55.25 ($C_{1,6}$), 36.93 (C_7, J_{CP} = 33 Hz), 16.89 (CH_2 (α)), 16.75 (CH_2 (β)). IR (CH_2Cl_2): 1998, 1942, 1905 cm^{-1}.

Preparation of the Phosphonium Ring Adduct VI and the Diphosphine Ring Linked Dimer VII. In the case of dppp, the analogous reaction yielded a red product which gave unsatisfactory analyses despite repeated chromatography and recrystallization. The ^{31}P NMR spectra showed peaks at δ 22.5, 22.1, and −16.8, indicating a mixture of the ring adduct $[(\eta^6\text{-}C_7H_7\text{-}exo\text{-dppp})Cr(CO)_3]BF_4$ (VI) and the ring–ring linked dimer $[(7,7'\text{-}exo\text{-dppp})\{(\eta^6\text{-}C_7H_7)Cr(CO)_3\}_2]\{BF_4\}_2$ (VII) analogous to VIII.

Preparation of the Diphosphine Ring Linked Dimer $[(7,7'$-*exo*-dppb$)\{(\eta^6\text{-}C_7H_7)Cr(CO)_3\}_2][BF_4]_2$ (VIII). Bis(diphenylphosphino)butane (0.5 g, 1.2 mmol) and I (0.74 g, 2.4 mmol) were stirred in CH_2Cl_2 at −40 °C for 60 min, after which time the infrared peaks due to I were replaced by those of VIII. Filtration, removal of solvent, and recrystallization from CH_2Cl_2 gave cherry-colored crystals of VIII (0.83 g, 67.4%). Anal. Calcd for $C_{50}H_{46}Cr_2O_6P_2B_2F_8$: C, 53.9; H, 4.1; P, 6.1. Found: C, 54.6; H, 4.0; P, 5.8. ^1H NMR (CD_2Cl_2): δ 5.59 (dt, H_7, $J_{6,7}$ = 8.8 Hz), 5.48 (dt, $H_{3,4}$), 4.95 (dt, $H_{2,4}$), 3.84 (dt, $H_{1,6}$), 1.37 (m, CH_2 (β)), 2.62 (m, CH_2 (α)). ^{13}C NMR (CD_2Cl_2): δ 104.95 ($C_{3,4}$), 98.45 ($C_{2,5}$), 55.39 ($C_{1,6}$), 34.1 (C_7, J_{CP} = 30 Hz), 17.12 (CH_2 (β)), 22.24 (CH_2 (α)). IR (CH_2Cl_2): 2000, 1942, 1905 cm^{-1}.

Preparation of the Diphosphine Metal Chelate $[(\eta^7\text{-}C_7H_7)Cr(CO)(\eta^2\text{-dppm})]BF_4$ (IX). Bis(diphenylphosphino)methane (dppm; 0.6 g, 1.6 mmol) and I (0.5 g, 1.6 mmol) were refluxed in acetone (100 mL) for 3 h. Solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2 and chromatographed on alumina. Elution with CH_2Cl_2 gave orange crystals of $[mer\text{-}Cr(CO)_3(\eta^2\text{-dppm})(\eta^1\text{-dppm}]$ (X). Elution with CH_2Cl_2/CH_3CN (60/40) and concentration to 10 mL followed by dropwise addition of 5 mL of diethyl ether gave dark green crystals of IX (0.153 g, 15.1%). Anal. Calcd for $C_{33}H_{29}CrOP_2BF_4$: C, 60.2; H, 4.4; P, 9.6. Found: C, 60.3; H, 4.4; P, 9.4. ^1H NMR (d_6-acetone): δ 5.79 (s, C_7H_7), 1.97 (H (α)), 2.11 (H (β)). ^{13}C NMR (d_6-acetone): δ 97.83 (C_7H_7), 43.21 (CH_2). IR (acetone): 1942 cm^{-1}. The final elution with benzene gave on workup light green crystals of $Cr(CO)_4(\eta^2\text{-dppm})$.

Thermal Reactions with Other Diphosphines (dppe, dppp, and dppb). Reaction of I with the other diphosphines (dppe, dppp, and dppb) using the same procedure as described above for dppm gave only the analogous ring displaced series $[mer\text{-}Cr(CO)_3(\eta^2\text{-dppx})(\eta^1\text{-dppx})]$ (x = e, p) and $[Cr(CO)_4(\eta^2\text{-dppx})]$ (x = e, p, b) with no formation of ring chelate products analogous to IX.

Decomplexation and Hydride Abstraction Reactions of IV, V, and VIII. Hydride Abstration. To a solution of IV (0.83 g, 1.2 mmol) in CH_2Cl_2 at −60 °C was added a solution of *N*-bromosuccinimide (0.21 g, 1.2 mmol). Rapid reaction occurred. Filtration and recrystallization from acetone/ether gave orange crystals of I, $[(\eta^7\text{-}C_7H_7)Cr(CO)_3]BF_4$. Similar results were obtained with V and VIII. Use of trityl tetrafluoroborate as a hydride abstracting agent again led to the formation of I from IV, V and VIII.

Decomplexation Reactions. Oxidation by Iodine and Ce(IV) of IV, V, and VIII. Oxidation by Iodine. A solution of IV (1 g, 1.3 mmol) in CH_2Cl_2 (100 mL) was stirred with iodine (2.1 g, 3.9 mmol) at room temperature for 6 h when the carbonyl infrared stretching frequencies of IV were replaced by those of I. The crude mixture was filtered and the volume reduced to 10 mL and then 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, filtered, and on reduction in volume gave crystals of $[C_7H_7]BF_4$. Similar results were obtained for V and VIII and also on treatment of IV, V, and VIII with ceric ammonium nitrate as oxidant.

Hydride Addition to IV, V, and VIII. A solution of lithium triethylborohydride (0.053 g, 0.5 mmol) in THF (0.5 mL) was added to a solution of IV (0.35 g, 0.5 mmol) in CH_2Cl_2 (100 mL) at −70 °C when the color changed from purple to red. Solvent was removed under pressure, followed by chromatography on alumina and elution with CH_2Cl_2. Solvent volume reduction to 10 mL followed by dropwise addition of hexane gave dark red crystals of $[(\eta^6\text{-}C_7H_8)Cr(CO)_3]$. V and VIII gave similar results.

Low-Temperature Reactions of $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]BF_4$ (II) and $[(\eta^7\text{-}C_7H_7)W(CO)_3]$ (III) with Diphosphines and PPh_3. A typical procedure is as follows: dppm (0.4 g, 1.0 mmol) was added to a stirred solution of II (0.37 g, 1.0 mmol) in CH_2Cl_2 at −78 °C. An immediate color change from orange to red occurred. A sample was then transferred by syringe to the precooled (−78 °C) low-temperature infrared cell and a spectrum taken immediately. Three new ν_{CO} peaks appeared at 2004, 1940, and 1904 cm^{-1}, and both the peak positions and relative intensities

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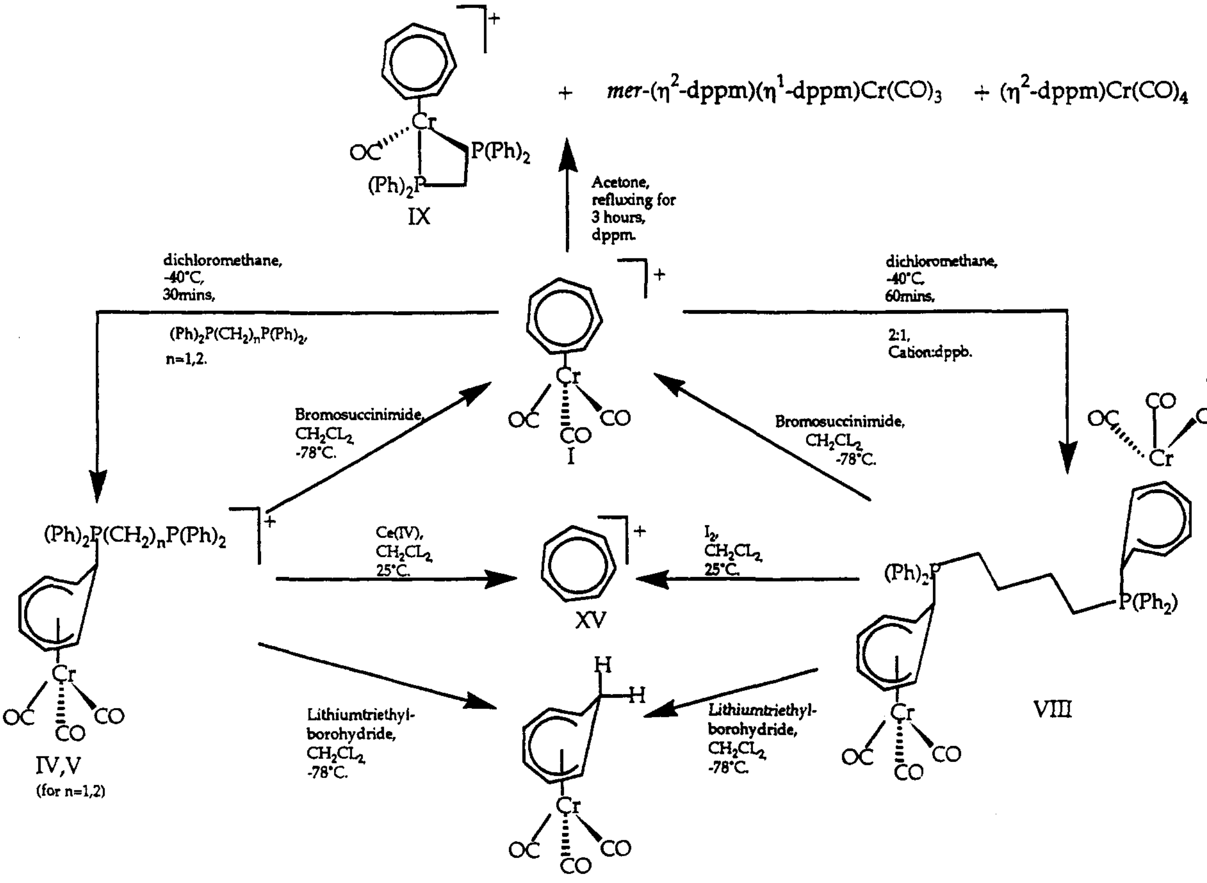
Scheme 1



were very similar to those of IV and are therefore attributed to XI; when the temperature was raised, the peaks disappeared and were replaced by those previously reported for the thermal reaction.[12] Similar results were obtained with PPh_3 in place of dppm to give $[(\eta^6\text{-}C_7H_7\text{-}exo\text{-}P(Ph)_3)Mo(CO)_3]BF_4$ (ν_{CO} 2006, 1944, 1901 cm^{-1}) and with III in place of II to give $[(\eta^6\text{-}C_7H_7\text{-}exo\text{-}dppm)W(CO)_3]BF_4$ (ν_{CO} 2000, 1934, 1896 cm^{-1}) and $[(\eta^6\text{-}C_7H_7\text{-}exo\text{-}P(Ph)_3)W(CO)_3]BF_4$ (ν_{CO} 2002, 1937, 1900 cm^{-1}), respectively. The reaction between II and dppm was also followed by ^1H NMR spectroscopy in d_6-acetone at −70 °C. The proton resonances of II were rapidly replaced by those of XI, which are very close to those in IV (see above): ^1H NMR (CD_2Cl_2) 5.99 (dt, H_7, $J_{6,7}$ = 8.06 Hz), 5.74 (dt, $H_{3,4}$), 5.31 (dt, $H_{2,5}$), 4.04 (dt, $H_{1,6}$), 3.97 (t, CH_2).

Determination of the Crystal Structure of VIII. The structure was solved by direct methods using SHELX86[14] and refined by full-matrix least squares using SHELXL-93,[15] which minimizes R_w^2 (based on F^2). The F-based R_1 is also given in Table 2. The space group $P\bar{1}$ was chosen on the basis of an analysis of E values and on the reasonable results from the subsequent refinement. Attempts to refine the complete molecule in space group $P1$ were not successful, as the least squares became unstable. Data were corrected for Lorentz and polarization effects but not for absorption. Hydrogen atoms were included in calculated positions with common thermal parameters, except those on C(12), which were located and refined. The non-hydrogen atoms were refined anisotropically. The asymmetric unit consists of a half-molecule with an inversion center at the midpoint of the butyl group. The six ring carbons bonded to chromium are planar (maximum deviation from the mean plane is 0.04 Å), and the chromium atom is 1.60 Å from that plane. The relatively high R index is due to problems associated with the dichloromethane of solvation. Attempts to model the dichloromethane using various types of disorder were all unsuccessful. All calculations were performed on a VAX 6610 computer. The ORTEP program was used to obtain the drawings.[16]

Results and Discussion

7-*exo* Ring Adducts IV and V. Reaction of I with an equimolar quantity of dppm in CH_2Cl_2 at −40 °C proceeded rapidly to completion (~30 min) with formation of the 7-exo ring adduct IV, $[(\eta^6\text{-}C_7H_7\text{-}7\text{-}exo\text{-}dppm)Cr(CO)_3]BF_4$. A similar reaction occurred with dppe and formation of V (Scheme 1). The structures of IV and V are fully consistent with their ^1H, ^{13}C, and ^{31}P NMR spectra (Table 1) and those of IV are similar to those of the closely related iron complex $[(\eta^4\text{-}C_7H_9\text{-}5\text{-}exo\text{-}dppm)Fe(CO)_3]BF_4$[2,3] and the analogous monophosphine ring adducts.[11] Thus, in the ^1H NMR spectra of IV and V, the relative positions of protons 1,6, 2,5, and 3,4 lie close to those of the analogous PPh_3 ring adduct,[11] while H_7 is the most deshielded proton, occurring as a doublet of triplets at δ 5.87 ($J_{6,7}$ − 9.0 Hz; $J_{P,H_{endo}}$ = 12.5 Hz) and 5.95 ($J_{6,7}$ = 8.8 Hz; $J_{P,H_{endo}}$ = 11.7) for IV and V, respectively, typical of an *exo* ring adduct. Similarly the ^{13}C spectrum shows C_7 at δ 36.9 with $J_{P,C}$ = 33 Hz for both IV and V. The ^{31}P spectra show clearly the presence of pendant phosphorus atoms at δ −27.8 and −11.1 and phosphorus bonded to C_7 at δ 26.8 and 23.4 in IV and V, respectively. When the temperature was raised, it was noted that solutions of IV and V showed evidence for free ligand peaks, indicating that some dissociation of the ring

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Table 1. ^{31}P NMR Spectral Data for Diphosphonium Complexes[a]

	δ(P)						
	P_{Fl}	P_a	P_b	P_c	P_d	$J_{P,P}$ (Hz)	Δ(pend) (ppm)
$[(\eta^6\text{-}C_7H_7\text{-}exo\text{-dppm})Cr(CO)_3][BF_4]$ (IV)[b]	−23.6	−20.9 (d)	21.8 (d)			58	2.7
$[(\eta^6\text{-}C_7H_7\text{-}exo\text{-dppe})Cr(CO)_3][BF_4]$ (V)[b]	−12.5	−11.0 (d)	23.4 (d)			43.7	1.48
$[(\eta^6\text{-}C_7H_7\text{-}exo\text{-dppp})Cr(CO)_3][BF_4]$ (VI)[c]	−17.3	−16.7 (s)	22.5 (s)				0.53
$[(7,7'\text{-}exo\text{-dppp})(\eta^6\text{-}C_7H_7)Cr(CO)_3\}_2][BF_4]_2$ (VII)[c]			22.1 (s)				
$[(7,7'\text{-}exo\text{-dppb})\{(\eta^6\text{-}C_7H_7)Cr(CO)_3\}_2][BF_4]_2$ (VIII)[b]			22.4 (s)				
$[(\eta^7\text{-}C_7H_7)Cr(CO)(\eta^2\text{-dppm})][BF_4]$ (IX)[d]				36.47			
mer-$(\eta^2\text{-dppm})(\eta^1\text{-dppm})Cr(CO)_3$ (X)[e]		−25.4 (d)				45.8	
						18.3	
				50.23 (d, η^2-dppm; P trans to P)			
						27.5	
				27.05(d, η^2-dppm; P trans to CO)	65.91(h)		

[a] Fl = free ligand; P_a = uncoordinated phosphorus; P_b = phosphorus bonded to tropylium ring; P_c = chelated phosphorus; P_d = phosphorus coordinated monodentate to metal; Δ(pend) = $\delta(P_{Fl}) - \delta(P_a)$. [b] $[^2H_6]$acetone. [c] $[^2H_2]$dichloromethane. [d] $[^2H_3]$acetonitrile. [e] $[^2H_6]$benzene.

adducts was occurring, as observed to a greater extent in the case of the ring adduct formed by PPh_3.[11] Attempts at hydride abstraction from IV and V with either *N*-bromosuccinimide or trityl tetrafluoroborate resulted in loss of the exo diphosphine, even at low temperatures, and formation of I. Attempted decomplexation of IV and V with either iodine or ceric ammonium nitrate led to initial loss of diphosphine and formation of I followed by metal–ring bond fission and formation of $[C_7H_7]BF_4$. Hydride addition of IV and V with lithium triethylborohydride even at −60 °C led in both cases to diphosphine substitution and formation of $C_7H_8Cr(CO)_3$.

Diphosphine Ring Linked Dimers VII and VIII. Reaction of I with a $^1/_2$ molar equiv of dppp (n = 3) in CH_2Cl_2 at −40 °C resulted in rapid reaction (~30 min) and formation of a mixture of the mono-ring adduct VI, analogous to IV and V, and the ring–ring dimer VII ($[(7,7'\text{-}exo\text{-dppp})\{(\eta^6\text{-}C_7H_7)Cr(CO)_3\}_2][BF_4]_2$, as indicated by ^{31}P NMR spectroscopy (see Experimental Section and Table 1). Unfortunately, we were not able to achieve a complete separation of VI and VII; however, the analogous reaction of I with dppb in CH_2Cl_2 at −40 °C for about 60 min gave a pure sample of the ring–ring dimer VIII, $[(7,7'\text{-}exo\text{-dppb})\{(\eta^6\text{-}C_7H_7)Cr)CO)_3\}_2][BF_4]_2$, as confirmed by microanalytical and spectroscopic data. Again, the ^1H, ^{13}C, and ^{31}P NMR spectra are fully consistent with the proposed structures and, in particular, the ^{31}P spectrum clearly differentiates the ring–ring linked dimer VIII from the mono-ring adducts IV and V, exhibiting only one phosphorus peak at δ 22.4 ($J_{C,P}$ = 30 Hz) assigned to the phosphorus atoms bonded to carbon atoms 7 and 7′ of the two C_7 rings and no absorptions due to pendant phosphorus atoms, as observed for IV and V. The ^1H NMR spectra are similar to those of IV and V except for the additional CH_2 peaks of dppb. Again H_7 is the most deshielded proton with $J_{6,7}$ = 8.8 Hz, confirming the *exo* arrangement of the diphosphine about C_7 and $C_{7'}$. Bonding at C_7 and $C_{7'}$ is further confirmed by the ^{13}C spectrum, C_7 and $C_{7'}$ occurring at δ 34.1 with $J_{C,P}$ = 30 Hz. Attempts to obtain suitable crystals of VIII for an X-ray structural determination were unsuccessful; however, while attempting to obtain suitable crystals of the mixed metal–ring complex $[P(Ph)_2(CH_2)_4P(Ph)_2\{(\eta^4\text{-}C_6H_7\text{-}exo)Fe(CO)_3\}\{(\eta^6\text{-}C_7H_7\text{-}exo)Cr(CO)_3\}][BF_4]_2$ for X-ray analysis,[2] we were surprised to obtain crystals of VIII which did prove suitable for X-ray study, a rather bizarre example of serendipity. The structure of VIII is shown in Figure 1 and clearly proves the existence of a diphosphine ring–ring linked structure in the solid state with the $Cr(CO)_3$ moieties occupying opposite sides of the diphosphine linked ring systems. The ring C_7–phosphorus distance of 1.852 Å is almost identical with the value of 1.856 Å reported in our preliminary communication for the mono-ring adduct $[(\eta^4\text{-}C_7H_9\text{-}5\text{-}exo\text{-dppm})Fe(CO)_3]BF_4$[2] and is considerably longer than the phosphorus–carbon (alkane chain) bond of 1.79 Å. The long ring–phosphorus bonds in these complexes imply C–P bonds weaker than a normal single C–P bond, which may account for the facile breaking of this bond during the reactions of VIII with nucleophiles such as hydride and during attempted decomplexation reactions as described below.

Reactions of VIII. As in the case of IV and V, attempts at hydride abstraction from VIII by either NBS or CPh_3BF_4 resulted in loss of diphosphine and formation of I even at low temperatures. Attempted decomplexation of VIII, e.g. by oxidation with iodine, again resulted in cleavage of the carbon–phosphorus bond and formation of I. Subsequent oxidation and decomplexation yielded the tropylium salt $[C_7H_7]BF_4$. Hydride addition to VIII with lithium triethylborohydride at −60 °C again led to substitution of the diphosphine and formation of $C_7H_8Cr(CO)_3$ as the case of IV and V.

Formation of only the monomeric ring adducts IV and V by dppe and dppm, respectively, contrasts with formation of the diphosphine ring–ring linked dimers VII and VIII by dppp and dppb, respectively. Comparing the ^{31}P δ values of the pendant P atom in IV–VI with the corresponding free ligand values (see Table 1) shows a decreasing deshielding effect (Δ) in the series dppm > dppe > dppp consistent with a greater charge withdrawal from and therefore decreasing nucleophilicity of the pendant P atom in the above series. As a consequence, the lower members of the series show no tendency for the second phosphine center to bond to another positive center. However, for the longer chain diphosphines attenuation of this charge withdrawal occurs and so the second phosphorus atom is sufficiently nucleophilic to form ring–ring dimers such as VII and VIII.

Reaction of I with Diphosphines at Elevated Temperatures. The mono-ring adducts IV–VI and the diphosphine ring–ring linked dimers VII and VIII are all formed by low-temperature reactions (−40 to −60 °C) of I with the appropriate diphosphine in either 1:1 or 2:1 molar ratios. In contrast, when dppm and I in a 1:1 molar ratio were refluxed in acetone for 3 h, a complex reaction mixture resulted which after chromatography and recrys-

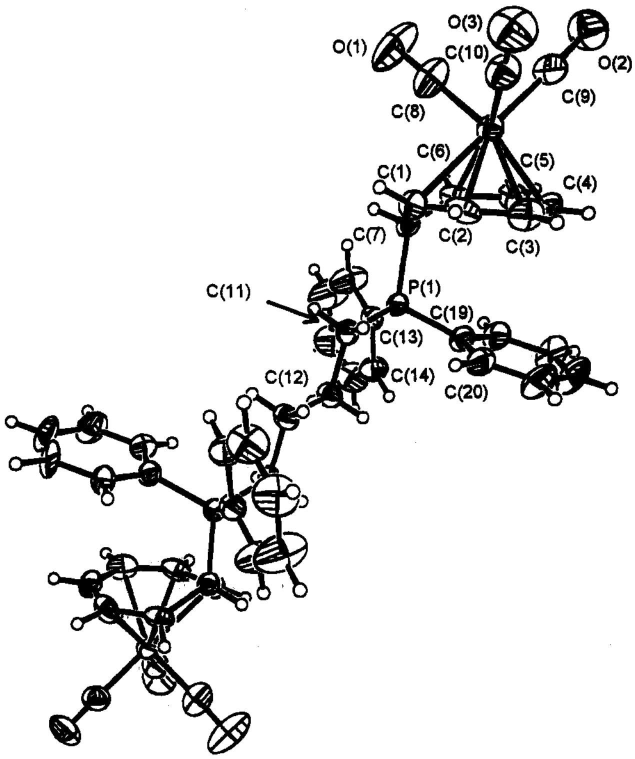

Figure 1. Crystal structure of $[(7,7'\text{-}exo\text{-dppb})\{(\eta^6\text{-}C_7H_7)Cr(CO)_3\}_2][BF_4]_2$ (VIII).

Table 2. Crystal Data and Structure Refinement[a]

empirical formula	$C_{25}H_{23}BCl_2CrF_4O_3P$
color	orange
fw	612.11
temp	293 (2) K
wavelength	0.710 69 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	a = 10.679 (2) Å, b = 11.391 (2) Å, c = 11.599 (1) Å, α = 76.20 (1)°, β = 86.40 (1)°, γ = 81.73 (2)°
V	1355 (5) Å^3
Z	1
density (calcd)	1.500 Mg/m^3
abs coeff	0.732 mm^{-1}
$F(000)$	622
cryst size	0.45 × 0.33 × 0.28 mm
θ range for data collection	2.27–24.97°
index ranges	$0 \le h \le 12, -13 \le k \le 13, -13 \le l \le 13$
no. of rflns collected	5186
no. of indep rflns	4773 (R(int) = 0.0818)
refinement method	full-matrix least squares on F^2
no. of data/no. of restraints/ no. of params	4773/0/339
goodness of fit on F^2	1.991
final R indices ($I > 2\sigma(I)$)	R_1 = 0.0847, R_{w2} = 0.2394
R indices (all data)	R_1 = 0.0927, R_{w2} = 0.2455
largest diff peak and hole	1.134 and −0.802 e Å^{-3}

[a] R indices: $R_1 = [\sum \| F_o | - | F_c \|] / \sum | F_o |$; $R_{w2} = [[\sum w(|F_o - F_c|)^2] / [\sum w(|F_o|)^2]]^{1/2}$. $w = q/[(\sigma F_o)^2 + (aP)^2 + bP + d + e \sin\theta]$. goodness of fit $= [\sum w(|F_o^2| - |F_c^2|)^2/(N_{obs} - N_{params})]^{1/2}$.

tallization yielded the chelate $[(\eta^7\text{-}C_7H_7)Cr(CO)(\eta^2\text{-dppm})]BF_4$ (IX), the ring displaced product [*mer*-$Cr(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})$] (X), the hydride addition product $(C_7H_8)Cr(CO)_3$, and a second ring displaced product, [$Cr(CO)_4(\eta^2\text{-dppm})$]. Both ring displaced products have been reported previously.[17,18] The infrared and ^{1}H, ^{13}C, and ^{31}P NMR spectra of IX are fully consistent with chelate formation, and it should be noted that this is the first example of a chelate formed from I. Reaction of I with longer chain diphosphines dppx (x = e, p, b) under conditions similar to those employed for dppm resulted

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3)

	x	y	z	U(eq)[a]
Cr(1)	171 (1)	2660 (1)	1543 (1)	43 (1)
P(1)	−2503 (1)	−5 (1)	2965 (1)	37 (1)
C(1)	−1271 (4)	1974 (4)	3034 (4)	52 (1)
C(2)	−1793 (4)	3003 (4)	2225 (5)	58 (1)
C(3)	−1808 (4)	3216 (4)	978 (5)	60 (1)
C(4)	−1195 (4)	2455 (5)	277 (4)	58 (1)
C(5)	−428 (4)	1343 (4)	659 (4)	53 (1)
C(6)	−201 (4)	647 (4)	1788 (4)	48 (1)
C(7)	−1026 (3)	702 (3)	2862 (2)	41 (1)
C(11)	−3436 (3)	408 (3)	4181 (2)	43 (1)
C(12)	−4626 (4)	−217 (4)	4493 (4)	49 (1)
C(13)	−2155 (4)	−1627 (4)	3247 (3)	44 (1)
C(14)	−3095 (5)	−2306 (5)	3098 (5)	61 (1)
C(15)	−2858 (6)	−3571 (5)	3406 (5)	75 (2)
C(16)	−1751 (6)	−4133 (5)	3853 (7)	84 (2)
C(17)	−842 (7)	−3494 (6)	4001 (9)	110 (3)
C(18)	−1033 (5)	−2230 (5)	3706 (6)	83 (2)
C(19)	3335 (4)	539 (4)	1617 (3)	44 (1)
C(20)	−4232 (4)	1564 (5)	1479 (4)	59 (1)
C(21)	−4728 (5)	2085 (6)	357 (6)	79 (2)
C(22)	−4311 (6)	1572 (7)	−588 (5)	81 (2)
C(23)	−3449 (6)	564 (7)	−445 (4)	80 (2)
C(24)	−2946 (4)	15 (5)	644 (4)	58 (1)
C(8)	1417 (6)	2027 (5)	2642 (5)	70 (1)
C(9)	1401 (4)	2979 (5)	358 (5)	59 (1)
C(10)	357 (5)	4189 (5)	1721 (4)	60 (1)
O(1)	2201 (6)	1642 (5)	3326 (5)	125 (2)
O(2)	2162 (4)	3248 (5)	−363 (4)	90 (1)
O(3)	543 (5)	5138 (4)	1819 (5)	95 (1)
B(1)	2399 (6)	7901 (6)	3642 (5)	62 (1)
F(1)	3611 (4)	8092 (5)	3488 (4)	114 (2)
F(2)	2244 (5)	6941 (3)	4581 (3)	112 (2)
F(3)	1637 (3)	8909 (3)	3940 (3)	90 (1)
F(4)	1943 (4)	7696 (5)	2634 (3)	110 (1)
Cl(1)	4962 (2)	3826 (2)	3930 (2)	115 (1)
Cl(2)	4114 (5)	4887 (4)	1577 (3)	214 (2)
C(25)	3727 (10)	4704 (11)	3105 (9)	143 (4)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Selected Bond Lengths (Å) and Angles (deg)

Cr(1)–C(10)	1.841 (5)	Cr(1)–C(6)	2.331 (4)
Cr(1)–C(8)	1.848 (5)	P(1)–C(19)	1.780 (4)
Cr(1)–C(9)	1.849 (5)	P(1)–C(13)	1.786 (4)
Cr(1)–C(5)	2.192 (4)	P(1)–C(11)	1.792 (3)
Cr(1)–C(4)	2.206 (5)	P(1)–C(7)	1.856 (3)
Cr(1)–C(2)	2.209 (4)	C(8)–O(1)	1.155 (7)
Cr(1)–C(3)	2.211 (5)	C(9)–O(2)	1.148 (6)
Cr(1)–C(1)	2.311 (4)	C(10)–O(3)	1.159 (6)
C(10)–Cr(1)–C(9)	83.3(2)	O(1)–C(8)–Cr(1)	179.3(5)
C(8)–Cr(1)–C(9)	89.9(2)	O(2)–C(9)–Cr(1)	175.7(5)
C(8)–Cr(1)–C(10)	88.1(2)	O(3)–C(10)–Cr(1)	176.3(5)

only in the formation of analogous ring displaced products, all of which have been reported previously.[17,18]

Low-Temperature Reactions of II and III with Diphosphines. As mentioned in the Introduction, thermal reaction of $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]BF_4$ (II) with diphosphines gave a series of carbonyl substitution products;[12] however, in view of previous reports of ring addition by some monophosphines to II at low temperatures,[10] it seemed of interest to study the low-temperature reactions of II and III with diphosphines to see if any spectroscopic evidence could be obtained for the formation of ring adducts analogous to those formed by I, if only as initial products. The reaction of II (III) with dppm in CH_2Cl_2 at −60 °C was monitored by infrared spectroscopy using a Specac low-temperature cell. The carbonyl stretching frequencies of II at 2071 and 2033 cm^{-1} were replaced by new bands at 2004, 1940, and 1901 cm^{-1}, which lie very close to those of the analogous mono-ring adduct of chromium (IV) and therefore may be assigned to the analogous molybdenum complex $[(\eta^6\text{-}C_7H_7\text{-}exo\text{-dppm})Mo(CO)_3]BF_4$ (XI). Similar results were obtained with III to yield XIII, and finally the monophosphine PPh_3 reacted similarly under these conditions with both II and III to give the monophosphine adducts XII and XIV. The low-temperature reaction of II with dppm in d_6-acetone was also monitored at −60 °C by ^1H NMR spectroscopy. The single peak at δ 6.58 due to II was replaced by a typical mono-ring adduct spectrum (see above) and provides further confirmation of the formation by II of the mono-ring adduct XII. Unlike the chromium series, complexes XII–XV dissociate when the temperature is raised and thermal reaction forms the carbonyl substitution products.[12]

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Supplementary Material Available: Tables of hydrogen atom coordinates and anisotropic displacement parameters for VIII (2 pages). Ordering information is given on any current masthead page.

OM9307747

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