ionic T-type silicate nuclei are typically observed (−94 to −97 ppm).[10] The ^{13}C NMR spectrum of **6c** also exhibited a characteristic singlet resonance (δ 10.39) for five-coordinate Me_4SbOR ethers.[4]

The reaction[11] of **6c** with **2** gave high yields of **7**, which was identified on the basis of multinuclear (^{1}H, ^{13}C, ^{29}Si) NMR data. A single-crystal X-ray diffraction study on one of many well-formed but poorly diffracting crystals confirmed the identity of 7. Unfortunately, a serious discussion of metrical data is not warranted due to the marginal quality of the diffraction data and the severely disordered nature of the cyclohexyl groups.[12]

The preparation of **6c** and its use for the synthesis of **7** clearly suggests that a number of other interesting silicate clusters could be synthesized from **6c**. More tantalizing, though, are the prospects for achieving syntheses of very large, structurally well-defined clusters and/or entirely new framework silicates by using multifunctional precursors (e.g., $[HSiO_{1.5}]_n$; $n = 8, 10, 12, 14$).[6,13] We are currently exploring these possibilities and will present the details of this work in due course.

Acknowledgment. We express our thanks to Theodore A. Budzichowski for assistance with the X-ray structural study of 7 and for suggesting the use of $Me_4SbOSiMe_3$ as a mild source of siloxide anions. These studies were supported by the National Science Foundation (Grant No. CHE-8703016) and an NSF-Presidential Young Investigator Award (Grant No. CHE-8657262). Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Financial support from the UCI Academic Senate Committee on Research is also gratefully acknowledged. Funds for the purchase of the X-ray diffraction equipment were made available from NSF Grant No. CHE-85-14495.

Registry No. 1, 47904-22-3; 2, 122487-88-1; 4, 129193-59-5; 5, 3809-29-8; **6a**, 129174-78-3; **6b**, 129174-79-4; **6c**, 129193-57-3; 7, 129193-61-9; $Me_4SbOSiMe_3$, 18279-58-8; $HSiCl_3$, 10025-78-2.

Supplementary Material Available: An ORTEP drawing, a summary of the crystal structure determination, and listings of atomic coordinates, interatomic distances and angles, and hydrogen atomic coordinates for 7 (10 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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(10) (a) Marsmann, H. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: New York, 1980; Vol. 17, and references cited therein. (b) Williams, E. A. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 235 and referenced cited therein. (c) Williams, E. A. *Annu. Rep. NMR Spectrosc.* **1979**, *9*, 221 and referenced cited therein.

(11) In a typical reaction dimer **2** (81 mg, 0.0404 mM) and **7c** (98 mg, 0.0819 mM) were refluxed in benzene (3 mL) for 12 h. Evaporation of the solvent gave a quantitative (NMR) yield of **7** (based on **2**), which was recrystallized from C_6H_6/MeCN to give large colorless crystals. Spectroscopic and analytical data for **7** are as follows. ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): δ 2.30–2.04 (complex m, 28 H), 2.04–1.55 (complex m, 70 H), 1.55–1.17 (complex m, 42 H, with sharp singlet (12 H) at 1.35 for $SbMe_4$), 1.17–0.85 (complex m, 14 H). $^{13}C\{^{1}H\}$ NMR (125.03 MHz, C_6D_6, 25 °C): δ 28.76, 28.36, 28.25, 28.13, 28.03, 27.93, 27.88, 27.85, 27.82, 27.66, 27.61, 27.48, 27.44, 27.41, 27.37, 27.29 (CH_2), 25.75, 24.75, 24.26, 25.15, 23.92 (3:3:1:3:4 for CH), −0.43 ($SbMe_4$). $^{29}Si\{^{1}H\}$ NMR (99 MHz, C_6D_6, 25 °C): δ −66.94, −68.44, −68.52, −68.57, −68.74, −70.07, −106.21 (3:3:1:3:1:3:1). Anal. Calcd (found after removal of benzene and MeCN of crystallization in vacuo) for $C_{82}H_{155}AlO_{25}SbSi_{13}$: C, 47.93 (47.42); H, 7.60 (7.61). Mp >400 °C dec.

(12) Compound 7 crystallizes as a benzene–$(CH_3CN)_3$ solvate in the space group $P6_3$ ($a = 14.734$ (1) Å, $c = 35.498$ (6) Å; $V = 6674$ (1) Å^3; $D_{calcd} = 1.270$ g/cm^3 ($Z = 2$)). A total of 2930 independent reflections with $4.0 < 2\theta < 45.0°$ were collected on a Nicolet R3m/V diffractometer at −100 °C using graphite-monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXTL PLUS), and all non-hydrogen atoms were located by a series of difference-Fourier syntheses. The crystallographic 3-fold rotational axis is aligned along the Si–O–Al linkage joining both silsesquioxane frameworks. (The dihedral angle for the gauche $O_3Al(-O-)SiO_3$ conformation is 35°.) All of the cyclohexyl groups are severely disordered. Although efforts to model the disordered cyclohexyl groups as 1-adamantyl groups were moderately successful, the final *R* factor for isotropic refinement of all non-hydrogen atoms was 10.2%.

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A New Class of Silicon Compounds with Interesting Nonlinear Optical Effects

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Summary: The synthesis and characterization of a new class of silicon compounds with high transparency and nonlinear optical properties have been carried out.

The growing interest in new organic products for quadratic nonlinear optics, related to intramolecular electronic charge transfer (CT), has led to numerous studies of various classes of molecules.[1] In most compounds, previously published, this CT between an electron-donor and an electron-acceptor group takes place through a conjugated π system. For many applications (optical processing, integrated optics, ...) new compounds combining high nonlinear optical activities (NLO) with good transparency are needed. In this study, we have examined a new class of silicon compounds, whose general

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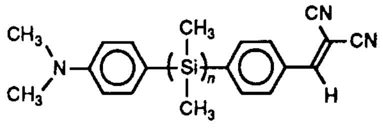
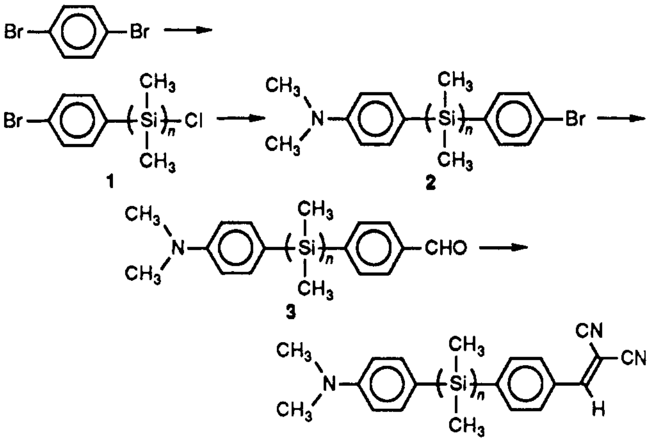
formula is[2]



n = 1, 2, 6

Our interest in silicon compounds that are active in nonlinear optics is guided by the following features:[3] increased polarizability of a silicon backbone compared to that of carbon, σ–π interaction (σ(Si)–π(C)), and σ-delocalization over the Si–Si bonds.

In order to obtain good NLO properties, donor and acceptor groups were grafted onto both sides of a polysilane. The synthesis of these new compounds is schematically presented:



4a (n = 1), 4b (n = 2), 4c (n = 6)

Experimental Section. All manipulations were performed under a dry nitrogen or dry argon atmosphere with use of standard Schlenk techniques. Tetrahydrofuran (THF) and Et_2O were distilled under N_2 from sodium benzophenone ketyl. All other solvents were nitrogen-saturated and dried according to standard procedures. Dimethylformamide (DMF) was allowed to stand over 3-Å molecular sieves (activated by heating to 360 °C for 5 h and cooling in a desiccator). All chlorosilanes (Me_2SiCl_2, $ClSiMe_2SiMe_2Cl$, and $ClSiMe_2(SiMe_2)_4SiMe_2Cl$) were distilled under nitrogen before use.[4]

Malonodinitrile (Aldrich), piperidine (Aldrich), 1,4-dibromobenzene (Aldrich), 4-bromo-*N*,*N*-dimethylaniline (Merck), methanol (Prolabo), ethanol (Prolabo), iodine (Prolabo), magnesium (turnings, 98%, Aldrich), and *n*-butyllithium (Aldrich) were used as obtained from their commercial sources.

Column chromatography was performed with silica gel (230–400 mesh ASTM, Merck). Preparative HPLC was done on a Waters Prep/LC 500 with two silica gel columns (50 cm^3/min). All melting points are uncorrected. The FTIR spectra (KBr) were taken on a Perkin-Elmer PE/750 spectrophotometer. The UV–visible spectra were recorded on a Varian Cary 219 spectrophotometer. ^1H NMR spectra were taken on a 360-MHz Bruker spectrometer, and ^{13}C NMR and ^{29}Si NMR spectra were recorded on a 250-MHz Bruker OAM spectrometer; chemical shifts refer to HMDS (^1H NMR) and TMS (^{29}Si NMR, ^{13}C NMR) as internal standards. The mass spectra were measured on a AEI MS30 spectrometer.

(4-Bromophenyl)chlorodimethylsilane (1a; *n* = 1). To a suspension of magnesium (12.15 g, 0.50 mol) in ether (50 mL) was added one crystal of iodine and slowly (4 h) a solution of 1,4-dibromobenzene (128 g, 0.54 mol) in ether (250 mL). During this procedure, the temperature was maintained at 35–37 °C. The mixture was heated at reflux for 4 h. After the mixture was cooled to room temperature, the Grignard reagent was added to dimethyldichlorosilane (212.5 g, 1.65 mol). The mixture was heated at reflux for 16 h. After the mixture was cooled and filtered, the solvent was removed at 30 °C/30 mmHg and the residue was distilled under reduced pressure. A colorless oil (80 g) was obtained (77–83 °C/1 mmHg). This material was used without further purification (purity 90% by GC); yield 57.7%. Mass spectrum (CI): *m*/*e* 248 (M^+). ^1H NMR ($CDCl_3$): δ 0.55 (s, SiMe, 6 H), 7.46 (m, C_6H_4, 4 H).

(4-Bromophenyl)(4-(dimethylamino)phenyl)dimethylsilane (2a; *n* = 1). To a suspension of magnesium (10.2 g, 0.42 mol) in ether (30 mL) was added one crystal of iodine and slowly (75 min) a solution of 4-bromo-*N*,*N*-dimethylaniline (80 g, 0.4 mol) in ether (250 mL). During the introduction the temperature rose to 35 °C. The mixture was stirred for 16 h at room temperature. The Grignard reagent was added to **1a** (80 g, 0.29 mol, purity 90%, GC) in THF (50 mL), and this mixture was refluxed for 16 h. After the mixture was cooled and filtered, the solvent was removed. To the resulting material was added 100 mL of hexane, and this solution was washed three times with water (200 mL). The organic layer was dried over $MgSO_4$. After evaporation (70 °C/30 mmHg), the crude material was distilled under reduced pressure and 62.5 g of a white solid was isolated (bp 155–160 °C/0.25 mmHg, mp 58 °C); yield 64.5%. The mass spectrum (70 eV) showed a molecular ion at *m*/*e* 333. FTIR (KBr): 2860–2820 cm^{-1} ($\nu(NMe_2)$). ^1H NMR ($CDCl_3$): δ 0.41 (s, $SiCH_3$, 6 H), 2.85 (s, NMe_2, 6 H), 7.48–7.35 (AA′BB′, C_6H_4Br, 4 H), 7.26–6.73 (AA′BB′, $C_6H_4NMe_2$, 4 H).

(4-Formylphenyl)(4-(dimethylamino)phenyl)dimethylsilane (3a; *n* = 1). To a suspension of magnesium (1.4 g, 58 mmol) in THF (80 mL) was added one crystal of iodine and slowly (30 min) compound **2a** (16.7 g, 50 mmol). The mixture was refluxed for 16 h. This Grignard reagent was added slowly (1 h) to a solution of DMF (7.31 g, 0.1 mol) in THF (40 mL). The mixture was stirred at room temperature over 16 h. Brine (100 mL) was added, and the resulting mixture was extracted with AcOEt. The organic layer was dried over $MgSO_4$; the solvent was removed, and a white solid was collected. After recrystallization in hexane, 6.3 g of a light yellow substance was isolated; yield 44.5%. Mass spectrum (CI): *m*/*e* 283 (M^+). ^1H NMR ($CDCl_3$): δ 0.25 (s, $SiCH_3$, 6 H), 2.90 (s, $N(CH_3)_2$, 6 H), 7.33–7.68 (AA′BB, $C_6H_4NMe_2$, 4 H), 7.76–7.63 (AA′BB′, C_6H_4CHO, 4 H), 9.95 (s, CHO, 1 H). FTIR (KBr): 1700 cm^{-1} (ν(CHO)).

(4-(2,2-Dicyanoethenyl)phenyl)(4-(dimethylamino)phenyl)dimethylsilane (4a; *n* = 1). To a solution of **3a** (2.83 g, 10 mmol) in methanol (30 mL) was added malonodinitrile (0.66 g, 10 mmol) and 1 drop of piperidine. This mixture was stirred at room temperature for 3 h. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel) with 90/10 hexane–THF (v/v) as the mobile phase. **4a** was isolated as a red oil in 56% yield (1.85 g). An analytical sample was obtained by HPLC (silica gel, hexane–ethyl acetate (95/5, v/v)). The mass spectrum (70 eV) showed the molecular ion at *m*/*e* 331. FTIR (KBr): 2230 cm^{-1} (ν-

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Table I[11]

entry no.	compd	μ, D	λ_{max}, nm (ϵ)[a]	β, 10^{-30} esu	β_{add}, 10^{-30} esu	β_{CT}, 10^{-30} esu
1	**4a**	6 ± 0.5	320 (27 200)	16 ± 4	14 ± 4	0
2	**4b**	7 ± 1	334 (25 680)	22 ± 5	16 ± 4	6 ± 4
3	**4c**	6.8 ± 0.6	276 (36 600) 320, 385 (CT)	38 ± 4	16 ± 4	22 ± 4

[a] In CHCl$_3$.

(CN)). ^{1}H NMR (CDCl$_3$): δ 0.49 (s, SiMe, 6 H), 2.91 (s, NMe$_2$, 6 H), 6.68–7.32 (AA′BB′, $C_6\mathit{H}_4NMe_2$, 4 H), 7.61–7.76 (AA′BB′, $C_6\mathit{H}_4CH{=}C(CN)_2$, 4 H), 7.68 (s, $-CH{=}C(CN)_2$, 1 H). ^{13}C NMR (CDCl$_3$): δ −2.5 (SiMe$_2$), 40.0 (−NMe$_2$), 151.4, 112.0, 135.2, 120.9 ($Me_2N\mathit{C}_6H_4$), 149.7, 135.1, 129.4, 131.0 ($\mathit{C}_6H_4CH{=}C(CN)_2$), 82.6, 160.0 ($\mathit{C}H{=}\mathit{C}(CN)_2$), 113.8, 112.6 (CN). ^{29}Si NMR (CDCl$_3$): δ −8.08. UV (CHCl$_3$): 320 nm (ϵ = 27 200). UV (CH$_3$OH): 313 nm (ϵ = 26 650). UV (hexane): 312 nm (ϵ = 28 580). Anal. Calcd for $C_{20}H_{21}N_3Si$: C, 72.46; H, 6.38; N, 12.67. Found: C, 72.31; H, 6.43; N, 12.62.

1-(4-Bromophenyl)-2-chloro-1,1,2,2-tetramethyldisilane (1b; *n* = 2). The same procedure as for **1a** was used, with Mg (14.6 g, 0.60 mol), 1,4-dibromobenzene (142 g, 0.60 mol), and 1,2-dichlorotetramethyldisilane (122 g, 0.65 mol). Compound **1b** was isolated (colorless oil) in 53% yield (102.7 g) by a distillation under reduced pressure (102–104 °C/0.5 mmHg; purity 95% by GC). Mass spectrum (CI): *m/e* 306 (M$^+$). FTIR (KBr) 1570–1480 cm^{-1} (aryl), 1250 cm^{-1} (ν(SiCH$_3$)). ^{1}H NMR (CDCl$_3$): δ 0.38 ($BrC_6H_4Si\mathit{Me}_2$, 6 H), 0.39 ($ClSi(Me_2)_2$, 6 H), 7.44–7.29 (AA′BB′, BrC_6H_4, 4 H). ^{29}Si NMR (CDCl$_3$): δ −22.2 ($SiMe_2Cl$), −21.0 ($BrC_6H_4SiMe_2$).

1-(4-Bromophenyl)-2-(4-(dimethylamino)phenyl)-1,1,2,2-tetramethyldisilane (2b; *n* = 2). The same procedure as for **2a** was used, with Mg (10.2 g, 0.42 mol), 4-bromo-*N*,*N*-dimethylaniline (80 g, 0.40 mol), and **1b** (100 g, purity 95% by GC, 0.31 mol). Compound **2b** was isolated (white cream solid) in 44.8% yield (54.5 g) by a distillation under reduced pressure: bp 161–162 °C/0.2 mmHg; mp 58 °C. Mass spectrum (CI): *m/e* 391 (M$^+$). FTIR (KBr): 2800 cm^{-1} (ν(NMe$_2$)), 1100 cm^{-1} (ν(SiC$_6$H$_4$)). ^{1}H NMR (CDCl$_3$): δ 0.21 (s, $Me_2NC_6H_4Si\mathit{Me}_2$, 6 H), 0.24 ($BrC_6H_4Si\mathit{Me}_2$, 6 H), 2.89 (s, −NMe$_2$, 6 H), 7.17–6.64 (AA′BB′, $Me_2NC_6\mathit{H}_4$, 4 H), 7.36–7.18 (AA′BB′, $BrC_6\mathit{H}_4$, 4 H). ^{29}Si NMR (CDCl$_3$): δ −21.4 ($SiMe_2C_6H_4Br$), −23.0 ($SiMe_2C_6H_4NMe_2$).

1-(4-Formylphenyl)-2-(4-(dimethylamino)phenyl)-1,1,2,2-tetramethyldisilane (3b; *n* = 2). The same procedure as for **3a** was used, Mg (1.40 g, 58 mmol), **2b** (19.6 g, 50 mmol), and DMF (7.3 g, 0.1 mol). **3b** was isolated (yellow solid) in 47% yield (8 g) by chromatography on silica gel (hexane–ether (50/50, v/v)); mp 66 °C. Mass spectrum (CI): *m/e* 341 (M$^+$). FTIR (KBr): 1700 cm^{-1} (ν(CHO)), 2800 cm^{-1} (ν(NMe$_2$)), 1105 cm^{-1} (ν(SiC$_6$H$_4$)). ^{1}H NMR (CDCl$_3$): δ 0.22 (s, $Me_2NC_6H_4Si\mathit{Me}_2$, 6 H), 0.29 (s, $OHCC_6H_4Si\mathit{Me}_2$, 6 H), 2.89 (s, −NMe$_2$, 6 H), 6.63–7.15 (AA′BB′, $Me_2NC_6\mathit{H}_4$, 4 H), 7.11–7.48 (AA′BB′, $OHCC_6\mathit{H}_4$, 4 H), 9.94 (s, CHO, 1 H).

1-(4-(2,2-Dicyanoethenyl)phenyl)-2-(4-(dimethylamino)phenyl)-1,1,2,2-tetramethyldisilane (4b; *n* = 2). The same procedure as for **4a** was used, with **3b** (3.41 g, 10 mmol) and NCCH$_2$CN (0.73 g, 11 mmol); **4b** was isolated (yellow-orange solid) in 90% yield (3.5 g) by filtration; mp 98–100 °C. Mass spectrum (CI): *m/e* 389. FTIR (KBr): 2230 cm^{-1} (ν(CN)). ^{1}H NMR (CDCl$_3$): δ 0.21 (s, $Me_2NC_6H_4Si\mathit{Me}_2$, 6 H), 0.28 (s, $(NC)_2C{=}CHC_6H_4Si\mathit{Me}_2$, 6 H), 2.89 (s, NMe$_2$, 6 H), 6.62–7.12 (AA′BB′, $C_6\mathit{H}_4NMe_2$, 4 H), 7.45–7.71 (AA′BB′, $C_6\mathit{H}_4CH{=}C(CN)_2$, 4 H), 7.46 (s, $CH{=}C(CN)_2$, 1 H). ^{29}Si NMR (CDCl$_3$): δ −22.42 (s, $SiMe_2C_6H_4NMe_2$), −20.42 (s, $SiMe_2C_6H_4CH{=}C(CN)_2$)). ^{13}C NMR (CDCl$_3$): δ −3.7 ($Si\mathit{Me}_2C_6H_4NMe_2$), −4.2 ($Si\mathit{Me}_2C_6H_4CH{=}C(CN)_2$), 40.1 (NMe$_2$), 150.9, 112.1, 134.8, 122.3 ($\mathit{C}_6H_4NMe_2$), 150.8, 134.8, 129.2, 130.5 ($\mathit{C}_6H_4CH{=}C(CN)_2$), 160.0, 82.1 ($-\mathit{C}H{=}\mathit{C}(CN)_2$), 113.9, 112.7 (CN). UV (CHCl$_3$): 334 nm (ϵ = 25 680). UV (CH$_3$OH): 328 nm (ϵ = 22 380). UV (hexane): 326 (ϵ = 24 600). Anal. Calcd for $C_{22}H_{27}N_3Si_2$: C, 67.81; H, 6.98; N, 10.78. Found: C, 67.93; H, 7.02; N, 10.66.

The aldehyde **3c** was obtained as a red oil in the same way as described for compounds **3a** and **3b**.

1-(4-(2,2-Dicyanoethenyl)phenyl)-6-(4-(dimethylamino)phenyl)-1,1,2,2,3,3,4,4,5,5,6,6-dodecamethylhexasilane (4c; *n* = 6). A 11.6-g (20.44-mmol) amount of the aldehyde **3c** was dissolved in 100 mL of boiling ethanol. After the addition of 1.74 g (26.4 mmol) of malonodinitrile 2 drops of piperidine were added, and the mixture was stirred for 1.5 h. The product was precipitated on cooling in the refrigerator over the weekend and collected by filtration (5.1 g, 8.21 mmol, 40.5%). An additional preparative HPLC separation (silica gel, hexane–ethyl acetate (90/10, v/v)) gave a yellow crystalline powder, mp 138.5–139 °C. Mass spectrum (CI): *m/e* 621. FTIR (KBr): 2230 cm^{-1} (ν(CN)). ^{1}H NMR (CDCl$_3$): δ 0.01 (s, SiMe$_2$, 12 H), 0.04 (s, SiMe$_2$, 12 H), 0.27 (s, SiMe$_2$, 6 H), 0.35 (s, SiMe$_2$, 6 H), 2.89 (s, NMe$_2$, 6 H), 6.66–7.24 (AA′BB′, $C_6\mathit{H}_4NMe_2$, 4 H), 7.54–7.78 (AA′BB′, $C_6\mathit{H}_4CH{=}C(CN)_2$, 4 H), 7.67 (s, $CH{=}C(CN)_2$, 1 H). ^{29}Si NMR (CDCl$_3$): δ −11.26, −18.87, −38.6, −38.9, −42.5, −43.2 (s, SiMe$_2$). ^{13}C NMR (CDCl$_3$): δ −2.5, −3.3, −4.4, −5.2, −5.4 ($(-Si(CH_3)_2-)_6$), 40.2 (NMe$_2$), 112.1, 124.5, 134.8, 151.1 ($\mathit{C}_6H_4NMe_2$), 129.3, 130.5, 134.7, 150.7 ($\mathit{C}_6H_4CH{=}C(CN)_2$), 159.9, 82.3 ($-\mathit{C}H{=}\mathit{C}(CN)_2$), 112.7, 113.9 (CN). UV (CHCl$_3$): 276 nm (ϵ = 36 600). UV (CH$_3$OH): 274 nm (ϵ = 39 700). UV (*n*-hexane): 274 nm (ϵ = 37 600). Anal. Calcd for $C_{30}H_{51}N_3Si_6$: C, 57.90; H, 8.26; N, 6.75. Found: C, 58.18; H, 8.54; N, 6.65.

Discussion. We have significantly improved the optical first-order hyperpolarizability β of organosilicon compounds by increasing the number of Si atoms separating the acceptor and donor groups (Table I). This improvement is due to the delocalization of σ electrons along the silicon–silicon backbone. This effect is connected to the presence of the lowest energy transition state in the absorption spectra of compound **4c** compared to the absorption spectra of **4a** and **4b**. We believe that this CT process is due to the σ delocalization. Compound **4c** shows an interesting nonlinearity/transparency compromise; if one takes into account the level at 385 nm for calculating the dispersion correction derived from a two-level model,[5] we obtain, for compound **4c**, $\beta_0 = 25.4 \times 10^{-30}$ esu. This value is 1.6 times larger than the highest β_0 value of *p*-nitroaniline reported in the literature[1,5] in methanol (λ_{max} = 370 nm). It must be pointed out that more recent and more sophisticated studies gave much smaller values of β_0 for *p*-nitroaniline: 8.4×10^{-30} esu in dioxane (λ_{max} = 354 nm)[6] or 7.5×10^{-30} esu (λ_{max} = 365 nm).[7] Therefore, the

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increase in β_0 value relative to that of *p*-nitroaniline can reach a factor of 3. Comparison to a "fully conjugated" molecule with a more extended conjugation such as 4-amino-4′-nitrostilbene illustrates the role of the silicon atoms in the reduction of both maximum absorption wavelength (λ_{max} = 385 nm instead of 430 nm in acetone) and intramolecular charge transfer (by a factor of 2 for β_0 as compared to the EFISH-deduced value given by Oudar.[8] These results can be interpreted by the following model:[9] $\beta = \beta_{add} + \beta_{CT}$; β_{add} is obtained by a vectorial addition of the contributions of each side group, which are considered to be independent; this addition is made with respect to the geometrical considerations of the sp^3 orbitals of silicon. β_{CT} is the difference between β and β_{add}. For compound **4c** the important contribution of the CT through the silicon chain is clearly pointed out. The nonlinear optical properties of compounds **4a**, **4b**, and **4c** are listed in Table I.[10]

The work done currently concerns the studies of the CT behavior in donor/acceptor substituted silanes and their efficiency in NLO. The results of this investigation will soon be published in a subsequent paper.

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(10) β measurements were performed with use of the electric field induced second harmonic (EFISH) method.[8] The laser sources consisted of a Q-switched, mode-locked Nd^{III}:YAG laser emitting pulse trains (duration 160 ps) at 1.34 μm and a Q-switched Nd^{III}:YAG laser emitting 10-ns pulses at 1.06 μm. The second-harmonic signal was measured at 670 nm from solutions of various concentrations in acetone.

(11) Dipole moment measurements were made with use of the Hedestrand method in 1,4-dioxane: Hedestrand, G. *Z. Phys. Chem., Abt. B* **1929**, *2*, 428.

A Revisionist View of Fluxionality in Metal Polyhydrides: The Role of Exchange Coupling

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Summary: A reinterpretation of the ^1H NMR spectra of (η-C_5R_5)Ru(PPh_3)H_3 (R = H, **1**; R = Me, **2**) is proposed on the basis of new data from the ^1H NMR spectra of **1** and **1**-d_2. A single resonance is observed in the hydride region of the $^1H\{^{31}P\}$NMR spectrum of **1** down to 190 K, consistent with previous reports. A low-temperature limiting ^1H NMR spectrum of the A_2BX type (X = ^{31}P) was ultimately observed for **1** at 170 K. Computer simulation of the spectrum of **1** at 170 K gives a value of 900 Hz for J_{A-B}. In contrast, the $^1H\{^{31}P\}$ NMR spectrum of **1**-d_2 at 190 K exhibits two distinct hydride resonances in the ratio 2:1, which coalesce at 210 K. From the coalescence temperature, the barrier to thermally activated hydride site exchange is $\Delta G^{\ddagger}_{210}$ = 9.5 kcal/mol. The exceptionally large value for J_{A-B} in **1** is attributed to a quantum-mechanical exchange process, which is effectively quenched by deuterium substitution. A similar interpretation of the previously reported spectra for **2** gives J_{A-B} = 290 Hz at 180 K.

There is currently great interest in the structure and reactivity of transition-metal polyhydride complexes. In light of the discovery of transition-metal dihydrogen complexes by Kubas[1] and theoretical work by Burdett and co-workers indicating that other polyhydrogen "ligands" such as H_3 and H_4 may exist,[2] we[3] and others[4-6] have investigated the possible role of H–H bonding interactions in transition-metal polyhydrides. While there is currently no evidence for H_3 or H_4 ligands as ground-state structures, such polyhydrogen ligands are possible intermediates in the well-studied rearrangement processes of stereochemically nonrigid or fluxional polyhydrides.[7]

A particularly interesting class of polyhydrides are neutral ruthenium(IV) complexes of the form (η-C_5R_5)-Ru(L)H_3 (R = H, Me; L = tertiary phosphine ligand). The first such complex, (η-C_5H_5)Ru(PPh_3)H_3 (**1**), was reported by Davies and co-workers in 1983.[8] It was reported that complex **1** exhibits a single doublet resonance in the hydride region of the ^1H NMR spectrum ($^2J_{H-P}$ = 18 Hz) down to 193 K, the lowest temperature reported. This observation, in conjunction with the observation of two bands in the infrared spectrum attributed to ν(Ru–H), led to the assignment of a trigonal-bipyramidal structure, with the three hydride ligands in the equatorial plane. Subsequent work by Suzuki and co-workers[9] on the closely related complex (η-C_5Me_5)Ru(PPh_3)H_3 (**2**) cast some doubt on this assertion, since the results of an X-ray study of **2** clearly showed that the structure is a distorted capped square pyramid, with the cyclopentadienyl ligand capping. In the case of **2**, Suzuki reports that the ^1H NMR spectrum

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