X-Ray Analysis of Tricarbonylchromium(0) Complexes of *E*-Bis(2,4,6-tri-t-butylphenyl)diphosphene

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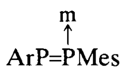
X-Ray analysis of mono- and bis-tricarbonylchromium(0) complexes of *E*-bis(2,4,6-tri-t-butylphenyl)diphosphene shows that the carbonylchromium groups in the complexed arenes play an important role in determining the conformations even in bulky diphosphenes.

We have been successful in the preparation and characterisation of unusual organophosphorus compounds with phosphorus in a low co-ordination state as the *E*-diphosphenes (**1**)[1a] and (**2**).[1b] The reaction of (thf)$Cr(CO)_5$ (thf = tetrahydrofuran) with (**2**) gave the corresponding mesityl-*P*-co-ordinated pentacarbonylchromium(0) complex,[2] whereas the reaction with (**1**) did not proceed because of the very large steric hindrance around the P=P unit due to the four bulky *o*-t-butyl groups. In contrast, when (**1**) was heated with hexacarbonylchromium(0), mono- (**4**) and bis- (**5**) tricarbonylchromium(0) complexes co-ordinated *via* the benzene rings were obtained as stable compounds.[3] We now report the *X*-ray analysis of the chromium(0) complexes (**4**) and (**5**) of (**1**).[4]

ArP=PAr
(**1**)

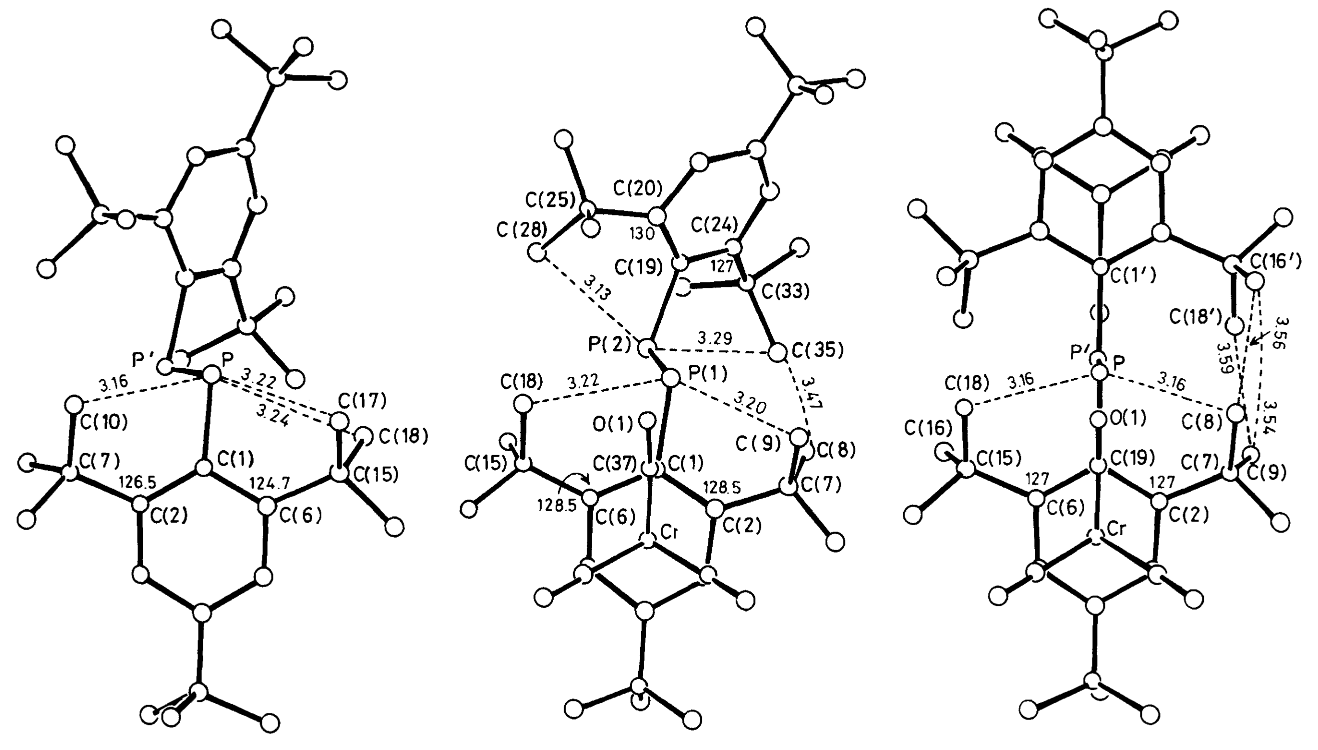

$\mathrm{ArP{=}\overset{\overset{m}{\uparrow}}{P}Mes}$
(**2**) m = lone pair
(**3**) m = $Cr(CO)_5$

$(\mathrm{ArP{=}PAr})[\mathrm{Cr(CO)_3}]_n$
(**4**) *n* = 1
(**5**) *n* = 2

Ar = $2,4,6\text{-}Bu^t_3C_6H_2$, Mes = $2,4,6\text{-}Me_3C_6H_2$

$(C_6H_6)Cr(CO)_3$
(**6**)

Figure 1 shows the *X*-ray structures[5] of (**4**) and (**5**) together with that of the parent diphosphene (**1**) which has already been reported,[1a] and Table 1 gives selected bond distances



(1) (4) (5)

Figure 1. *X*-Ray structures of (**1**) (already reported[1a]), (**4**), and (**5**). *Crystal data* (**4**): $C_{39}H_{58}CrO_3P_2$, monoclinic, space group $P2_1/m$, $a = 31.227(6)$, $b = 12.293(2)$, $c = 10.394(2)$ Å, $\beta = 95.99(3)°$, $U = 3968(1)$ Å^3, $Z = 4$, $D_c = 1.15$ g cm^{-3}. 4142 Reflections with $2\theta \leqslant 40°$ were recorded on a four-circle diffractometer using graphite-monochromated Mo-K_α radiation. Of these only 1468 [with $I > 3\sigma(I)$] were judged as observed. The structure was solved using MULTAN.[6] Full-matrix least squares refinement with anisotropic temperature factors for non-hydrogen atoms converged to $R = 0.059$.[7] *Crystal data* (**5**): $C_{42}H_{58}Cr_2O_6P_2$, monoclinic, space group $P2_1/a$, $a = 18.817(1)$, $b = 11.081(1)$, $c = 10.457(1)$ Å, $\beta = 99.92(1)°$, $U = 2147.8(2)$ Å^3, $Z = 2$, $D_c = 1.28$ g cm^{-3}. 3169 Reflections with $2\theta \leqslant 46°$ were recorded. Of these 2275 [with $I > 3\sigma(I)$] were judged as observed. The structure was solved as for (**4**) ($R = 0.036$). The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

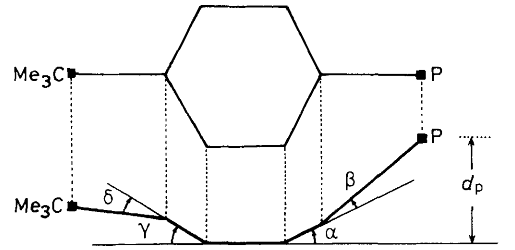


Figure 2. Deformation of the aromatic ring to boat form and definition of angles α, β, γ, and δ (°) and distance d_P (Å) in the deformed Ar ring. Hydrogen atoms and *o*-t-butyl groups are omitted for clarity.

and angles. The complex (**5**) has a crystallographic inversion centre at the centre of the P=P bond and has $2/m$ symmetry.

All the carbonyl groups are situated *gauche* to the t-butyl groups with one of the CO groups eclipsing[8a] the phosphorus atom in the complexed arenes (**4**) and (**5**); there are no significant interactions between chromium and the P=P unit. It should be noted that the P–C and P=P bonds become longer when the $Cr(CO)_3$ group is complexed to the aryl rings while the ∠PPC bond angle remains unchanged between (**1**) and (**5**). It is interesting that the aryl rings are almost perpendicular to the P=P nodal plane in (**5**) (see ∠φ in Table 1) making the two aryl rings parallel ($\theta = 0$), probably because of the large $Cr(CO)_3$ groups. The mean distances from chromium to the carbon atoms of the complexed aromatic ring, $Cr–C_{ring}$, are 2.238 Å [for (**4**), plane II] and 2.243 Å [for (**5**)], both of which are longer than the 2.229 Å observed for (benzene)tricarbonylchromium (**6**).[8b] The perpendicular distances of chromium from the mean plane of the carbon atoms are 1.720(5) Å for (**4**) and 1.738(2) Å for (**5**) [(**6**): 1.726 Å].[8b]

Deformation of the aryl rings to the boat form[9,10] is observed for every Ar–P containing compound regardless of whether they are of the non-bridged type.[10] Figure 2 shows the mean side view of the boat benzene, and defines the deformation parameters:[10] the angles α, β, γ, and δ (°), and the distance of the phosphorus atom from the bottom plane of the boat, d_P (Å). It would be expected that complex formation with chromium would make the aryl increase the planarity of the aromatic π-electron framework and, indeed, the deformation parameters are small for the complexed aryl rings. In complex (**4**) the complexed ring is less deformed than the uncomplexed one (planes I and II). More interestingly, the angle β becomes negative on complex formation resulting in a shortening of d_P. The aryl groups, however, are not completely flat because of the bulky substituents, showing the unusually large steric hindrance of t-butyl groups. From the point of view of intramolecular short contacts between the methyl carbon atoms of the t-butyl groups, (**5**) has six distances shorter than 3.6 Å, whereas (**4**) and (**1**) have one and

Table 1. Some selected bond distances (Å), angles (°), and deformation parameters (Å, °) in (**1**), (**4**), and (**5**).

Compd.		P–C	P–P	∠PPC	∠CPPC	ϕ^{c}	θ^{d}	α^{e}	β^{e}	γ^{e}	δ^{e}	d_{P}^{e}
(**1**)		1.862(2)^{f}	2.034(2)^{f}	102.8(1)^{f}	172.2(1)^{f}	63.9	52.1	10.7	2.2	4.3	−3.9	0.550(4)
(**4**)	I^{a}	1.873(11)		100.6(4)		63.5		14	4	6	−8	0.74(3)
			2.042(5)		169.3(5)		51.5					
	II^{b}	1.905(12)		105.4(4)		70.7		6	−5	3	−1	0.11(3)
(**5**)		1.899(3)	2.045(2)	102.9(1)	180	88.5	0	9.0	−2.3	4.8	1.7	0.336(8)

[a] Non-complexed Ar ring in (**4**). [b] Complexed Ar ring in (**4**). [c] Angle between Ar and the nodal P=P plane. [d] Angle between Ar substituents. [e] See Figure 2. [f] Data taken from ref. 1a.

none, respectively (Figure 1). The results indicate the greater steric congestion caused by the complexed aromatic ring(s) of the diphosphene (**1**) leading to large deformation of the uncomplexed aromatic ring [plane I in (**4**)] or to reduced interplanar angle [θ in (**5**)].

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