was stirred for 4 h at 23 °C, during which time a yellow precipitate formed. The slurry was concentrated to 18 mL, and the lemon-yellow product was collected by filtration, washed with CH_2Cl_2, and dried under vacuum at 23 °C overnight (yield 1.38 g, 77%). A second crop of product (0.21 g) was recovered from the filtrate, bringing the total yield to 88%. Anal. Calcd for $C_{44}H_{42}BNZr$: C, 76.93; H, 6.18; N, 2.04; Zr, 13.28. Found: C, 76.86; H, 6.00; N, 2.02; Zr, 13.25.

Reaction of 10 with CD_3CN. NMR Scale. A solution of **10** (13 mg, 0.019 mmol) in CD_3CN (0.4 mL) was prepared in a sealed NMR tube and monitored by ^1H NMR. The resonances for **10** were shifted as described in the text and decreased in intensity while resonances for **13**-d_3 and **14** grew in intensity. After 4.5 h at 23 °C the yield of both **13**-d_3 and **14** were 74%. After 19 h the yield of **14** was 100%.[51]

Preparative Scale. A solution of **10** was generated by reaction of a solution of **6** (5.15 g, 7.31 mmol) in CH_2Cl_2 (110 mL) with propylene (22.1 mmol) for 22 h at 23 °C. The CH_2Cl_2 and excess propylene were removed under vacuum, and CH_3CN (100 mL) was added. The CH_3CN solution was stirred for 3.5 days at 23 °C. The resulting slurry was exposed to air, diluted with 30 mL of ether, and filtered. The filtrate was extracted with 2 N HCl, and the aqueous portion was made basic by the addition of solid KOH and extracted with hexane. Evaporation of the hexane gave **14** (0.61 g, 63%) as a yellow liquid. Anal. Calcd for $C_9H_{11}N$: C, 81.14; H, 8.34; N, 10.52. Found: C, 80.50; H, 8.35, N, 10.24. MS calcd for $C_9H_{11}N$ 133.0891, found 133.0895.

Reaction of 10 with PMe_3. A solution of **10** (8.1 mg, 0.012 mmol) in CD_2Cl_2 (0.4 mL) was charged with PMe_3 (0.47 mmol) from a calibrated gas bulb and sealed in an NMR tube. The reaction was monitored by ^1H NMR at 23 °C. The resonances for **10** were shifted as described in the text and decreased in intensity, while resonances for **14** and **17** grew in intensity. After 78 h the yields of **14** and **17** were 60%. Cp_2ZrCl_2 (13%) and an unknown Cp_2Zr product or products (δ 6.32, 6.07 Cp) were also present.

X-ray Structure Determinations of 8 and 9. Suitable crystals of **8** were grown by slow evaporation of a CH_2Cl_2 solution, mounted in capillaries, and sealed under N_2. Suitable crystals of **9** were grown by cooling a concentrated CH_2Cl_2 solution and mounted in capillaries under N_2 in a drybox. X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer as summarized in Table VI.

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Supplementary Material Available: For **8** and **9**, tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions (9 pages); listings of *h*, *k*, *l*, F_o, F_c, and $\sigma(F_o)$ for **8** and **9** (23 pages). Ordering information is given on any current masthead page.

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(51) Complex **13** slowly decomposes under these conditions to unidentified products. After 19 h the yield of **13** was 56%.

Synthesis, Structure, and Dynamics of (Organosilyl)anilides

Julie C. Otter, Christine L. Adamson, and Claude H. Yoder*

Department of Chemistry, Franklin and Marshall College, Lancaster, Pennsylvania 17604-3003

Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, Delaware 19716

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A series of (organosilyl)formanilides of the type $HCONPhSiR^1R^2R^3$, where $R^1R^2R^3$ = Me_2H, MePhH, Me_3, Et_3, $(n\text{-}Pr)_3$, $(i\text{-}Pr)_3$, $(n\text{-}Bu)_3$, $(OEt)_3$, $(OSiMe_3)_3$, Me_2OMe, Me_2Et, $Me_2CH{=}CH_2$, $Me_2\text{-}i\text{-}Pr$, $Me_2C_3H_6Cl$, $Me_2C_2H_4OAc$, $Me(n\text{-}Bu)_2$, Me_2Ph, and $Ph_2\text{-}t\text{-}Bu$, and a series of (organosilyl)acetanilides of the form $CH_3CON(p\text{-}R^4C_6H_4)SiMe_2H$, where R^4 = OMe, H, and Cl, were prepared by amination and transsilylation. Most of the (organosilyl)formanilides exist as rapidly equilibrating mixtures of amide and imidate tautomers and exhibit hindered rotation about the C–N bond in the amide tautomer. Bulky groups and alkoxy groups at silicon favor the imidate tautomer. The size of the silyl group has no effect on the barrier to either silyl tautomerism or hindered rotation, while electron-withdrawing alkoxy groups on the silicon lower both barriers. The effect of substituents on the rate of tautomerism is consistent with an intramolecular, concerted mechanism. The rotamer populations are relatively insensitive to variations in the silyl group. The more stable rotamer has the silyl moiety cis to the carbonyl. The (dimethylsilyl)acetanilides also exist as a dynamic mixture of amide and imidate tautomers. The attempted preparation of the $SiMe_2CHCl_2$ formanilide derivative led to substitution at carbon rather than silicon. The product, $(HCONPh)_2CHSiMe_2Cl$, was shown by X-ray crystallography to have distorted trigonal-bipyramidal geometry at Si, with two nonequivalent dative bonds from carbonyl oxygen atoms to silicon. For $C_{17}H_{19}ClN_2O_2Si$: monoclinic, $P2_1/c$, a = 10.420 (3) Å, b = 17.322 (5) Å, c = 10.561 (2) Å, β = 112.26 (2)°, V = 1764.3 (10) Å^3, Z = 4, $R(F)$ = 5.29% for 1796 reflections, $F_o \geq 3\sigma(F_o)$.

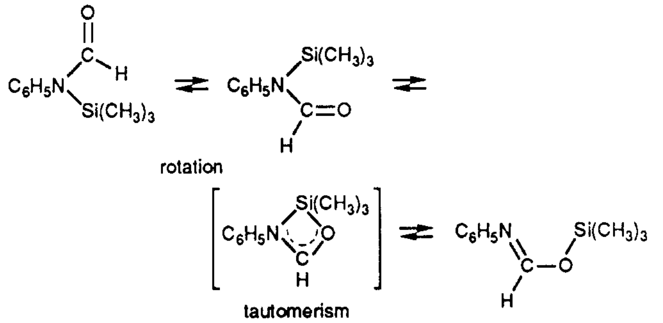
The ambident nature of the amide function makes it ideal for the study of bonding and tautomerism in organometallic congeners of carbon. Previous studies of trimethylsilyl-, germyl-, and stannylamides have demonstrated the unique position of silicon among the group IV elements. Only these derivatives undergo rapid amide/imidate silyl tautomerism, display fluxionality, and have severely lowered barriers to rotation about the C–N bond in the *N*-(trimethylsilyl)amide form. The strong Si–O bond is presumably responsible for the presence of the imidate tautomer, while the lower rotational barrier can be attributed to (p–d)π-bonding in the transition state.

Table I. Boiling Point and Chemical Shift Data (ppm) for HCONPhSiR^{1}R^{2}R^3 and CH$_3$CON(p-R^{4}C$_6$H$_4$)SiMe$_2$H (1-21)

						NMR (δ), ppm		
	R^1	R^2	R^3	R^4	bp, °C/mmHg	^{1}H^b HC=O A cis, A trans, I	^{13}C^c HC=O A, I	^{29}Si^d I, A
1	CH$_3$	CH$_3$	H		57-8/1.0	8.42, 8.26, 7.43	169.6, 154.8	0.3, -0.1
2	CH$_3$	Ph	H		112-5/0.04	8.57, 8.23, 7.68	169.2 (br)	6.28 (6.26)
3	CH$_3$	CH$_3$	CH$_3$		39/0.09^a	8.40, 8.23, 7.44	169.3, 154.6	23.1, 11.1
4	Et	Et	Et		76-8/0.05	8.35, 8.22, 7.39	169.3, 154.4	25.4, 15.4
5	n-Pr	n-Pr	n-Pr		119-20/0.34	8.39, 8.24, 7.37	168.8, 154.0	22.2, 11.2
6	i-Pr	i-Pr	i-Pr		100-2/0.04	7.78	154.0	21.8
7	n-Bu	n-Bu	n-Bu		138-140/0.09	8.38, 8.21, 7.38	168.9, 154.2	23.1, 12.1
8	OEt	OEt	OEt		91-2/0.09	8.78, 8.23, 7.44	164.3, 152.3	-76.2, -84.9
9	OSiMe$_3$	OSiMe$_3$	OSiMe$_3$		89-91.5/0.07	8.74, 8.13, 7.22	165.7, 152.2	12.3, 10.7
10	Me	Me	OMe		63-4/0.09	8.49, 8.24, 7.37	169.5, 153.7	2.4, 0.9
11	Me	Me	Et		61-2/0.048	8.39, 8.22, 7.42	169.2, 154.5	24.5, 13.2
12	Me	Me	CH=CH$_2$		60-1/0.11	8.45, 8.23, 7.42	169.4, 154.3	10.5, 0.4
13	Me	Me	i-Pr		86-7.500.024	8.37, 8.21, 7.39	169.3, 154.5	24.9, 14.6
14	Me	Me	CH$_2$CH$_2$CH$_2$Cl		89.7-90/0.07	8.33, 8.16, 7.35	170.6, 155.6	23.6, 12.2
15	Me	Me	C$_2$H$_4$OAc		109-9.5/1.6	8.40, 8.17, 7.38	170.7, 155.6	21.5, 10.1
16	Me	n-Bu	n-Bu		107-8/0.02	8.40, 8.24, 7.39	169.1, 154.2	23.7, 12.5
17	Me	Me	Ph		105-6/0.08	8.50, 8.26, 7.38	169.4, 154.2	12.2, 2.4
18	Ph	Ph	i-Bu		160-1/0.08	7.52	152.7	-1.1
19				OMe	77.5-8.5/0.05		176.8, 158.3^e	-6.14, 2.02^f
20				H	41-2/0.08		176.1, 160.8	-5.69, 2.64
21				Cl	62.5-3/0.05		176.3, 161.9	-5.05, 3.22

^{a} Lit.[1d] bp 85 °C/3 mmHg. ^{b} T = -20 °C, reference CD$_3$C$_6$D$_5$, 2.09 ppm. ^{c} T = 26 °C, reference CD$_3$COCD$_3$ coaxial inner tube, 206.0 ppm. ^{d} T = 26 °C, reference TMS coaxial inner tube, 0.0 ppm. ^{e} CH$_3$CO shifts at -40 °C. ^{f} Si shifts at -40 °C.

Scheme I. Rotation and Exchange Processes in (Trimethylsilyl)formanilide



The tautomerization and rotational processes and the proposed mechanisms[1,2] relating them are shown for (trimethylsilyl)formanilide in Scheme I.

The effects of substituents at the carbonyl carbon and nitrogen on the structure and dynamics of (trimethylsilyl)amides have been extensively explored.[1-4] From these studies, it is clear that the size and electronic nature of the substituents control the extent and rate of tautomerism, as well as the rate of rotation in the amide form. For example, small groups at the carbonyl carbon favor the amide form in bis(trimethylsilyl)amides, while electron-withdrawing groups attached to nitrogen favor the imidate form. However, there have been few studies directed to the effect of substituents at the silicon atom. Although ($tert$-butyldimethylsilyl)formanilide has been prepared,[5] other attempts to study silyl substituents were sidetracked by the discovery of the preferential nucleophilic substitution at the ClCH$_2$ site in ClCH$_2$Si(CH$_3$)$_2$Cl and subsequent formation of a five-coordinate silicon.[6] The present study completes our investigation of structural effects on tautomerism and hindered rotation in silyl amides. Because the anilides have previously been found to exist in both tautomeric forms and therefore permit the determination of barriers to both exchange and rotation,[2] a series of silylformanilides and acetanilides containing groups on the silicon of different size and electronic effects were prepared. The structures and barriers to exchange and rotation were determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectrometry.

Experimental Section

Syntheses. All reactions were carried out under an argon atmosphere. Chlorosilane precursors (Petrarch Systems, Inc.) were used as received. Triethylamine and THF were purified and dried prior to use by standard procedures. All boiling and melting points are uncorrected. Elemental analyses for carbon and hydrogen were obtained from Schwarzkopf Microanalytical Laboratory (Woodside, NY) and were in excellent agreement with the theoretical percentages. Boiling point and NMR data are given in Table I.

HCONPhSiR^{1}R^{2}R^3 (1-16) and CH$_3$CON(p-R^{4}C$_6$H$_4$)SiMe$_2$H (19-21). Amination was used to prepare 1-16 and 19-21 in a 70-90% yield. The appropriate organosilyl chloride precursor (0.07 mol) was added dropwise to a solution of Et$_3$N (9.8 mL, 0.07 mol) and either acetanilide (6.8 g, 0.05 mol) or formanilide (6.1 g, 0.05 mol) in THF (ca. 50 mL). A precipitate formed immediately, and the mixture was stirred at room temperature for ca. 24 h. Triethylamine hydrochloride was removed by vacuum filtration. Removal of THF under vacuum was followed by a second filtration when necessary to remove residual anilide. Reduced pressure distillation afforded clear, colorless, hygroscopic liquids.

HCONPhSiR^{1}R^{2}R^3 (17 and 18). Transsilylation of (trimethylsilyl)formanilide (vide supra) with the appropriate organochlorosilane in equimolar ratio was carried out in a two-neck flask fitted with a thermometer and a condenser with a take-off arm. Trimethylchlorosilane was removed at ca. 60 °C. For 17, Me$_2$PhSiCl (3.6 mL, 0.023 mol) was added to (trimethylsilyl)-

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Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $(HCONPh)_2CMSiMe_2Cl$ (22)

	x	y	z	U^a
Si	7261 (1)	981 (1)	1470 (1)	38 (1)
Cl	7386 (1)	−251 (1)	793 (1)	58 (1)
C(1)	6098 (5)	737 (3)	2387 (5)	56 (2)
C(2)	6413 (5)	1349 (3)	−309 (5)	56 (2)
C(3)	9224 (4)	918 (2)	2680 (4)	33 (2)
C(4)	8639 (5)	2202 (3)	3059 (5)	44 (2)
O(1)	7450 (3)	2053 (2)	2203 (3)	49 (1)
O(2)	9547 (4)	1671 (2)	563 (4)	66 (2)
C(5)	10281 (5)	1110 (3)	1026 (5)	51 (2)
N(1)	10249 (3)	701 (2)	2106 (4)	35 (1)
N(2)	9636 (3)	1673 (2)	3403 (4)	35 (1)
C(11)	10791 (2)	−593 (2)	3101 (3)	45 (2)
C(12)	11746	−1176	3717	56 (2)
C(13)	13146	−1069	3954	63 (2)
C(14)	13589	−379	3575	62 (2)
C(15)	12634	205	2959	54 (2)
C(16)	11235	98	2722	37 (2)
C(21)	11704 (3)	1352 (2)	5410 (3)	46 (2)
C(22)	13044	1530	6314	60 (2)
C(23)	13703	2193	6113	67 (2)
C(24)	13022	2678	5008	76 (3)
C(25)	11682	2501	4104	62 (2)
C(26)	11023	1838	4305	36 (2)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

formanilide (4.23, 0.023 mol) and refluxed for 27 h. For **18**, Ph_2-*t*-BuSiCl (3.30 g, 0.012 mol) was added to (trimethylsilyl)formanilide (4.0 g, 0.021 mol) and refluxed for 24 h. Reduced pressure distillation afforded clear, colorless, hygroscopic **17** and **18** in 70–90% yields.

22. $Cl_2CH(CH_3)_2SiCl$ (10.0 mL, 0.07 mol) was added dropwise to a mixture of formanilide (6.1 g, 0.05 mol), Et_3N (9.8 mL, 0.07 mol), and THF (ca. 50 mL). A precipitate formed immediately. After 12 h the reaction mixture was filtered, and THF was removed by distillation. Twofold recrystallization from toluene afforded the white, crystalline **22** with a final yield of 50%: mp 157–160 °C; ^1H NMR δ 0.3 (s, 6 H), 5.1 (s, 1 H), 6.7–7.2 (m, 10 H) and 8.0 (s, 2 H); ^{13}C NMR δ 163.6, 139.1, 129.6, 128.3, 125.3, 64.9, 7.6; ^{29}Si NMR δ −33.7; IR ($CHCl_3$) 3000 (aromatic C–H), 2900 (aliphatic C–H), 1640 (C=O), 1600, 1580 and 1500 (aromatic C=C), 700 (C–Cl). Anal. Calcd for $C_{17}H_{19}SiO_2N_2Cl$: C, 58.86; H, 5.52; N, 8.08; Cl, 10.22. Found: C, 59.31; H, 5.41; N, 8.17; Cl, 10.52.

IR and NMR Data. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer. NMR spectra were recorded on a JEOL FX-90Q spectrometer and are reported (ppm) relative to internal $(Me)_4Si$. Room-temperature ^{13}C and ^{29}Si spectra were obtained on neat samples. All ^1H and variable-temperature experiments were performed on a 25% v/v solution in toluene-d_8 (a neat sample of compound **5** was used to measure its tautomerism coalescence temperature).

X-ray Crystallographic Study for $(HCOPhN)_2CHSiMe_2Cl$ (22). A suitable single crystal was obtained by slow recrystallization from toluene and had dimensions of 0.17 × 0.23 × 0.32 mm. Data were collected at room temperature (22 ± 1 °C) on a Nicolet R3m diffractometer. Systematic absences uniquely defined the space group. No correction for absorption was required (I_{max}/I_{min} = 1.08). The structure was solved by direct methods. All nonhydrogen atoms were refined anisotropically, and all hydrogen atoms were treated as idealized contributions. Phenyl rings were constrained to rigid hexagonal structures (d(CC) = 1.395 Å). All software used was contained in the SHELXTL (S.1) program library (G. Sheldrick, NicoletXRD Madison, WI).

Crystal Data. The unit cell for $(HCOPhN)_2CHSiMe_2Cl$ was monoclinic with a = 10.420 (3) Å, b = 17.322 (5) Å, c = 10.561 (4) Å, β = 112.26 (2)°, V = 1764.3 (11) Å^3, and Z = 4 and belonged to the $P2_1/c$ space group. A total of 3041 independent reflections was measured of which 2760 were independent and 1796 were observed, $F_o \geq 3\sigma(F_o)$. Experimental parameters: 2θ limits 4 → 48°; radiation Mo Kα (λ = 0.71073 Å); $R(F)$ 5.29%; $R(wF)$ 5.72%; GOF 1.377; $\Delta(\rho)$ 0.43 e Å^{-3}. Atomic coordinates and isotropic thermal parameters are given in Table II; bond lengths are given in Table III; bond angles are given in Table IV. Figure 1 presents the ORTEP representation of **22**.

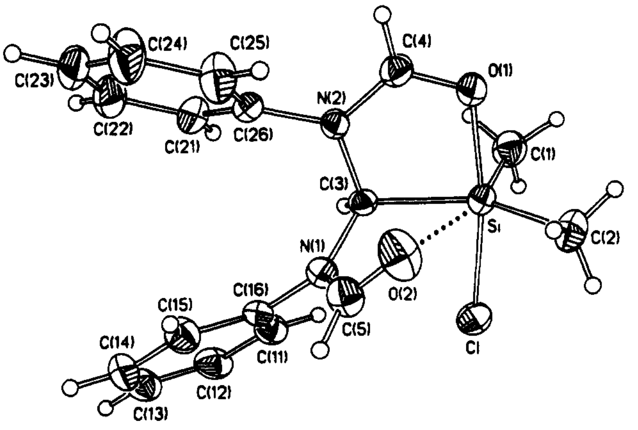

Figure 1. ORTEP diagram of **22** (thermal ellipsoids are drawn with 40% probability contours).

Table III. Bond Lengths (Å) for $(HCONPh)_2CHSiMe_2Cl$ (22)

Si–Cl	2.271 (2)	Si–C(1)	1.863 (7)
Si–C(2)	1.860 (5)	Si–C(2)	1.961 (4)
Si–O(1)	1.992 (3)	C(3)–N(1)	1.463 (6)
C(3)–N(2)	1.493 (5)	C(4)–O(1)	1.253 (5)
C(4)–N(2)	1.328 (6)	O(2)–C(5)	1.218 (6)
C(5)–N(1)	1.355 (7)	N(1)–C(16)	1.436 (4)
N(2)–C(26)	1.426 (4)	Si···O(2)	3.123 (3)

Table IV. Bond Angles (deg) for $(HCONPh)_2CHSiMe_2Cl$ (22)

Si···O(2)–Cl	97.0 (2)	Si–C(3)–N(1)	119.3 (3)
Si···O(2)–C(1)	165.5 (2)	Cl–Si–O(1)	171.6 (1)
Si···O(2)–C(2)	71.6 (3)	Cl–Si–C(2)	93.8 (2)
Si···O(2)–C(3)	59.5 (2)	C(3)–N(2)–C(4)	114.8 (3)
Si···O(2)–O(1)	77.8 (2)	N(2)–C(26)–C(25)	119.7 (2)
Cl–Si–C(1)	94.4 (2)	Cl–Si–C(2)	93.8 (2)
C(1)–Si–C(2)	116.7 (2)	Cl–Si–C(3)	89.0 (1)
C(1)–Si–C(3)	111.8 (2)	C(2)–Si–C(3)	131.0 (2)
C(3)–N(1)–C(16)	120.6 (3)	C(1)–Si–O(1)	89.9 (2)
N(1)–C(16)–C(15)	120.3 (2)	C(3)–Si–O(1)	82.7 (1)
C(3)–N(2)–C(26)	122.6 (3)	Si–C(3)–N(2)	108.2 (2)
C(5)–N(1)–C(16)	121.3 (4)	O(1)–C(4)–N(2)	120.8 (4)
C(3)–N(1)–C(5)	117.9 (4)	O(2)–C(5)–N(1)	122.9 (5)
Si–O(1)–C(4)	113.4 (3)	C(4)–N(2)–C(26)	122.3 (3)
N(1)–C(3)–N(2)	108.9 (3)		

Determination of $\Delta G^{\ddagger}$ and Isomer Populations. Coalescence temperatures and isomer populations for amide/imidate and rotamer interconversions were determined with variable-temperature proton NMR for the (organosilyl)formanilides (HC=O or $Si(CH_3)R^2R^3$) and by ^{13}C NMR for the (dimethylsilyl)acetanilides (HC=O). Sample temperature was determined from a thermocouple/digital thermometer. The isomer populations were determined by cutting and weighing peaks; free energies of activation were determined by using the Shanan-Atidi and Bar-Eli approximate method,[7] as described previously.[2] Isomer populations (p) at the coalescence temperature (T_c) were determined from least-squares plots of the log p vs $1/T$ at three or four temperatures 20–50 °C below coalescence. Peak separations at T_c were similarly determined from least-squares plots of chemical shifts vs T.

The measurement of T_c is believed to be the major source of error in $\Delta G^{\ddagger}$ because of the unequal isomer populations. A series of repetitive measurements resulted in a standard deviation of ±0.3 kcal/mol for $\Delta G^{\ddagger}$ and ±0.04 for isomer populations. The values listed in Table V were determined from a single set of measurements.

Rotamer Assignment. The two amide peaks in the low-temperature ^1H spectra were assigned to the cis and trans rotamers by the method of differential solvent shifts.[8]

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Table V. Thermodynamic Data for Exchange and Rotation[a] for 1–21

	exchange					rotation				
	T_c,[b] °C	P_I[c]	$\Delta\nu$, Hz	$\Delta G^\ddagger_{I\to A}$[d]	$\Delta G^\ddagger_{A\to I}$	T_c,[b] °C	P_a[c]	$\Delta\nu$, Hz	$\Delta G_a^\ddagger$[d]	$\Delta G_b^\ddagger$
1	64.0	0.27	74.9	16.5	17.1	17.0	0.94	12.8	16.6	15.0
2	[e]					15.0	0.97	26.9	16.5	14.5
3	83.5*	0.34	10.3	18.9	19.4	22.2	0.86	17.2	16.1	15.2
	108.8	0.32	74.0	18.8	19.4	22.0	0.87	17.8	16.2	15.1
4	103.5	0.31	73.8	18.5	19.1	16.0	0.92	13.6	16.3	14.9
5	110.0	0.33	68.5	18.9	19.5	20.0	0.92	16.1	16.5	15.0
6		1.00								
7	108.5	0.51	74.7	18.8	18.8	[f]				
8	41.0	0.76	84.6	15.9	15.2	6.0	0.57	46.3	14.0	13.9
9	85.0*	0.99	1.91	23.3	20.0	−1.5	0.86	8.52	15.2	14.3
10	67.5	0.80	79.2	17.5	16.6	12.5	0.91	23.6	15.7	14.4
11	88.0*	0.33	10.7	19.1	19.6	19.0*	0.91	12.9	16.5	15.1
12	70.0*	0.31	5.99	18.5	19.1	19.0*	0.81	18.4	15.8	15.0
13	89.0*	0.69	19.0	19.3	18.8	19.0*	0.84	11.6	16.2	15.2
14	106.5	0.45	74.7	18.7	18.9	20.5	0.85	14.3	16.2	15.2
15	74.0*	0.28	14.3	18.1	18.8	21.2	0.91	19.7	16.4	15.0
16	89.0*	0.50	7.17	19.3	19.3	15.5	0.91	15.0	16.2	14.9
17	74.0*	0.36	11.8	18.3	18.7	21.5	0.86	23.7	16.0	14.9
18		1.00								
19	[g]					[h]				
20	14.0	0.17	340.0	14.0	13.0	[h]				
21	23.0	0.42	323.5	13.8	13.6	[h]				

[a] Error in $\Delta G^\ddagger$, ±0.3 kcal/mol; error in P, ±0.04. [b] An asterisk indicates coalescence of trimethylsilyl protons; all others correspond to coalescence of formyl protons. [c] P_I(exchange) = imidate population; P_a(rotation) = population of rotamer with SiR_3 cis to carbonyl. [d] kcal/mol, $\Delta G^\ddagger_{I\to A}$(exchange) = imidate → amide; $\Delta G_a^\ddagger$(rotation) = cis → trans. [e] Could not be determined because the formly imidate peak is among the aromatic multiplets. [f] Was not determined. [g] Imidate population too small, approximately 97% amide tautomer. [h] No hindered rotation observed.

Results

The preparation of all compounds, even those with bulky groups attached to silicon, was accomplished by simple amination of the appropriate chlorosilane with formanilide or acetanilide. The phenyl derivatives were more easily isolated through transsilylation of (trimethylsilyl)formanilide with the appropriate chlorophenylsilane.

(Organosilyl)formanilides. The ^1H room-temperature spectra of (organosilyl)formanilides **1–5** and **7–17** contain two formyl peaks at ca. 8.2 and 7.4 ppm that coalesce as the temperature is raised. At low temperatures, the high-frequency formyl signal split into two peaks of unequal intensities with chemical shifts of ca. 8.2 and 8.4 ppm. On the basis of a previous investigation of (trimethylsilyl)formanilides[2] and (dimethyl-*tert*-butylsilyl)formanilides,[4] the higher coalescence temperature was assigned to the amide/imidate process and the lower coalescence temperature to hindered rotation. Thus, the lower frequency formyl peak is due to the imidate tautomer, and the two higher frequency formyl peaks are due to the cis/trans amide rotamers. The more intense rotamer peak at ca. 8.2 ppm was assigned to the cis rotamer (silyl cis to carbonyl) by the method of differential solvent shifts. For **11**, **12**, **14**, and **16**, dilution with an aromatic solvent produced the smaller upfield chemical shift for the $SiCH_3$ peak of the major rotamer, behavior characteristic of a group cis to the carbonyl. The imidate assignment was confirmed by the lack of shift upon dilution.

Only one set of tautomer resonances was observed in the ^1H, ^{13}C, and ^{29}Si NMR spectra for **6** and **18**. Furthermore, the appearance of these spectra did not change as a function of temperature. The ^1H NMR spectra of these compounds each contained one formyl peak at 7.78 and 7.52 ppm, respectively, indicating that compounds **6** and **18** exist exclusively in the imidate form.

Comparison of the ^{13}C APT spectra of **4** with those of **18** and **6** enabled all but a few of the aromatic resonances in the ^{13}C spectra to be assigned to either the amide or imidate tautomer. For example, the ^{13}C APT spectrum of **4** shows two "formyl" peaks at 169.3 and 154.4 ppm and two quaternary carbon peaks at 149.0 and 141.9 ppm. The ^{13}C APT spectra of the two imidate compounds, **6** and **18**, contain only two peaks in this region: a N=CH peak at ca. 154 ppm and a quaternary peak at ca. 149 ppm. Therefore, the 154 and 149 ppm peaks correspond to the imidate N=CH and quaternary aromatic carbon, respectively, and the 169.3 and 141.9 ppm peaks are due to the amide carbonyl and quaternary aromatic carbon, respectively.

Contrary to the results of previous studies of amide–imidate tautomerism, the IR spectra of the (organosilyl)formanilides offer definitive support of these structural assignments.[1,2] The IR spectrum of **6**, which exists solely in the imidate form, contained only one peak in the C=O/C=N region at 1637 cm^{-1}, while the spectrum of **4**, which exists in both tautomeric forms, contained two peaks, at 1678 and 1635 cm^{-1}. Thus, the lower frequency peak in the IR spectra corresponds to the C=N stretch. The IR spectra of derivatives **1**, **2**, and **16** also showed both C=O and C=N stretches, confirming that these compounds exist as amide/imidate mixtures.

(Dimethylsilyl)acetanilides. The ^1H, ^{13}C, and ^{29}Si NMR spectra for **19–21** were temperature dependent; however, only one coalescence process was observed and was attributed to a rapid exchange of the silyl group between amide and imidate tautomers. Like the silylformanilides, where the $SiMe_2H$ derivative (**1**) has a $\Delta G^\ddagger$ that is 2 kcal/mol less than the $SiMe_3$ derivative (**3**), the $\Delta G^\ddagger$ for **20** was determined to be 14.0 kcal/mol, nearly 2 kcal/mol less than the trimethylsilyl analogues. As reported for other acetanilides, the amide peaks were temperature invariant to −60 °C, presumably due to 100% population of the cis rotamer.[2,8]

Discussion

Populations and free energies of activation, $\Delta G^\ddagger$, for both tautomerism and hindered rotation are shown in

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(8) Stewart, W. E.; Siddall, III, T. H. *Chem. Rev.* **1970**, *70*, 517.

Table V.

(Organosilyl)formanilides. The presence of alkoxy groups on silicon results in high imidate populations (8–10 have an imidate population of ca. 80%), presumably as a result of destabilization of the amide resonance structure by electron withdrawal from the amide nitrogen. The free energy of activation for amide/imidate tautomerism is lowered by approximately 2–3 kcal/mol by the presence of alkoxy groups at silicon, as in **8** and **10**. The partial negative charge on the Si in the transition state for amide/imidate tautomerism (Scheme I) is stabilized by electron-withdrawing silyl substituents. Paradoxically, the free energy of activation for **9** ($Si(OSiMe_3)_3$) is ca. 2 kcal/mol *greater* than that for the alkyl derivatives, presumably due to an overwhelming steric effect (but vide infra).

The free energy of activation for amide/imidate tautomerism is generally insensitive to the *size* of the silyl group (Table III); that is, the free energies of activation for derivatives **1–5**, and **11–17** are within experimental error. This can be attributed to similar steric repulsions in both the ground and transition states for the exchange process and is consistent with the proposed concerted mechanism (Scheme I).

The size of the silyl group does affect the *extent* of tautomerism. Derivatives **6** and **18** have three bulky alkyl groups and exist exclusively in the imidate form. By contrast, derivatives **3–5** have smaller alkyl substituents on the silicon and have imidate populations of approximately 30%. Space-filling models show that bulky groups on silicon encounter more steric repulsions in the amide tautomer than in the imidate tautomer because the silyl group is closer to the phenyl ring in the amide tautomer. Derivatives with only one or two bulky groups can orient the silyl group so that the smallest group comes closest to the phenyl ring, thereby minimizing steric repulsions. Also, derivatives with large but linear alkyl groups, such as *n*-Bu, can rotate about the C–C bonds to position the major portion of the alkyl chain away from the phenyl ring, again making the amide tautomer less sterically unfavorable but at the cost of a decrease in entropy. The repulsive steric interaction appears to be more significant than the entropy, and hence the *effective size* of the substituents depends on the number and size of the bulky groups.

The effect of the size and electronic nature of substituents at nitrogen on the barrier to rotation has been thoroughly investigated in a variety of *N*,*N*-dialkyl and -diarylamides[8,9] and it is known that electron-withdrawing groups decrease the barrier due to destabilization of the dipolar amide resonance structure and that large groups result in a decrease in the barrier due to greater repulsive forces in the ground state. For the compounds studied here, the free energy of activation is lowered slightly by three ethoxy groups (**8**), but, surprisingly, the size of the groups do not affect the rotational barrier. In these compounds the substituents are further removed from the nitrogen because of the intervening silicon; that is, the N–Si and Si–C bond lengths are longer than the C–N and C–C bond lengths in dialkyl- or diarylamides. Consequently, differences in steric interactions in the ground state relative to the transition state are minimized.

(Dimethylsilyl)acetanilides. The free energy of activation for exchange in dimethylsilylacetanilide is approximately 3 kcal/mol lower than that of (dimethylsilyl)formanilide. The lower energy barrier for the silylacetanilides is supported by previous studies of similar silylamide systems.[2,8]

The barrier to silyl exchange is insensitive to the addition of a *p*-Cl substituent. The addition of an electron-withdrawing substituent to the para-phenyl position, however, does affect the isomer populations. As with the (organosilyl)formanilides, the imidate tautomer is favored by the electronegative substituent.[2] The absence of a trans rotamer is in accord with previous findings for other (organosilyl)acetanilide systems.[2]

$(HCONPh)_2CHSiClMe_2$ (22). The attempted synthesis of ((dichloromethyl)dimethylsilyl)formanilide resulted in compound **22**. The spectral and crystallographic data indicate that 2 equiv of formanilide attacked (dichloromethyl)dimethylchlorosilane at the dichloromethyl site rather than the Si–Cl site, leaving the silicon–chlorine bond intact. Compound **22** has one strong dative O(1)→Si dative bond (1.992 (3) Å) and one very weak O(2)→Si dative bond (3.123 (3) Å), as indicated in Figure 1 and Table III. The short dative O→Si distance is similar to that reported for the five-coordinate silicon formed in the reaction of bis(trimethylsilyl)acetamide with (chloromethyl)dimethylchlorosilane.[6b] The two dative bonds must be in dynamic equilibrium in solution because the NMR spectra indicate that the formanilide groups are equivalent. Unfortunately, this process was not detected by variable-temperature NMR experiments down to –65 °C.

The O→Si dative bonds result in two nearly planar five-membered rings and the geometry at the silicon atom is best described as distorted trigonal bipyramidal. The interaction between O(2) and Si is demonstrated by the large C(2)–Si–C(3) angle of 131.0 (2)° and an O(2)–Si bond distance that is less than the sum of the van der Waals radii of Si and O (3.4 Å). The high-frequency ^{29}Si resonance at –33.7 ppm is consistent with a coordination number for the silicon atom greater than four.

Derivative **14** supports the previous findings of size constraints on the ring formed in the dative interaction. With the substrate $Cl(CH_2)_nSiMe_2Y$, attack occurred at carbon to form the five-membered ring and a five-coordinate silicon when Y = Cl, Br, and NEt_2 but not when Y = OEt, Me, Vn, or Ph, or when $n > 1$.[6a,c] In **14** $n = 3$ and substitution occurred at the Si–Cl site to yield a mixture of amide and imidate tautomers.

Compound **15** was prepared to further understand the features that promote an O–Si dative bond. In derivative **15** it possible for a dative bond to form between the carbonyl of the 2-acetoxyethyl group and the silicon. However the peaks in the ^{29}Si NMR spectrum, 21.5 and 10.1 ppm, are in regions characteristic of a four-coordinate silicon atom.

Conclusion

The electronegativity of the silyl group has a much greater effect on the dynamics of (organosilyl)anilides than does the size of the silyl group. Electronegative substituents on the silicon lower the barrier to exchange and rotation by 1–2 kcal/mol. The imidate tautomer is favored when electronegative or several bulky groups are present at silicon. The effects of size and electronegativity of the silyl substituents on the barrier to exchange are consistent with an intramolecular, concerted mechanism.

The factors that promote the formation of a dative Si–O bond and reaction at the C–Cl site (rather than reaction at the Si–Cl site) are still not well understood, but the formation of **22** demonstrates that the driving force is sufficiently strong to cause two nucleophilic substitutions at carbon. The compound also shows a strong tendency for higher coordination at silicon, while compounds **14** and

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[9] Yoder, C. H.; Sandberg, J. A.; Moore, W. S. *J. Am. Chem. Soc.* 1974, *96*, 2260.

15 reveal some of the structural constraints that control this coordination.

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Supplementary Material Available: Tables of anisotropic thermal parameters for **22** and analytical data for compounds **1–21** (3 pages); a listing of observed and calculated structure factor amplitudes for the X-ray structure of **22** (11 pages). Ordering information is given on any current masthead page.

Cycloaddition of Imines and $Bu^tN{=}O$ with the Carbyne Complexes $[Cp(CO)_2M{\equiv}CTol]^+$ (M = Mn, Re)

Beth M. Handwerker, Kevin E. Garrett, Kathy L. Nagle, and Gregory L. Geoffroy*

The Pennsylvania State University, University Park, Pennsylvania 16802

Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, Delaware 19716

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The cationic carbyne complex $[Cp(CO)_2Re{\equiv}CTol]^+$ (**2**) reacts with the imines $PhCH{=}NCH_3$ and $PhCH{=}N{-}N{=}CHPh$ to give a net [2 + 2] cycloaddition of the imine across the metal–carbyne linkage and form the metallacycles $[Cp(CO)_2Re(\eta^2(C,C)\text{-}C\{Tol\}N\{R\}CH\{Ph\})]^+$ (**3**, R = CH_3; **4**, R = $N{=}CHPh$). Complex **3** is hydrolytically unstable and reacts with water to form benzaldehyde and the carbene complex $Cp(CO)_2Re{=}C(NHMe)Tol$. Trimethylphosphine adds to the tolyl-substituted carbon of complex **3** to form the new metallacycle $[Cp(CO)_2Re(\eta^2(C,C)\text{-}CH\{Ph\}N\{Me\}C\{Tol\}\{PMe_3\}]^+$. Upon photolysis, the BCl_4^- salt of complex **3** loses CO and abstracts Cl^- from the BCl_4^- anion to form $Cp(CO)ClRe(\eta^2(C,C)\text{-}C\{Tol\}N\{Me\}CH\{Ph\})$. A similar chloride abstraction occurs when the BCl_4^- salt of $[Cp(CO)_2Re{\equiv}CTol]^+$ reacts with $Bu^tN{=}O$ to give $Cp(CO)(Cl)Re\{\eta^2(C,O)\text{-}C(O)C(Tol)N(Bu^t)O\}$, **15**, in which a CO ligand has also inserted between the Re atom and the carbyne carbon. In contrast, the BPh_4^- salt of $[Cp(CO)_2Re{\equiv}CTol]^+$ reacts with $Bu^tN{=}O$ by a net [2 + 2] cycloaddition reaction to form $[Cp(CO)_2Re\{\eta^2(C,O)\text{-}C(Tol)N(Bu^t)O\}]BPh_4$, **16**. The metallacycle **15** can be converted into **16** by abstraction of chloride with Ag^+, and complex **16** reacts with excess PMe_3 to form $(CO)_2(PMe_3)_2Re\{\eta^2(C,O)\text{-}C(Tol)N(Bu^t)O\}$, **18**, in which the metallacycle has been retained but the Cp ligand has been displaced. Reaction of the BCl_4^- salt of $[Cp(CO)_2Re{\equiv}CTol]^+$ with the dimer $[Bu^tN{=}O]_2$ leads to the formation of the five-membered metallacycle $[Cp(CO)_2Re\{\eta^2\text{-}(C,O)\text{-}C(O)C(Tol)N(Bu^t)O\}]BCl_4$. In contrast to the reactions of **2**, the manganese carbyne complex $[Cp(CO)_2Mn{\equiv}CPh]^+$ reacts with $PhCH{=}NCH_3$ and $PhCH{=}N{-}N{=}CHPh$ to give new carbene complexes which result from insertion of the imine between the carbyne carbon and a carbon atom of the Cp ligand. The complex $[Cp^*(CO)_2Mn{\equiv}CTol]BCl_4$ (**12**) reacts with $PhCH{=}NCH_3$ to give an analogous product formed by an unprecedented substitution of a Cp* methyl group by the imine carbon. Complexes **3**, **15**, **16**, and **18** were crystallographically characterized: **3**, triclinic, $P\bar{1}$, $a = 10.367$ (2), $b = 11.306$ (2), $c = 11.858$ (2) Å, $\alpha = 83.96$ (2), $\beta = 83.04$ (2), $\gamma = 67.78$ (2)°, $V = 1274.6$ (5) Å^3, $Z = 2$, $R(F) = 3.56\%$, $R(wF) = 4.53\%$ for 4804 reflections with $F_o > 5\sigma(F_o)$; **15**, orthorhombic, $Fdd2$, $a = 21.700$ (4), $b = 38.016$ (7), $c = 11.120$ (2) Å, $V = 9173.4$ (22) Å^3, $Z = 16$, $R(F) = 5.22\%$, $R(wF) = 5.76\%$ for 4144 reflections with $F_o \geq 5\sigma(F_o)$; **16**, monoclinic, $P2_1/c$, $a = 9.007$ (2), $b = 15.003$ (4), $c = 27.839$ (6) Å, $\beta = 95.67$ (2)°, $V = 3743$ (2) Å^3, $Z = 4$, $R(F) = 4.73\%$, $R(wF) = 4.72\%$ for 5084 reflections with $F_o > 5\sigma(F_o)$; **18**, triclinic, $P\bar{1}$, $a = 10.026$ (2), $b = 11.075$ (2), $c = 11.201$ (2) Å, $\alpha = 85.76$ (2), $\beta = 86.99$ (2), $\gamma = 85.59$ (2)°, $V = 1235.3$ (4) Å^3, $Z = 2$, $R(F) = 3.88\%$, $R(wF) = 4.21\%$ for 3724 reflections with $F_o > 5\sigma(F_o)$.

Introduction

Transition metal–carbene complexes have found numerous applications in synthetic organic chemistry through a variety of carbene transfer and cycloaddition reactions.[1] In contrast, carbyne complexes have far fewer applications, in part because their overall chemistry is significantly less developed.[2] Particularly scarce have been well-defined cycloaddition reactions of metal carbynes. The only well-documented reactions of this class are those involving the formation of metallacyclobutadiene complexes from metal carbynes and alkynes,[3] e.g., eq 1,[3a] mainly because of the relevance of this reaction to alkyne metathesis.[4]

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