

Electronically Tunable Compact Trialkylphosphines: SMAPs-bridged Bicyclic Phosphines

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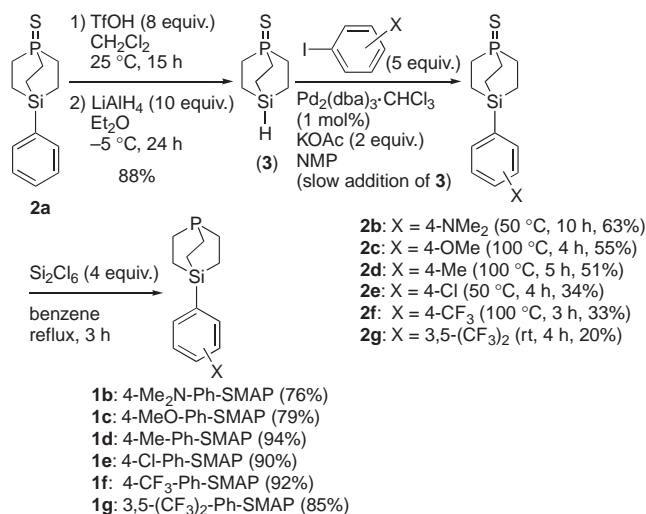
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A series of silicon-constrained monodentate trialkylphosphines SMAPs bearing a *Si* substituent with diverse electronic natures were synthesized. DFT calculations and NMR measurements indicated that these compounds constitute a class of electronically tunable trialkylphosphines. The tunable range of donor power overlaps those of tri(*tert*-butyl)phosphine and monoalkyldiarylphosphines.

Modification of the properties of a metal complex with electronically tunable ligands can be a powerful means for the development of a catalyst with specific properties. Such ligands also are useful for mechanistic research and the development of functional materials. To gain an electronic effect without limitation by accompanying steric effects, a modifying group must operate at the position distal to the metal-coordinating center. This is possible with ligands of a sp^2 -hybridized donor atom such as pyridine derivatives or with those of a sp^3 -hybridized donor atom having an aromatic substituent such as an arylphosphine.¹ On the other hand, electronic tuning of trialkylphosphines, which are a class of ligands with strong σ -donor ability, is not possible with existing compounds. We report here that the silicon-constrained bicyclic phosphines SMAPs (**1a–1g**, Figure 1)² bearing *Si* substituents with varied electronic natures constitute a class of electronically tunable trialkylphosphines. DFT calculations indicated that the tunable range of the donor power overlaps those of (*t*-Bu)₃P and RAr₂P (R: alkyl, Ar: aryl).

SMAP derivatives with a substituted phenyl group on the bridgehead silicon were synthesized through a hydrosilane-type compound H-SMAP sulfide (**3**), a pivotal compound of diverse reactivity. The hydrosilane **3** was obtained as an air-stable crystalline material from Ph-SMAP sulfide (**2a**) in 88% yield through protodesilylation with TfOH followed by reduction with LiAlH₄ (Scheme 1). Note that the Si–Ph bond in Ph-SMAP sulfide was stable against protodesilylation when compared to that in acyclic phenylsilane PhSiBu₃. While the latter was totally cleaved on treatment with 1.1 equiv. of TfOH in CH₂Cl₂ at 0 °C for 3 h, the former needed 8 equiv. of TfOH and a reaction time of 15 h at 25 °C for 100% cleavage. The low reactivity of Ph-SMAP sulfide likely is due to instability of the leaving non-planar



Scheme 1. Synthesis of SMAP derivatives with a substituted phenyl group at the bridgehead silicon atom (**1b–1g**).

bridgehead silyl cation.

The palladium-catalyzed hydrosilane–iodoarene coupling developed by Masuda was applied to H-SMAP sulfide (**3**) to afford a series of SMAP sulfides (**2b–2g**).³ The yield of the cross-coupling product depended on the iodoarenes and the reaction conditions. Generally, the yield was improved (20–63%) by slow addition of a solution of hydrosilane **3** into a solution of the catalyst and iodoarene. Reduction of the phosphine sulfides with Si₂Cl₆ afforded the corresponding phosphines (Ar-SMAPs, **1b–1g**). These phosphines are air-stable, crystalline, colorless solids that do not produce a noxious phosphine odor.

DFT calculations [B3LYP/6-31G(d,p)] indicated that the electronic character of the *P*-lone pair of the SMAP derivatives is strongly influenced by the distal *Si* substituents.⁴ We used the molecular electrostatic potential minimum V_{min} (kcal/mol) value associated with the phosphine lone pair region as a quantitative measure of donor power (Table 1).⁵ A larger negative V_{min} value corresponds to a stronger electron-donating ability of the phosphine. As reported previously, Ph-SMAP (**1a**) is comparable with Me₃P in donor power (Table 1, Entries 7 and 8).² Calculations indicated that the donor powers of 4-MeO-Ph-SMAP (**1c**) and 4-Me-Ph-SMAP (**1d**) apparently were stronger than those of Me₃P and Ph-SMAP (**1a**), and comparable with those of Bu₃P and (*i*-Pr)₃P (Entries 3–8). The *para*-Me₂N group exerts a much larger effect, increasing the donor ability of the aniline-type derivative 4-Me₂N-Ph-SMAP (**1b**) even more than (*t*-Bu)₃P, which is one of the σ -donor ligands possessing the

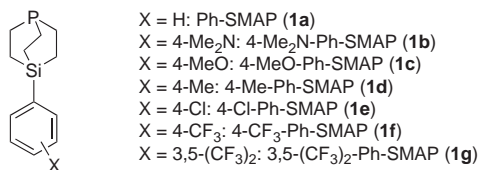
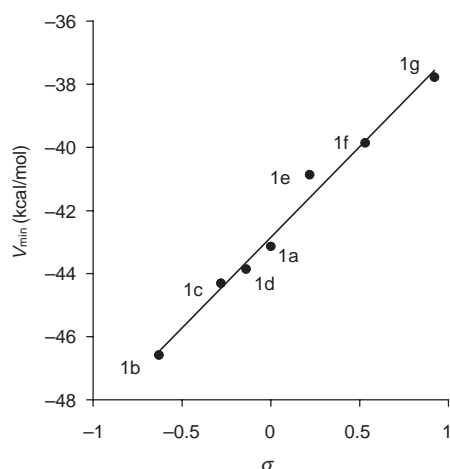


Figure 1. Structures of SMAP family of compounds (**1**).

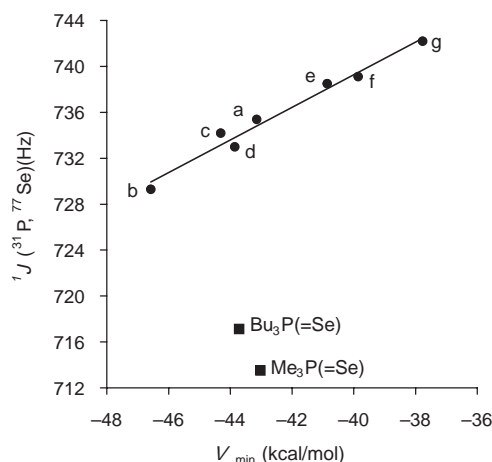
Table 1. V_{\min} (kcal/mol) for various phosphines and $^1J(^{31}\text{P}, ^{77}\text{Se})$ (Hz) for phosphine selenides

Entry	SMAP	R_3P	V_{\min} kcal mol $^{-1}$	$^1J(^{31}\text{P}, ^{77}\text{Se})$ /Hz
1	4-Me ₂ N-Ph-SMAP (1b)		-46.58	729.3
2		(<i>t</i> -Bu) ₃ P	-45.48 ^a	n.d.
3		(<i>i</i> -Pr) ₃ P	-44.47 ^a	n.d.
4	4-MeO-Ph-SMAP (1c)		-44.30	734.2
5	4-Me-Ph-SMAP (1d)		-43.86	733.0
6		Bu ₃ P	-43.71 ^a	717.1
7	Ph-SMAP (1a)		-43.14	735.4
8		Me ₃ P	-43.02 ^a	713.5
9	4-Cl-Ph-SMAP (1e)		-40.86	738.5
10		Me ₂ PhP	-40.41 ^a	n.d.
11	4-CF ₃ -Ph-SMAP (1f)		-39.85	739.1
12	3,5-(CF ₃) ₂ -Ph-SMAP (1g)		-37.77	742.2
13		MePh ₂ P	-36.76 ^a	n.d.

^aData taken from Ref. 5.**Figure 2.** A plot of V_{\min} (kcal/mol) vs Hammett's substituent constants σ 's for SMAP derivatives **1a–1g**. A value two-fold greater than the σ value of *m*-CF₃ was used for **1g**.

strongest donor power (Entries 1 and 2). In contrast, substitution at the para-position with an electron-withdrawing group decreased donor power; the donating power of 4-Cl-Ph-SMAP (**1e**) and 4-CF₃-Ph-SMAP (**1f**) were comparable with monoaryl-dialkylphosphine Me₂PhP (Entries 9–11). Donor power of 3,5-(CF₃)₂-Ph-SMAP (**1g**) is as weak as that of MePh₂P (Entries 12 and 13). Figure 2 shows that the substitution effect at the *para*-position of Ph-SMAP on V_{\min} is proportional to Hammett's substituent constant σ .

The $^1J(^{31}\text{P}, ^{77}\text{Se})$ measurements for phosphine selenides provided experimental evidence for the substituent effect at the bridgehead silicon atom on phosphine donor power. The selenides were prepared by heating a mixture of the phosphine and selenium in C₆D₆ in an NMR tube, and the $^1J(^{31}\text{P}, ^{77}\text{Se})$ values were measured in situ. It is commonly accepted that the stronger the donor power is, the smaller the $^1J(^{31}\text{P}, ^{77}\text{Se})$ value.⁶ Values for SMAP selenides (**4a–4g**) and Me₃P=Se and Bu₃P=Se are listed in Table 1. The $^1J(^{31}\text{P}, ^{77}\text{Se})$ values for the SMAP sele-

**Figure 3.** A plot of $^1J(^{31}\text{P}, ^{77}\text{Se})$ vs V_{\min} of the phosphine derivatives. The correlation line is associated with **1a–1g/4a–4g**.

nides increase by 12.9 Hz upon examination of the selenide (**4b**) possessing the strongest donating aryl-SMAP (**1b**) to that (**4g**) of the weakest donating one (**1g**). Figure 3 demonstrates that $^1J(^{31}\text{P}, ^{77}\text{Se})$ values for SMAP selenides **4a–4g** show good linear correlation with the theoretical measures (V_{\min} 's). Figure 3 also shows that the values for Me₃P=Se and Bu₃P=Se are far below the correlation line for **4a–4g**. This drastic deviation is attributable to the change in steric environment around the P center.

In conclusion, the SMAP series of compounds with various Si substituents were synthesized. The donor properties of the P-lone pair varied over a wide range depending upon the electronic nature of the Si substituent, with retention of the steric demand around the phosphorus center. These characteristics should allow SMAPs to find diverse utility in mechanistic studies of organometallic reactions and in the development of efficient catalytic reactions.⁷

References and Notes

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- Although we have been unsuccessful in finding a dramatic ligand substituent effect in relation to catalysis, we have confirmed that the SMAP ligands can be used as Me₃P-like ligands and have found noticeable substituent effects in some transition metal-catalyzed reactions. Details are forthcoming.