Nonvolatile Me₃P-like *P*-Donor Ligand: Synthesis and Properties of 4-Phenyl-1-phospha-4-silabicyclo[2.2.2]octane

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ABSTRACT



A new trialkylphosphine ligand with Me₃P-like steric and electronic properties, 4-phenyl-1-phospha-4-silabicyclo[2.2.2]octane (Ph-SMAP), was synthesized. Given a phenyl group at the silicon atom, the Ph-SMAP ligand displayed nonvolatility with retention of Me₃P-like properties. The new ligand was air-stable, crystalline, and easy to handle.

Trialkylphosphines have found wide application in coordination chemistry and organometallic chemistry as metalcoordinating ligands with strong σ -donating ability. One ligand with an extremely low steric demand is trimethylphosphine (Me₃P), which is especially important in the metal-mediated C–H bond activation of hydrocarbons.¹ We have designed a new Me₃P-like trialkylphosphine ligand 1 (SMAP, named after silicon-constrained monodentate alkylphosphine) (Figure 1). A new feature of this ligand is the presence of a site for functionalization at the backside of the *P*-lone pair, which is not the case for Me₃P. The SMAP ligand 1 contains phosphorus and silicon atoms at each bridgehead of the bicyclo[2.2.2]octane framework. The molecular constraint of the bicyclic framework makes the steric demand around the phosphorus center as small as that of Me₃P and projects the *P*-lone pair and the Si-substituent (R) in diametrically opposite directions on the straight line defined by the two bridgehead atoms (see Figure 1). P-Donor ligands that can be functionalized with such a directional

constraint are rarely found and are limited to phosphaalkynes (2),² phosphabenzenes (3),³ bicyclic phosphites (4),⁴ and phosphatriptycenes (5).⁵ To the best of our knowledge, no analogous trialkylphosphine ligand exists.⁶ We expected that the rigidity of this framework would promote molecular



Figure 1. Structures of SMAP and related P-donor ligands.

^{(1) (}a) Jones, W. D. In *Topics in Organometallic Chemistry 3: Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer: Berlin, 1999; pp 9–46. (b) Kakiuchi, F.; Murai, S. In *Topics in Organometallic Chemistry 3: Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer: Berlin, 1999; pp 47–79.

assembly into a crystal phase, yielding an odorless, crystalline SMAP stable against air oxidation. We report the synthesis and characterization of the first example of SMAP (**1a**, Ph-SMAP), which contains a phenyl group on the Si atom that provides a property of nonvolatility.

The synthesis of Ph-SMAP (1a) is illustrated in Scheme 1. Phenyltrivinylsilane (6) was converted into triol 7 in 68%



^{*a*} Reagents and conditions: (a) (i) (Ipc)₂BH, THF, -25 °C → rt; (ii) H₂O₂, NaOH. (b) (i) MsCl, Et₃N, THF, 0 °C; (ii) NaI, acetone, 0 °C → reflux. (c) BH₃·SMe₂/PhPH₂/BuLi (1:1:2), THF, -78 °C → rt. (d) 1-Octene, DME, reflux. (e) (i) Lithium naphthalenide, toluene, 40 °C; (ii) S₈, toluene, 80 °C. (f) (i) MeOTf, CH₂Cl₂, rt; (ii) P(NMe₂)₃, CH₂Cl₂, rt. (g) (i) Lithium naphthalenide, toluene, 40 °C; (ii) BH₃·SMe₂, 0 °C.

yield through 3-fold hydroboration with diisopinocampheylborane followed by $H_2O_2/NaOH$ oxidation.⁷ The hydroboration proceeded with complete regioselectivity to give the primary alcohol against the electronic requirement of the silicon atom to induce the opposite selectivity. Mesylation of **7** and subsequent substitution with iodide anion afforded tris(2-iodoethyl)phenylsilane (**8**) in 82% yield. Then, [5 + 1] annulation between the triiodide (**8**) and dilithium salt⁸ of PhPH₂-BH₃ produced the borane complex of monocyclic tertiary phosphine (**9**) carrying a 2-iodoethyl substituent at the Si atom (47%). NMR analysis indicated that the product

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 (b) Nixon, J. F. *Chem. Soc. Rev.* 1995, 24, 319–328.
 (3) Le Floch, P.; Mathey, F. *Coord. Chem. Rev.* 1998, 178–180, 771–
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- (4) Wadsworth, W. S., Jr.; Emmons, W. D. J. Am. Chem. Soc. 1962, 84, 610–617.
- (5) (a) Jongsma, C.; De Kleijn, J. P.; Bickelhaupt, F. *Tetrahedron* **1974**, *30*, 3465–3469. (b) Rot, N.; De Wijs, W.-J. A.; De Kanter, F. J. J.; Dam, M. A.; Bickelhaupt, F.; Lutz, M.; Spek, A. L. *Main Group Met. Chem.*
- **1999**, 22, 519–526. (6) For a diphosphine with a related structure, 1,4-diphosphabicvclo-

contained both trans- and cis-isomers (major:minor = ca. 60:40). Upon heating with excess 1-octene in refluxing DME, the isomeric mixture of **9** was transformed into phosphonium salt **10** in 88% yield.^{9,10} Subsequent reductive cleavage of the P–Ph bond of **10** with lithium naphthalenide followed by reaction with sulfur afforded phosphine sulfide **11** in 40% yield. Alternatively, addition of BH₃·SMe₂ instead of S₈ gave borane complex **12** in 46% yield. Finally, desulfuration of **11** through S-methylation followed by treatment with HMPT¹¹ afforded white crystalline solid Ph-SMAP (**1a**) in 68% yield: mp 90.5–90.7 °C (in a sealed tube); sublimes at 40 °C/0.04 mmHg; ³¹P NMR (C₆D₆, 85% H₃PO₄) δ –59.2 (+3.0 relative to Me₃P/C₆D₆).¹²

Solid Ph-SMAP is highly air-stable, with no detectable oxidation observed after exposure to air for several days.¹³ Moreover, being almost odorless, Ph-SMAP does not produce the noxious phosphine odor characteristic of volatile phosphines.

Single-crystal X-ray diffraction analysis revealed a rodlike shape of Ph-SMAP (1a) and Ph-SMAP $-BH_3$ (12) (Figure 2).^{14,15} Analyses also showed that the bicyclic cage



Figure 2. ORTEP drawings of the molecular structures of Ph-SMAP (1a, left) and Ph-SMAP-BH₃ (12, right).

possesses some flexibility and twists toward chiral C_3 -symmetric conformations. In free phosphine **1a**, the values for the average C-P-C and P-C-C-Si dihedral angles and the P-Si distance are 100.9°, 15.5°, and 3.105 Å,

^[2.2.2]octane, see: Hinton, R. C.; Mann, F. G. J. Chem. Soc. **1959**, 2835–2843.

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⁽⁸⁾ Bourumeau, K.; Gaumont, A.-C.; Denis, J.-M. J. Organomet. Chem. 1997, 529, 205–213.

⁽⁹⁾ Uziel, J.; Riege, N.; Aka, B.; Figuière, P.; Jugé, S. *Tetrahedron Lett.* **1997**, *38*, 3405–3408.

⁽¹⁰⁾ High yield indicates that both isomers were converted into the phosphonium salt 10.

⁽¹¹⁾ Omelanczuk, J.; Mikolajczyk, M. Tetrahedron Lett. 1984, 25, 2493–2496.

⁽¹²⁾ In the ¹³C{¹H} NMR spectra of cage compounds **10–12** and **1a**, the signals for the *ipso*-carbons of the *Si*-phenyl groups were observed as doublets with ⁴J_{C-P} coupling constants of 3.5, 3.5, 3.4, and 4.5 Hz, respectively. In contrast, no ⁴J_{C-P} coupling was observed for monocyclic compound **9**. The long-range electronic interaction through the cage may suggest that the electron-donating power of a SMAP ligand can be controlled by a *Si*-substituent.

respectively. In BH₃ complex **12**, the P atom bonds to the B atom with a distance of 1.922(2) Å.¹⁶ The average C–P–C angle is enlarged to 104.2°. Such a slight enlargement of the angles around the P atom is typical for the metal coordination of a *P*-donor ligand. The BH₃ coordination also causes shrinkage of the cage as indicated by enlargement of the P–C–C–Si dihedral angles (22.3°, averaged) and shortening of the P–Si distance (3.031 Å). Although the cage possesses some flexibility for twisting and stretching, almost no bending of the longest molecular axes was observed for both **1a** and **12**.

Figure 3 represents densely packed crystal structures of **1a** and **12**. The former consists of the two enantiomeric



Figure 3. Crystal packing of Ph-SMAP (**1a**, left) and Ph-SMAP–BH₃ (**12**, right).

molecules $(P2_1/n)$, while only a single enantiomer is involved in the latter (chiral space group: $P2_1$).¹⁷ The feature common to the crystal packing of **1a** and **12** is the columnar stacking along the *a*-axis through van der Waals contacts between neighboring 1-phospha-4-silabicyclo[2.2.2]octane cages. In both cases, the one-dimensional columns are further stacked along the longest molecular axis in a head-to-tail manner to form a sheet structure on the *a*,*c* plane. In the case of **1a**,

(14) Crystal data for **1a**: monoclinic, $P2_1/n$ (#14), a = 6.3438(3) Å, b = 18.0866(5) Å, c = 10.4720(6) Å, $\beta = 100.732(1)^\circ$, V = 1180.52(9) Å³, Z = 4. Data collection: Rigaku RAXIS-RAPID Imaging Plate diffractometer, T = -153 °C. $2\theta_{max} = 54.9^\circ$, R = 0.041, $R_w = 0.076$, $I > 1.5\sigma(I)$, GOF = 1.96.

(15) Crystal data for **12**: monoclinic, $P2_1$ (#4), a = 6.3632(3) Å, b = 7.6482(3) Å, c = 13.6844(7) Å, $\beta = 660.93$ Å³, Z = 2. Data collection: Rigaku RAXIS-RAPID Imaging Plate diffractometer, T = -153 °C, $2\theta_{\text{max}} = 54.9^{\circ}$, R = 0.028, $R_{\text{w}} = 0.037$, $I > 3\sigma(I)$, GOF = 1.26.

(16) P-B bond length of **12** (1.922(2) Å) is apparently longer than that of Me₃P-BH₃ (1.901 Å) as determined by microwave spectroscopy. See: Bryan, P. S.; Kuczkowski, R. L. *Inorg. Chem.* **1972**, *11*, 553–559. The reason of the elongation is not clear at present. Correlation between steric/ electronic properties of phosphines and P-B bond lengths is not clear in general. For a review, see: Brunel, J. M.; Faure, B.: Maffei, M. *Coord. Chem. Rev.* **1998**, *178–180*, 665–698.

 $\left(17\right)$ This is a case of chiral crystallization of an achiral molecule with chiral conformations.

the sheets are then stacked along the *b*-axis so that the cage and the aromatic ring are alternatively arranged to allow van der Waals contacts. In contrast, the sheet of **12** is stacked through $C-H\cdots\pi$ interactions between neighboring aromatic rings.

DFT calculations [B3LYP/6-31G(d,p)] indicated that Ph-SMAP possesses an electron-donating ability as strong as that of Me₃P, and replacement of the Si atom of Ph-SMAP with a carbon atom drastically decreases the donor power. We optimized the geometry of Ph-SMAP and evaluated donor ability by the value of the molecular electrostatic potential minimum V_{min} (kcal/mol) according to Koga's method.¹⁸ A larger negative V_{min} value corresponds to a stronger electron-donating ability of a phosphine. For comparison, we also performed calculations for 4-phenyl-1-phosphabicyclo[2.2.2]octane (13), an analogue of Ph-SMAP that has a bridgehead carbon atom instead of the Si atom.¹⁹ As shown in Table 1, the V_{min} (-43.14 kcal/mol) of

Table 1.	Results	of DFT	Calculations	for	Various	Tertiary
Phosphine	s					

entry	phosphine	V _{min} (kcal/mol)	average C-P-C angle (deg) ^a
1^b	(t-Bu) ₃ P	-45.48	107.5
2^b	(<i>i</i> -Pr) ₃ P	-44.47	101.6
3^b	Et ₃ P	-43.51	99.5
4	Ph-SMAP (1a)	-43.14	99.7
5^b	Me ₃ P	-43.02	99.4
6^b	Me ₂ PhP	-40.41	
7	13	-39.06	96.2
8^{b}	MePh ₂ P	-36.76	

^a Values of optimized structures. ^b Data were taken from ref 18.

Ph-SMAP is much more negative than the value of monoaryldialkylphosphine PhMe₂P and is in the range for trialkylphosphines, being between the values of Me₃P and Et₃P. However, the V_{min} of **13** is less negative than that of PhMe₂P. The drastic decrease in donor ability upon placement of a carbon atom at the bridgehead may be due to the increase in *s*-character of the *P*-lone pair caused by the strain in the 1-phosphabicyclo[2.2.2]octane cage. The strain is evident from the comparison of the C-P-C angles of the optimized structures; the avarage angle of **13** (96.2°) is much smaller than that of Ph-SMAP (99.7°), and the latter is almost the same as the values of Me₃P (99.4°) and Et₃P (99.5°).

We presented a new trialkylphosphine Ph-SMAP with steric and electronic features that guarantee its wide application as a robust ligand for transition metal coordination. SMAP derivatives with various *Si*-substituents can be easily synthesized either by starting with the corresponding organosilicon compounds or by transforming Ph-SMAP through

⁽¹³⁾ To our surprise, Ph-SMAP showed considerable air-stability even in solutions. A solution of Ph-SMAP in C₆D₆ prepared without exclusion of air underwent no oxidation detectable by ¹H NMR after standing for 3 days in the air. Similar experiments with CD₂Cl₂ and acetone- d_6 produced only a trace amount (<3%) of the corresponding phosphine oxide after 1 h.

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⁽¹⁹⁾ Phosphine oxide form of 1-phosphabicyclo[2.2.2]octane was synthesized, and its strain around the *P* atom was discussed. However, it has not been converted to the free phosphine. See: Wetzel, R. B.; Kenyon, G. L. *J. Am. Chem. Soc.* **1974**, *96*, 5189–5198.

Si-Ph bond cleavage. The molecular rigidity and flexibility of functionalization allows the preparation of a sophisticated series of SMAP ligands providing useful components for supramolecular architectures based on coordination chemistry.

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Supporting Information Available: Experimental procedures and spectroscopic data for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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