

## [2-(Anilinomethyl)phenyl]diphenylphosphine and {2-[(*N*-methylanilino)methyl]phenyl}diphenylphosphine

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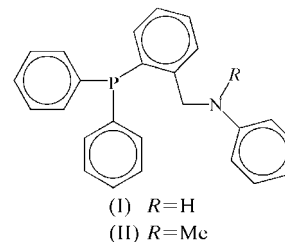
The title compounds,  $\text{Ph}_2\text{PCH}_2\text{N(H)Ph}$  or  $\text{C}_{25}\text{H}_{22}\text{NP}$  and  $\text{Ph}_2\text{PCH}_2\text{N(CH}_3\text{)Ph}$  or  $\text{C}_{26}\text{H}_{24}\text{NP}$ , respectively, are isomorphous, with calculated theoretical Tolman angles of 174 and 182°.

### Comment

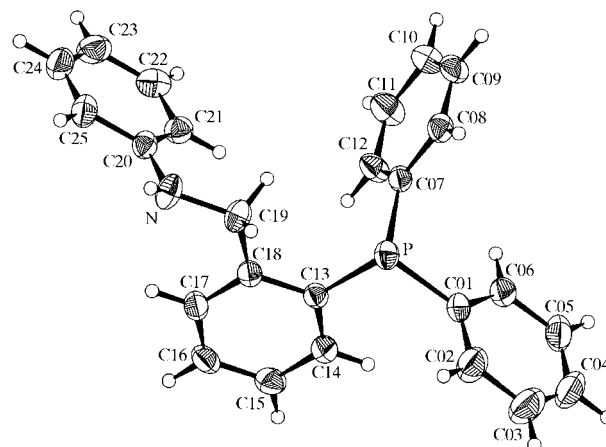
Part of our interest in exploring catalytic reactions has led to the manipulation of multifunctional phosphorus-based ligands for evaluation in well known model systems. Aminophosphines, containing both soft (P) and hard (N) Lewis bases, have the ability to stabilize various oxidation states of metals, generating complexes which exhibit different spectroscopic properties, reactivities and applications. Various examples of palladium(II) aminophosphine complexes showing catalytic behaviour have been reported (Koprowski *et al.*, 2002; Reddy *et al.*, 2002) and have also been shown to have potential radiopharmaceutical applications (Chen *et al.*, 2001). The title phosphines, (I) and (II), are bidentate and possess a P–N motif which has the potential to bind soft metal centres strongly *via* the P atom and weakly *via* the N atom, allowing for the facile displacement of the chelating N-moiety. This situation is frequently desirable in catalysed reactions and can lead to enhanced stability in the catalyst without sacrificing kinetic or selectivity parameters. By manipulating the substituents on the phosphine, it can be tailored for specific needs in various fields of catalysis, as well as for further development for radiopharmaceutical use. We report here the structures of (I) and (II).

Compound (I) (Fig. 1) was synthesized previously by Reddy *et al.* (2002). Compound (II) (Fig. 2) is the methyl derivative of (I). The two compounds are isomorphous, with individual molecules in the centrosymmetric space group  $C2/c$  ( $Z = 8$ ). The bonds and angles in the two compounds are typical compared with other phosphines. An r.m.s. overlay (P coordination sphere, r.m.s. error = 0.0146 Å) of the two compounds

shows remarkable similarities (Fig. 3), differing only at the periphery of the molecules. Further investigation into this is required to check whether different electronic and steric groups can be introduced on the N atom without creating additional effects on packing.

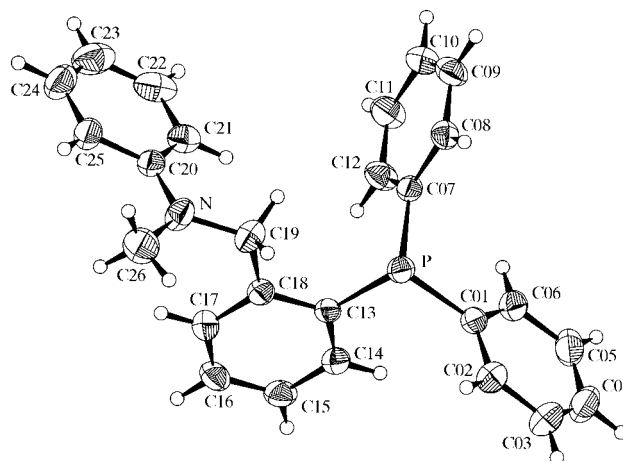


The most widely used method for determining ligand steric behaviour at a metal centre is the calculation of the Tolman cone angle (Tolman, 1977), using an  $M\text{--}P$  bond distance of 2.28 Å, C–H bond distances of 0.97 Å and a van der Waals radius of 1.2 Å for the H atoms. For (I) and (II), dummy atoms were created 2.28 Å from the P atoms and used for the



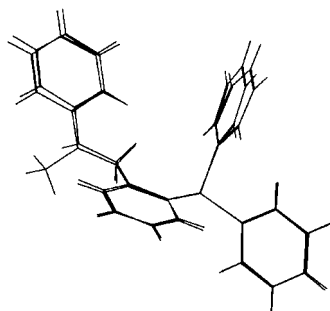
**Figure 1**

A view of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.



**Figure 2**

A view of the structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.



**Figure 3**  
An r.m.s. overlay of (I) and (II).

determination of the theoretical Tolman angles, yielding a value of  $174^\circ$  for (I) and  $182^\circ$  for (II). The determined value for (II) is slightly larger due to the contribution from the methyl group on the N atom. However, this may not be an exact indication of the cone angle when bonded to a metal centre, since some degree of freedom for rotation exists on atom C19 and the N atom. The Tolman cone angle is important mainly for monodentate or monocoordinated ligands, while in bidentate ligands or ligands bound to a metal in a bidentate mode the bite angle becomes more important. In the present instance, the Tolman cone angles calculated for (I) and (II) will be an important parameter in assessing differences (e.g. in reaction rates or selectivities) observed in catalysed reactions, which can be related to a monodentate mode of binding.

No hydrogen-bonding interaction is observed for the N—H group in (I), which is not uncommon (Cambridge Structural Database, Version 5.25 of January 2004; Allen, 2002).

## Experimental

Compound (I) was prepared by reduction of the imino precursor under the action of 2.5 equivalents of  $\text{LiAlH}_4$  in ether as solvent. The formation of the product at room temperature was followed *via* thin-layer chromatography analysis and took about 8–12 h. The reaction was quenched by the addition of ice to the reaction mixture. Ether was removed *in vacuo*, followed by extraction with dichloromethane and water, and the product was isolated by flash silica chromatography in a yield of 80%. Compound (II) was synthesized by treatment of (I) in dry tetrahydrofuran with 1.1 mole equivalents of *n*-butyllithium at 195 K, followed by the addition of 1.1 equivalents of methyl iodide. After 2 h, the reaction was quenched using water and the tetrahydrofuran was removed *in vacuo*. Dichloromethane and water were used to extract the product, which was purified *via* flash silica chromatography and obtained in a yield of 65%. For both compounds, crystals were obtained from solutions in hexane.

### Compound (I)

#### Crystal data

$\text{C}_{25}\text{H}_{22}\text{NP}$   
 $M_r = 367.41$   
Monoclinic,  $C2/c$   
 $a = 22.174$  (4) Å  
 $b = 7.9968$  (16) Å  
 $c = 22.519$  (5) Å  
 $\beta = 94.50$  (3) $^\circ$   
 $V = 3980.7$  (14) Å $^3$   
 $Z = 8$

$D_x = 1.226$  Mg m $^{-3}$   
Mo  $K\alpha$  radiation  
Cell parameters from 789 reflections  
 $\theta = 2.7$ – $21.5^\circ$   
 $\mu = 0.15$  mm $^{-1}$   
 $T = 293$  (2) K  
Plates, colourless  
 $0.38 \times 0.24 \times 0.04$  mm

#### Data collection

Bruker SMART 1K CCD area-detector diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan (SADABS; Bruker, 1998)  
 $T_{\min} = 0.95$ ,  $T_{\max} = 0.97$   
16 110 measured reflections

4943 independent reflections  
2201 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.075$   
 $\theta_{\max} = 28.4^\circ$   
 $h = -29 \rightarrow 29$   
 $k = -10 \rightarrow 10$   
 $l = -30 \rightarrow 24$

#### Refinement

Refinement on  $F^2$   
 $R(F) = 0.046$   
 $wR(F^2) = 0.103$   
 $S = 0.86$   
4943 reflections  
248 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0411P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.15$  e Å $^{-3}$   
 $\Delta\rho_{\min} = -0.19$  e Å $^{-3}$

**Table 1**

Selected geometric parameters (Å,  $^\circ$ ) for (I).

P—C01	1.829 (2)	N—C20	1.383 (2)
P—C07	1.830 (2)	N—C19	1.450 (2)
P—C13	1.8378 (19)		
C01—P—C07	101.66 (9)	C07—P—C13	102.09 (8)
C01—P—C13	102.61 (9)	C20—N—C19	121.23 (18)
C20—N—C19—C18	−83.4 (2)		

### Compound (II)

#### Crystal data

$\text{C}_{26}\text{H}_{24}\text{NP}$   
 $M_r = 381.43$   
Monoclinic,  $C2/c$   
 $a = 23.518$  (5) Å  
 $b = 8.2811$  (17) Å  
 $c = 21.892$  (4) Å  
 $\beta = 93.04$  (3) $^\circ$   
 $V = 4257.6$  (15) Å $^3$   
 $Z = 8$

$D_x = 1.19$  Mg m $^{-3}$   
Mo  $K\alpha$  radiation  
Cell parameters from 920 reflections  
 $\theta = 2.7$ – $21.3^\circ$   
 $\mu = 0.14$  mm $^{-1}$   
 $T = 293$  (2) K  
Cuboid, colourless  
 $0.34 \times 0.24 \times 0.12$  mm

#### Data collection

Bruker SMART 1K CCD area-detector diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan (SADABS; Bruker, 1998)  
 $T_{\min} = 0.94$ ,  $T_{\max} = 0.97$   
14 295 measured reflections  
5216 independent reflections

2474 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.051$   
 $\theta_{\max} = 28.3^\circ$   
 $h = -28 \rightarrow 31$   
 $k = -10 \rightarrow 10$   
 $l = -29 \rightarrow 26$

#### Refinement

Refinement on  $F^2$   
 $R(F) = 0.046$   
 $wR(F^2) = 0.114$   
 $S = 0.91$   
5216 reflections  
253 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0494P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.18$  e Å $^{-3}$   
 $\Delta\rho_{\min} = -0.16$  e Å $^{-3}$

The aromatic, methylene and methyl H atoms were placed in geometrically idealized positions (C—H = 0.97–0.98 Å) and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . In (I), the position of the amine H atom was determined from a difference Fourier map.

**Table 2**

Selected geometric parameters (Å, °) for (II).

P—C01	1.825 (2)	N—C20	1.375 (2)
P—C07	1.832 (2)	N—C26	1.437 (3)
P—C13	1.8400 (18)	N—C19	1.443 (2)
<hr/>			
C20—N—C19—C18	−86.9 (2)		

For both compounds, data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 1999); program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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2053397, 2053399 and 2053664. Opinions, findings, conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the NRF.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1003). Services for accessing these data are described at the back of the journal.

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