

Cationic Silane σ -Complexes of Ruthenium with Relevance to Catalysis

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Silane σ -complexes attract a lot of attention as possible intermediates in metal catalyzed transformations of organosilanes, although only in a few instances their involvement in catalytic process has been established directly.¹ Most of the isolated silane σ -complexes are neutral species met in η^2 - or η^3 -coordination modes.² In contrast, isolable cationic silanes σ -complexes are very rare,^{3,4} and virtually nothing is known about substituent effects on the Si–H interaction in these species.

We have recently reported carbonyl hydrosilylation catalyzed by the iron complex [Cp(Me₂PrP)Fe(NCMe)₂]⁺ (**1**).⁵ Thinking that the analogous ruthenium chemistry will be more effective due to the larger size of the metal, we opted to study the catalytic chemistry of compounds [Cp(R₃P)Ru(NCMe)₂]⁺. This led us to the discovery of a series of surprisingly stable cationic silane σ -complexes which exhibit unexpected substituent effects.

The compound [Cp(Prⁱ₃P)Ru(NCMe)₂]⁺BAF[−] (**2**, BAF = B(C₆H₅)₄) has been found to catalyze a variety of hydrosilylation reactions under mild conditions and more effectively than **1**.⁶ Rewardingly, the corresponding BF₄[−] derivative (**2'**) showed a very similar catalytic activity and due to its lower cost is a preferable catalyst. Of several silanes screened in the hydrosilylation of benzaldehyde, the fastest rate was observed for HSiMe₂Ph (Table 1). Hydrosilylation of ketones is sluggish (entries 2–4) and does not reach completion for bulkier ketones (entries 3–4). Noteworthy, complex **2** also catalyzes the hydrosilylation of ethyl acetate (entry 5), which is known to be a very inert substrate.^{7,8,9b} In spite of this, the reaction with benzoic acid (entry 6) stops at the silyl ester. Fast silane alcoholysis (entries 7–10), aminolysis (entry 11),¹⁰ and hydrolysis (entry 12) were observed.¹¹ Slow catalytic dehalogenation of CDCl₃ by HSiMe₂Ph also takes place.¹² In contrast, CH₂Cl₂ and chlorobenzene proved unreactive.

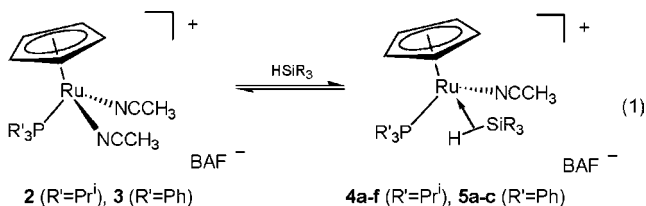
To establish the mechanism of hydrosilylation, stoichiometric reactions were attempted. EXSY NMR showed fast exchange between coordinated and free nitrile, suggesting that NCMe dissociation is a reasonable first step. There is no coordination of carbonyl substrates even when the reaction is monitored in neat carbonyl. In contrast, reactions of **2** and its PPh₃ analogue, [Cp(Ph₃P)Ru(NCMe)₂]⁺BAF[−], with silanes easily give silane σ -complexes [Cp(R₃P)Ru(NCMe)(η^2 -HSiR₃)]⁺ (**4** and **5** in eq 1; R₃ = Cl₃ (**a**), MeCl₂ (**b**), Me₂Cl (**c**), H₂Ph (**d**), HMePh (**e**), PhMe₂ (**f**)). Compounds **4** and **5** were characterized by NMR and IR spectroscopy. The stability of these species is significantly reduced in comparison with related neutral compounds Cp(Prⁱ₃P)Ru(Cl)(η^2 -HSiR₃) (**6**).¹³ Nevertheless, complexes **4a** (R = SiCl₃) and **4b** (R = SiMeCl₂) are remarkably stable, surviving several days in CDCl₃ solutions. For less stable derivatives the NMR spectra were recorded in neat silane.

To evaluate the extent of Si–H activation by the cationic Ru center, Si–H coupling constants were measured from the ²⁹Si

Table 1. Hydrosilylation and Coupling Reactions Catalyzed by **2**^a

	Substrate	Silane	Time	Conv.	Products
1	PhC(O)H	HSiMe ₂ Ph	30 min	100%	PhCH ₂ OSiMe ₂ Ph
		HSiEt ₃	36 h,	82%	PhCH ₂ OSiEt ₃
			50 °C		
		H ₂ SiMePh	20 h	100%	PhCH ₂ OSiHMePh
		H ₃ SiPh	4 h	60%	PhCH ₂ OSiH ₂ Ph +
			20 h	99%	(PhCH ₂ O) ₂ SiHPh
2	Cyclohexanone	HSiMe ₂ Ph	18 h	100%	C ₆ H ₁₁ OSiMe ₂ Ph
3	PhC(O)Me	HSiMe ₂ Ph	24 h	30%	PhCH(OSiMe ₂ Ph)Me
4	MeC(O)Et	HSiMe ₂ Ph	24 h	11%	<i>s</i> -BuOSiMe ₂ Ph
5	MeC(O)OEt	HSiMe ₂ Ph	24 h	100%	EtOSiMe ₂ Ph
6	PhCOOH	HSiMe ₂ Ph	20 min	100%	PhCOOSiMe ₂ Ph
7	EtOH	HSiMe ₂ Ph	5 min	100%	EtOSiMe ₂ Ph
		HSiEt ₃	50 h	100%	EtOSiEt ₃
8	<i>i</i> -PrOH	HSiMe ₂ Ph	30 min	100%	<i>i</i> -PrOSiMe ₂ Ph
9	<i>t</i> -BuOH	HSiMe ₂ Ph	1 h	100%	<i>t</i> -BuOSiMe ₂ Ph
10	PhOH	HSiMe ₂ Ph	30 min	100%	PhOSiMe ₂ Ph
11	PhNH ₂	HSiMe ₂ Ph	10 min	100%	PhNHSiMe ₂ Ph
12	H ₂ O	HSiMe ₂ Ph	10 min	100%	HOSiMe ₂ Ph + O(SiMe ₂ Ph) ₂

^a Catalyst load 3–5%, substrate/silane ratio 1:1, room temperature, CDCl₃.



satellites in the ¹H NMR spectra (Table 2). Unexpectedly, the *J*(Si–H) values showed a V-type dependence on the electron-withdrawing ability of the SiR₃ group, first decreasing from 53 Hz for R₃ = Cl₃ to 45 Hz for R₃ = ClMe₂ and then increasing to 50 Hz for R₃ = Me₂Ph. The reduced stability of **4** and unusual behavior of their Si–H coupling constants suggests significantly reduced back-donation from the cationic Ru center,² so that the variation of *J*(Si–H) is mainly affected by the change of hybridization at Si.^{2a,14} For comparison, in neutral complexes **6** the *J*(Si–H) shows the opposite trend.¹³ The PPh₃ derivatives **5** are more labile and demonstrate increased *J*(Si–H) values in comparison with their Prⁱ₃P analogues, signifying a further decrease of back-donation from the less electron-rich metal.

A DFT study of complexes **4** revealed η^2 -silane coordination without any Si...N interligand interactions.¹⁵ The calculated Si–H coupling constants, although systematically lower (Table 2), correlate well with experimental values.¹⁶ Surprisingly, there is no direct correlation between the magnitude of Si–H coupling and the Si–H distance: complex **4g** having the shortest Si–H bond (1.898 Å) shows almost the same calculated *J*(Si–H) as that for

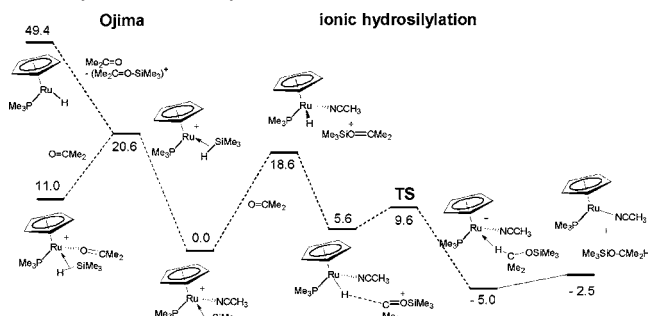
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Table 2. Experimental and Calculated $J(\text{Si}-\text{H})$ Values (in Hz) and Calculated $\text{Si}-\text{H}$ Bond Lengths (in Å) for Silane σ -Complexes **4**–**6**

	a	b	c	d	e	f
4 (exp.)	53	45	45	48	48	50
(calc.)	-34.8	-19.9	-17.8			-33.2 ^a
5	59	48	47	–	–	–
6	33	45	50	39	–	46
Si–H	1.996	1.980	1.947	–	–	1.898 ^a

^a Calculated data for complex **4g** with $\text{R}_3 = \text{Me}_3$.

Scheme 1. Ionic Hydrosilylation and Dissociative Ojima-Type Pathways Calculated by DFT^a



^a Gibbs energies are given in $\text{kcal}\cdot\text{mol}^{-1}$.²¹

complex **4a** with the longest Si–H bond (1.996 Å). The rationale for this anomaly is that the Si–H bond in **4a**, although more activated than that in **4g**, has increased Si 3s character. Previously, such unusually increased Si–H coupling has been found only in complexes with interligand hypervalent interactions and agostic Si–H bonds.¹⁷

¹H EXSY spectra of complexes **4** do not show any exchange with free nitrile. However, a reaction of **4b** with 15 equiv of acetone leads to the bis(nitrile) **2** and a new labile mono(phosphine) silane σ -complex ($J(\text{H}-\text{Si}) = 40$ Hz), which may suggest a usual Ojima type mechanism of hydrosilylation based on nitrile dissociation, η^2 -carbonyl coordination, and silyl migration.¹⁸ However, DFT COSMO calculations taking into account solvent effects show that acetone addition to $[\text{Cp}(\text{Me}_3\text{P})\text{Ru}(\eta^2\text{-HSiMe}_3)]^+$ gives only the η^1 -O=CMe₂ derivative $[\text{Cp}(\text{Me}_3\text{P})\text{Ru}(\eta^2\text{-HSiMe}_3)(\eta^1\text{-OCMe}_2)]^+$ which resists silyl migration to the oxygen atom. For an alternative mechanism, the ionic hydrosilylation (Scheme 1),^{8,19} we found that direct Me_3Si^+ transfer to the carbonyl is the rate-determining step ($\Delta^\ddagger G^\circ_{298} = 18.6$ $\text{kcal}\cdot\text{mol}^{-1}$). This is followed by a low-barrier ($\Delta^\ddagger G^\circ_{298} = 4$ $\text{kcal}\cdot\text{mol}^{-1}$) hydride transfer from $\text{Cp}(\text{Me}_3\text{P})\text{Ru}(\text{NCMe})(\text{H})$ to $[\text{Me}_2\text{C}=\text{O}-\text{SiMe}_3]^+$ to form the σ -complex $\text{Cp}(\text{Me}_3\text{P})\text{Ru}(\text{NCMe})(\eta^1\text{-H}-\text{CMe}_2-\text{O}-\text{SiMe}_3)^+$, which easily dissociates $\text{Me}_2\text{HC}-\text{OSiMe}_3$. Similar pathways were suggested for borane-catalyzed hydrosilylation,^{9a} for dialkyl ether cleavage with silanes mediated by a cationic Ir complex,^{1b} and for silane alcoholysis on electrophilic metal centers.²⁰

Further support for this mechanistic proposal was found in the dependence of silane alcoholysis on the nucleophilicity of alcohol (Table 1, entries 7–10) suggesting that alcohol attack on the silane ligand in **4f** is the rate-determining step.

In conclusion, we found evidence that hydrosilylation of carbonyl substrates catalyzed by **2** goes via intermediate formation of cationic silane σ -complexes **4** and **5**, whose Si–H coupling constants suggest significantly reduced back-donation from the cationic ruthenium center in comparison with neutral analogues. DFT studies of the mechanism of hydrosilylation favored a reaction pathway based

on silylium ion abstraction in **4**, by a carbonyl substrate followed by hydride transfer to the silyloxy carbenium ion.

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Supporting Information Available: Experimental and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Lachaize, S.; Sabo-Etienne, S.; Donnadieu, B.; Chaudret, B. *Chem. Commun.* **2003**, 214. (b) Yang, J.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2008**, *130*, 17509.
- (2) (a) Nikonov, G. I. *Adv. Organomet. Chem.* **2005**, *53*, 217–309. (b) Lin, Z. *Chem. Soc. Rev.* **2002**, *31*, 239. (c) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175. (d) Kubas, G. J. *Metal Dihydrogen and σ -Bond Complexes*; Kluwer Academic/Plenum: New York, 2001. (e) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789.
- (3) Labile, NMR characterized: (a) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527. (b) Huhmann-Vincent, J.; Scott, B. L.; Kubas, G. J. *Inorg. Chim. Acta* **1999**, *294*, 240. (c) Scharer, E.; Chang, S.; Brookhart, M. *Organometallics* **1995**, *14*, 5686. (d) Fang, X.; Huhmann-Vincent, J.; Scott, B. L.; Kubas, G. J. *J. Organomet. Chem.* **2000**, *609*, 95. (e) Fang, X.; Scott, B. L.; John, K. D.; Kubas, G. J. *Organometallics* **2000**, *19*, 4141.
- (4) Isolated, X-ray characterized: (a) Freeman, S. T. N.; Lemke, F. R.; Brammer, L. *Organometallics* **2002**, *21*, 2030. (b) Yang, J.; White, P. S.; Schauer, C. K.; Brookhart, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4141.
- (5) Gutsulyak, D. V.; Kuzmina, L. G.; Howard, J. A. K.; Vyboishchikov, S. F.; Nikonov, G. I. *J. Am. Chem. Soc.* **2008**, *130*, 3732.
- (6) For recent reviews on hydrosilylation of carbonyls, see: (a) Carpentier, J.-F.; Bette, V. *Curr. Org. Chem.* **2002**, *6*, 913. (b) Riant, O.; Mosterfaï, N.; Courmarcel, J. *Synthesis* **2004**, *18*, 2943.
- (7) For hydrosilylation of esters, see: (a) Mao, Z.; Gregg, B. T.; Cutler, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 10139. (b) Ojima, I.; Kogure, T.; Kumagai, M. *J. Org. Chem.* **1977**, *42*, 1671. (c) Igarashi, M.; Mizuno, R.; Fuchikami, T. *Tetrahedron Lett.* **2001**, *42*, 2149. (d) Berc, S. C.; Kreutzer, K. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 5093. (e) Berc, S. C.; Buchwald, S. L. *J. Org. Chem.* **1992**, *57*, 3751.
- (8) Dioumaev, V. K.; Bullock, R. M. *Nature* **2003**, *424*, 530.
- (9) For metal-free reactions with a similar mechanism, see: (a) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090. (b) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440. (c) Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 6179. (d) Scott, V. J.; Celenligil-Cetin, R.; Ozerov, O. V. *J. Am. Chem. Soc.* **2005**, *127*, 2852.
- (10) For dehydrogenative coupling of silanes with amines and ammonia, see: (a) Nametkin, N. S.; Chernysheva, T. I.; Gevenyan, M. L.; Lashenko, I. N.; Pritula, N. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, *10*, 2230. (b) Wang, W. D.; Eisenberg, R. *Organometallics* **1991**, *10*, 2222. (c) Biran, C.; Blum, Y. D.; Glaser, R.; Tse, D. S.; Youngdahl, K. A.; Laine, R. M. *J. Mol. Catal.* **1988**, *48*, 183. (d) Blum, Y.; Laine, R. M. *Organometallics* **1986**, *5*, 2081. (e) Kono, H.; Ojima, I. *Org. Prep. Proc. Int.* **1973**, *5*, 135.
- (11) For the coupling of silanes with water as a source of H₂, see: (a) Ison, E. A.; Corbin, R. A.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 11938. (b) Corbin, R. A.; Ison, E. A.; Abu-Omar, M. M. *Dalton Trans.* **2009**, 2850.
- (12) For selected examples of catalytic dehalogenation of haloalkanes and arenes by hydrosilanes, see: (a) Yang, J.; Brookhart, M. *Adv. Synth. Catal.* **2009**, *351*, 175. (b) Karstedt, D.; Bell, A. T.; Tilley, T. D. *Organometallics* **2006**, *25*, 4471. (c) Petersen, A. A.; McNeill, K. *Organometallics* **2006**, *25*, 4938. (d) Esteruelas, M. A.; Herrero, J.; Oliván, M. *Organometallics* **2004**, *23*, 3891, and references therein.
- (13) Gutsulyak, D. V.; Kuzmina, L. G.; Howard, J. A. K.; Vyboishchikov, S. F.; Nikonov, G. I. *Organometallics* **2009**, *28*, 2655.
- (14) This trend can be rationalized in terms of a combination of reduced back-donation from metal and reduced Si 3s character in the Si–H bond in the less chlorinated species.
- (15) Significant Si···Cl bonding was found in neutral complexes **6** (ref 13).
- (16) Experimental Si–H coupling constants are given in absolute values, calculated $J(\text{H}-\text{Si})$ are negative due to negative gyromagnetic ratio of Si.
- (17) (a) Dubberley, S. R.; Ignatov, S. K.; Rees, N. H.; Razuvaev, A. G.; Mountford, P.; Nikonov, G. I. *J. Am. Chem. Soc.* **2003**, *125*, 644. (b) Ignatov, S. K.; Rees, N. H.; Tyrrell, B. R.; Dubberley, S. R.; Razuvaev, A. G.; Mountford, P.; Nikonov, G. I. *Chem.-Eur. J.* **2004**, *10*, 4991.
- (18) (a) Ojima, I.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Sato, T. *J. Organomet. Chem.* **1976**, *122*, 83. (b) Ojima, I. *The Hydrosilylation Reaction. In The Chemistry of Organic Silicon Compounds*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 25.
- (19) Du, G.; Fanwick, P. E.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2005**, *129*, 5180.
- (20) (a) Kubas, G. J. *Adv. Inorg. Chem.* **2005**, *56*, 127. (b) Bühl, M.; Mauschick, F. T. *Organometallics* **2003**, *22*, 1422.
- (21) For a slightly more elaborated scheme, see Supporting Information.

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