Reaction of [{Cr(cp)(CO)$_3$}$_2$] (cp = η^5-C_5H_5) with Elemental Phosphorus. Isolation of [Cr_2(cp)$_2$(P_5)] as a Thermolysis Product and its *X*-Ray Crystal Structure†

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The reaction of [{Cr(cp)(CO)$_3$}$_2$] (**1**) with 2 mol equivalents of P_4 in toluene at 90 °C produces a mixture of [Cr_2(cp)$_2$(CO)$_4$(μ-η^2-P_2)] (**2**), [Cr(cp)(CO)$_2$(η^3-P_3)] (**3**), [{Cr(cp)(CO)$_2$}$_5$(P_{10})] (**4**), and [Cr_2(cp)$_2$(η^5-P_5)] (**5**), the relative proportion of which is dependent on the duration of the reaction. This, coupled with thermolysis studies on (**2**)—(**4**), demonstrates that these three complexes are the primary products of the reaction, whereas (**5**) arises mainly from the thermolysis of (**2**), which also yields (**3**) and [{Cr(cp)(CO)$_2$}$_2$] (**6**). Complex (**5**) has been isolated from a reaction of (**1**) with P_4 at 110 °C after *ca.* 5 h. A single-crystal *X*-ray diffraction study of (**5**) shows it to be a triple-decker sandwich complex with a cyclic P_5 ring bonded to two Cr(cp) groups. Crystal data: monoclinic, space group $P2_1/n$, $a = 7.921(2)$, $b = 15.04(1)$, $c = 11.704(4)$ Å, $\beta = 104.08(2)$°, and $Z = 4$. The spectral features of complex (**5**) are also presented.

There is much current interest in the syntheses and reactivity of transition-metal complexes containing bare P atoms or aggregates.[1–3] In extending our studies on the reactions of the Cr–Cr dimer [{Cr(cp)(CO)$_3$}$_2$] (1) (cp = η^5-C_5H_5) with main group elements,[4,5] we have treated it with elemental phosphorus under mild reaction conditions and obtained high yields of [Cr_2(cp)$_2$(CO)$_4$(μ-η^2-P_2)] (2) and [Cr(cp)(CO)$_2$(η^3-P_3)] (3).[6] In this paper, we describe conditions that led to the isolation of [Cr_2(cp)$_2$(P_5)] (5), together with evidence indicating that (5) arises from the thermolytic degradation of (2), (3), and a polyphosphidochromium complex [{Cr(cp)(CO)$_2$}$_5$(P_{10})] (4). Mechanistic pathways for the formation of (3) and (5) and the *X*-ray crystal structure of (5) are also presented.

Results and Discussion

Mechanistic Pathways.—In a previous study[6] we have shown that the reaction of [{Cr(cp)(CO)$_3$}$_2$] (1) with 1 mol equivalent of P_4 at 90 °C for 3—4 h produced the complexes [Cr_2(cp)$_2$(CO)$_4$(μ-η^2-P_2)] (2) and [Cr(cp)(CO)$_2$(η^3-P_3)] (3) in 53 and 40% yields, respectively. Further investigation now demonstrates that this product composition is drastically altered with prolonged reaction times. Thus as shown in the results presented in Table 1, a 10-h reaction produced a substantial yield (24%) of [Cr_2(cp)$_2$(η^5-P_5)] (5) apparently at the expense of (2), which is totally degraded at *ca.* 15 h, when the yield of (5) has achieved 43%. Indeed, an exhaustive thermal reaction at 110 °C for 5—6 h, using a Cr:P mol ratio of 1:4, led to the isolation of (3) (28%) and (5) (37%) as the predominant products with a minor amount of an elementally characterised polyphosphido complex [{Cr(cp)(CO)$_2$}$_5$(P_{10})] (4) (6%).[7] It can be deduced from these observations that complexes (2)—(4) are the primary products of the reaction of (1) with P_4, and (5) results from the thermolytic degradation of (2) or from a cothermolysis of (2) with (3) or with P_4. In effect, this is substantiated by the observed facile degradation of (2) in toluene at 110 °C. Thus its thermolysis was found to be complete in 1.5 h, giving a mixture of complexes (3) (12), (5) (70), and [{Cr(cp)(CO)$_2$}$_2$] (6) (18% yield) in solution [routes (ii)—(iv) in the Scheme], which on work-up led to the isolation of (3), (5), and (6) in 7.5, 66.4, and 17% yields respectively. Likewise, the cothermolysis of (2) with P_4 at a Cr:P mol ratio of 1:4, though not noticeable after 21 h at 70 °C, was found to be almost complete after 2.5 h at 110 °C, resulting in a 96% conversion into (3) (35%) and (5) (60%) [routes (ii) and (iii) in the Scheme]. The absence of (6) in this case is consistent with the reaction of the triply bonded pentamethylcyclopentadienyl analogue of (6) with P_4 as reported by Scherer *et al.*[8] [equation (v) in the Scheme].

Complex (3) is thermally more stable than (2). It was observed that thermolysis at 110 °C for 4.5 and 15.5 h led only to 10 and 15% conversion, respectively, into [Cr_2(cp)$_2$(P_5)] (5) [pathway (vi) in the Scheme]. In the presence of 4 equivalents of P, its reaction was even more sluggish, and after 6 h at 110 °C the solution remained practically unchanged, except for slight precipitation of a fine brown-black unidentified solid, and no spectral evidence of (5) was observed.

Like (2), the polyphosphido complex (4) degraded quite readily to the cyclic η^5-P_5 complex (5) [pathway (vii) in the Scheme]. An unidentified cp-containing species (δ 4.09) along with trace amounts of (3) and (6) were detected during the reaction which took *ca.* 8 h to complete at 110 °C. In the presence of a large excess of P (25 mol equivalents), and under similar reaction conditions, the degradation produced (5) as the major product and a substantial yield (30%) of (3) [routes (vii) and (viii) in the Scheme].

The above findings show that the triple-decker complex (5) is the ultimate thermolytic product of (2)—(4), as shown in the Scheme. In this context, it may be noted that the mass fragment *m/z* 389 [Cr_2(cp)$_2$(P_5)] was previously observed in the mass spectra of both (2) and (3).[6] In view of the thermal lability of complexes (2)—(4) established here, it is not surprising that in the reaction of [{Cr(η-C_5Me_5)(CO)$_2$}$_2$] with P_4 under more forcing conditions (140 °C, 5 h) Scherer[8] obtained only 0.2%

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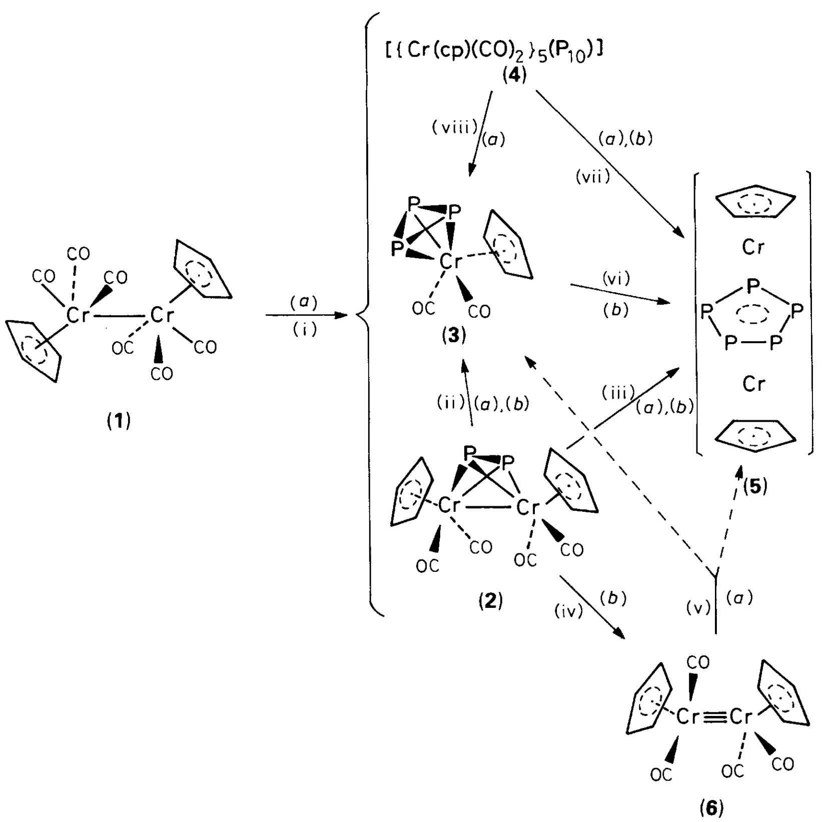
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



Scheme. (*a*) Cothermolysis with P_4; (*b*) thermolysis

Table 1. Product composition from the reaction of $[\{Cr(cp)(CO)_3\}_2]$ (**1**) with 2 mol equivalents of P_4

Temperature (°C)	Time (h)	Product (% yield) $[Cr_2(cp)_2(CO)_4(P_2)]$ (**2**)	$[Cr(cp)(CO)_2(P_3)]$ (**3**)	$[\{Cr(cp)(CO)_2\}_5(P_{10})]$ (**4**)	$[Cr_2(cp)_2(P_5)]$ (**5**)
90[a]	3.5	37	45	18	0
	10	12	50	14	24
	15	2	33	22	43
110[b]	5—6	0	28	6	37

[a] Product yields estimated from ^1H n.m.r. spectra of aliquots of reaction mixture. [b] Yields from isolated complexes.

yield of $[Cr(\eta\text{-}C_5Me_5)(CO)_2(P_3)]$ and none of $[Cr_2(\eta\text{-}C_5Me_5)_2(CO)_4(P_2)]$. However, the low yield obtained also for $[Cr_2(\eta\text{-}C_5Me_5)_2(P_5)]$ (8.3%) is not in agreement with our findings for the unmethylated system. It may well be that low thermal stabilities are responsible for the low yields of the $\mu\text{-}\eta^2\text{-}P_2$ and $\eta^3\text{-}P_3$ complexes of Mo and W obtained from the reactions of $[\{M(\eta\text{-}C_5Me_5)(CO)_2\}_2]$ with P_4 at 140—150 °C at 5 h (M = Mo) and 12 h (M = W) respectively,[9] though the equally low yields of $[M_2(\eta\text{-}C_5Me_5)_2(P_6)]$ (*ca.* 1%) could indicate that these cyclic $\eta^6\text{-}P_6$ complexes arise from a different pathway, *e.g. via* the reaction of P_4 with the bis($\mu\text{-}\eta^2\text{-}P_2$) complex $[\{Mo(cp)(CO)(\mu\text{-}\eta^2\text{-}P_2)\}_2]$, as suggested by Scherer.[2] A recent report described the decarbonylation of $[Mo(\eta\text{-}C_5Me_5)(CO)_2(\eta^3\text{-}P_3)]$ under irradiation to give a substantial yield of $[Mo_2(\eta\text{-}C_5Me_5)_2(P_6)]$.[10]

As is speculated in the formation of the $\eta^5\text{-}P_5$ ligand in the mixed sandwich $[Fe(C_5Me_5)(P_5)]$,[11] it is probable that the $\eta^5\text{-}P_5$ ring in (**5**) is formed from a direct bimolecular interaction of the $\mu\text{-}\eta^2\text{-}P_2$ (**2**) and $\eta^3\text{-}P_3$ (**3**) complexes [equation (ix)],

$$\underset{(\mathbf{2})}{[Cr_2(cp)_2(CO)_4(P_2)]} + \underset{(\mathbf{3})}{[Cr(cp)(CO)_2(P_3)]} \longrightarrow \underset{(\mathbf{5})}{[Cr_2(cp)_2(P_5)]} \quad \text{(ix)}$$

especially since (**3**) was also one of the thermolytic products of (**2**). However, this pathway cannot exclude reaction (x).

$$\underset{(\mathbf{2})}{[Cr_2(cp)_2(CO)_4(P_2)]} \longrightarrow \underset{(\mathbf{3})}{[Cr(cp)(CO)_2(P_3)]} + \underset{(\mathbf{5})}{[Cr_2(cp)_2(P_5)]} \quad \text{(x)}$$

Although the presence of P_4 is found to be not essential for the conversion of (**2**) into (**5**), the interaction of (**2**) and P_4 [equation (xi)] also cannot be completely discounted. Experimentally, it is

$$[Cr_2(cp)_2(CO)_4(P_2)] + P_4 \longrightarrow [Cr(cp)(CO)_2(P_3)] + [Cr_2(cp)_2(P_5)] \quad \text{(xi)}$$

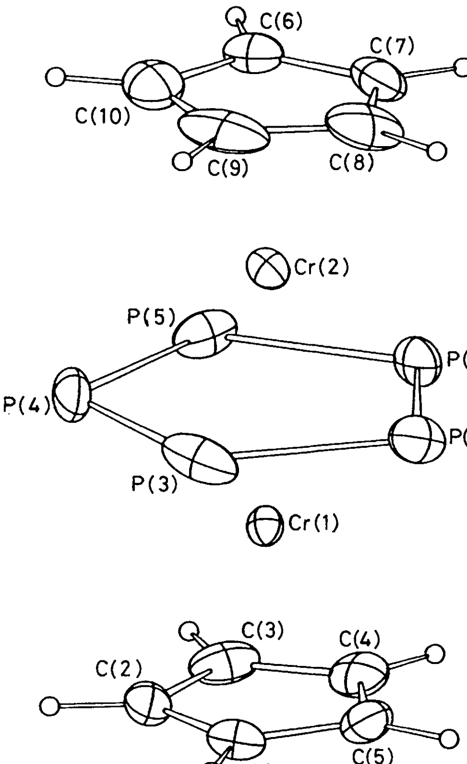


Figure. Molecular structure of [$Cr_2(cp)_2(\eta^5\text{-}P_5)$] (**5**)

Table 2. Phosphorus-31 chemical shifts for cyclic P_5 and P_6 triple decker complexes and metallocenes

Complex	δ/p.p.m.	Ref.
[$Cr_2(cp)_2(P_5)$]	−100.5	This work
[$Cr_2(\eta\text{-}C_5Me_5)_2(P_5)$]	−290.5	8
[$Cr_2(cp)_2(P_5)$] (?)	−285	8
[$Cr_2(C_5H_4Me)_2(P_5)$](?)	−283	8
[$Fe(\eta\text{-}C_5Me_5)(P_5)$]	153.0	*a*
[$Fe(C_5Me_4Et)(P_5)$]	152.8	*a*
[$Ru(\eta\text{-}C_5Me_5)(P_5)$]	83.8	*a*
[$Ru(C_5Me_4Et)(P_5)$]	84.4	*a*
[$Mo_2(\eta\text{-}C_5Me_5)_2(P_6)$]	−315.6	*b*
[$W_2(\eta\text{-}C_5Me_5)_2(P_6)$]	−338.2	9
[$V_2(\eta\text{-}C_5Me_5)_2(P_6)$]	164.9	9
[$V_2(C_5Me_4Et)_2(P_6)$]	160.3	9

[a] O. J. Scherer, T. Brück, and G. Wolmershäuser, *Chem. Ber.*, 1988, **121**, 935. [b] O. J. Scherer, H. Sitzmann, and G. Wolmershäuser, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 351.

not possible to establish which of the above is the main or only contributory route. Until more definitive studies can be realised the exact mechanism of formation of the P_5 ring remains a matter of speculation. In this context, one may note that *ab initio* calculations show that the formation of cyclic N_5 ion from N_3^- and N_2 could be feasible in a matrix at low temperatures, and that likewise $\eta^5\text{-}N_5$ complexes, *e.g.* [$Fe(CO)_3(N_5)$]$^+$, [$Mn(CO)_3(N_5)$], and [$Cr(CO)_3(N_5)$]$^-$, could be formed by bringing together the fragments, possibly *via* diffusion in an inert matrix at low temperatures.[12,13]

It is interesting that whereas cyclic X_5 or X_6 rings in triple-decker sandwich complexes seem to be a characteristic feature of the thermolytic product of complexes of P and As[14] the thermal degradation of analogous $\mu\text{-}\eta^2\text{-}E_2$ (E = S or Se) and related complexes of Cr produces ultimately cubane-like derivatives [$M_4(cp)_4(\mu_3\text{-}E)_4$].[5,15,16]

Properties and Spectral Characteristics of [$Cr_2(cp)_2(P_5)$] (**5**).—The complex is obtained as an air-stable fine black crystalline solid, insoluble in n-hexane but moderately soluble in benzene, toluene and tetrahydrofuran (thf). The orange-yellow solutions obtained are very air-sensitive, producing a green precipitate. The ^1H n.m.r. spectrum in C_6D_6 shows a very broad signal at δ 18.8 ($\nu_{\frac{1}{2}}$ 80—127 Hz) but no signal could be detected in the ^{13}C spectrum. In $C_6D_5CD_3$, this broad cp resonance shifts from δ 16.8 ($\nu_{\frac{1}{2}}$ *ca.* 90 Hz) at +90 °C to δ 27.0 ($\nu_{\frac{1}{2}}$ *ca.* 200 Hz) at −90 °C. The cause of this phenomenon is still unclear. The ^{31}P n.m.r. spectrum shows a sharp singlet at δ −100.5 p.p.m. and this is compared with those of other $\eta^5\text{-}P_5$ as well as $\eta^6\text{-}P_6$ complexes in Table 2. It is also perplexing that Scherer *et al.*[8] reported ^{31}P resonances at δ −285 p.p.m. for the identical complex and δ −283 p.p.m. for the C_5H_4Me analogue. Since complex (**5**) is definitively characterised here, we believe that Scherer's ^{31}P chemical shifts belong to some as yet unidentified species. Inconsistent with the permethylcyclopentadienyl analogue was the absence of any observed e.s.r. signal in a freshly prepared solution in toluene between 30 and −70 °C. However, upon deliberate admission of a trace amount of air into the e.s.r. tube, resulting in the formation of a light blue surface layer, the solution after being shaken still remained clear yellowish orange but now showed an e.s.r. signal (g_{iso} = 2.021, peak-to-peak distance 1.5 mT) very similar to that reported for the C_5Me_5 analogue (g_{iso} = 2.022, peak-to-peak distance 1.2 mT), which Scherer *et al.*[8] had attributed to the paramagnetic nature of the 27-valence electrons of the system. Splittings of 1.8 mT due to the mononuclear Cr ($I = \frac{3}{2}$) were also observed for the partially oxidised cp complex. The absence of an e.s.r. signal in the freshly prepared solution of complex (**5**) is unexpected. It may be conjectured that there is a dynamic distortion of the P_5 ring in solution, resulting in a deviation of the ring from axial symmetry as observed in some metallocene complexes.[17,18] The mass spectrum shows the parent ion *m*/*z* 389 [$Cr_2(cp)_2(P_5)$], and mass fragments at *m*/*z* 327 [$Cr_2(cp)_2(P_3)$], 262 [$Cr_2(cp)(P_3)$], 213 [$Cr(cp)_2P$], 200 [$Cr_2(cp)P$], 182 [$Cr(cp)_2$], 124 (P_4), 117 [$Cr(cp)$], and 62 (P_2).

Structure of [$Cr_2(cp)_2(P_5)$] (**5**).—A stereoview is shown in the Figure. Positional parameters are given in Table 3. The structural analysis confirms the presence of a cyclic P_5 group co-ordinated to two cyclopentadienylchromium groups. The three rings are parallel to within 3°. Least-squares planes through each of the five-membered rings reveal no deviations from planarity greater than 0.01 Å. The Cr atoms lie 1.83 Å from the planes of the cp rings and 1.37 Å from the P_5 ring. Selected bond distances and bond angles are given in Table 4 and some of the bonding parameters are compared with those of other cyclic P_3, P_5, and P_6 complexes in Table 5. The P–P distances range from 2.206(3) to 2.276(2) Å, marginally longer than the distances [2.15(2)—2.21(2) Å] observed in the analogous pentamethylcyclopentadienyl complex [$Cr_2(C_5Me_5)_2(P_5)$],[8] which are closer to those observed in $\mu\text{-}\eta^3\text{-}P_3$ and $\mu\text{-}\eta^6\text{-}P_6$ and metallocene complexes. The P–Cr bonds [2.318(2)—2.366(2) Å] are also longer than those in the C_5Me_5 compound[8] [2.29(1)—2.32(1) Å]. Curiously the Cr–Cr distances in the two structures are very similar 2.738(1) and 2.727(5) Å, respectively. In the report of the C_5Me_5 structure the P atoms are said to exhibit strong anisotropy[9] and it may be that this results in artificially shortened Cr–P and P–P bond lengths. Another cause for this effect may be an increased synergic back donation from (C_5Me_5)Cr to the P_5 ring. The Cr–C bond distances in (**5**)

Table 3. Positional parameters (× 10^4) for $[\{Cr(cp)\}_2(P_5)]$

Atom	*x*	*y*	*z*
Cr(1)	5 615(1)	2 194(1)	1 647(1)
Cr(2)	3 742(1)	819(1)	2 256(1)
P(1)	6 030(2)	689(1)	1 343(2)
P(2)	3 514(2)	1 358(1)	368(2)
P(3)	2 679(2)	2 248(1)	1 662(2)
P(4)	4 612(3)	2 126(1)	3 371(2)
P(5)	6 636(2)	1 169(1)	3 181(2)
C(1)	5 580(8)	3 545(4)	938(6)
C(2)	6 740(9)	3 524(4)	2 038(6)
C(3)	8 049(8)	2 930(5)	1 985(7)
C(4)	7 731(8)	2 587(4)	862(7)
C(5)	6 190(9)	2 965(4)	212(6)
C(6)	3 721(9)	−396(4)	3 291(7)
C(7)	3 241(10)	−612(4)	2 135(7)
C(8)	1 692(10)	−160(5)	1 633(8)
C(9)	1 311(9)	355(5)	2 549(11)
C(10)	2 590(10)	208(5)	3 598(9)

Table 4. Bond lengths (Å) and angles (°) for $[\{Cr(cp)\}_2(P_5)]$

Cr(2)–Cr(1)	2.738(1)	P(1)–Cr(1)	2.327(2)
P(2)–Cr(1)	2.320(2)	P(3)–Cr(1)	2.332(2)
P(4)–Cr(1)	2.344(2)	P(5)–Cr(1)	2.355(2)
C(1)–Cr(1)	2.191(6)	C(2)–Cr(1)	2.191(6)
C(3)–Cr(1)	2.174(6)	C(4)–Cr(1)	2.180(6)
C(5)–Cr(1)	2.178(6)	P(1)–Cr(2)	2.325(2)
P(2)–Cr(2)	2.318(2)	P(3)–Cr(2)	2.350(2)
P(4)–Cr(2)	2.366(2)	P(5)–Cr(2)	2.345(2)
C(6)–Cr(2)	2.197(6)	C(7)–Cr(2)	2.188(6)
C(8)–Cr(2)	2.183(6)	C(9)–Cr(2)	2.153(6)
C(10)–Cr(2)	2.200(8)	P(1)–P(2)	2.276(2)
P(1)–P(5)	2.209(3)	P(2)–P(3)	2.238(3)
P(3)–P(4)	2.212(4)	P(4)–P(5)	2.206(3)
C(1)–C(2)	1.388(9)	C(1)–C(5)	1.384(9)
C(2)–C(3)	1.382(10)	C(3)–C(4)	1.376(10)
C(4)–C(5)	1.393(9)	C(6)–C(7)	1.353(10)
C(6)–C(10)	1.384(10)	C(7)–C(8)	1.400(10)
C(8)–C(9)	1.413(11)	C(9)–C(10)	1.406(12)
P(2)–Cr(1)–P(1)	58.6(1)	P(3)–Cr(1)–Cr(2)	54.5(0)
P(1)–P(2)–P(3)	107.0(1)	P(2)–P(3)–P(4)	108.0(1)
P(3)–P(4)–P(5)	108.9(1)	P(4)–P(5)–P(1)	108.7(1)
P(5)–P(1)–P(2)	107.5(1)	C(1)–C(2)–C(3)	107.9(6)
C(2)–C(3)–C(4)	108.7(6)	C(3)–C(4)–C(5)	107.5(6)
C(4)–C(5)–C(1)	108.2(6)	C(5)–C(1)–C(2)	107.7(6)
C(6)–C(7)–C(8)	107.9(8)	C(7)–C(8)–C(9)	106.0(7)
C(8)–C(9)–C(10)	109.5(7)	C(9)–C(10)–C(6)	104.6(8)
C(10)–C(6)–C(7)	112.0(8)		

are in the range observed in other complexes containing cp bound to Cr.

The non-distorted nature of the P_5 ring has been rationalised on the basis of extended-Hückel calculations,[19,20] which gave an electronic structure with a singly occupied non-degenerate highest occupied molecular orbital (h.o.m.o.) for **(5)**[19] This differs from the observed distortion of the As_5 ring of $[Mo_2(cp)_2(As_5)]$[21] which has been attributed to the presence of three electrons in a degenerate h.o.m.o.,[19] and very recently by Hoffmann and co-workers[20] to the simultaneous operation of first- and second-order Jahn–Teller effects. The observed difference (*ca.* 0.01 Å) between the Cr–Cr distances of **(5)** and its C_5Me_5 analogue and the shorter M–M distances of the μ-η^6-P_6 complexes of Mo, W, and V are also consistent with the extended-Hückel calculations which showed that the m.o. overlap between the interacting orbitals of (cp)M ··· M(cp) and the middle ring increases with ring size.[19] Indeed it may be inferred from these theoretical studies that the preferential formation of the cyclic P_5 middle deck with Cr *versus* cyclic P_6 with the heavier congeners Mo and W and its neighbour V[9] arises from a delicate balance between the relative size of the individual metal atom, the M–M distance, and the ring size of the middle deck.

Experimental

General Procedures and Physical Measurements.—Inert-atmosphere manipulation techniques, sources, and preparation of reagents and solvents were as described previously.[5,6] Proton and ^{13}C n.m.r. spectra were measured on a JEOL FX100 100-MHz spectrometer, and chemical shifts are relative to residual C_6H_6 in C_6D_6 or to $SiMe_4$. The ^{31}P n.m.r. spectrum was measured on a JEOL FX9Q FT spectrometer (36.23 MHz) and the chemical shift referenced to external H_3PO_4. E.s.r. spectra were measured on a Bruker B-R 70 spectrometer (23-cm magnet) and the field determined with the aid of a n.m.r. oscillator; the *g* value was calibrated using diphenylpicrylhydrazyl. I.r. spectra were measured on a Perkin-Elmer 1330 instrument, mass spectra on a Kratos AEI MS 3074. Carbon and hydrogen analyses were made by the Analytical Unit of the Research School of Chemistry, Australian National University, phosphorus analysis by Pascher Laboratories of Bonn, and we analysed Cr as CrO_4^{2-}.[22]

Reaction of $[\{Cr(cp)(CO)_3\}_2]$ *with* P_4: *Isolation of* $[Cr_2(cp)_2(P_5)]$ **(5)**.—A deep green mixture of $[\{Cr(cp)(CO)_3\}_2]$ (500 mg, 1.24 mmol) and yellow P_4 (308 mg, 2.48 mmol) in toluene (25 cm^3) was refluxed with stirring for 5—6 h. A gradual colour change through reddish brown to dark brown was observed. The homogeneous product solution was filtered and eluted through an alumina disc (3 × 1.5 cm) with toluene (*ca.* 20 cm^3). Concentration of the filtrate-eluate to *ca.* 5 cm^3, followed by cooling at −17 °C, gave a fine black crystalline solid of $[Cr_2(cp)_2(P_5)]$ **(5)** (150 mg, 0.39 mmol, 31% yield) (Found: C, 30.60; H, 2.65; Cr, 26.15; P, 37.8. $C_{10}H_{20}Cr_2P_5$ requires C, 30.85; H, 2.60; Cr, 26.70; P, 39.85%). I.r.(Nujol): ν(cp) 810s cm^{-1}.

The mother-liquor was concentrated to *ca.* 2 cm^3 and loaded onto an alumina column (1.5 × 15 cm) prepared in n-hexane. Elution with n-hexane (20 cm^3) followed by n-hexane–toluene (4:1) (20 cm^3) gave a yellow solution, from which was isolated yellowish brown flaky crystals of $[Cr(cp)(CO)_2(P_3)]$ **(3)** (170 mg, 0.64 mmol, 26% yield) [^1H n.m.r.(C_6D_6), δ(cp) 3.92].[6] Further elution with n-hexane–toluene (1:1) (15 cm^3) and toluene (25 cm^3) gave a golden brown solution which on evaporation to dryness yielded a brown-black crystalline solid (115 mg), the ^1H n.m.r. spectrum of which indicated a 2:1:1 molar mixture of complexes **(3)**, $[\{Cr(cp)(CO)_2\}_5(P_{10})]$ **(4)**, and **(5)**. Rechromatography of this mixture on a 1 × 10 cm alumina column led to the separation of **(3)** (n-hexane, 10 mg, 0.07 mmol, 2% yield), **(5)** [n-hexane–toluene (1:1); 30 mg, 0.077 mmol, 6% yield], and reddish brown crystalline needles of **(4)** [toluene–diethyl ether (1:1); 35 mg, 0.0297 mmol, 6.0% yield].

A similar reaction on 1/10 scale of the above was also carried out at 90 °C, and aliquots taken at 3.5, 10, and 15 h to monitor the ^1H n.m.r. spectrum of the products, the composition of which is given in Table 1.

Thermolysis Reactions.—$[Cr_2(cp)_2(CO)_4(P_2)]$ **(2)**. A stirred magenta solution of complex **(2)** (40 mg, 0.098 mmol) in toluene (20 cm^3) was maintained at *ca.* 110 °C for 1.5 h, by which time the colour had turned yellowish brown. An n.m.r. spectrum in C_6D_6 showed a 2:12:3 molar mixture of $[Cr(cp)(CO)_2(P_3)]$ **(3)**, $[Cr_2(cp)_2(P_5)]$ **(5)**, and $[\{Cr(cp)(CO)_2\}_2]$ **(6)** (*i.e.* in 12, 70, and

Table 5. Comparison of some bonding parameters (Å) in metallocenes and triple-decker sandwich complexes with μ-η^3-P_3, μ-η^5-P_5, and μ-η^6-P_6 ligands

Complex	P–P	M–P_x(centre)	M–cp(centre)	M–M	P–M	Ref.
$[Cr_2(cp)_2(P_5)]$	2.206(3)—2.238(3)	1.37	1.83	2.738(1)	2.318(2)—2.366(2)	This work
$[Cr_2(\eta$-$C_5Me_5)_2(P_5)]$	2.15(2)—2.21(2)	1.36[9]	1.86[9]	2.727(5)	2.29(1)—2.32(1)	8
$[Fe(\eta$-$C_5Me_4Et)(P_5)]$	2.088(3)—2.108(3)	1.526	1.707		2.344(2)—2.350(2)	*a*
$[Ru(\eta$-$C_5Me_4Et)(P_5)]$	2.082(3)—2.118(4)	1.652	1.850		2.430(2)—2.442(2)	*a*
$[Mo_2(\eta$-$C_5Me_5)_2(P_6)]$	2.167(3)—2.175(3)	1.32	2.00	2.647(1)	2.541(2)—2.542(2)	9
$[W_2(\eta$-$C_5Me_5)_2(P_6)]$	2.168(4)—2.177(4)	1.32	1.99	2.639(1)	2.541(2)—2.543(2)	9
$[V_2(\eta$-$C_5Me_4Et)_2(P_6)]$	2.085(4)—2.163(4)	1.31	1.94	2.627(1)	2.474(3)—2.542(3)	9
$[LM(\eta^3$-$P_3)ML]^{n+}$ [b]	2.14—2.18					1, 3

[a] O. J. Scherer, T. Bruck, and G. Wolmershäuser, *Chem. Ber.*, 1988, **121**, 935. [b] M = Co, Ni, or Pd; L = $MeC(CH_2PPh_2)_3$.

18% yields, respectively). The product solution was concentrated to *ca.* 1 cm^3 and loaded on to an alumina column (1.5 × 10 cm) prepared in n-hexane. Elution gave three fractions: (*i*) a pale yellow solution in n-hexane (15 cm^3) which gave yellowish brown flakes of complex (**3**) (4 mg, 0.015 mmol, 7.5% yield); (*ii*) a golden yellow solution in n-hexane–toluene (9:1 to 5:1, 30 cm^3), which on concentration to *ca.* 0.5 cm^3 and cooling to −28 °C gave (**5**) as a fine black crystalline solid (20 mg, 0.051 mmol, 51.4% yield), with an additional 6 mg (0.015 mmol, 15% yield) in the mother-liquor; and (*iii*) a green solution in n-hexane–toluene (1:1, 40 cm^3), from which was obtained $[\{Cr(cp)(CO)_2\}_2]$ (**6**) (*ca.* 6 mg, 0.017 mmol, 17% yield).

$[Cr(cp)(CO)_2(P_3)]$ (**3**). A yellow solution of complex (**3**) (10 mg, 0.038 mmol) in $C_6D_5CD_3$ (1 cm^3) in a serum-capped 5-mm n.m.r. tube, vented into a nitrogen line *via* a syringe needle, was maintained at 90 °C and its ^1H n.m.r. spectrum [δ(cp) 3.99] monitored at intervals. No reaction was observed up to 3.5 h. The temperature was then raised to 110 °C. A slow conversion into $[Cr_2(cp)_2(P_5)]$ (**5**) (δ 18.8) was observed (10% after 4.5 h and 15% after 15.5 h).

$[\{Cr(cp)(CO)_2\}_5(P_{10})]$ (**4**). A brown saturated solution of complex (**4**) (*ca.* 10 mg, 0.0085 mmol) in $C_6D_5CD_3$ (0.5 cm^3) in a 5-mm n.m.r. tube was maintained at 110 °C as above and its ^1H n.m.r. spectrum recorded at intervals. After 40 min, there was an approximate 60% conversion into a 1:1 molar mixture of $[Cr_2(cp)_2(P_5)]$ (**5**) (δ 18.8) and an unidentified cp-containing species (δ 4.09). At 2—4 h weak resonances of complexes (**3**) (δ 3.99) and (**6**) (δ 4.23) were present. Total decomposition of (**4**), as indicated by the complete disappearance of its cp resonances (δ 5.06, 4.90, and 4.50 of relative intensity 1:1:3),[7] took *ca.* 8 h. This final product solution was estimated to contain 25% yield of complex (**5**), the bulk of which was precipitated as fine black solids on the walls and bottom of the tube.

Cothermolysis Reactions with P_4.—$[Cr_2(cp)_2(CO)_4(P_2)]$ (**2**). A suspension of P_4 (24 mg, 0.194 mmol) in a magenta solution of complex (**2**) (40 mg, 0.098 mmol) in toluene (20 cm^3) was initially stirred at 70 °C for 21 h without any sign of reaction. It was then refluxed for 2.5 h. The resultant yellowish brown solution possessed an ^1H n.m.r. spectrum indicating a 1:5:8 molar mixture of complexes (**2**), (**3**), and (**5**). Chromatography of the concentrated solution (*ca.* 1 cm^3) on an alumina column (1 × 10 cm) gave three fractions: (*i*) a yellow solution in n-hexane (*ca.* 10 cm^3) from which was isolated $[Cr(cp)(CO)_2(P_3)]$ (**3**) (18 mg, 0.068 mmol, 35% yield); (*ii*) a golden yellow solution in n-hexane–toluene (1:1, *ca.* 25 cm^3) which gave fine black crystals of $[Cr_2(cp)_2(P_5)]$ (**5**) (23 mg, 0.059 mmol, 60% yield); and (*iii*) a pale magenta solution of unreacted (**2**) (2 mg, 0.005 mmol, 5%).

$[Cr(cp)(CO)_2(P_3)]$ (**3**). A suspension of P_4 (23.6 mg, 0.19 mmol) in a yellow solution of complex (**3**) (50 mg, 0.19 mmol) in toluene (3 cm^3) was stirred at *ca.* 90 °C for 3.5 h. The ^1H n.m.r. spectrum indicated no change, though there was slight precipitation of a fine brown solid. The reaction was continued for a further 6 h at 110 °C. However, both the colour and ^1H n.m.r. spectrum remained unchanged with no sign of $[Cr_2(cp)_2(P_5)]$ (**5**), despite more precipitation of the brown-black unidentified solid.

$[\{Cr(cp)(CO)_2\}_5(P_{10})]$ (**4**). A suspension of P_4 (*ca.* 10 mg, 0.081 mmol) and complex (**4**) (*ca.* 15 mg, 0.013 mmol) in $C_6D_5CD_3$ (0.5 cm^3) in a 5-mm n.m.r. tube was agitated in an ultrasonic bath to achieve a homogeneous reddish-brown solution, which was then maintained at 80 °C for 3.5 h. Proton n.m.r. spectral scans recorded at intervals indicated no reaction. The temperature was therefore raised to 110 °C. After 1 h, a 20% conversion into $[Cr_2(cp)_2(P_5)]$ (**5**) (δ 18.85) was observed. At the end of 8 h, (**4**) had completely reacted and the cp integrals in the ^1H n.m.r. spectrum of the yellowish brown product solution indicated a 30% yield of $[Cr(cp)(CO)_2(P_3)]$ (**3**) (δ 3.98) and $[Cr_2(cp)_2(P_5)]$ (**5**), 15% yield in solution with the bulk precipitated as black particles on the tube walls.

E.S.R. Spectra.—A yellowish orange solution of (**5**) was prepared in toluene in a 2-mm serum-capped quartz tube and the spectrum immediately scanned between −70 and 30 °C. No signal was observed. The serum cap was then punctured with a syringe needle to admit a trace amount of air, whereupon the upper layer of the solution turned blue. The solution was shaken; the colour remained clear yellow. On scanning, the e.s.r. spectra showed a signal with highest intensity at around ambient temperature.

Crystal Structure Determination.—Diffraction quality crystals of $[Cr_2(cp)_2(P_5)]$ (**5**) were obtained as brown black triangular and diamond-shaped plates from a saturated solution in benzene in a 5-mm tube after 2 weeks at ambient temperature.

Crystal data. $C_{10}H_{10}Cr_2P_5$, M = 389.05, monoclinic, space group $P2_1/n$, a = 7.921(2), b = 15.04(1), c = 11.704(4) Å, β = 104.08(2)°, U = 1 352.1 (by least-squares refinement of diffractometer setting angles for 25 automatically centred reflections), Z = 4, D_c = 1.911 g cm^{-3}, brown plate-shaped crystals 0.28 × 0.22 × 0.05 mm; μ(Mo-K_α) = 20.67 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å, $F(000)$ = 748.

Data collection and processing. Reflections were measured on an Enraf–Nonius CAD4-F four-circle diffractometer, ω—θ scan mode with ω scan width (°) 1.00 + 0.35tanθ, aperture width (mm) 2.40 + 0.50tanθ. 2 488 Reflections measured ($2 < 2\theta < 50°$) ($+h, +k, \pm l$), 1 941 unique non-zero (merging R = 0.022). Lorentz, polarisation, crystal decay (less than 3%), and absorption (minimum 1.15, maximum 1.60) effects corrected for by the method of numerical integration.[23]

Structure analysis and refinement. The structure was solved by direct methods. Hydrogen atoms were included at calculated sites (C–H 0.97 Å) with individual isotropic thermal parameters. Full-matrix least-squares refinement converged with $R [= \Sigma(|F_o| - |F_c|)/\Sigma|F_o|] = 0.036$, $R' = 0.043$ [weighting scheme of the form $1.01/(\sigma^2 F_o - 0.0006 F_o^2)$], for 1 570 reflections with $I > 2.5\sigma(I)$. Maximum peaks in a final difference map were less than ± 0.5 e Å^{-3}.

Scattering factors and anomalous dispersion terms were taken from ref. 24. All calculations were carried out using SHELX 76,[25] ORTEP,[26] and data-reduction programs implemented on a CYBER computer. Final atomic co-ordinates are listed in Table 3 and bond lengths and angles in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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