The Crystal and Molecular Structure of Iminobis(aminodiphenylphosphorus) Chloride, $(Ph_2P{\cdot}NH_2)_2NCl$

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THE structure of $(Ph_2PNH_2)_2NCl$ has been determined by single crystal *X*-ray diffraction techniques. The compound crystallizes in space group $P\bar{1}$, and is triclinic, $a = 9{\cdot}363 \pm 0{\cdot}018$, $b = 11{\cdot}35 \pm 0{\cdot}02$, $c = 11{\cdot}71 \pm 0{\cdot}02$ Å, $\alpha = 81{\cdot}82 \pm 0{\cdot}16°$, $\beta = 99{\cdot}35 \pm 0{\cdot}19°$, and $\gamma = 101{\cdot}0 \pm 0{\cdot}2°$, $Z = 2$.

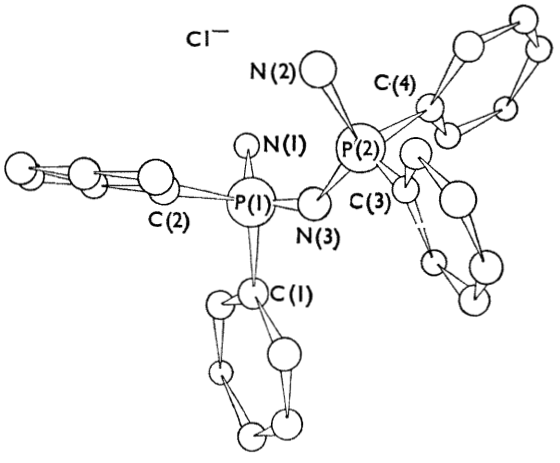
Multiple-film Weissenberg equi-inclination photographs taken with Mo-K_α radiation gave 1710 diffraction maxima. The two phosphorus and chlorine atom positions were located from the three-dimensional Patterson synthesis with coefficients that were sharpened for phosphorus and chlorine. The remaining non-hydrogen atom positions were established from a three-dimensional electron-density map phased on the two phosphorus atoms and the chlorine atom. A full-matrix least-squares refinement in which the four phenyl rings were treated as rigid bodies has yielded an unweighted discrepancy index, *R*, of 14·0% and a weighted value, *R'*, of 11·0%.

The compound is ionic and the P–P–N system of the $(Ph_2PNH_2)_2N^+$ cation is bent, with an angle of 136°. The cation has approximate non-crystallographic two-fold symmetry about the line which bisects the P–N–P angle; each of the phosphorus atoms has distorted tetrahedral co-ordination. The shortest chlorine–non-hydrogen atom distance is 3·28 Å (Figure and Table).

TABLE

Bond	Distances*	Bond	Angles*
P(1)–N(3)	1·58	P(1)–N(3)–P(2)	136
P(2)–N(3)	1·57	N(3)–P(1)–N(1)	122
P(1)–N(1)	1·64	N(3)–P(1)–C(1)	108
P(2)–N(2)	1·66	N(3)–P(1)–C(2)	110
P(1)–C(1)	1·76	C(1)–P(1)–C(2)	107
P(1)–C(2)	1·80	C(1)–P(1)–N(1)	105
P(2)–C(3)	1·79	C(2)–P(1)–N(1)	105
P(2)–C(4)	1·78	N(3)–P(2)–N(2)	121
* $\sigma = 0{\cdot}01$ Å		N(3)–P(2)–C(3)	107
		N(3)–P(2)–C(4)	114
		C(3)–P(2)–C(4)	107
		C(3)–P(2)–N(2)	106
		C(4)–P(2)–N(2)	103
		* $\sigma = 1{\cdot}0°$.	

The P–N bond lengths fall into two ranges. The central P(1)–N(3) and P(2)–N(3) values are 1·58 and 1·57 Å, and the terminal N(1)–P(1) and N(2)–P(2) distances are 1·64 and 1·66 Å. The accepted P–N single σ-bond distance is 1·78 Å,[1] and the calculated P–N bond length which results with maximum p_π–d_π overlap for the formation of one p_π–d_π bond in addition to the normal σ-bond is 1·64 Å.[2] Therefore, values of the P–N central bond lengths in this compound suggest that more than one p_π–d_π bond is formed while the terminal N–P bond distances suggest the presence of one p_π–d_π bond. The C(Ph)–P bond-lengths are those expected for a normal P–C σ-bond.



FIGURE

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