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HYDROSILYLATION OF HETEROCYCLIC ALDIMINES CATALYZED BY TRANSITION METAL COMPLEXES*

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The addition of triethylsilane to O- and S- heterocyclic Schiff bases in the presence of Rh, Pd, Pt, and Ir complexes has been studied. A series of the corresponding amines has been synthesized using the most active catalysts, which were the dimeric, monovalent complexes [Rh(1,5-cyclooctadiene)Cl]$_2$ and [Pd(allyl)Cl]$_2$.

Keywords: azomethines, heterocyclic amines, transition metal complexes, hydrosilylation, catalysis.

The addition of hydrosilanes to a C=N double bond has been studied much less than to the C=O bond of aldehydes, ketones, and their derivatives [1, 2]. To our knowledge, there has only been reported in the literature data for the hydrosilylation of aliphatic and aromatic heterocyclic azomethines. In this reaction saturated N-silyl derivatives are formed and these give the corresponding amines upon hydrolysis. In the presence of many catalysts these processes occur unselectively and are accompanied by hydrogenation, hydrogenolysis, and condensations. Basically positive results are obtained when different Rh and Pd complexes [3-5] are used. Palladium catalysts are most effective when used with monohydrosilanes and rhodium catalysts are more active with dihydrosilanes [6].

In recent years, starting with the work of Kagan [7, 8] and Brunner [9-11], the asymmetric hydrosilylation of imines and oximes have been vigorously developed [12-21]. However, this has not broadened the group of substrates investigated.

It is known that heterocyclic amines and, in particular, their fluorinated derivatives are potentially promising precursors of biologically active materials [22-24]. Hence our investigation is directed to the development of novel methods of synthesis of these compounds which have both academic and practical interest. Because the final reaction products are amines, it was of greatest benefit to use the cheapest alkylsilane ($HSiEt_3$) in their preparation.

In this work we have studied the hydrosilylation, using triethylsilane, of the Schiff bases **1a-h**, previously synthesized by us [25] via condensation of furan and thiophene aldehydes with trifluoromethyl anilines. In order to reveal the nature of the processes we additionally prepared some imines (**1i-k**) and studied their reactions. The reactions were carried out in the presence of a wide range of catalysts which included Rh, Pd, Pt, and Ir complexes. The results obtained are shown in Scheme 1 and in Table 1.

* Dedicated to Academician M. G. Voronkov on his 80th Birthday.

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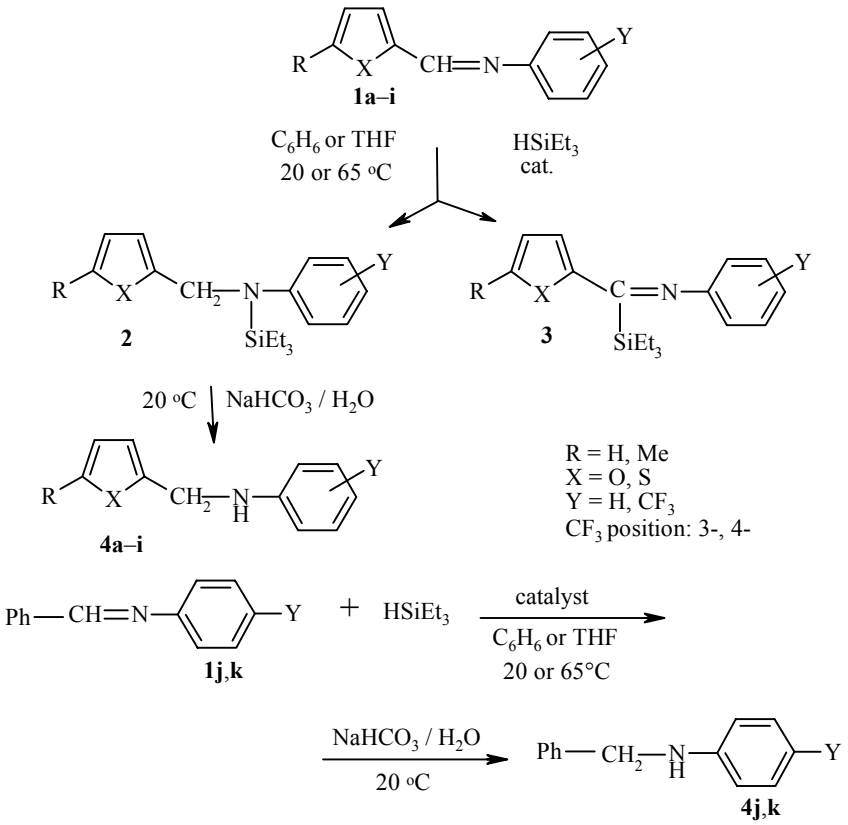
Scheme 1. Synthesis of amines **4a-k** by hydrosilylation of imines **1a-k**



Five different catalysts were tested in the hydrosilylation of the imine **1a**. In the presence of two of these the reaction did not occur (Table 1, experiments 3 and 4). Both platinum catalysts (experiments 1 and 2) were poorly active and only $[Rh(COD)Cl]_2$ catalyzed the process (even at room temperature) and allowed the preparation of the amine **4a** after hydrolysis of the reaction mixture. Amine **4b** was also prepared using this complex (at 65°C). The reaction of $HSiEt_3$ with the imine **1c** was studied in the presence of the five complexes Ir (I), Pd (0), Rh (0), Rh (I), and Pd (I). Only univalent complexes of rhodium and palladium catalyzed the reaction with the activity of the latter significantly higher (see experiments 10 and 12). Amines **4d** and **4e** were prepared by hydrosilylation in the presence of $[Rh(COD)Cl]_2$ in benzene at 65°C. Amine **4f** was synthesized using the same catalyst in benzene or tetrahydrofuran at 65°C. Both of the 3-trifluoromethyl thiophene derivatives (**1g** and **1h**) react slowly with $HSiEt_3$ in the presence of $[Rh(COD)Cl]_2$ (experiments 19, 22). The palladium catalyst $[Pd(CH_2CHCH_2)Cl]_2$ is significantly more active (as in the reaction with **1c**) (compare experiments 19 and 20).

In addition to these heterocyclic trifluoromethyl imine derivatives **1a-h,** azomethines with alternative structures were investigated, i.e. the thiophene without a CF_3 group (**1i**) and non heterocyclics both with and without this group (**1j** and **1k**). As in the other examples (experiments 8 and 21), the $[(C_6H_5)_3]_4Pd$ complex is not active (experiment 23) but $[Pd(CH_2CHCH_2)Cl]_2$ is more active than $[Rh(COD)Cl]_2$ (compare experiments 24 and 25, 27 and 28, 29 and 31). The corresponding amines (**4i-k**) were prepared using both of these catalysts.

When using the $[Rh(COD)Cl]_2$ catalyst the reaction in THF is significantly faster than in benzene (experiments 17 and 18) but the activity of the allyl-palladium complex in both of these solvents is little different (experiments 30 and 31). The corresponding amines were obtained from all of the studied imines in this way by the hydrosilylation method. Their yields after chromatographic column purification were 70-75% based on the reacted imine.

TABLE 1. Parameters for the Hydrosilylation of Imines **1a-k***

Experiment	Imine				Catalyst*[2] (mole %)	Solvent	T, °C	Reaction time, h	Conversion, % (GLC)	Product (yield, % (GLC))	
	Compound	X	R	CF_3 position						Before hydrolysis	After hydrolysis
1	2	3	4	5	6	7	8	9	10	11	12
1	**1a**	O	H	4	$H_2PtCl_6 \cdot 6H_2O$ (2)	THF	20	21	21		**4a** (15)
2	**1a**	O	H	4	$[(C_6H_5)_3P]_4Pt$ (2)	THF	20	21	15		**4a** (12)
3	**1a**	O	H	4	$RhCl_3 \cdot 4H_2O$ (2)	THF	20	32.5		No reaction	
4	**1a**	O	H	4	[Rh(COD)acac] (2)	THF	20	17.5			
							65	5.5		No reaction	
5	**1a**	O	H	4	$[Rh(COD)Cl]_2$ (2)	THF	20	21	56	**2a** (54)	**4a** (49)
6	**1b**	O	CH_3	4	$[Rh(COD)Cl]_2$ (2)	THF	20	20			
							65	5	100		**4b** (85)
7	**1c**	S	H	4	$[(C_6H_5)_3P]_2IrCl(CO)$ (2)	THF	65	10.5		No reaction	
8	**1c**	S	H	4	$[(C_6H_5)_3P]_4Pd$ (2)	THF	65	10.5		No reaction	
9	**1c**	S	H	4	[Rh(COD)acac] (2)	THF	65	10.5		No reaction	
10	**1c**	S	H	4	$[Rh(COD)Cl]_2$ (2)	THF	65	10.5	58		**4c** (50)
11	**1c**	S	H	4	$[Pd(CH_2CHCH_2)Cl]_2$ (2)	THF	20	5	48		**4c** (44)
12	**1c**	S	H	4	$[Pd(CH_2CHCH_2)Cl]_2$ (2)	C_6H_6	65	3	80	**2c** (76)	**4c** (73)
13	**1d**	S	CH_3	4	$[Rh(COD)Cl]_2$ (2)	C_6H_6	65	18			
					(3)			4	56		**4d** (48)
14	**1e**	O	H	3	$[Rh(COD)Cl]_2$ (2)	C_6H_6	65	10			
					(3)			2	90		**4e** (81)

TABLE 1 (continued)

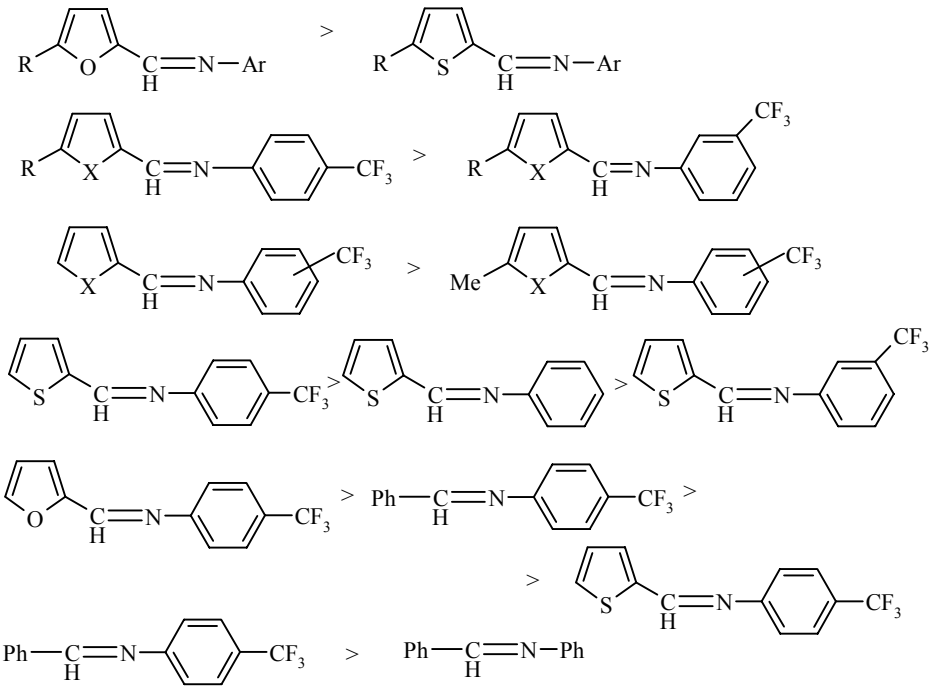
1	2	3	4	5	6	7	8	9	10	11	12
15	**1e**	O	H	3	$[Rh(COD)Cl]_2$ (2)	C_6H_6	65	19	97	**2e** (88)	**4e** (85)
16	**1f**	O	CH_3	3	$[Rh(COD)Cl]_2$ (3)	C_6H_6	65	19	88	**2f** (60), **3f** (17)	**4f** (58)
17	**1f**	O	CH_3	3	$[Rh(COD)Cl]_2$ (2)	C_6H_6	65	17	91	**2f** (86)	**4f** (80)
18	**1f**	O	CH_3	3	$[Rh(COD)Cl]_2$ (3)	THF	65	7	90	**4f** (69), **3f** (19)	**4f** (65)
19	**1g**	S	H	3	$[Rh(COD)Cl]_2$ (3)	C_6H_6	65	36	25	**2g** (22)	
20	**1g**	S	H	3	$[Pd(CH_2CHCH_2)Cl]_2$ (2)	C_6H_6	20	25			
							65	4	48	**2g** (46)	**4g** (42)
21	**1g**	S	H	3	$[(C_6H_5)_3P]_4Pd$ (2)	C_6H_6	20	25 }			
							65	4 }		No reaction	
22	**1h**	S	CH_3	3	$[Rh(COD)Cl]_2$ (3)	C_6H_6	65	41	22		**4h** (18)
23	**1i**	S	H	—	$[(C_6H_5)_3P]_4Pd$ (2)	C_6H_6	20	26		No reaction	
24	**1i**	S	H	—	$[Rh(COD)Cl]_2$ (2)	C_6H_6	65	30	38	**2i** (35)	
25	**1i**	S	H	—	$[Pd(CH_2CHCH_2)Cl]_2$ (2)	C_6H_6	20	26	96	**2i** (50), **3i** (38)	**4i** (48)
26	**1i**	S	H	—	$[Pd(CH_2CHCH_2)Cl]_2$ (2)	C_6H_6	65	14	96	**2i** (52), **3i** (39)	**4i** (50)
27	**1j**	Ph		4	$[Rh(COD)Cl]_2$ (2)	THF	65	5	54		**4j** (50)
28	**1j**	Ph		4	$[Pd(CH_2CHCH_2)Cl]_2$ (2)	THF	20	22	88		**4j** (80)
29	**1k**	Ph		—	$[Rh(COD)Cl]_2$ (2)	THF	65	14.5	39		**4k** (37)
30	**1k**	Ph		—	$[Pd(CH_2CHCH_2)Cl]_2$ (2)	C_6H_6	65	14.5	84		**4k** (76)
31	**1k**	Ph		—	$[Pd(CH_2CHCH_2)Cl]_2$ (2)	THF	65	14.5	87		**4k** (78)

* Compounds **1j-k** are $PhCH=N–C_6H_4Y$ where Y = H, CF_3.

*[2] COD is 1,5-cyclooctadiene; acac is acetylacetonate.

By comparison of the reactivity of the obtained imines (Table 1) it can be concluded that all of the furan azomethines are more active than the thiophene analogs. The presence of a methyl substituent in the heterocycle slows the reaction. A trifluoromethyl group in position 3 of the azo part of the molecule does not assist the reaction but in position 4 increases its rate. The latter is true both for the heteroaromatic and also the aromatic compounds. The activity of the benzylidene amine **1j** is less than the furan but greater than the thiophene analog. This variation is illustrated in Scheme 2.

Scheme 2. Reactivity of the imines towards silylation



The primary products of the reaction of $HSiEt_3$ with the imines are compounds of the structure **2** (Scheme 1). Compounds **2e** and **2f** (the furan derivatives with a 3-CF_3 group) were separated from their reaction mixtures. For the others (**2a**,**c**,**g**,**i**) the mass spectra were recorded for their reaction mixtures. The presence of unsaturated silicon compounds of structure **3** (**3f**,**i**) was also observed and identified by GLC-MS. The formation of the side products may be a result of a catalytic dehydrocondensation as noted in report [4] and occurring in parallel with the hydrosilylation.

We also carried out a comparison of the activity in this reaction of two homogeneous complexes and heterogeneous catalysts which were the metals Pd and Ru coated on different carriers. Reaction of $HSiEt_3$ with imine **1a** was studied in the presence of the following catalysts (2 mole %): $[(C_6H_5)_3P]_2PdCl_2$, $[(C_6H_5)_3P]_3RuCl_2$, and also 5% Pd/C and 5% Ru/Al_2O_3.

The reactions were performed in benzene at 65°C over 42 h. It was found that the Ru/Al_2O_3 complex was inactive in this process. In the presence of the palladium carbon catalyst the conversion was 40% and the yield of **4a** was 35% (GLC). The ruthenium complex was still less effective (32% conversion, 26% yield of amine). The activity of these two catalysts was marked less than for the monovalent rhodium and palladium complexes (Table 1).

TABLE 2. ^{1}H NMR Spectra of the Synthesized Compounds

Com-pound	δ, (ppm); J (Hz)
4a	1.5 (1H, br. s, NH); 4.33 (2H, s, CH_2); 6.24 (1H, m, J = 4.0, H_{Fur}-3); 6.31 (1H, m, J = 4.0, J = 2.0, H_{Fur}-4); 6.67 (2H, d, J = 9.4, H_{Ar}-3,5); 7.35 (1H, m, H_{Fur}-5); 7.40 (2H, d, J = 9.4, H_{Ar}-2,6)
4b	1.8 (1H, br. s, NH); 2.27 (3H, d, J = 1.2, CH_3); 4.28 (2H, s, CH_2); 5.89 (1H, dd, J = 3.6, J = 1.2, H_{Fur}-4); 6.11 (1H, d, J = 3.6, H_{Fur}-3); 6.55 (2H, d, J = 9.5, H_{Ar}-3,5); 7.40 (2H, d, J = 9.5, H_{Ar}-2,6)
4c	1.55 (1H, br. s, NH); 4.55 (2H, s, CH_2); 6.69 (2H, d, J = 9.0, H_{Ar}-3,5); 6.9-7.1 (2H, m, H_{Th}-3,4); 7.24 (1H, dd, J = 4.0, J = 2.0, H_{Th}-5); 7.42 (2H, d, J = 9.0, H_{Ar}-2,6)
4d	2.43 (3H, s, CH_3); 4.45 (2H, s, CH_2); 5.59 (1H, m, J = 3.4, J = 1.2, H_{Th}-4); 6.73 (2H, d, J = 8.4, H_{Ar}-3,5); 6.78 (1H, d, J = 3.4, H_{Th}-3); 7.42 (2H, d, J = 8.4, H_{Ar}-2,6)
2e	0.8-1.0 (15H, m, $SiEt_3$); 4.43 (2H, s, CH_2); 6.02 (1H, dd, J = 3.0, J = 1.0, H_{Fur}-3); 6.22 (1H, dd, J = 3.0, 2.0, H_{Fur}-4); 6.9-7.3 (4H, m, Ar); 7.42 (1H, dd, J = 2.0, J = 1.0, H_{Fur}-5)
4e	4.33 (2H, s, CH_2); 6.24 (1H, dd, J = 3.2, J = 0.7, H_{Fur}-3); 6.31 (1H, dd, J = 3.2, J = 1.9, H_{Fur}-4); 6.8-6.9 (2H, m, H_{Ar}-5,6); 6.9-7.0 (1H, m, H_{Ar}-4); 7.2-7.3 (1H, m, H_{Ar}-2); 7.36 (1H, dd, J = 0.7, J = 1.9, H_{Fur}-5)
2f	0.8-1.0 (15H, m, $SiEt_3$); 2.20 (3H, s, CH_3); 4.40 (2H, s, CH_2); 5.78 (1H, m, H_{Fur}-4); 5.87 (1H, m, H_{Fur}-3); 6.8-7.5 (4H, m, Ar)
4f	2.25 (3H, s, CH_3); 4.25 (2H, s, CH_2); 5.88 (1H, dd, J = 3.2, J = 1.0, H_{Fur}-4); 6.11 (1H, d, J = 3.2, H_{Fur}-3); 6.75-6.9 (2H, m, H_{Ar}-5,6); 6.9-7.0 (1H, m, H_{Ar}-4); 7.2-7.3 (1H, m, H_{Ar}-2)
4g	4.2 (1H, br. s, NH); 4.53 (2H, s, CH_2); 6.6-7.6 (7H, m, H_{Th}-3,4,5, Ar)
4h	2.43 (3H, s, CH_3); 4.43 (2H, s, CH_2); 6.59 (1H, m, J = 3.2, J = 1.2, H_{Th}-4); 6.79 (1H, d, J = 3.2, H_{Th}-3); 6.8-6.9 (2H, m, H_{Ar}-5,6); 6.9-7.0 (1H, m, H_{Ar}-4); 7.2-7.3 (1H, m, H_{Ar}-2)
1i	7.0-7.5 (8H, m, Th, Ph); 8.51 (1H, s, CHN)
4i	4.0 (1H, br. s, NH); 4.51 (2H, s, CH_2); 6.5-7.3 (6H, m, Ph, H_{Th}-3); 6.71 (1H, m, J = 2, H_{Th}-4); 7.18 (1H, m, J = 2, H_{Th}-5)
1j	7.22 (2H, d, J = 8.4, H_{Ar}-3,5); 7.3-7.6 (3H, m, H_{Ph}-2,4,6); 7.62 (2H, d, J = 8.4, H_{Ar}-2,6); 7.90 (2H, m, H_{Ph}-3,5); 8.42 (1H, s, CHN)
4j	4.33 (3H, s, CH_2NH); 6.60 (2H, d, J = 8.6, H_{Ar}-3,5); 7.33 (5H, s, Ph); 7.38 (2H, d, J = 8.6, H_{Ar}-2,6)
1k	7.1-7.7 (8H, m, H_{Ph}-2,4,6, Ph'H_5); 7.93 (2H, m, H_{Ph}-3,5); 8.49 (1H, s, CHN)
4k	3.9 (1H, br. s, NH); 4.27 (2H, s, CH_2); 6.5-6.8 (2H, m, H_{Ph}-2,6); 7.0-7.4 (7H, m, H_{Ph}-3,5, Ph')

TABLE 3. Mass Spectra of the Synthesized Compounds

Com-pound	*m/z* (I_{rel}, %)
1	2
2a	355 (14, M^+), 336 (5, $[M - F]^+$), 326 (37, $[M - Et]^+$), 224 (17), 188 (20), 154 (100), 145 (9, $[C_6H_4CF_3]^+$), 125 (29), 115 (5, $[SiEt_3]^+$), 97 (8), 87 (14), 81 (72, $[FurCH_2]^+$), 69 (2, $[CF_3]^+$), 59 (21), 53 (24)
4a	241 (28, M^+), 240 (6, $[M - H]^+$), 222 (4, $[M - F]^+$), 174 (4, $[M - Fur]^+$), 172 (3, $[M - CF_3]^+$), 145 (9, $[C_6H_4CF_3]^+$), 80 (6), 81 (100, $[FurCH_2]^+$), 69 (3, $[CF_3]^+$), 53 (25), 39 (5)
4b	255 (17, M^+), 236 (2, $[M - F]^+$), 211 (11), 174 (5), 172 (4), 160 (1, $[M - MeFur]^+$), 145 (9, $[C_6H_4CF_3]^+$), 95 (100, $[MeFurCH_2]^+$), 65 (4), 51 (5), 43 (10), 39 (5)
2c	371 (22, M^+), 353 (2, $[M - F]^+$), 342 (35, $[M - Et]^+$), 284 (1, $[M - 3Et]^+$), 256 (3, $[M - SiEt_3]^+$), 236 (8), 188 (20), 169 (36), 154 (100), 145 (8, $[C_6H_4CF_3]^+$), 141 (31), 127 (5), 113 (12), 97 (76, $[ThCH_2]^+$), 87 (13), 69 (2, $[CF_3]^+$), 59 (21), 45 (8)
4c	257 (16, M^+), 238 (5, $[M - F]^+$), 174 (5, $[M - Th]^+$), 172 (4), 145 (14, $[C_6H_4CF_3]^+$), 97 (100, $[ThCH_2]^+$), 69 (6, $[CF_3]^+$), 53 (7), 45 (8), 39 (5)
4d	271 (16, M^+), 252 (1, $[M - F]^+$), 211 (11), 174 (5), 145 (17, $[C_6H_4CF_3]^+$), 125 (6), 111 (100, $[MeThCH_2]^+$), 95 (7), 77 (12), 69 (10), 59 (7), 45 (9), 39 (6)
2e	355 (10, M^+), 336 (2, $[M - F]^+$), 326 (35, $[M - Et]^+$), 224 (16), 188 (11), 154 (100), 153 (35), 145 (6, $[C_6H_4CF_3]^+$), 125 (29), 115 (5, $[SiEt_3]^+$), 97 (8), 87 (12), 81 (54, $[FurCH_2]^+$), 69 (1, $[CF_3]^+$), 59 (19), 53 (18)

TABLE 3 (continued)

1	2
4e	242 (6, $[M + H]^+$), 241 (47, M^+), 222 (15, $[M – F]^+$), 213 (5), 172 (9, $[M – CF_3]^+$), 145 (23, $[C_6H_4CF_3]^+$), 125 (7), 113 (18), 95 (7), 81 (100, $[FurCH_2]^+$), 75 (9), 69 (7, $[CF_3]^+$), 63 (8), 53 (21), 39 (12)
2f	369 (6, M^+), 340 (11, $[M – Et]^+$), 246 (4), 216 (4), 188 (5), 167 (15), 154 (29), 139 (8), 95 (100, $[MeFurCH_2]^+$), 87 (6), 77 (3), 59 (10), 43 (11)
3f	367 (6, M^+), 352 (1, $[M – Me]^+$), 348 (1, $[M – F]^+$)337 (26), 338 (100, $[M – Et]^+$), 310 (12), 280 (7), 222 (47), 207 (82), 179 (21), 145 (19, $[C_6H_4CF_3]^+$), 128 (8), 109 (5), 95 (20, $[MeFurCH_2]^+$), 77 (14), 59 (9), 43 (30)
4f	255 (14, M^+), 236 (3, $[M – F]^+$), 174 (4), 145 (10, $[C_6H_4CF_3]^+$), 95 (100, $[MeFurCH_2]^+$), 51 (6), 43 (15)
2g	371 (19, M^+), 353 (2, $[M – F]^+$), 342 (33, $[M – Et]^+$), 256 (3, $[M – SiEt_3]^+$), 236 (5), 217 (4), 188 (13), 169 (31), 154 (100), 145 (9, $[C_6H_4CF_3]^+$), 141 (30), 127 (6), 113 (11), 97 (63, $[ThCH_2]^+$), 87 (9), 77 (5), 59 (17), 45 (6).
4g	257 (33, M^+), 238 (5, $[M – F]^+$), 174 (5, $[M – Th]^+$), 145 (15, $[C_6H_4CF_3]^+$), 113 (5), 97 (100, $[ThCH_2]^+$), 69 (6, $[CF_3]^+$), 53 (8), 45 (10), 39 (6)
4h	271 (20, M^+), 252 (1, $[M – F]^+$), 174 (5), 145 (14, $[C_6H_4CF_3]^+$), 111 (100, $[MeThCH_2]^+$), 95 (5), 77 (8), 69 (5), 45 (6)
1i	187 (85, M^+), 186 (100, $[M – H]^+$), 115 (6), 110 (2, $[M – Ph]^+$), 104 (4, $[M – Th]^+$), 95 (4), 97 (100, $[ThCH_2]^+$), 84 (5, $[ThH]^+$), 77 (40, Ph^+), 69 (5), 63 (5), 58 (5), 51 (26), 45 (9), 39 (14)
2i	306 (16), 305 (67, M^+), 276 (3, $[M – Et]^+$), 249 (20), 248 (100, $[M – 2Et – H]^+$), 244 (37), 218 (5), 200 (3), 190 (16), 156 (5), 130 (12), 115 (23, $[SiEt_3]^+$), 104 (6), 87 (47), 77 (28, Ph^+), 59 (50), 45 (8), 31 (5)
3i	304 (11), 303 (45, M^+), 273 (20), 274 (92, $[M – Et]^+$), 246 (5), 216 (2, $[M – 3Et]^+$), 170 (14), 169 (100), 149 (9), 142 (10), 141 (80), 121 (19), 120 (49), 113 (23), 97 (68), 87 (24), 77 (23, Ph^+), 59 (46), 53 (13), 45 (14)
4i	190 (6), 189 (48, M^+), 187 (8), 186 (10), 154 (2), 106 (4), 97 (100, $[ThCH_2]^+$), 77 (18, Ph^+), 65 (10), 51 (15), 45 (14), 39 (16).
1j	250 (12), 249 (75, M^+), 248 (100, $[M – H]^+$), 230 (4, $[M – F]^+$), 180 (7), 172 (8, $[M – Ph]^+$), 145 (38, $[C_6H_4CF_3]^+$), 126 (7), 125 (9), 95 (12), 89 (5), 77 (11, Ph^+), 75 (9), 69 (7, $[CF_3]^+$), 51 (10), 39 (5).
4j	252 (10), 251 (65, M^+), 250 (14, $[M – H]^+$), 232 (13, $[M – F]^+$), 182 (2), 174 (10, $[M – Ph]^+$), 172 (6), 145 (21, $[C_6H_4CF_3]^+$), 125 (4), 113 (5), 92 (7), 91 (100, $[PhCH_2]^+$), 77 (6, Ph^+), 65 (17), 51 (8), 39 (7)
1k	182 (10), 181 (81, M^+), 180 (100, $[M – H]^+$), 152 (7), 104 (10, $[M – Ph]^+$), 89 (7), 78 (10), 77 (56, Ph^+), 63 (10), 51 (37), 50 (14), 39 (9)
4k	184 (12), 183 (84, M^+), 182 (33, $[M – H]^+$), 154 (4), 152 (2), 106 (20, $[M – Ph]^+$), 104 (14, $[M – Ph – 2H]^+$), 92 (9), 91 ($[PhCH_2]^+$), 89 (5), 77 (37, Ph^+), 65 (38), 63 (11), 51 (25), 50 (9), 39 (22)

EXPERIMENTAL

^{1}H NMR spectra were recorded on Varian Mercury (200 MHz) and Bruker WH-90/DS instruments using $CDCl_3$ solvent and TMS internal standard. Mass spectra were obtained on an HP 6890 GC/MS chromatographic mass spectrometer fitted with an HP-5 MS capillary column (30.0 m × 250 μm × 0.25 μm) at a program temperature from 70-260°C at 10°C/min. Benzene and tetrahydrofuran were purified and dried using known methods before use. The aldehydes and amines were purified by vacuum distillation or recrystallization, after which their properties agreed with the corresponding literature data. The hydrosilane and transition metal complexes used in this work were obtained from Fluka, Merck, and Acros and the 4A molecular sieves from VEB Laborchemie Apolda. The synthesis of the azomethines **1i-k** was carried out as described in [25]. Their parameters agreed with those the data reported in [26-28].

General Method for the Synthesis of Amines 4a-k. A reaction tube (Pierce, volume 5 ml) was purged with argon and dry benzene or tetrahydrofuran (2 ml), catalyst (0.01 or 0.015 mmol), and the starting amine (0.5 mmol) were added to it. It was then stirred at room temperature for 30 min, the solution was cooled in ice to

0°C, and triethylsilane (96 μl, 0.6 mmol) was added by syringe. The reaction was carried out at room temperature or at 65°C, periodically removing a sample and analysing by TLC, GLC, or GLC-MS. At the end of the silylation (the reaction time is shown in Table 1) the reaction mixture was evaporated at reduced pressure (30°C, 15 mm) and hydrolyzed by the addition of methanol (2.5 ml) and aqueous $NaHCO_3$ solution (10%, 0.5 ml). The mixture was extracted with ether, the extract dried with anhydrous Na_2SO_4, filtered, and evaporated. The residue was then separated using liquid chromatography on a silica gel column (Kieselgel 60, 0.063-0.200 mesh, Merck) using benzene-ethyl acetate eluent (18:1 or 20:1). All of the products obtained are yellow or orange, oily materials. Their ^1H NMR and mass spectra are given in Tables 2 and 3.

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