

Dehydrogenative Silylation of Ketones Catalyzed by Diphosphinidenecyclobutene-Coordinated Platinum(II) Complexes

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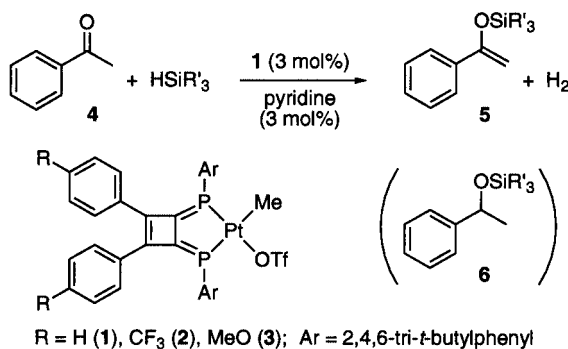
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Methylplatinum triflate coordinated with 1,2-diphenyl-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene serves as a highly selective catalyst for dehydrogenative silylation of ketones with HSiMe_2Ph in the presence of pyridine as a co-catalyst, giving silyl enol ethers in high yields.

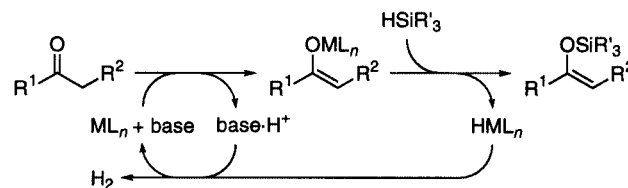
The coordination chemistry of sp^2 -hybridized phosphorus compounds has attracted a great deal of recent interest.¹ Unlike the sp^3 -hybridized phosphorus of tertiary phosphine ligands, the sp^2 -hybridized phosphorus has a marked propensity to engage in metal-to-phosphorus π -back-bonding and exhibits a strong π -acceptor property, comparable to carbonyl ligands. This feature should be useful in homogeneous catalysis. Recently, phospharomatic compounds such as phosphabenzene and phosphaferrrocene derivatives have been examined as the ligands of late transition metal catalysts.^{2,3} On the other hand, the use of the other sp^2 -hybridized phosphorus compounds in catalytic organic reactions has remained almost unexplored.⁴ We herein report that diphosphinidenecyclobutene-coordinated platinum complex **1** in Scheme 1 can be used as a highly selective catalyst for dehydrogenative silylation of ketones to give silyl enol ethers⁵ in high yields.



Scheme 1.

While ketones generally undergo hydrosilylation of carbonyl group in the presence of a transition metal catalyst, dehydrogenative silylation has also been documented in some instances.⁶ An early example of selective catalysis was reported by Sakurai et al. in 1977 using a mixed catalyst consisting of $\text{Co}_2(\text{CO})_8$ and pyridine, which converts a variety of ketones into the corresponding silyl enol ethers in high selectivities, except for acetophenone.^{6b} Selective conversion of acetophenone was accomplished later on by other research groups.^{6c,e} Although the catalytic mechanism has not been confirmed yet, a plausible explanation invokes the formation of a transition metal enolate, which subsequently reacts with hydrosilane to give silyl enol ether and a metal hydride

(Scheme 2). Since the enolate formation must be aided by π -acidic nature of transition metal complexes, we examined this catalysis using **1–3** with highly π -accepting ligands, 1,2-diaryl-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutenes.⁷



Scheme 2.

Complexes **1–3** were prepared by the reactions of the corresponding dimethyl complexes^{4b} with trifluoromethanesulfonic acid (HOTf) in Et_2O at room temperature and isolated as orange crystalline solids in 82–89% yields.⁸

Table 1 summarizes the results of catalytic dehydrogenative silylation of acetophenone (Scheme 1). All reactions were carried out at 50 °C without solvent. The use of pyridine as co-catalyst was of particular importance, otherwise the reaction was significantly slow.

Table 1. Catalytic dehydrogenative silylation of acetophenone^a

Run	Catalyst	HSiR'_3	Reaction time/h	Conversion/% ^b	Ratio ^b 5 : 6
1	1	HSiMe_2Ph	4.5	100	100 : 0
2	2	HSiMe_2Ph	2.5	100	98 : 2
3	3	HSiMe_2Ph	6	100	85 : 15
4	1	HSiEt_3	19	86	100 : 0
5	1	HSiMePh_2	26	76	100 : 0
6	1	HSi(OEt)_3	24	0	—

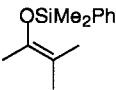
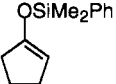
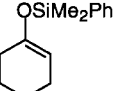
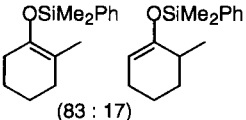
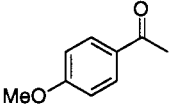
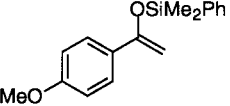
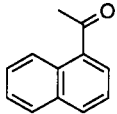
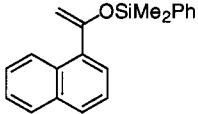
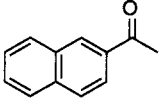
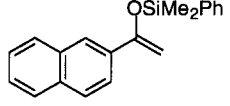
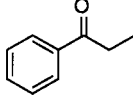
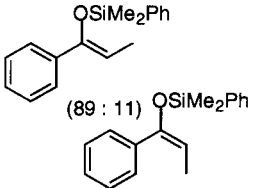
^aAll reactions were run at 50 °C using catalyst (3 mol%), pyridine (3 mol%), and hydrosilane (1.5 molar quantity) without solvent.

^bDetermined by GLC using anisole as an internal standard.

Complex **1** bearing non-substituted phenyl groups at the 1- and 2-positions of cyclobutene ring gave the best result, leading to silyl enol ether **5** in perfect selectivity (run 1). On the other hand, **2** and **3** having CF_3 and MeO substituents, respectively, formed hydrosilylation product **6** to some extent (runs 2, 3). Of hydrosilanes tested, HSiMe_2Ph showed the highest reactivity (run 1), whereas HSi(OEt)_3 was unreactive (run 6).

The present catalytic system consisting of **1**, pyridine, and HSiMe_2Ph was also effective towards a variety of ketones, giving silyl enol ethers in high yields (Table 2).

Table 2. Dehydrogenative silylation of ketones with HSiMe₂Ph catalyzed by **1**^a

Run	Ketone	Time/h	Product(s)	Yield/% ^b
1		9		89
2		6		92
3		11		100
4		6.5	 (83 : 17)	100
5		19		69 (86) ^c
6		8.5		97
7		25		75 (96) ^c
8		9.5	 (89 : 11)	100

^aAll reactions were run at 50 °C using **1** (3 mol%), pyridine (3 mol%), and HSiMe₂Ph (1.3–1.5 molar quantity) without solvent; except for runs 5 and 7, which were performed in toluene.

^bDetermined by GLC using anisole as an internal standard. ^cThe value in parentheses is conversion yield.

Highly electron-deficient nature of **1** is reflected in the NMR data for its ethylene-coordinated derivative [PtMe(C₂H₄)(P–P)]⁺. This complex shows the ¹H and ¹³C NMR signals of ethylene ligand at δ 5.11 (t, *J*_{PH} = 5.1 Hz, *J*_{PH} = 57.1 Hz) and 89.7 (d, *J*_{PC} = 13 Hz, *J*_{PC} = 103 Hz), respectively (CD₂Cl₂). These chemical shifts are significantly lower than

those of structurally analogous diimine complexes [PtMe(C₂H₄)(diimine)]⁺ (δ_H = 3.68–3.72, δ_C = 72.2–74.0).⁹ Thus the ¹H NMR signal is rather close to that of free ethylene (δ 5.30), and the ¹³C NMR value falls under the category of the lowest chemical shifts of platinum–ethylene complexes.¹⁰

In conclusion, we have found a highly selective catalyst (**1**) for dehydrogenative silylation of ketones. The reactions can be conducted without solvent when the substrate ketone is liquid, and dihydrogen gas is the sole by-product. Accordingly, extremely clean and simple reaction systems for synthesizing silyl enol ethers have been realized. The high-performance of **1** may be attributed to highly π-acidic nature of the platinum center, which is provided by the coordination with the sp²-hybridized phosphorus ligand.

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Dedicated to Professor Hideki Sakurai on the occasion of his 70th birthday.

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- Selected NMR data for **1** (CDCl₃, 20 °C). ¹H NMR: δ 1.06 (dd, *J*_{PH} = 2.7, 9.9 Hz, 3H, PtMe), 1.42, 1.44, 1.63, 1.66, 1.66 (each s, each 9H, *t*-Bu), 6.79 (d, *J*_{HH} = 7.5 Hz, 2H, *o*-Ph), 6.83 (d, *J*_{HH} = 8.4 Hz, 2H, *o*-Ph), 6.91 (t, *J*_{HH} = 8.1 Hz, 4H, *m*-Ph), 7.17 (t, *J*_{HH} = 7.2 Hz, 1H, *p*-Ph), 7.19 (t, *J*_{HH} = 7.2 Hz, 1H, *p*-Ph), 7.53 (d, *J*_{PH} = 2.7 Hz, 2H, PAr), 7.65 (d, *J*_{PH} = 4.2 Hz, 2H, PAr). ¹³C{¹H} NMR: δ 5.0 (dd, *J*_{PC} = 101, 6 Hz, *J*_{PC} = 545 Hz, PtMe), 149.3 (dd, *J*_{PC} = 59, 33 Hz, P=C), 151.7 (dd, *J*_{PC} = 54, 27 Hz, P=C), 162.2 (dd, *J*_{PC} = 92, 25 Hz, P=C-C), 166.3 (dd, *J*_{PC} = 48, 5 Hz, P=C-C). ³¹P{¹H} NMR: δ 98.1 (d, *J*_{PP} = 14 Hz, *J*_{PtP} = 6819 Hz), 186.2 (d, *J*_{PP} = 14 Hz, *J*_{PtP} = 1618 Hz). Anal. Calcd for C₅₄H₇₁F₃O₃P₂SPt: C, 58.21; H, 6.42%. Found: C, 57.99; H, 6.48%.
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