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Cationic Silane *o*-Complexes of Ruthenium with Relevance to Catalysis

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

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 $[Cp(Me_2PrP)Fe(NCMe)_2]^+$ (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 $[Cp(R_3P)Ru(NCMe)_2]^+$. This led us to the discovery of a series of surprisingly stable cationic silane σ -complexes which exhibit unexpected substituent effects.

The compound $[Cp(Pr_{3}^{i}P)Ru(NCMe)_{2}]^{+}BAF^{-}$ (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 BF_4^- 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, $[Cp(Ph_3P)Ru(NCMe)_2]^+BAF^-$, with silanes easily give silane σ -complexes [Cp(R'₃P)Ru(NCMe)(η^2 -HSiR₃)]⁺ (4 and 5 in eq 1; $R_3 = Cl_3$ (a), $MeCl_2$ (b), Me_2Cl (c), H_2Ph (d), HMePh (e), $PhMe_2$ (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 $Cp(Pr_{3}^{i}P)Ru(Cl)(\eta^{2} HSiR_3$) (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 29 Si

	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%	s-BuOSiMe ₂ Ph
5	MeC(O)OEt	HSiMe ₂ Ph	24 h	100%	EtOSiMe ₂ Ph
				(silane)	
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-PrOSiMe2Ph
9	t-BuOH	HSiMe ₂ Ph	1 h	100%	t-BuOSiMe2Ph
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_2O	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 electronwithdrawing 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 Calc	ulated J	(Si-H)	Values ((in Hz)	and
Calculate	ed Śi−H Bond	Lengths	(in Å) fo	r Silane	ο-Com	plexes	4-6

	а	b	с	d	е	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 $R_3 = Me_3$.

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



^{*a*} Gibbs energies are given in kcal·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(H-Si) = 40 Hz), which may suggest a usual Ojima type mechanism of hydrosilylation based on nitrile dissociation, η^2 -carbonyl coordination, and silvl migration.¹⁸ However, DFT COSMO calculations taking into account solvent effects show that acetone addition to $[Cp(Me_3P)Ru(\eta^2-HSiMe_3)]^+$ gives only the η^1 -O=CMe₂ derivative $[Cp(Me_3P)Ru(\eta^2-HSiMe_3)(\eta^1-OCMe_2)]^+$ which resists silvl migration to the oxygen atom. For an alternative mechanism, the ionic hydrosilylation (Scheme 1),^{8,19} we found that direct Me₃Si⁺ 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 Cp(Me₃P)Ru(NCMe)(H) to $[Me_2C-O-SiMe_3]^+$ to form the σ -complex Cp(Me₃P)Ru(NCMe)(η^{1} -H-CMe₂-O-SiMe₃)⁺, which easily dissociates Me₂HC-OSiMe₃. 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 silvlium ion abstraction in 4, by a carbonyl substrate followed by hydride transfer to the silvloxy 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.

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