Multiple intramolecular hydrogen bonds in 2,4-di-*tert*-butyl-6-[*N*-(2,6-diisopropylphenyl)-*P*,*P*-diphenyl-phosphorimidoyl]phenol

Jong-Dae Lee,[a] Il-Hwan Suh[b] and Sang Ook Kang[c]

[a]Department of Chemistry, College of Natural Sciences, Chosun University, Gwangju 501-759, Republic of Korea, [b]ReSEAT Program, Korea Institute of Science and Technology Information, 335 Eoeun-dong, Yuseong-gu, Daejeon 305-806, Republic of Korea, and [c]Department of Advanced Materials Chemistry, Korea University, Sejong Campus, Chungnam 339-700, Republic of Korea

Correspondence e-mail: sangok@korea.ac.kr

The title compound, $C_{38}H_{48}NOP$, isolated from the reaction of (2-diphenylphosphanyl-4,6-di-*tert*-butyl)phenol with 2,6-diisopropylphenyl azide at 273 K, can act as an *N,O*-bidentate ligand. Crystal structure analysis shows a deviation from ideal tetrahedral symmetry around the P atom. The molecule exists as a monomer in the solid state, whose conformation is stabilized *via* multiple intramolecular hydrogen bonds. Geometric parameters from both experimental and theoretical calculations are compared.

Comment

The search for nonmetallocene transition metal complexes to catalyse olefin polymerization has resulted in a wide range of new catalysts based on new or known ancillary ligands (Hlatky, 2000; Gibson & Spitzmesser, 2003). In recent years, there has been considerable and growing interest in the coordination chemistry of sterically hindered phosphinimine and phosphiniminate complexes (Masuda *et al.*, 2003; Cristau *et al.*, 2002; Said *et al.*, 2001). Among these, titanium complexes bearing phosphinimide ligands have been shown by Stephan *et al.* (2003) to be highly active ethylene polymerization catalysts. At the same time, Fujita and co-workers (Mitani *et al.*, 2002, 2003) developed a series of group IV metal complexes containing bis(phenoxyimine) ligands, and these complexes have proved to be excellent precatalysts for olefin polymerization. Subsequently, Zhang and co-workers (Qi *et al.*, 2005; Qi & Zhang, 2006) reported that group IV metal complexes with phenoxy–phosphinimine ligands reacted similarly. Intrigued by the possibility that increasing the bulk of the N-containing substituents could improve catalytic activity, we investigated the use of the title compound, (I), containing the bulky 2,6-diisopropylphenyl group on atom N1

and *tert*-butyl groups on the phenol unit. As part of our efforts in the development and structural studies of these molecules, we report the synthesis and X-ray crystal structure of (I), supported by density functional theory (DFT) calculations.

(I)
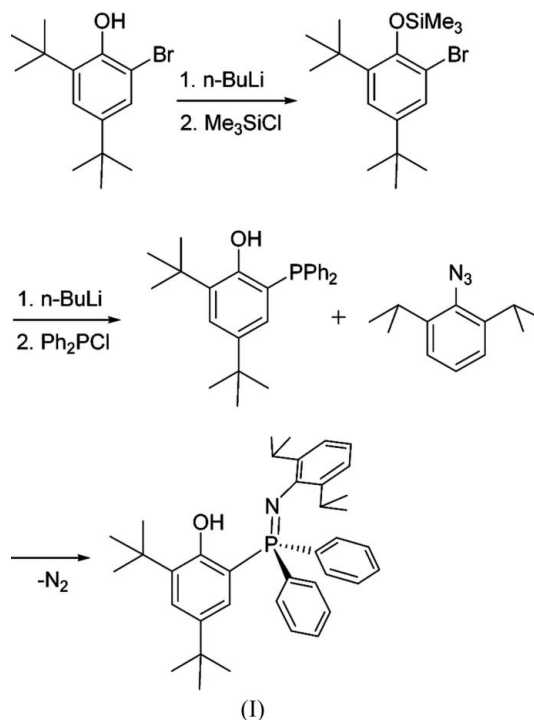
As shown in Fig. 1 and Table 1, compound (I) has five intramolecular hydrogen bonds. The strong O1—H1···N1 hydrogen-bond O···N distance of 2.601 (2) Å is in good
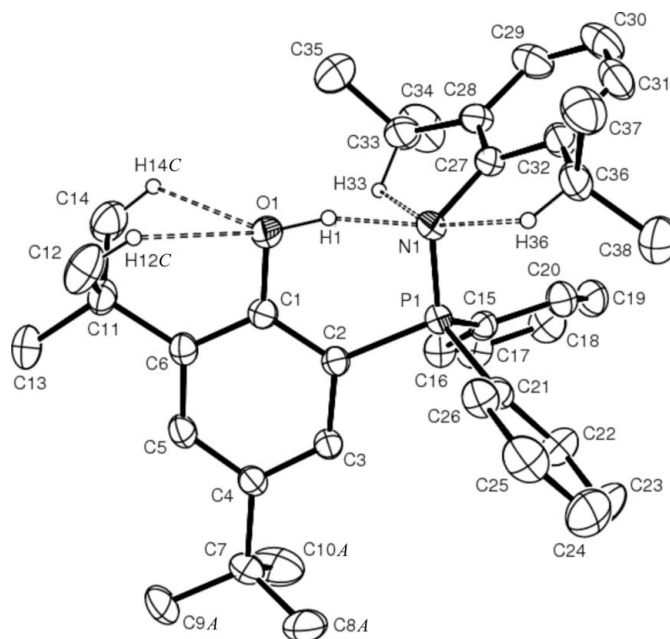

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level, and H atoms (except for H1, H12*C*, H14*C*, H33 and H36) and the minor component of the disordered *tert*-butyl group have been omitted for clarity. Dashed lines indicate intramolecular hydrogen bonds.

agreement with the values of 2.580 (6) and 2.619 (6) Å reported for (1Z,3Z)-1,4-di(pyridin-2-yl)buta-1,3-diene-2,3-diol (Ośmiałowski *et al.*, 2002), and 2.600 (2) and 2.540 (2) Å in bis[2-(2-hydroxy-3-methoxybenzylideneamino)phenolato-κO]dimethylsilane (Böhme & Fels, 2010). The six-membered N1/P1/C2/C1/O1/H1 ring, containing the phosphinimine unit and the O1—H1···N1 hydrogen bond, is planar to within 0.042 (1) Å and nearly coplanar with the phenoxy ring, with a dihedral angle of 2.9 (3)°. The remainder of the hydrogen bonds are weak and occur between the heteroatoms (O1 and N1) and the alkyl substituents [C—H of –C(CH$_3$)$_3$ and –CH(CH$_3$)$_2$] of the aromatic rings, with C···O distances varying from 2.912 (3) to 3.021 (3) Å. These hydrogen bonds appear to play an important role in controlling the molecular conformation of (I). Presumably, the additional steric requirement of the bulky 2,6-diisopropylphenyl substituent prevents the formation of intermolecular hydrogen bonds. In fact, the closest intermolecular contact [O1···H10A^i = 2.88 Å; symmetry code: (i) $x + 1$, y, z] suggests that the molecular packing of (I) is governed only by van der Waals forces. There are also no significant intermolecular π–π interactions in the structure as the shortest centroid–centroid distance between any parallel phenyl rings is greater than 5 Å. Examination of the structure with *PLATON* (Spek, 2009) showed that there are solvent-accessible voids in the crystal structure.

The P1=N1 bond distance in (I) [1.5826 (18) Å] is similar to the value of 1.592 (2) Å in 2-methoxy-3-methyl-6-[(triphenylphosphoranylidene)amino]pyrimidin-4(3H)-one and 1.588 (2) Å in 3-methyl-2-methylthio-6-[(triphenylphosphoranylidene)amino]pyrimidin-4(3H)-one (Low *et al.*, 1998). Recently, however, Hayes and co-workers reported a 4,6-bis[N-(2,4,6-trimethylphenyl)-P,P-diphenylphosphorimidoyl]-dibenzofuran system, and this compound displayed a significant difference in the P=N bond distances [1.549 (1) and 1.565 (1) Å; Ireland *et al.*, 2010]. In comparison with the structure of (I), the P=N bonds of the dibenzofuran system are shortened as a result of the presence of sterically less hindered methyl groups instead of isopropyl groups on the phenyl ring attached to the phosphinimine N atom. As shown in Table 2 and Fig. 1, the range of angles around the P1 atom [104.92 (9)–115.89 (10)°] in (I) indicates a distorted tetrahedral geometry. These values are similar to the range of 105.50 (9)–118.22 (13)° observed in the pyrimidinone compounds (Low *et al.*, 1998). The dibenzofuran compound also shows comparable bond angles [100.54 (7)–116.31 (7)°; Ireland *et al.*, 2010] around the P center even in the absence of strain.

All four aromatic rings of (I) are planar, with a maximum deviation of 0.027 (2) Å for atom C27 from the least-squares plane defined by atoms C27–C32. The phenoxy ring is almost perpendicular to the C21–C26 phenyl ring attached to atom P1, with a dihedral angle of 89.48 (7)°, and the dihedral angle between the C15–C20 phenyl ring attached to atom P1 and the C27–C32 phenyl ring attached to atom N1 is 42.21 (10)°.

A molecular orbital calculation was performed using the *GAUSSIAN03* package (Frisch *et al.*, 2004). The geometries obtained from the X-ray analysis were used in the input file for the calculation of total energy. The calculations were carried out using the B3LYP/6-31+G(d) level of theory. As shown in Table 2, the atomic bond lengths including P calculated by DFT are slightly longer than those from the X-ray data, and it may safely be said that all the rest are similar. However, improved agreement might be obtained if still higher level basis sets were used, at the expense of additional computational time.

Experimental

For the preparation of (I), a solution of 2,6-diisopropylphenyl azide (0.61 g, 3 mmol) in tetrahydrofuran (THF, 10 ml) was added dropwise to a solution of 4,6-di-*tert*-butyl-2-(diphenylphosphanyl)-phenol (1.17 g, 3 mmol) in THF (10 ml) at 273 K and the resulting mixture stirred for 12 h at room temperature. The solvent was evaporated and a crude product obtained. Pure pale-yellow crystals of (I) were obtained after recrystallization from toluene at 263 K and these were dried *in vacuo* (yield 87%; m.p. 356–358 K). Analysis found: C 80.69, H 8.54, N 2.51%; calculated for C$_{38}$H$_{48}$NOP: C 80.67, H 8.55, N 2.48%.

Crystal data

C$_{38}$H$_{48}$NOP	$\gamma = 89.380$ (3)°
$M_r = 565.74$	$V = 1683.0$ (5) Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 9.4499$ (15) Å	Mo $K\alpha$ radiation
$b = 11.9323$ (19) Å	$\mu = 0.11$ mm^{-1}
$c = 15.247$ (3) Å	$T = 293$ K
$\alpha = 88.658$ (3)°	$0.40 \times 0.10 \times 0.10$ mm
$\beta = 76.925$ (3)°	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	22883 measured reflections
	8349 independent reflections
Absorption correction: integration (*SADABS*; Sheldrick, 2008)	4194 reflections with $I > 2\sigma(I)$
$T_{min} = 0.957$, $T_{max} = 0.989$	$R_{int} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.157$	
$S = 1.02$	
8349 reflections	$\Delta\rho_{max} = 0.24$ e Å^{-3}
420 parameters	$\Delta\rho_{min} = -0.38$ e Å^{-3}

One of the *tert*-butyl groups is disordered over two orientations. Two positions were defined for the methyl groups at atoms C8, C9, and C10 and the site-occupation factors of the two orientations were constrained to sum to unity. The major orientation (atom labels with the suffix 'A') has an occupation of 0.619 (12). All C—C bonds involving the disordered C atoms were restrained to a similar length within a tolerance s.u. value of 0.005 Å.

Aromatic H atoms were included in the model in idealized sp^2 geometries, with C—H = 0.93 Å and with U_{iso}(H) = 1.2U_{eq}(C). Methyl H atoms were included in the model in sp^3 geometries found from difference Fourier syntheses, with C—H = 0.96 Å and with U_{iso}(H) = 1.5U_{eq}(C). The remaining H atoms (H1, H33 and H36) were found in an electron-density difference map and were allowed to refine both positionally and isotropically. The final difference map

Table 1
Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O1—H1⋯N1	0.99 (3)	1.63 (3)	2.601 (2)	163 (2)
C12—H12C⋯O1	0.96	2.38	3.021 (3)	124
C14—H14C⋯O1	0.96	2.31	2.948 (3)	123
C33—H33⋯N1	1.03 (2)	2.52 (2)	2.912 (3)	101.6 (15)
C36—H36⋯N1	0.96 (2)	2.48 (2)	2.935 (3)	109.0 (15)

Table 2
Comparison of selected geometric parameters (Å, °) with those derived from DFT calculations.

	X-ray	DFT
P1—N1	1.5826 (18)	1.60
P1—C2	1.784 (2)	1.82
P1—C15	1.803 (2)	1.84
P1—C21	1.811 (2)	1.85
O1—C1	1.355 (2)	1.35
N1—C27	1.429 (3)	1.42
N1—P1—C2	107.42 (9)	106.63
N1—P1—C15	113.93 (10)	114.56
N1—P1—C21	115.89 (10)	116.85
C2—P1—C15	108.95 (10)	109.69
C2—P1—C21	104.92 (9)	103.77
C15—P1—C21	105.24 (10)	104.73
P1—N1—C27	123.48 (14)	129.13
C2—P1—N1—C27	−152.14 (17)	159.01
C15—P1—N1—C27	−31.4 (2)	37.47
C21—P1—N1—C27	90.98 (19)	85.54
N1—P1—C2—C1	7.6 (2)	7.62
O1—C1—C2—P1	−5.9 (3)	2.11

was essentially free of any chemically significant features, with the highest electron-density 0.70 Å from atom N1 and the deepest hole 0.83 Å from atom P1.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

References

Böhme, U. & Fels, S. (2010). *Acta Cryst.* C**66**, o202–o205.
Bruker (1999). *SMART* (Version 5.0) and *SAINT-Plus* (Version 6.0). Bruker AXS Inc., Madison, Wisconsin, USA.
Cristau, H. J., Taillefer, M. & Rahier, N. (2002). *J. Organomet. Chem.* **646**, 94–106.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Frisch, M. J., *et al.* (2004). *GAUSSIAN03*. Revision D.01. Gaussian Inc., Wallingford, Connecticut, USA.
Gibson, V. C. & Spitzmesser, S. K. (2003). *Chem. Rev.* **103**, 283–316.
Hlatky, G. G. (2000). *Coord. Chem. Rev.* **199**, 235–329.
Ireland, B. J., Wheaton, C. A. & Hayes, P. G. (2010). *Organometallics*, **29**, 1079–1084.
Low, J. N., Ferguson, G., Cobo, J., Nogueras, M., Sanchez, A. & Marchal, A. (1998). *Acta Cryst.* C**54**, 1355–1357.
Masuda, J. D., Wei, P. & Stephan, D. W. (2003). *J. Chem. Soc. Dalton Trans.* pp. 3500–3505.
Mitani, M., Furuyama, R., Mohri, J., Saito, J., Ishii, S., Terao, H., Kashiwa, N. & Fujita, T. (2002). *J. Am. Chem. Soc.* **124**, 7888–7889.
Mitani, M., Furuyama, R., Mohri, J., Saito, J., Ishii, S., Terao, H., Nakano, T., Tanaka, H. & Fujita, T. (2003). *J. Am. Chem. Soc.* **125**, 4293–4305.
Ośmiałowski, B., Kolehmainen, E., Nissinen, M., Krygowski, T. M. & Gawinecki, R. (2002). *J. Org. Chem.* **67**, 3339–3345.
Qi, C.-H. & Zhang, S.-B. (2006). *J. Organomet. Chem.* **691**, 1154–1158.
Qi, C.-H., Zhang, S.-B. & Sun, J.-H. (2005). *J. Organomet. Chem.* **690**, 3946–3950.
Said, M., Thornton-Pett, M. & Bochmann, M. (2001). *J. Chem. Soc. Dalton Trans.* pp. 2844–2849.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Stephan, D. W., Stewart, J. C., Guérin, F., Courtenay, S., Kickham, J., Hollink, E., Beddie, C., Hoskin, A., Graham, T., Wei, P., Spence, R. E. v. H., Xu, W., Koch, L., Gao, X. & Harrison, D. G. (2003). *Organometallics*, **22**, 1937–1947.