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Ligand Immobilization

Monocoordinating, Compact Phosphane Immobilized on Silica Surface: Application to Rhodium-Catalyzed Hydrosilylation of Hindered Ketones[**]

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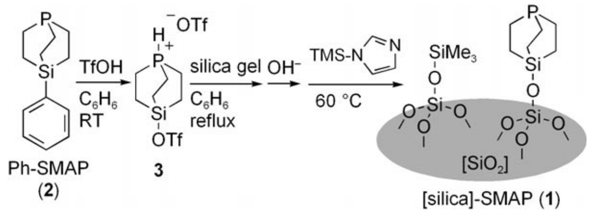
In memory of Yoshihiko Ito

Compact phosphanes such as Me_3P are useful for the preparation of well-defined organometallic compounds, but their use as a ligand for metal catalysis is not so common, owing in part to the difficulty in controlling their coordination number. Because of their compactness, they tend to "over-coordinate" to the metal center, giving an inactive species that is resistant to affording a vacant coordination site. This situation may, in turn, mean that one could have a highly active species by limiting the P coordination number. But, unfortunately, such a sterically unprotected active species would immediately encounter self-aggregation and decomposition, leading to the loss of activity. One may expect that immobilization of compact P centers on a rigid support to allow catalyst-site isolation would be a reasonable method to create a highly active catalytic environment, but such a system has not been demonstrated experimentally.[1,2]

We report herein the immobilization of a sterically undemanding, caged trialkylphosphane (SMAP)[3] on a silica gel surface ([silica]-SMAP, **1**) and its unique coordination behavior to form a 1:1 Rh/P complex as well as its use as a platform to create a highly active catalytic center. A heterogeneous catalyst, prepared from **1** and $[\{RhCl(C_2H_4)_2\}_2]$, showed an exceptionally high activity for the hydrosilylation of sterically hindered ketones, as represented by the transformations of diisopropyl ketone (**4b**) and di(*tert*-butyl) ketone (**4c**) into the corresponding tBuMe$_2$Si-protected secondary alcohols at ambient temperature. These transformations have not been achieved with any other catalyst system to date.

We used the SMAP ligand as a compact phosphane to attach to silica gel, taking advantage of its structure variability at the bridgehead silicon atom, molecular rigidity, and air stability.[3] The cage of SMAP was grafted on a silica gel surface through a direct connection between the cage and a surface oxygen atom as shown in Scheme 1. Treatment of Ph-SMAP (**2**) with TfOH in benzene afforded silyl triflate **3**, which was treated with HCl-activated silica gel in refluxing benzene. Filtration and elution of soluble materials and subsequent neutralization afforded phosphane-functionalized silica gel. The surface silanols that remained intact were end-capped with a Me_3Si group to give [silica]-SMAP (**1**).[4]



Scheme 1. Immobilization of a compact phosphane on a silica surface. Tf = trifluoromethanesulfonyl; TMS = trimethylsilyl.

The ^{31}P CP/MAS NMR spectra of **1** displayed a single resonance at $\delta = -58$ ppm, which was assigned to the free phosphane group on the basis of the characteristic high-field resonance of Ph-SMAP at $\delta = -59.2$ ppm in C_6D_6 solution (Figure 1a). The lack of a signal corresponding to the oxidized phosphorus nucleus confirms the intrinsic air stability of the phosphane moiety of the SMAP molecule, despite being exposed to air on the surface. Accordingly, [silica]-SMAP (**1**) is easy to handle.

The monocoordinating property of [silica]-SMAP (**1**) was established by NMR observations (Figures 1 and 2). Thus, the interaction between **1** and $[\{RhCl(cod)\}_2]$ (cod = 1,5-cyclooctadiene) was investigated by mixing varying amounts of the Rh complex with a benzene slurry of **1**. NMR spectra were measured after filtration, washing with benzene, and drying.

Figure 1b shows the ^{31}P CP/MAS NMR spectrum consisting of signals for both the free phosphane and a Rh-coordinated phosphane (P/Rh 1:0.48; see below for the determination of P concentration in **1**). With an increase in the amount of the added $[\{RhCl(cod)\}_2]$, the signal intensity of the free phosphane decreased and the signal intensity for the Rh–phosphane complex increased. When **1** was mixed with excess $[\{RhCl(cod)\}_2]$ (P/Rh 1:1.52) in benzene, the supernatant became yellow. The remaining $[\{RhCl(cod)\}_2]$ that did not interact with **1** was recovered from the filtrate upon washing with benzene. The spectrum of the gel showed only the signal for the Rh–phosphane complex as shown in

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

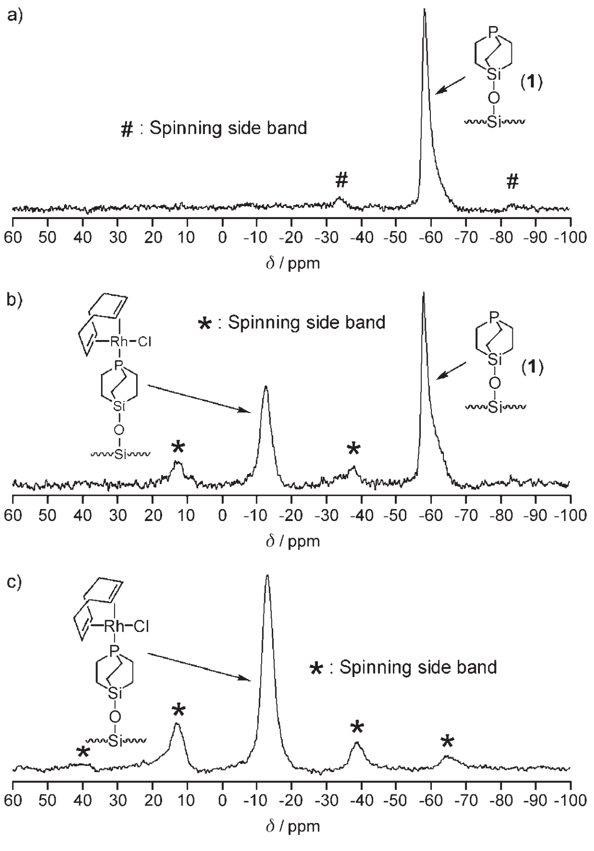


Figure 1. a) ^{31}P CP/MAS NMR spectrum of **1**; b) ^{31}P CP/MAS NMR spectrum that was obtained from **1** and a substoichiometric amount of [{RhCl(cod)}$_2$] (P/Rh 1:0.48); c) ^{31}P CP/MAS NMR spectrum that was obtained by treating **1** with excess [{RhCl(cod)}$_2$] (P/Rh 1:1.52) before washing and drying.

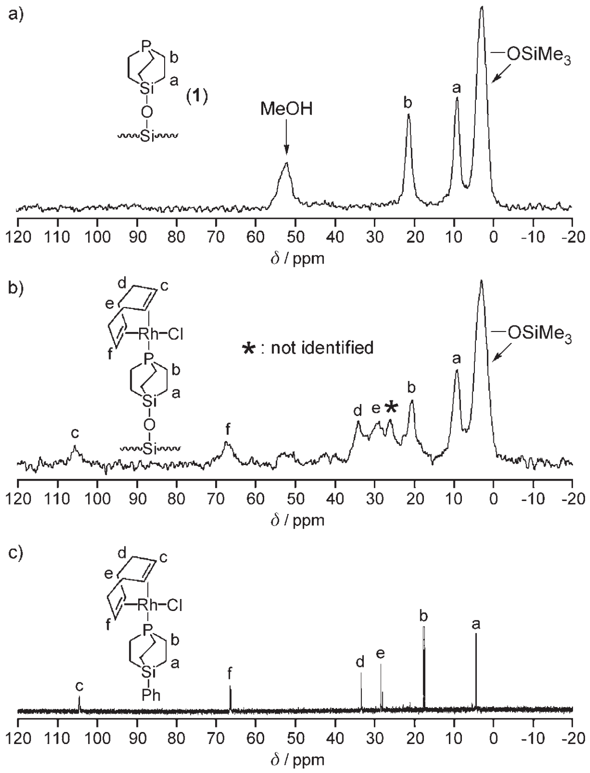


Figure 2. a) ^{13}C CP/MAS NMR spectrum of **1**; b) ^{13}C CP/MAS NMR spectrum obtained by treating **1** with excess [{RhCl(cod)}$_2$] (the same sample used in Figure 1 c); c) ^{13}C NMR of [RhCl(cod)(**2**)] in C_6D_6.

Figure 1 c. With this procedure the amount of Rh loaded on the functionalized silica gel was determined to be 0.19 mmol g^{-1}.

Next, ^{13}C CP/MAS NMR spectra were measured with free ligand **1** and the sample that gave the spectrum in Figure 1 c, and were compared with the solution spectrum of [RhCl(cod)(**2**)], which was prepared by mixing [{RhCl(cod)}$_2$] and Ph-SMAP (**2**) with a Rh/P ratio of 1:1 in C_6D_6 (Figure 2). The chemical shifts obtained in the solid-state NMR spectra matched well with the solution data, and thus confirmed the formation of a monocoordinated SMAP-Rh structure, [silica]-[RhCl(cod)(smap)] (C_s symmetry with Rh–P free rotation). Having established the composition of the Rh–phosphane complex, we were able to determine the amount of the phosphane in **1** to be 0.20 mmol g^{-1}.

The effect of immobilization was critical for the monocoordinating ability of the compact trialkylphosphane. The reaction of [{RhCl(cod)}$_2$] with Ph-SMAP (**2**) in a Rh/P ratio of 1:2 gave a complex mixture, leaving no free phosphane.

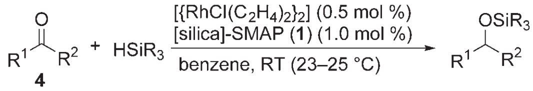
To demonstrate ligand characteristics of [silica]-SMAP (**1**) for catalytic applications, we examined the Rh-catalyzed hydrosilylation of ketones with triorganosilanes, as a monophosphane–Rh species had been proposed by Tsuji and coworkers to be critically important in this type of catalysis.[5] In addition to the monocoordination effect, we expected a geminating effect of the ligand compactness on catalytic performance.

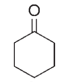
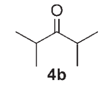
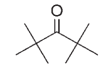
In fact, a heterogeneous rhodium(I) complex bound on **1** exhibited high catalytic activity. A striking advantage of our protocol is its applicability to sterically hindered ketones and silanes. The hydrosilylation was carried out in the presence of the silica-supported Rh catalyst prepared in situ from [{RhCl(C_2H_4)$_2$}$_2$] (0.005 mmol) and **1** (0.010 mmol) in benzene (1 mL) at room temperature (Table 1).

The hydrosilylation of cyclohexanone (**4a**) with $PhMe_2SiH$ and Et_3SiH was complete within 5 min (Table 1, entries 1 and 2). These reactions are much faster than those with the bowl-shaped phosphane (Rh/P 1:2; 3 h with $PhMe_2SiH$, 21 h with Et_3SiH),[5] which had been identified to be one of the most effective ligands to promote these rhodium-catalyzed transformations. The [silica]-SMAP-Rh catalysis is also applicable to the hydrosilylation with *t*BuMe$_2$SiH (Table 1, entry 3). Replacing cyclohexanone (**4a**) with the much bulkier diisopropyl ketone (**4b**) caused a considerable decrease in the rate, but the reactions with $PhMe_2SiH$, Et_3SiH, and *t*BuMe$_2$SiH produced the corresponding silyl ethers in quantitative yields with reasonable reaction times (Table 1, entries 4–6). The catalysis with **1** tolerates the hydrosilylations of an even more challenging substrate, di(*tert*-butyl) ketone (**4c**; Table 1, entries 7–9).[6,7]

The bond between the P atom of **1** and the Rh atom is fairly robust. Leaching of Rh after the reaction (Table 1, entry 6) was below the quantification limit of the ICP analysis (< 0.1 % of the catalyst loading). The [silica]-SMAP-Rh

Table 1: Hydrosilylation catalyzed by the [silica]-SMAP-Rh system.[a]



Entry	Ketone	Hydrosilane	t[b]	Yield [%]
1	 **4a**	$PhMe_2SiH$	< 5 min	93[c]
2		Et_3SiH	< 5 min	100[c]
3		$t$$BuMe_2SiH$	30 min	100[c]
4	 **4b**	$PhMe_2SiH$	1 h	99[c]
5		Et_3SiH	4 h	99[c]
6		$t$$BuMe_2SiH$	10 h	100[c]
7	 **4c**	$PhMe_2SiH$	96 h	92[c]
8		Et_3SiH	12 h	96[d]
9		$t$$BuMe_2SiH$	30 h	97[d]

[a] Reagents and conditions: **4** (1 mmol), R_3SiH (1.2 mmol), [{RhCl(C_2H_4)$_2$}$_2$] (0.005 mmol), **1** (0.010 mmol), benzene (1 mL). Conversion of **4** is 100% in all entries. [b] Approximate time required for 100% conversion. [c] Yield based on GC. [d] Yield of isolated product.

catalyst could be recovered by simple filtration and be reused for the same transformation (100% conv. of **4b** with 1.2 equiv of $t$$BuMe_2SiH$, 10 h, 23 °C, six times, total TON = 700).

The impact of the immobilization on the tolerance toward the hindered substrates is overwhelming. The catalysts (1 mol% Rh) prepared from the homogeneous Ph-SMAP (**2**) ligand or other various conventional phosphanes including PPh_3, P$t$$Bu_3$, and 1,2-bis(diphenylphosphanyl)ethane (dppe) showed almost no activity for the transformation corresponding to entry 6 in Table 1 (**4b**, $t$$BuMe_2SiH$, 1 mol% Rh, RT, 10 h, < 2% conv.), irrespective of the Rh/P ratio ranging from 1:1 to 1:2. The most likely reason for the lower activity of the homogeneous catalysts for Rh/P 1:1 as compared with that of the [silica]-SMAP-Rh system would be the lack of a monophosphane–rhodium species in the former.[8] In fact, the strong tendency of compact phosphane **2** to congregate on the rhodium center was confirmed in the ^{31}P NMR spectra for a mixture of [{RhCl(C_2H_4)$_2$}$_2$] and Ph-SMAP (**2**) (P/Rh 1:1, 2:1, 3:1, 4:1) in C_6D_6 in ethylene atmosphere (see the Supporting Information).

As reasonably expected from the aforementioned results of the titration of [silica]-SMAP (**1**) with [{RhCl(cod)}$_2$], the use of excess **1** caused no change in the rate of the hydrosilylations. This result is in sharp contrast to the results with a homogeneous catalyst system involving the soluble phosphane Ph-SMAP (**2**) in the hydrosilylation with reactive substrate couples such as cyclohexanone/$PhMe_2SiH$. The reaction proceeded smoothly with a P/Rh ratio of 1:1 (1 mol% Rh, 1 h, 100% conv.; even faster than with a BSP ligand; BSP = bowl-shaped phosphane), but the second equivalent of **2** drastically inhibited the reaction (see the Supporting Information).

It is presumed that the monocoordination of the compact ligand creates an exceptionally sparse catalytic environment[9] and induces a unique reaction mechanism that is indispensable for the activity toward the sterically demanding substrates. Besides the major effects of the P coordination number and the compactness, the electronic effect of the strongly σ-donating SMAP ligand may also have some influence on the catalytic properties of the [silica]-SMAP-Rh system.

In summary, a functionalized silica gel, [silica]-SMAP, consisting of a compact, bridged bicyclic trialkylphosphane was developed. The monocoordinating character and usefulness as a ligand for heterogeneous catalysts were demonstrated in the Rh-catalyzed hydrosilylation, which showed unprecedented high tolerance toward hindered ketones and silanes. More detailed analysis of the surface structure, use of other silica supports such as mesoporous silica, and the application to other synthetically useful reactions will be the subjects of future work.

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[1] $Ph_2P(CH_2)_n$-functionalized silicas were used for the Rh-catalyzed hydrosilylation of 1-hexene. The activity with the Ph_2PCH_2 group was tenfold higher than those with the longer-chain analogues: a) M. Czaková, M. Čapka, *J. Mol. Catal.* **1981**, *11*, 313; b) Z. M. Michalska, M. Čapka, J. Stoch, *J. Mol. Catal.* **1981**, *11*, 323.

[2] For a related study, in which a bulky phosphane attached to a rigid polymer support was used for the Suzuki–Miyaura coupling, see: Q.-S. Hu, Y. Lu, Z.-Y. Tang, H.-B. Yu, *J. Am. Chem. Soc.* **2003**, *125*, 2856.

[3] SMAP = *s*ilicon-constrained *m*onodentate *a*lkyl*p*hosphane. a) A. Ochida, K. Hara, H. Ito, M. Sawamura, *Org. Lett.* **2003**, *5*, 2671; b) A. Ochida, S. Ito, T. Miyahara, H. Ito, M. Sawamura, *Chem. Lett.* **2006**, *35*, 294.

[4] The approximate SMAP/Me_3Si ratio for **1** was 1:4 according to the ^{29}Si CP/MAS NMR spectrum.

[5] a) O. Niyomura, M. Tokunaga, Y. Obora, T. Iwasawa, Y. Tsuji, *Angew. Chem.* **2003**, *115*, 1325; *Angew. Chem. Int. Ed.* **2003**, *42*, 1287; b) O. Niyomura, T. Iwasawa, N. Sawada, M. Tokunaga, Y. Obora, Y. Tsuji, *Organometallics* **2005**, *24*, 3468; see also: c) A. Ochida, M. Sawamura, *Chem. Asian J.*, **2007**, *2*, 609; d) H. Ito, T. Kato, M. Sawamura, *Chem. Lett.* **2006**, *35*, 1038.

[6] Lipshutz et al. reported that some Cu–bisphosphane catalysts are effective for the ketone hydrosilylation with $t$$BuMe_2SiH$, but their reactivity toward highly hindered ketones has not extensively been studied: B. H. Lipshutz, C. C. Caires, P. Kuipers, W. Chrisman, *Org. Lett.* **2003**, *5*, 3085.

[7] Nolan and co-workers reported on Cu–NHC catalysts that are effective for the hydrosilylation of hindered ketones with Et_3SiH. The Cu–NHC-catalyzed reaction, however, demands high catalyst loading (3 mol%) and high temperature (55–80 °C); furthermore, its applicability using hindered silanes, such as $t$$BuMe_2SiH$, has yet to be demonstrated: a) S. Díez-González, H. Kaur, F. K. Zinn, E. D. Stevens, S. P. Nolan, *J. Org. Chem.* **2005**, *70*, 4784; b) S. Díez-González, N. M. Scott, S. P. Nolan, *Organometallics* **2006**, *25*, 2355.

[8] DFT calculations of the P-donor power of MeO-SMAP, a model compound for **1**, indicated that the electronic effect of the support is negligible; see reference [3a].

[9] The reaction of **1** with [{RhCl(C_2H_4)$_2$}$_2$] should form [silica]-[RhCl(C_2H_4)$_2$(smap)]. This catalyst precursor should release the two ethylene ligands upon rapid hydrosilylation prior to entering a catalytic cycle. [silica]-[RhCl(cod)(smap)] can also be used but needs to be aged with a hydrosilane before the addition of a ketone.