ORGANOMETALLICS

Controlled Hydrosilylation of Carbonyls and Imines Catalyzed by a Cationic Aluminum Alkyl Complex

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Supporting Information

ABSTRACT: The synthesis, characterization, and unprecedented catalytic activity of cationic aluminum alkyl complexes toward hydrosilylation are described. X-ray crystallographic analysis of Tp^*AlMe_2 (1) and $[Tp^*AlMe][I_3]$ (3) revealed the preference of Al for a tetrahedral coordination environment and the versatility of the Tp^* ligand in stabilizing Al in bi- and tridentate coordination modes. $[Tp^*AlMe][MeB(C_{L}F_{c})_{2}]$ (2)



tridentate coordination modes. $[Tp*AlMe][MeB(C_6F_5)_3]$ (2) is highly active toward the hydrosilylation of a wide variety of carbonyls and imines, thus providing an inexpensive and versatile alternative to late transition metal catalysts.

The direct formation of silyl-protected alcohols via reduction of carbonyls, also known as hydrosilylation, is an exceptionally useful reaction and has therefore become an important synthetic tool in organic chemistry.¹ Few chemical transformations have received a comparable amount of attention, and thus a plethora of catalysts with high activities have been reported. Examples of active catalysts span the entire transition metal series, some of which have been highly refined to achieve extraordinary turnover numbers and unmatched potential for asymmetric synthesis.²

Although noble metals have excelled in this chemistry, recent interest has shifted toward catalyst systems based on inexpensive and readily available metals such as iron.³ Recent reports of a simple yet highly effective Fe amide catalyst show the potential of such approaches while eliminating the need for extensive ligand synthesis.⁴ Examples of active catalysts based on main group elements have lagged behind their transition metal counterparts, although some systems based on remarkably simple Lewis acids such as $B(C_6F_5)_3$ have recently been documented.⁵ The homoleptic and typically monodentate ligation of such species, however, does not allow for significant reactivity control and thus limits their synthetic utility. Despite the Lewis acidic character of Al, few Al-based catalysts have been shown to participate in productive hydrosilylation chemistry, with most examples limited to alkynes and strained cyclic substrates.⁶ A significant challenge using such Lewis acid catalysts is the typically difficult reaction control, often resulting in complex product mixtures. Partially masking the reactivity by using bulky ligands can alleviate some of the mentioned issues, although typically at the expense of catalytic activity.

We thus sought a catalyst system that would stabilize a highly Lewis acidic cationic Al complex by exploiting the distinct preference of Al for tetrahedral coordination geometry. Such systems, designed to display a unique balance of reactivity and stability, are expected to provide highly active catalysts with unprecedented reaction control. Tridentate scorpionate ligands such as hydro-tris(1,3-dimethylpyrazol-1-yl)borate (Tp*) seemed Scheme 1. Synthesis of Compounds 1-3



exceptionally qualified for this task, as they can support multiple coordination modes and potentially stabilize a highly reactive metal center. Al complexes featuring Tp* ligands have been known since the late 1980s, and their synthesis was achieved using a slightly modified literature procedure.⁷ Accordingly, simple salt metathesis between commercially available KTp* and AlMe₂Cl resulted in the formation of 1 in quantitative yield on a multigram scale via the elimination of KCl (Scheme 1).

¹H NMR spectroscopic analysis of 1 (CDCl₃ at 25 °C) revealed fluxional coordination of the Tp* ligand to the metal center, as evidenced by average ligand resonances at 5.81, 2.29, and 2.28 ppm, corresponding to the aromatic pyrazolyl protons and the methyl substituents, respectively. As expected, both Al-bound methyl moieties are magnetically equivalent, appearing as a single resonance at -0.57 ppm. Resonances observed by ¹³C NMR spectroscopy confirm the structural assignment. Expectedly, the fluxional η^3 -coordination observed in solution is not sustained in the solid state, as evidenced by the X-ray crystallographic analysis of 1 (Figure 1a). The Tp* ligand is found to adopt a bidentate coordination mode, likely a result of the preference of Al for tetrahedral coordination in combination with crystal packing forces. This effect is well documented in

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Figure 1. Thermal ellipsoid diagrams of the molecular structures of (a) 1 and (b) 3. Thermal ellipsoids are drawn at 50% probability. H atoms (except H1), counterions, and cocrystallized solvents are omitted for clarity. Selected bond lengths (Å) and angles (deg): 1: Al1–N1 1.9169(17), Al1–C11 1.956(3), Al1–C12 1.989(3), C11–Al1–C12 115.44(14); 3: Al1–C16 1.912(3), Al1–N1 1.896(3), Al1–N3 1.901(3), Al1–N5 1.898(3), N1–Al1–C16 120.65(13).

the literature for Al alkyl complexes bearing similar supporting ligands.⁸

On the basis of the similarities to known systems, we anticipated the facile abstraction of a methyl ligand by Lewis acidic reagents such as BAr^F₃, resulting in a cationic Al complex with the Tp* ligand adopting a nonfluxional η^3 -coordination mode. In fact, treating 1 with one equivalent of B(C₆F₅)₃ resulted in the almost instantaneous formation of 2, which was isolated in good yield. ¹H NMR analysis of 2 clearly shows two distinct methyl resonances at 0.26 and 0.41 ppm. The former corresponds to the Al-Me moiety and indicates a significantly more electron-deficient metal center compared to that of 1 ($\Delta\delta$ = 0.83 ppm). The latter broad resonance is diagnostic for a B-bound methyl group that is well-separated from the Al center.⁹ The average signals for the Tp* ligand are consistent with symmetric η^3 -coordination to Al.

Due to crystallization difficulties often observed for complexes involving B-based anions, we sought a similar complex bearing an alternative counterion. Treating 1 with two equivalents of I₂ resulted in the formation of complex 3 accompanied by elimination of MeI (Scheme 1). X-ray quality crystals of 3 can be grown within minutes from concentrated DCM solutions at -35 °C, likely a result of the improved crystal packing capability of the I₃⁻ anion. As expected, η^3 -coordination of the Tp* ligand is observed in the solid state, resulting in a tetrahedral coordination environment around Al (Figure 1b) with almost identical Al–N bonds (~1.90 Å). The Al–C16 bond (1.912(3) Å) is noticeably shorter compared to the Al–C bonds in compound 1 ($\Delta d > 0.05$ Å), reflecting the electron-deficient nature of the metal center. Both ¹H and ¹³C NMR data indicate that these structural features are maintained in solution (CDCl₃ at 25 °C).

Initial NMR-scale experiments (CDCl₃) revealed the activity of **2** toward hydrosilylation chemistry at temperatures above 75 °C, as evidenced by the clean conversion of acetophenone and H₂SiPh₂ to the corresponding silyl ether.¹⁰ Encouraged by these results, we screened various silanes for their efficiency toward this transformation (Table 1). H₃SiPh exhibited the highest activity, whereas secondary and tertiary silanes were significantly less reactive (entries 1–6). Furthermore, the absolute substrate/silane concentration had a major impact on the rate of the reaction, with reactions proceeding significantly faster at high concentrations (entries 7–9).

Although H_3 SiPh showed the highest activity, preparative scale (1 mmol) reactions were performed using HSiEt₃ as the

	$ \begin{array}{c} O \\ + HSiR_3 \end{array} \xrightarrow{2} OSiR_3 \\ \hline temp \\ time \end{array} $							
	cat	conc						
entry	(mol %)	(mol/L)	silane	temp (°C)	time (h)	conv (%)		
1	3.8	0.1	HSiPh ₃	75	17	0		
2	4.2	0.1	HSiEt ₃	75	19	73		
3	4.0	0.1	H_2SiPh_2	75	14	>98		
4	4.3	0.1	H_2SiEt_2	75	18	>98		
5	3.0	0.1	$\rm H_2SiMePh$	75	4	>98		
6	1.7	0.1	H_3SiPh	75	1.5	>98		
7	2.5	1.0	HSiEt ₃	100	1	>98		
8	1.0	1.0	H ₂ SiMePh	100	1	>98		
9	1.0	1.0	H_3SiPh	100	0.5	>98		

Table 1. Silane Screening and Reaction Optimization

reductant since hydrosilylation reactions involving tertiary silanes are of greater industrial importance and typically yield single products. A wide variety of substrates were successfully converted to their respective silvl ethers (4a-p), as illustrated in Table 2. Unsurprisingly, conversion of aldehydes was efficient at catalyst loadings of 1.0 mol % (entries 1-3), while undesired Lewis acid-catalyzed side reactions such as the Tishchenko dimerization were kept below the detection limit (entries 1-3).¹¹ Consistent with recent studies by Mayr and co-workers, 1,2-addition of HSiEt₃ to cinnamaldehyde was observed as a result of the highly electrophilic character of the carbonyl moiety, whereas 1,4-addition was prevalent for $\alpha_{,\beta}$ -unsaturated ketones (vide infra).¹² Aromatic ketones were identified as equally suitable substrates for hydrosilylation, demonstrated by the clean conversion of acetophenone and even the sterically demanding 4,4'-dichlorobenzophenone (entries 4, 5), although higher catalyst loadings (2.5 mol %) and extended reaction times were necessary to achieve quantitative conversion. Reduction of a wide variety of aliphatic ketones bearing various functional groups to the respective silvl ethers was successful under standard reaction conditions (entries 6-10).

The catalyst proved effective toward the hydrosilylation of more challenging substrates such as an electron-rich cyclic ester

Table 2. Hydrosilylation of Aldehydes, Ketones, and Imines

	х R (1.0 М	+ 1.1 HSiEt ₃ R' //)	2 CDCl ₃ 100 °C time	XSiEt₃ ► RR'		
entry	substrate	cat. load. (mol %)	time (h)	product		yield (%) ^a
1		1.0	0.5	OSiEt ₃	4a	77
2		1.0	0.5	OSIEt ₃	4b	73 ^b
3		1.0	0.5	OSIEt ₃	4c	99°
4		2.5	1	OSiEt ₃	4d	81
5	CI CI CI	2.5	4	CI	4e	99
6	\mathbf{O} $\mathbf{R} = \mathbf{E}\mathbf{t}$	1.0	1	OSiEt ₃	4f	80
7	$\mathbf{R} = {}^{i}\mathbf{P}\mathbf{r}$	1.0	1	R	4g	91
8	V	2.5	1	OSiEt ₃	4h	84
9	⇒~~	1.0	1	OSiEt ₃	4 i	93
10		2.5	1	OSiEt ₃	4j	86
11	° O	2.5	24	OSiEt ₃	4k	50 ^d
12	0 R = H	1.0	0.5	OSiEt ₃	41	94
13	R = Me	1.0	1	RR	4m	91
14		1.0	0.5	OSIEt ₃	4n	99 ^e
15		1.0	20	Et ₃ Si _N	40	50 ^{d,f}
16	NTs	2.5	17	Et ₃ Si~ _{NTs}	4p	74 ^f

^{*a*} Isolated yields. ^{*b*} +20% of unidentified product. ^{*c*} Reaction run at 75 °C. ^{*d*} NMR yields, determined by integration of product signals versus internal standard. ^{*c*} Product isolated as mixture of Z:E (4:1) isomers. ^{*f*} Reaction run at 135 °C.

(δ -valerolactone), which was converted to the corresponding acetal (entry 11) even though Al complexes are known for the ring-opening polymerization of such species.¹⁴ As noted previously, complex **2** was highly active toward the direct conversion of α , β -unsaturated ketones to the corresponding silyl enol ethers (entries 12–14), a rare transformation typically observed only with late transition metal catalysts.¹³ Conversion of *N*-benzylideneaniline and *N*-benzylidene-4-methylbenzene-sulfonamide to the respective amines required higher temperatures and longer

reaction times (entries 15, 16), although these examples illustrate the versatility of **2** as a hydrosilylation catalyst.

Although mechanistic details of this transformation remain largely unexplored, clean formation of compound **4h** in the absence of ring-opening byproduct is inconsistent with a radical pathway.¹⁵ Moreover, coordination of acetophenone to complex **2** was not observed during variable-temperature ¹H NMR studies (see Supporting Information). On the contrary, loss of the *J* coupling between Si–H and the methylene protons of the ethyl groups suggests an interaction of $HSiEt_3$ with 2 (at elevated temperatures) analogous to other Lewis acid-catalyzed systems.^{5c} These findings are corroborated by deuterium labeling studies, which show the statistical H/D redistribution between DSiEt₃ and H₂SiPh₂ in the presence of catalytic amounts of 2 (eq 1). Undoubtedly, additional studies are required for the conclusive mechanistic elucidation of these Al-catalyzed hydrosilylation reactions.

$$DSiEt_3 + H_2SiPh_2 \xrightarrow[ODC]{2 (1 \mod \%)}_{UOC_3} HSiEt_3 + H_xD_{2-x}SiPh_2 \quad (1)$$

In conclusion, cationic Al alkyl complexes supported by scorpionate ligands have been prepared and structurally characterized. Crystallographic analysis revealed the versatility of the Tp* ligand as well as a change in coordination geometry upon formation of the cationic complexes. Compound 2 is active toward the hydrosilylation of a variety of substrates, including ketones, aldehydes, imines, and even electronically unfavorable lactones, highlighting the curiously gentle yet highly active character of the cationic Al complex. Such catalysts may thus provide a cheap and effective alternative for expensive late transition metal species in addition to a remarkably broad substrate scope.

ASSOCIATED CONTENT

Supporting Information. Experimental details, X-ray crystallographic data (CIF), and additional characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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DEDICATION

This paper is dedicated to the memory of Prof. Gordon Stone, with gratitude for the immense impact that his scientific contributions have made to the field of organometallic chemistry.

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