ORGANIC LETTERS

2003
Vol. 5, No. 15
2671−2674

Nonvolatile Me_3P-like *P*-Donor Ligand: Synthesis and Properties of 4-Phenyl-1-phospha-4-silabicyclo[2.2.2]octane

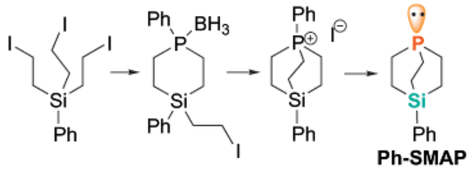
Atsuko Ochida, Kenji Hara, Hajime Ito, and Masaya Sawamura*

Division of Chemistry, Graduate School of Science, Hokkaido University,
Sapporo 060-0810, Japan

sawamura@sci.hokudai.ac.jp

Received May 23, 2003

ABSTRACT



Ph-SMAP

A new trialkylphosphine ligand with Me_3P-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 Me_3P-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 metal-coordinating ligands with strong σ-donating ability. One ligand with an extremely low steric demand is trimethylphosphine (Me_3P), which is especially important in the metal-mediated C−H bond activation of hydrocarbons.[1] We have designed a new Me_3P-like trialkylphosphine ligand **1** (SMAP, named after **s**ilicon-constrained **m**onodentate **a**lkyl**p**hosphine) (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 Me_3P. 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 Me_3P 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

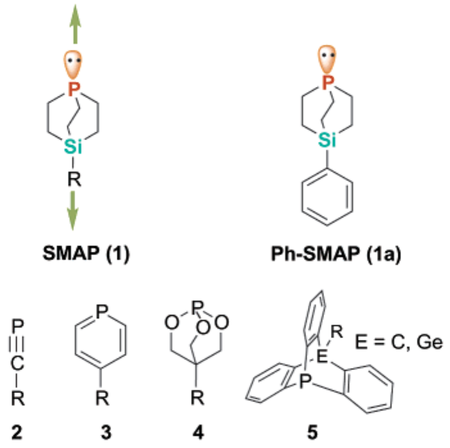


Figure 1. Structures of SMAP and related *P*-donor ligands.

---

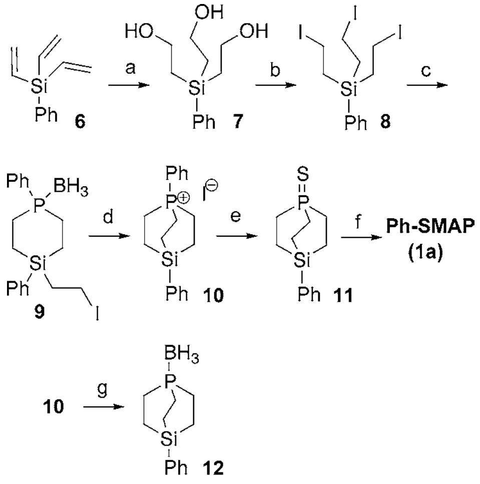
(1) (a) Jones, W. D. In *Topics in Organometallic Chemistry 3: Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer: Berlin, 1999; pp 9−46. (b) Kakiuchi, F.; Murai, S. In *Topics in Organometallic Chemistry 3: Activation of Unreactive Bonds and Organic Synthesis*; Murai, S.,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

10.1021/ol0349099 CCC: $25.00

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% 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 salt[8] of $PhPH_2-BH_3$ 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 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 $BH_3{\cdot}SMe_2$ instead of S_8 gave borane complex **12** in 46% yield. Finally, desulfuration of **11** through S-methylation followed by treatment with HMPT[11] 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; ^{31}P NMR (C_6D_6, 85% H_3PO_4) δ −59.2 (+3.0 relative to Me_3P/C_6D_6).[12]

Scheme 1. Synthesis of Ph-SMAP[a]



[a] Reagents and conditions: (a) (i) $(Ipc)_2BH$, THF, −25 °C → rt; (ii) H_2O_2, NaOH. (b) (i) MsCl, Et_3N, THF, 0 °C; (ii) NaI, acetone, 0 °C → reflux. (c) $BH_3{\cdot}SMe_2/PhPH_2$/BuLi (1:1:2), THF, −78 °C → rt. (d) 1-Octene, DME, reflux. (e) (i) Lithium naphthalenide, toluene, 40 °C; (ii) S_8, toluene, 80 °C. (f) (i) MeOTf, CH_2Cl_2, rt; (ii) $P(NMe_2)_3$, CH_2Cl_2, rt. (g) (i) Lithium naphthalenide, toluene, 40 °C; (ii) $BH_3{\cdot}SMe_2$, 0 °C.

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 rod-like shape of Ph-SMAP (**1a**) and Ph-SMAP−BH_3 (**12**) (Figure 2).[14,15] Analyses also showed that the bicyclic cage 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,

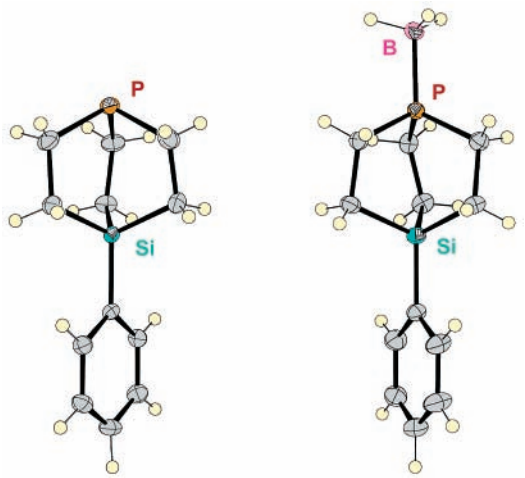


Figure 2. ORTEP drawings of the molecular structures of Ph-SMAP (**1a**, left) and Ph-SMAP−BH_3 (**12**, right).

---

(2) (a) Markovskii, L. N.; Romanenko, V. D. *Tetrahedron* **1989**, *45*, 6019−6090. (b) Nixon, J. F. *Chem. Soc. Rev.* **1995**, *24*, 319−328.

(3) Le Floch, P.; Mathey, F. *Coord. Chem. Rev.* **1998**, *178−180*, 771−791.

(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-diphosphabicyclo-[2.2.2]octane, see: Hinton, R. C.; Mann, F. G. *J. Chem. Soc.* **1959**, 2835−2843.

(7) Brown, H. C.; Desai, M. C.; Jadhav, P. K. *J. Org. Chem.* **1987**, *47*, 5065−5069.

(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 $^{13}C\{^1H\}$ 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 BH$_3$ 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 BH$_3$ 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**.

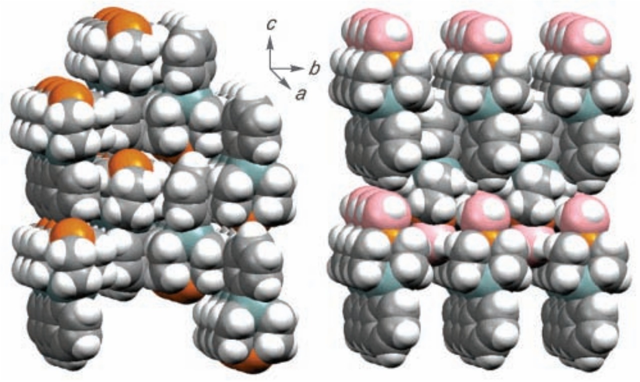


Figure 3. Crystal packing of Ph-SMAP (**1a**, left) and Ph-SMAP−BH$_3$ (**12**, right).

Figure 3 represents densely packed crystal structures of **1a** and **12**. The former consists of the two enantiomeric 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**, 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···π 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 Me$_3$P, 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 Ph-SMAP is much more negative than the value of monoaryldialkylphosphine PhMe$_2$P and is in the range for trialkylphosphines, being between the values of Me$_3$P and Et$_3$P. However, the V_{min} of **13** is less negative than that of PhMe$_2$P. 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 Me$_3$P (99.4°) and Et$_3$P (99.5°).

Table 1. Results of DFT Calculations for Various Tertiary Phosphines

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-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.

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 C$_6$D$_6$ prepared without exclusion of air underwent no oxidation detectable by ^{1}H NMR after standing for 3 days in the air. Similar experiments with CD$_2$Cl$_2$ and acetone-d_6 produced only a trace amount (<3%) of the corresponding phosphine oxide after 1 h.

(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, β = 100.732(1)°, V = 1180.52(9) Å^3, Z = 4. Data collection: Rigaku RAXIS-RAPID Imaging Plate diffractometer, T = −153 °C. $2\theta_{\mathrm{max}}$ = 54.9°, 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, β = 660.93 Å^3, Z = 2. Data collection: Rigaku RAXIS-RAPID Imaging Plate diffractometer, T = −153 °C, $2\theta_{\mathrm{max}}$ = 54.9°, R = 0.028, R_{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 Me$_3$P−BH$_3$ (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.

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

(18) Suresh, C. H.; Koga, N. *Inorg. Chem.* **2002**, *41*, 1473−1578.

(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.

Acknowledgment. The present research was supported by a Grant-in-Aid for Scientific Research (No. 13874095), a grant from Sumitomo Foundation, and the PRESTO program of JST. We thank D. Sato and T. Kato for their help in the early stages of this work and N. Kobayashi for assistance in the X-ray structure analysis.

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.

OL0349099