R= Me: P(tm-tp)$_3$
R= H: P(tp)$_3$

Table 1: Effects of ligands in the hydrosilylation of cyclohexanone.[a]

Entry	Ligand[b]	Yield [%][c]
1	P(tm-tp)$_3$	97 (13)[d]
2	P(tp)$_3$	25 (<1)[d]
3	PPh$_3$	7 (<1)[d]
4	P(2-furyl)$_3$	22
5	P(o-tol)$_3$	32
6	PMes$_3$	25
7	PEt$_3$	<2
8	PCy$_3$	<2
9	PtBu$_3$	31

[a] Reaction conditions: cyclohexanone (1.0 mmol), HSiMe$_2$Ph (1.2 mmol), [{RhCl(C$_2$H$_4$)$_2$}$_2$] (0.0050 mmol), ligand (0.020 mmol), tridecane (0.25 mmol, as an internal standard), benzene (1.0 mL), RT, 3 h. [b] tol = tolyl, Mes = mesityl, Cy = cyclohexyl. [c] Yield of cyclohexanol by GC after desilylation with HCl/MeOH. [d] In CH$_2$Cl$_2$ as solvent.

High-Speed Hydrosilylation

Rate Enhancement with a Bowl-Shaped Phosphane in the Rhodium-Catalyzed Hydrosilylation of Ketones**

*Osamu Niyomura, Makoto Tokunaga, Yasushi Obora, Tetsuo Iwasawa, and Yasushi Tsuji**

Since the nature of P ligands is very important in transition-metal-catalyzed reactions, a wide variety of these ligands has been designed to realize high catalytic activity and selectivity.[1] So far, most P ligands are rather small, and their design and modification have hitherto been performed within close proximity of the P atom. Recently, several large (nanosized) phosphorus ligands were developed for transition-metal-catalyzed reactions.[2, 3] In the course of our studies,[3] we found that a bowl-shaped[4] phosphane ligand markedly enhances the rate of rhodium-catalyzed hydrosilylation of ketones.[5]

The two triarylphosphanes tris(2,2″,6,6″-tetramethyl-*m*-terphenyl-5′-yl)phosphane[6] (denoted as P(tm-tp)$_3$) and tris(*m*-terphenyl-5′-yl)phosphane (denoted as P(tp)$_3$) were prepared and compared with common phosphanes in the rhodium-catalyzed hydrosilylation of cyclohexanone with a trisubstituted silane (Table 1). P(tm-tp)$_3$ was first prepared in 2001[6a] and its Pd^0 complex [Pd{P(tm-tp)$_3$}$_2$] was reported in

[*] Prof. Dr. Y. Tsuji, Dr. O. Niyomura, Dr. M. Tokunaga, Dr. Y. Obora, T. Iwasawa
Catalysis Research Center and Division of Chemistry
Graduate School of Science
Hokkaido University
Sapporo 060-0811 (Japan)
Fax: (+081) 11-706-3698
E-mail: tsuji@cat.hokudai.ac.jp

2002.[6b] In the presence of catalytic amounts of P(tm-tp)$_3$ and [{RhCl(C$_2$H$_4$)$_2$}$_2$] (P/Rh = 2), the reaction proceeded smoothly in benzene at room temperature over 3 h, and cyclohexanol was obtained in 97% yield after desilylation (Table 1, entry 1). In contrast, the same reaction with P(tp)$_3$ afforded the product in only 25% yield (entry 2). Furthermore, other representative triarylphosphanes (entries 3–6) and trialkylphosphanes (entries 7–9) were also much less effective than P(tm-tp)$_3$. With these ligands (entries 2–9), the reactions were sluggish at room temperature, and much longer reaction times (40–500 h) were required to obtain the products in good yields (70–95%). A kinetic study indicated that the P(tm-tp)$_3$ catalyst system (entry 1) realized 154, 31, and 28 times faster reactions than PPh$_3$ (entry 3), P(tp)$_3$ (entry 2), and P(o-tol)$_3$ (entry 5), respectively.[7] Benzene is a better solvent than CH$_2$Cl$_2$ in the reactions of entries 1–3.

The rate enhancement with P(tm-tp)$_3$ was further confirmed with various silanes and ketones, and compared with P(tp)$_3$ and PPh$_3$ (Table 2). With HSiEt$_3$ (Table 2, entries 1–3) or HSiMePh$_2$ (entries 4–6), the hydrosilylation of cyclohexanone proceeded much faster with P(tm-tp)$_3$ (entries 1 and 4) than with P(tp)$_3$ (entries 2 and 5) and PPh$_3$ (entries 3 and 6). Furthermore, in the hydrosilylation of various ketones such as acetophenone (entries 7–9), 2-octanone (entries 10–12), and (−)-menthone (entries 13–15), rate enhancement with P(tm-tp)$_3$ was also evident. As catalyst precursor, the cationic rhodium complex [Rh(cod)$_2$]BF$_4$ (cod = cyclooctadiene) showed a similar rate enhancement with P(tm-tp)$_3$ (entries 16–18).

P(tm-tp)$_3$ is a much more efficient than P(tp)$_3$, although the two ligands strongly resemble each other. The structures of P(tm-tp)$_3$ and P(tp)$_3$ were optimized by HF/6-31G(d) calculations[8a] on initial structures generated by CON-

Table 2: Hydrosilylation with various substrates.[a]

Entry	Ketone	Silane	Ligand	t [h]	Yield [%][b]
1	cyclohexanone	HSiEt$_3$	P(tm-tp)$_3$	21	81
2			P(tp)$_3$	21	36
3			PPh$_3$	21	13
4	cyclohexanone	HSiMePh$_2$	P(tm-tp)$_3$	20	97
5			P(tp)$_3$	20	37
6			PPh$_3$	20	27
7	acetophenone	HSiMe$_2$Ph	P(tm-tp)$_3$	5	96
8			P(tp)$_3$	5	15
9			PPh$_3$	5	15
10[c]	2-octanone	HSiMe$_2$Ph	P(tm-tp)$_3$	6	91
11[c]			P(tp)$_3$	6	41
12[c]			PPh$_3$	6	31
13	(−)-menthone	HSiMe$_2$Ph	P(tm-tp)$_3$	20	92 (45/55)[d]
14			P(tp)$_3$	20	8 (43/57)[d]
15			PPh$_3$	20	12 (38/62)[d]
16[e]	cyclohexanone	HSiMe$_2$Ph	P(tm-tp)$_3$	6	95
17[e]			P(tp)$_3$	6	65
18[e]			PPh$_3$	6	9

[a] Reaction conditions: ketone (1.0 mmol), silane (1.2 mmol), [{RhCl(C$_2$H$_4$)$_2$}$_2$] (0.0050 mmol), ligand (0.020 mmol), tridecane (0.25 mmol, as internal standard), benzene (1.0 mL), RT. [b] Yield of alcohol by GC after desilylation with HCl/MeOH. [c] At 50°C. [d] Product ratio (neomenthol/menthol). [e] [Rh(cod)$_2$]BF$_4$ (0.010 mmol) was used instead of [{RhCl(C$_2$H$_4$)$_2$}$_2$], in CH$_2$Cl$_2$ as solvent.

FLEX[8b]/MM3.[8c] They showed that P(tm-tp)$_3$ and P(tp)$_3$ both have nanosized bowl-shaped structures with the phosphorus atom at the bottom and diameters of 1.99 and 1.95 nm, respectively (Figure 1). The cone angles of P(tm-tp)$_3$ and P(tp)$_3$, determined for the optimized structures in Figure 1,
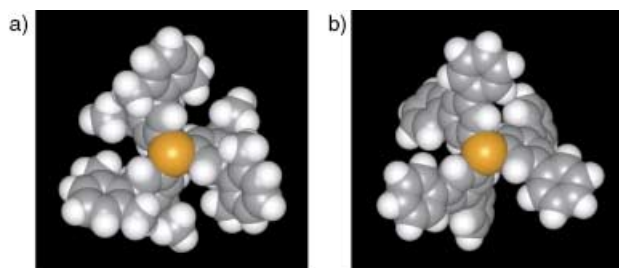
Figure 1. Optimized structures of a) P(tm-tp)$_3$ and b) P(tp)$_3$.

are 205 and 193°, respectively.[9a] Hence, they are more bulky than PCy$_3$ and PtBu$_3$, and less congested than P(o-tol)$_3$ and PMes$_3$.[9a] It is well-known that $^1J(^{31}P,^{77}Se)$ coupling constants of phosphane selenides Se=PR$_3$ are reliable measures of the basicity of the parent phosphane PR$_3$: larger coupling constants mean lower basicities.[10a–c] The $^1J(^{31}P,^{77}Se)$ coupling constants of Se=P(tm-tp)$_3$ and Se=P(tp)$_3$ of 769.7[10d] and 765.5 Hz,[10d] respectively, indicate that P(tm-tp)$_3$ and P(tp)$_3$ have comparable basicities. They are less basic than PPh$_3$ (735 Hz)[10b] and P(o-tol)$_3$ (732 Hz),[10d] and more basic than P(2-furyl)$_3$ (793 Hz).[10a]

Thus, the cone angles and basicities cannot explain the difference in reactivity between P(tm-tp)$_3$ and P(tp)$_3$. The most important difference between P(tm-tp)$_3$ and P(tp)$_3$ is the depth of the bowl: P(tm-tp)$_3$ (depth: 0.208 nm) is a much deeper bowl than P(tp)$_3$ (0.132 nm). The dihedral angles between the phosphanated phenyl ring (ring A) and the phenyl rings in the *meta* position (rings B) are 85.3 ± 0.5° for P(tm-tp)$_3$ and 44.7 ± 0.3° for P(tp)$_3$. This difference in dihedral angle alters the depth of the bowl.

While the mechanism of the rate enhancement is not completely understood, the high catalytic activity realized with P(tm-tp)$_3$ might be attributable to the prevalence of the monophosphane species. In rhodium-catalyzed hydrosilylation of alkenes, the rate of the reaction also increased in the order P/Rh = 3 < 2 < 1.[11] Bulky phosphanes such as PCy$_3$ and PtBu$_3$ are also known to afford low-coordinate species.[12] However, severe congestion around the phosphorus atom must lower the efficiency of ligands in the hydrosilylation reaction. In contrast, the deeper bowl-shaped P(tm-tp)$_3$ ensures substantial empty space around the phosphorus atom and, at the same time, is bulky enough to provide low-coordinate species (long-range steric effect). This unique bowl-shaped structure could facilitate the rate enhancement.

Further studies are now in progress to elucidate the mechanism of the acceleration and to explore the benefit of nanosized well-defined phosphane ligands in transition-metal-catalyzed reactions.

Experimental Section

Synthesis of P(tp)$_3$: n-Butyllithium (1.59 M in n-hexane, 0.982 mL, 1.56 mmol) was added to a solution of 5′-bromo-m-terphenyl[13] (0.482 g, 1.56 mmol) in THF (9 mL) at −78°C over 10 min. The solution was maintained at this temperature for an additional 1 h. Trichlorophosphane (0.071 g, 0.52 mmol) in toluene (1.4 mL) was added dropwise to the cooled solution over 15 min. The reaction mixture was further stirred at −78°C for 1.5 h, and at room temperature for 15 h. After evaporation of the solvent, toluene (8 mL) and water (3 mL) were added to the residue and the mixture was stirred vigorously. The organic layer was separated, and the aqueous layer was extracted with toluene (4×2 mL). The organic extracts were combined and dried over anhydrous MgSO$_4$, and then filtered through a glass filter under argon. The solvent was removed from the filtrate in vacuo to give a wet solid. Recrystallization of the residue from CHCl$_3$/MeOH (1/4) yielded white microfine crystals. Yield: 0.310 g, 83%. M.p. 219–220°C; FD-MS: m/z 718 [M^+]; ^{1}H NMR (400.13 Hz, CDCl$_3$, 23°C): δ = 7.83 (t, ^4J(H,H) = 1.5 Hz, 3 H; H2′), 7.75 (dd, ^3J(P,H) = 7.9 Hz, ^4J(H,H) = 1.5 Hz, 6 H; H4′,6′), 7.61–7.59 (m, 12 H; H2,2″,6,6″), 7.46–7.41 (m, 12 H; H3,3″5,5″), 7.37–7.33 ppm (m, 6 H; H4,4″); ^{13}C{^{1}H} NMR (100.61 Hz, CDCl$_3$, 23°C): δ = 142.0 (d, ^3J(C,P) = 7.2 Hz; C1′,3′), 140.7 (C1,1″), 138.0 (d, ^1J(C,P) = 11.5 Hz; C5′), 131.5 (d, ^2J(C,P) = 20.0 Hz; C4′,6′), 128.8 (C3,3″,5,5″), 127.6 (C4,4″), 127.3 (C2,2″,6,6″), 127.0 ppm (C2′); ^{31}P{^{1}H} NMR (161.98 Hz, CDCl$_3$, 23°C, H$_3$PO$_4$): δ = −2.0 ppm; elemental analysis (%) calcd for C$_{54}$H$_{39}$P: C 90.22, H 5.47; found: C 90.21, H 5.51.

General procedure for hydrosilylation of ketones (Tables 1 and 2): A typical reaction procedure is described for entry 1 in Table 1. [{RhCl(C$_2$H$_4$)$_2$}$_2$] (1.9 mg, 0.0050 mmol) and P(tm-tp)$_3$ (18 mg, 0.020 mmol) were placed in a 5-mL flask under argon. Anhydrous benzene (1.0 mL) was added by syringe, and then the mixture was stirred at room temperature in a water bath for 2 h. Cyclohexanone (98 mg, 1.0 mmol), tridecane (46 mg, 0.25 mmol), and dimethylphenylsilane (163 mg, 1.2 mmol) were then added by syringe. The reaction mixture was stirred at room temperature. Hydrolysis was performed by adding 1% HCl/MeOH, and yields of cyclohexanol

were determined by GC analysis relative to an internal standard (tridecane).

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