Unusual Metal-Dependent Acceleration and Deceleration in the Metal-Catalyzed Hydrosilylation of Olefin Using Pyridyldimethylsilanes

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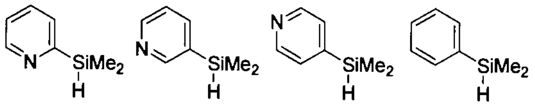
The Rh- and Pt-catalyzed hydrosilylations of olefin utilizing 2-pyridyl-, 3-pyridyl-, 4-pyridyl-, and phenyldimethylsilane are described. Whereas huge rate acceleration was observed with 2-$PyMe_2SiH$ in the Rh-catalyzed reaction, huge rate deceleration was observed with 2-$PyMe_2SiH$ and 4-$PyMe_2SiH$ in the Pt-catalyzed reaction.

The metal-catalyzed hydrosilylation of carbon–carbon unsaturated molecules has proved to be an extremely valuable tool for the carbon–silicon bond formation by virtue of its high regio- and stereoselectivities.[1] Although there are many factors governing the hydrosilylation, most of the works in this area were devoted to a catalyst tuning for controlling the reactivity and selectivity of the reaction. We envisioned that the reactivity- and selectivity-control might possibly be achieved by appending the secondary interaction moiety on the hydrosilane scaffold. During the course of our program utilizing a 2-pyridyldimethylsilyl (2-$PyMe_2Si$) group in metal-catalyzed processes,[2–4] we have found that 2-$PyMe_2SiH$ behaves quite different from other related hydrosilanes such as 3-$PyMe_2SiH$, 4-$PyMe_2SiH$, and $PhMe_2SiH$ in hydrosilylation reaction.[5]



We first examined the hydrosilylation of 1-octene with 2-$PyMe_2SiH$, 3-$PyMe_2SiH$, 4-$PyMe_2SiH$, and $PhMe_2SiH$ in the presence of $RhCl(PPh_3)_3$ (5 mol%) in CH_3CN. The mixture was stirred at 28 °C for 15 min to 2 h and the yield of hydrosilylated product was determined by GC analysis (Figure 1). The hydrosilylation using 2-$PyMe_2SiH$ completed within 30 min. On the other hand, hydrosilylation was extremely slow when using 3-$PyMe_2SiH$, 4-$PyMe_2SiH$, or $PhMe_2SiH$. We also subjected other olefins and found that the reactivity trend (2-$PyMe_2SiH$ >> 3-$PyMe_2SiH$, 4-$PyMe_2SiH$, $PhMe_2SiH$) was a universal phenomenon for the Rh-catalyzed olefin hydrosilylation.[6]

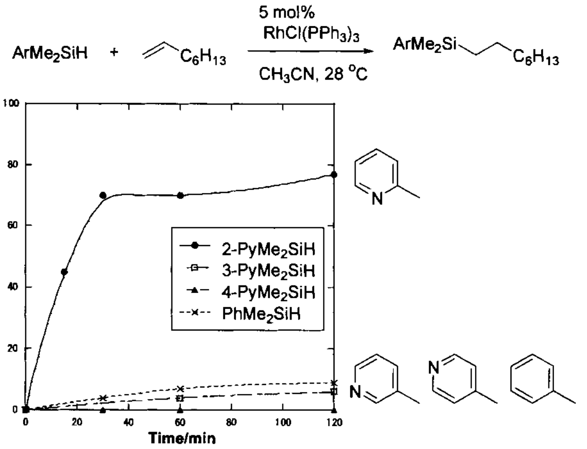


Figure 1. Rh-catalyzed hydrosilylation of 1-octene.

Next, we examined the hydrosilylation of 1-octene with 2-$PyMe_2SiH$, 3-$PyMe_2SiH$, 4-$PyMe_2SiH$, and $PhMe_2SiH$ in the presence of $Pt[(CH_2{=}CHSiMe_2)_2O]$ (1 mol%) and PPh_3 (1 mol%) in EtCN. The mixture was stirred at 80 °C for 30 min to 2 h and the yield of hydrosilylated product was determined by GC analysis (Figure 2). Quite interestingly, the reactivity trend was completely different from that observed in the Rh-catalyzed reaction. Whereas the hydrosilylation using 3-$PyMe_2SiH$ and $PhMe_2SiH$ proceeded smoothly, the hydrosilylation was much slower when using 2-$PyMe_2SiH$ and 4-$PyMe_2SiH$ (Figure 2).

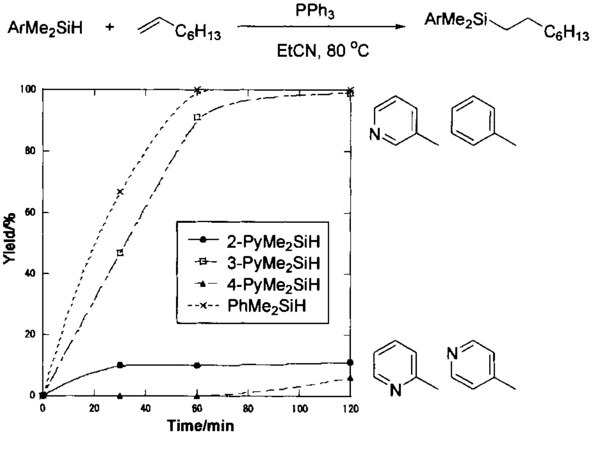
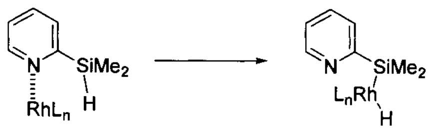


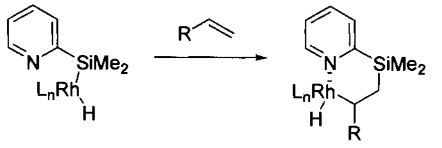
Figure 2. Pt-catalyzed hydrosilylation of 1-octene.

The mechanistic rationale for this unusual metal-dependent acceleration and deceleration is of special interest. In the case of Rh-catalyzed hydrosilylation, the electronic nature of 2-$PyMe_2SiH$ cannot be a decisive factor for its high reactivity since none of 3-$PyMe_2SiH$, 4-$PyMe_2SiH$, or $PhMe_2SiH$ rivals 2-$PyMe_2SiH$ in terms of reactivity. The coordination of the pyridyl group on silicon might have some accelerating effects at a certain stage of the reaction. Previously,[5] we presumed that the acceleration might be attributed to the facile oxidative addition of Si–H to Rh based on the pre-coordination effect (Scheme 1, a).[7] Alternatively, it may be also plausible to surmise that the pyridyl group on silicon coordinates to the catalyst rhodium after the insertion of olefin thereby stabilizing the olefin-inserted intermediate (Scheme 1, b). This coordination might enhance the olefin insertion process that has been theoretically uncovered as the rate-determining step in the Rh-catalyzed hydrosilylation of ethylene.[8] Noteworthy is that the latter coordination effect (Scheme 1, b) can only be expected in Rh-catalyzed reaction where the olefin insertion takes place to Rh–Si bond (Figure 3).[9]

(a) Coordination-Induced Facile Oxidative Addition



(b) Coordination-Induced Facile Olefin Insertion



Scheme 1.

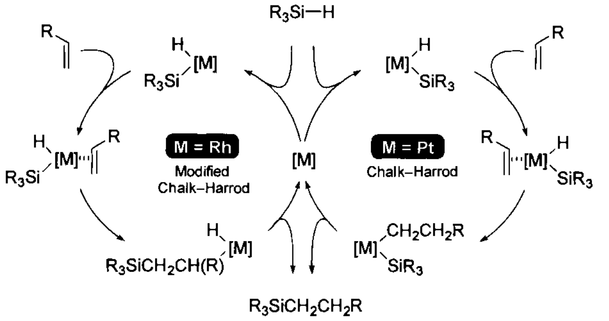
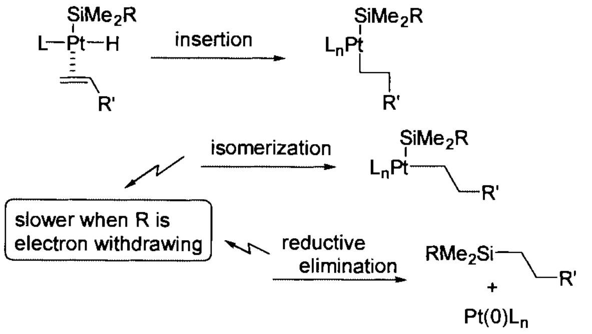


Figure 3. The Chalk–Harrod and modified Chalk–Harrod mechanism for the metal-catalyzed hydrosilylation of olefin.

In the case of Pt-catalyzed hydrosilylation, electronic effect of aryl group on silicon should have played the key role since the rate deceleration was observed with 2-$PyMe_2SiH$ and 4-$PyMe_2SiH$. It is well known that 2-pyridyl and 4-pyridyl groups are better electron-withdrawing groups than 3-pyridyl and phenyl groups because of resonance-oriented reason.

Sakaki recently determined by theoretical calculations that Pt-catalyzed hydrosilylation proceeds with the Chalk–Harrod mechanism (Figure 3)[10] and the overall rate is determined by the isomerization of olefin-inserted intermediate and subsequent reductive elimination.[11] According to their report, the isomerization of olefin-inserted intermediate occurs readily when the silyl group exhibits strong trans influence. Eaborn has reported that the trans influence of silyl group becomes weaker when electron-withdrawing group is attached on silicon.[12] Thus, 2-pyridyl and 4-pyridyl groups on silicon are expected to decelerate the isomerization step (Scheme 2).



Scheme 2.

Electronic properties of silyl groups might have influenced on the reductive elimination step as well. Ozawa has reported that the reductive elimination from (alkyl)(silyl)platinum complex is slower when electron-withdrawing group is attached on silicon.[13] Sakaki also observed the same trend in the theoretical calculations.[10] Therefore, one might expect that the reductive elimination is slower when 2-pyridyl and 4-pyridyl groups, which are better electron-withdrawing groups than 3-pyridyl or phenyl group, are attached on silicon. However, since there are many factors governing this elemental step,[14] it is impossible to conclude any clear rationale at this stage.

In summary, unusual metal-dependent acceleration and deceleration were observed in the Rh- and Pt-catalyzed hydrosilylation of olefins using pyridyldimethylsilanes. Although further investigation is needed to settle the precise mechanism, the present study clearly implies the alternative controlling factors in the hydrosilylation chemistry.

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

References

1 B. Marciniec, “Comprehensive Handbook on Hydrosilylation,” Pergamon Press, Oxford (1992).
2 K. Itami, K. Mitsudo, T. Kamei, T. Koike, T. Nokami, and J. Yoshida, *J. Am. Chem. Soc.*, **122**, 12013 (2000).
3 K. Itami, T. Nokami, and J. Yoshida, *J. Am. Chem. Soc.*, **123**, 5600 (2001).
4 K. Itami, T. Koike, and J. Yoshida, *J. Am. Chem. Soc.*, **123**, 6957 (2001).
5 J. Yoshida, K. Itami, K. Mitsudo, and S. Suga, *Tetrahedron Lett.*, **40**, 3403 (1999).
6 Other than simple olefins, vinylsilane also underwent hydrosilylation in a similar reactivity trend.
7 a) M. J. Auburn, R. D. Holmes-Smith, and S. R. Stobart, *J. Am. Chem. Soc.*, **106**, 1314 (1984). b) P. I. Djurovich, A. L. Safir, N. L. Keder, and R. J. Watts, *Inorg. Chem.*, **31**, 3195 (1992).
8 S. Sakaki, M. Sumimoto, M. Fukuhara, and M. Sugimoto, 46th Symposium on Organometallic Chemistry, Osaka, September, 1999; Abstr., No. A111.
9 a) M. A. Schroeder and M. S. Wrighton, *J. Organomet. Chem.*, **128**, 345 (1977). b) A. Millan, E. Towns, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, **1981**, 673. c) I. Ojima, T. Fuchikami, and M. Yatabe, *J. Organomet. Chem.*, **260**, 335 (1984). d) C. L. Randolph and M. S. Wrighton, *J. Am. Chem. Soc.*, **108**, 3366 (1986).
10 A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 16 (1965).
11 a) S. Sakaki, N. Mizoe, and M. Sugimoto, *Organometallics*, **17**, 2510 (1998). b) S. Sakaki, N. Mizoe, M. Sugimoto, and Y. Musashi, *Coord. Chem. Rev.*, **192**, 933 (1999).
12 J. Chatt, C. Eaborn, S. D. Ibekwe, and P. N. Kapoor, *J. Chem. Soc., Sect. A*, **1970**, 1343.
13 F. Ozawa, *J. Organomet. Chem.*, **611**, 332 (2000).
14 For an example, see: K. Hasebe, J. Kamite, T. Mori, H. Katayama, and F. Ozawa, *Organometallics*, **19**, 2022 (2000).