

Improved Transparency-Efficiency Trade-Off in a New Class of Nonlinear Organosilicon Compounds

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Synthesis and characterization of a new class of organosilicon compounds with a wide transparency range and enhanced nonlinear optical properties are presented. The quadratic hyperpolarizabilities (β) have been measured by the electric field induced second-harmonic generation (EFISH) technique. The effectiveness of the trimethylsilyl substituent is tested both as an electron-donor and as an electron-acceptor group in adequately substituted compounds. Experimental results support evidence that $(\text{CH}_3)_3\text{Si}$ is markedly more efficient as an electron-releasing group. Si has also been included as part of the conjugation path connecting two and three phenyl rings. It is found to be a weak charge transmitter when donor and acceptor phenyl-Si-phenyl moieties are connected. A vectorially additive model of β 's is then shown to account satisfactorily for such an interaction.

Introduction

The increasing interest in new organic and organometallic compounds for quadratic nonlinear optics led to numerous studies of various classes of molecules related to intramolecular electronic charge transfer (ICT) in conjugated systems. High β values have been obtained by the synthesis of donor-acceptor substituted molecules.¹ However, many molecules which show high β values are deeply colored in the visible spectrum, which may be detrimental for some applications requiring visible or near-UV transparency. For many applications (optical processing, integrated optics, ...) new compounds are needed which combined high nonlinear optical activities (NLO) with good transparency.

Recently, we have reported the synthesis and characterization of a new class of silicon compounds combining an extended transparency range with interesting nonlinear optical properties.²

Our main goal, in this series of studies, is to extend molecular engineering ground rules, so far mainly established in the context of standard organic compounds, to more advanced structures where the presence of heteroatoms such as Si, S, P,³ or transition elements⁴ is meant to improve the transparency-efficiency trade-off via specific interactions at the molecular level.

Properties of Si-containing compounds in nonlinear optics are expected to depend on the following features:⁵ (i) increasing polarizability of the Si backbone via σ delocalization as compared to the saturated carbon chain; (ii) p-d orbital bonding; (iii) σ - π interactions.

The quadratic hyperpolarizabilities of a series of Si-containing compounds (see Figure 1) have been measured in solution by use of the EFISH technique. The trimethylsilyl group is known potentially to be able to act both as an electron-donor and a weak electron-acceptor group. To test this potential, $(\text{CH}_3)_3\text{Si}$ was linked through a phenyl ring to either a strong donor (dimethylamino: compound 1) or a strong acceptor (dicyanovinyl, compound

2) group. These syntheses and subsequent measurements are meant to reveal the magnitude of the latent functionality of the $(\text{CH}_3)_3\text{Si}$ group in interaction with these donor and acceptor groups. Experimental results provide evidence that $(\text{CH}_3)_3\text{Si}$ is more effective as an electron-releasing group. The effectiveness of $(\text{CH}_3)_3\text{Si}$ is, however, reduced as compared to other donor groups with a filled p orbital. Following a well-established strategy where studies on stilbenes, phenylbutadienes, phenanthrenes, etc. have pointed out, in the context of "classical" systems, the increased efficiency of extended systems at the price of a reduced transparency, we explore the nonlinear properties of larger molecular systems where aromatic moieties are bridged by (an) Si atom(s). The path, connecting phenyl rings (compounds 3-6) is made to contain one or two silicon atoms, and an additive vectorial model of β is shown to satisfactorily account for such interaction. In conclusion, although the Si acceptor contribution is predominant, the Si donor contribution is weak but not negligible.

Experimental Section

Chemistry. The description of the synthesis of compounds 1-18 is shown in Figure 2. Compound 1 was prepared by a method described in the literature.⁶

General Procedure. Tetrahydrofuran (THF) and Et_2O were distilled under N_2 from sodium benzophenone ketyl. Di-

(1) (a) Chemla, D. S.; Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: Orlando, FL, 1987. (b) Hann, R. A.; Bloor, D., Eds. *Organic Materials for Nonlinear Optics*; Royal Society of Chemistry: London, 1989.

(2) Mignani, G.; Krämer, A.; Pucetti, G.; Ledoux, I.; Soula, G.; Zyss, J.; Meyrueix, R. *Organometallics* 1990, 9, 2640.

(3) (a) Barzoukas, M.; Josse, D.; Zyss, J.; Gordon, P.; Morley, J. *Chem. Phys.* 1989, 139, 359. (b) Zyss, J. *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics*; Bredas, J. L., Chance, R. R., Eds.; Kluwer Academic Publishers: Amsterdam, 1990; pp 545-557.

(4) Kanis, D.; Ratner, M.; Marks, T. *J. Am. Chem. Soc.* 1990, 112, 8203.

(5) (a) Sakurai, H. *J. Organomet. Chem.* 1980, 200, 261. (b) Bassindale, A.; Taylor, P. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 14, p 893. (c) Fujino, M. *Chem. Phys. Lett.* 1987, 136, 451. (d) Kepler, R. *Synth. Met.* 1989, 28, C573. (e) Ziegler, J. *Synth. Met.* 1989, 28 C591. Yokoyama, K.; Yokoyama, M. *Solid State Commun.* 1989, 70, 241.

(6) Gilman, H.; Marshall, F. *J. Am. Chem. Soc.* 1949, 71, 2066. Gilman, H.; Melvin, W.; Goodman, J. *J. Am. Chem. Soc.* 1954, 76, 3219.

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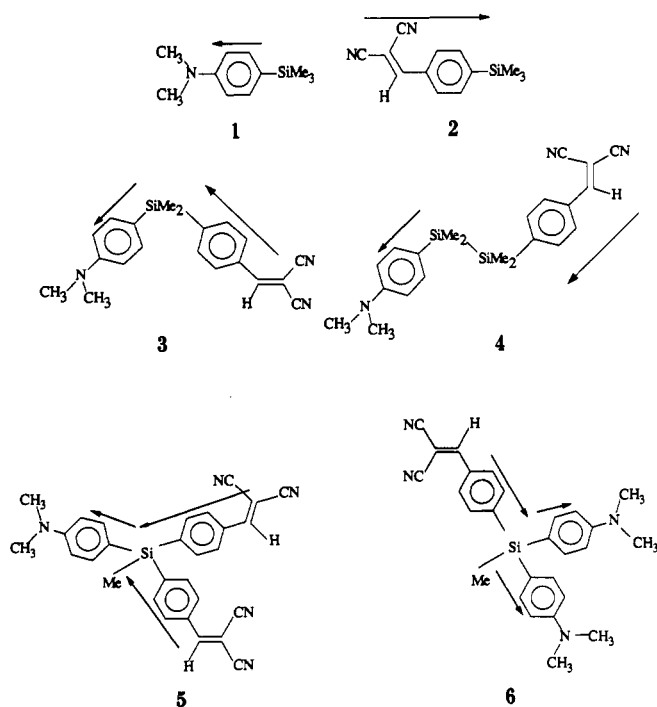


Figure 1. Structural formulas of compounds 1–6. Compounds 1–6 are divided into acceptor and donor subunits. For each of these moieties the β -tensor is approximately one-dimensional along the CT direction. β is represented as a vector pointing from the acceptor to the donor group.

methylformamide (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 , MeSiCl_3 , $\text{ClSiMe}_2\text{-SiMe}_2\text{Cl}$, Rhône-Poulenc) were distilled under nitrogen before use.

Malonodinitrile (Aldrich), piperidine (Aldrich), 1,4-dibromobenzene (Aldrich), 4-bromodimethylaniline (Merck), methanol (Prolabo), iodine (Prolabo), and magnesium (turning, 98%, Aldrich) were used without purification.

All reactions were carried out under a nitrogen atmosphere. Column chromatography was performed using silica gel (230–400 mesh A STM, Merck). Preparative HPLC was done on a Waters-Preps/LC 500 chromatograph with two silica gel columns (50 mL/min).

^1H NMR spectra were recorded 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 UV-visible spectra were recorded on a Varian Cary 219 spectrophotometer. Mass spectra were recorded on a MS 30 (EI) instrument.

IR spectra were obtained on a FT IR, Perkin-Elmer PE 1750 or on a FT IR, Bruker-IFS 85 system.

Melting points were measured by using an Electro Thermal melting points apparatus and are uncorrected.

Gas chromatography was carried out with a Intersmat (SE 30 column) apparatus and with a Spectra Physics integrator.

4-(2,2-Dicyanoethenyl)(trimethylsilyl)benzene (2). To a solution of 4-(trimethylsilyl)benzaldehyde⁷ (6.3 g, 35.4 mmol) in methanol (50 mL) were added one drop of piperidine and malonodinitrile (2.5 g, 37.8 mmol). The mixture was stirred at room temperature (4 h). The formed cream-white solid was collected by filtration. After recrystallization from hexane, 3.1 g of a white solid was obtained in 39% yield (mp 93 °C).

The mass spectrum (70 eV) gave a molecular ion at m/e 226 and a peak at m/e 211 ($\text{M} - \text{CH}_3^+$). FTIR (KBr): 2230 cm^{-1} (ν_{CN}). ^1H NMR (CDCl_3): δ 0.25 (s, SiCH_3 , 9 H), 7.79–7.62 (AA'BB', C_6H_4 , 4 H), 7.70 (s, $\text{CH}=\text{C}(\text{CN})_2$, 1 H). ^{29}Si NMR (CDCl_3): δ 2.60. ^{13}C NMR (CDCl_3): δ -1.5 (Me_3Si), 150.3–131.0 134.4–129.4 (C_6H_4), 160.0–82.8 ($-\text{CH}=\text{C}(\text{CN})_2$), 113.8 (CN). UV: (CHCl_3) 322 nm

($\epsilon = 27950$); (CH_3OH) 316 nm ($\epsilon = 26700$). Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{Si}$: C, 68.97; H, 6.23; N, 12.37. Found: C, 69.01; H, 6.31; N, 12.25.

(4-Bromophenyl)chlorodimethylsilane (7). To a suspension of magnesium (12.15 g, 0.50 g-atom) in ether (50 mL) were 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 cooling 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 cooling and filtering, 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, SiCH_3 , 6 H), 7.46 (m, C_6H_4 , 4 H).

(4-Bromophenyl)(4'-(dimethylamino)phenyl)dimethylsilane (8). To a suspension of magnesium (10.2 g, 0.42 g-atom) in ether (30 mL) were added one crystal of iodine and slowly (1 h 15 min) a solution of 4-bromodimethylaniline (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 7 (80 g, 0.29 mol, purity 90% by GC) in THF (50 mL). The mixture was refluxed for 16 h. After cooling and filtering, 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 of solvents (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} ($\nu_{\text{N}(\text{CH}_3)_2}$). ^1H NMR (CDCl_3): δ 0.41 (s, SiCH_3 , 6 H), 2.85 (s, $\text{N}(\text{CH}_3)_2$, 6 H), 7.48–7.35 (AA'BB', $\text{C}_6\text{H}_4\text{Br}$, 4 H), 7.26–6.73 (AA'BB', $\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$, 4 H).

(4-Formylphenyl)(4'-(dimethylamino)phenyl)dimethylsilane (9). To a suspension of magnesium (1.4 g, 58 mg-atom) in THF (80 mL) were added one crystal of iodine and slowly (30 min) compound 8 (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 ethyl acetate. The organic layer was dried over MgSO_4 ; the solvent was removed and a white solid collected. After recrystallization from 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, $\text{N}(\text{CH}_3)_2$, 6 H), 7.33–7.68 (AA'BB', $\text{C}_6\text{H}_4\text{-N}(\text{CH}_3)_2$, 4 H), 7.76–7.63 (AA'BB', $\text{C}_6\text{H}_4\text{-CHO}$, 4 H), 9.95 (s, CHO, 1 H). FTIR (KBr): 1700 cm^{-1} (ν_{CHO}).

(4-(2,2-Dicyanoethenyl)phenyl)(4'-(dimethylamino)phenyl)dimethylsilane (3). To a solution of 9 (2.83 g, 10 mmol) in methanol (30 mL) were added malonodinitrile (0.66 g, 10 mmol) and one 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. 3 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_{CN}). ^1H NMR (CDCl_3): δ 0.49 (s, SiCH_3 , 6 H), 2.91 (s, $\text{N}(\text{CH}_3)_2$, 6 H), 6.68–7.32 (AA'BB', $\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$, 4 H), 7.61–7.76 (AA'BB', $\text{C}_6\text{H}_4\text{-CH}=\text{C}(\text{CN})_2$, 4 H), 7.68 (s, $-\text{CH}=\text{C}(\text{CN})_2$, 1 H). ^{13}C NMR (CDCl_3): δ 40.0 ($-\text{N}(\text{CH}_3)_2$), 151.4–112.0, 135.2–120.9 ($(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_4$), -2.5 (SiCH_3), 149.7, 135.1–129.4, 131.0 ($\text{C}_6\text{H}_4\text{-CH}=\text{C}(\text{CN})_2$), 160.0–82.6 ($\text{C}=\text{C}(\text{CN})_2$), 113.8–112.6 (CN). ^{29}Si NMR (CDCl_3): δ -8.08. UV: (CHCl_3) 320 nm ($\epsilon = 27200$); (CH_3OH) 313 nm ($\epsilon = 26650$); (hexane) 312 nm ($\epsilon = 28580$). Anal. Calcd for $\text{C}_{20}\text{H}_{21}\text{N}_3\text{Si}$: C, 72.46; H, 6.38; N, 12.67. Found: C, 72.31; H, 6.43; N, 12.62.

1-(4-Bromophenyl)-2-chlorotetramethylsilane (10). The procedure followed was that used for 7, with Mg (14.6 g, 0.60 g-atom), 1,4-dibromobenzene (142 g, 0.60 mol), and 1,2-dichlorotetramethylsilane (122 g, 0.65 mol). Compound 10 was

(7) Sakata, Y. *Yakugaku Zasshi* 1962, 82, 929.

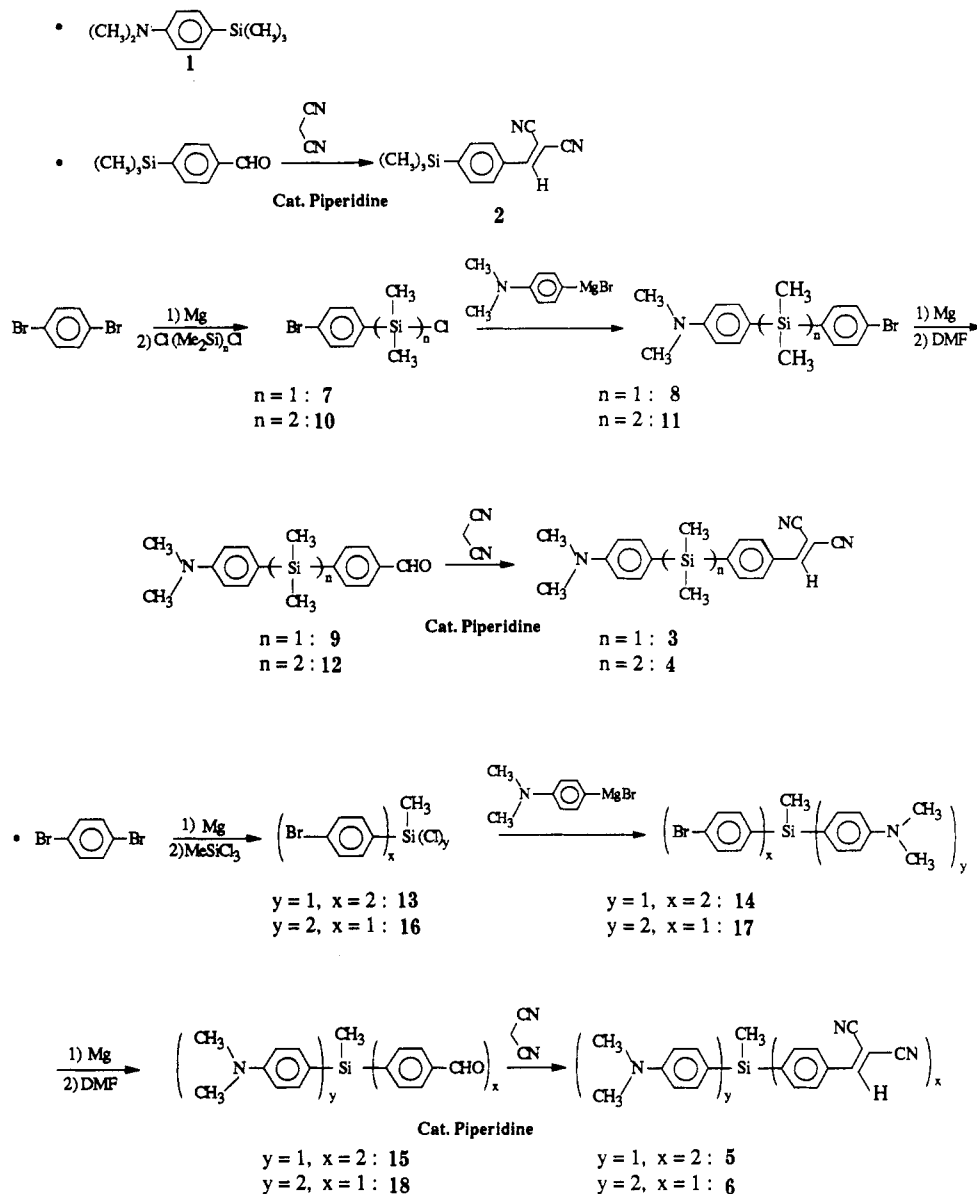


Figure 2. Synthesis of compounds 1–18.

isolated (colorless oil) in 53% yield (102.7 g) by distillation under reduced pressure (102–104 °C/0.5 Torr), purity 95% by GC.

Mass spectrum (CI): m/e 306 (M^+). FTIR (KBr): 1570–1480 cm^{-1} (aryl), 1250 cm^{-1} ($\nu_{\text{Si-CH}_3}$). $^1\text{H NMR}$ (CDCl_3): δ 0.38 ($\text{Br-C}_6\text{H}_4\text{-Si(CH}_3)_2$, 6 H), 0.39 ($\text{ClSi(CH}_3)_2$, 6 H), 7.44–7.29 (AA'BB', $\text{Br-C}_6\text{H}_4$, 4 H). $^{29}\text{Si NMR}$ (CDCl_3): δ -22.2 (SiMe_2Cl), -21.0 ($\text{Br-C}_6\text{H}_4\text{-Si(CH}_3)_2$).

1-(4-Bromophenyl)-2-(4-(dimethylamino)phenyl)tetramethyldisilane (11). The procedure followed was that used for **8**, with Mg (10.2 g, 0.42 g-atom), 4-bromodimethylaniline (80 g, 0.40 mol), and **10** (100 g, purity 95% by GC, 0.31 mol). Compound **11** was isolated (white cream solid) in 44.8% yield (54.5 g) by distillation under reduced pressure (bp 161–162 °C/Torr, mp 58 °C).

Mass spectrum (CI): m/e 391 (M^+). FTIR (KBr): 2800 cm^{-1} ($\nu_{\text{N(CH}_3)_2}$), 1100 cm^{-1} ($\nu_{\text{Si-C}_6\text{H}_4}$). $^1\text{H NMR}$ (CDCl_3): δ 0.21 (s, $(\text{C}_6\text{H}_5)_2\text{N-C}_6\text{H}_4\text{-Si(CH}_3)_2$, 6 H), 0.24 ($\text{Br-C}_6\text{H}_4\text{-Si(CH}_3)_2$, 6 H), 2.89 (s, $-\text{N(CH}_3)_2$, 6 H), 7.17–6.64 (AA'BB', $(\text{CH}_3)_2\text{N-C}_6\text{H}_4$, 4 H), 7.36–7.18 (AA'BB', $\text{Br-C}_6\text{H}_4$, 4 H). $^{29}\text{Si NMR}$ (CDCl_3): δ -21.4 ($\text{Si(CH}_3)_2\text{-C}_6\text{H}_4\text{Br}$), -23.0 ($\text{Si(CH}_3)_2\text{-C}_6\text{H}_4\text{-N(CH}_3)_2$).

1-(4-Formylphenyl)-2-(4-(dimethylamino)phenyl)tetramethyldisilane (12). The procedure followed was that used for **9**, with Mg (1.40 g, 58 g-atom), **11** (19.6 g, 50 mmol), and DMF (7.3 g, 0.1 mol). **12** 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} ($\nu_{\text{N(CH}_3)_2}$), 1105 cm^{-1} ($\nu_{\text{Si-C}_6\text{H}_4}$). $^1\text{H NMR}$ (CDCl_3): δ 0.22 (s, $(\text{CH}_3)_2\text{N-C}_6\text{H}_4\text{-Si(CH}_3)_2$, 6 H), 0.29 (s, $\text{OHC-C}_6\text{H}_4\text{-Si(CH}_3)_2$, 6 H), 2.89 (s, $-\text{N(CH}_3)_2$, 6 H), 6.63–7.15 (AA'BB', $(\text{C}_6\text{H}_5)_2\text{NC}_6\text{H}_4$, 4 H), 7.48–7.11 (AA'BB', $\text{OHC-C}_6\text{H}_4$, 4 H), 9.94 (s, CHO, 1 H).

1-(4-(2,2-Dicyanoethenyl)phenyl)-2-(4-(dimethylamino)phenyl)tetramethyldisilane (4). The procedure followed was that used for **3**, with **12** (3.41 g, 10 mmol) and NCCH_2CN (0.73 g, 11 mmol). **4** 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}). $^1\text{H NMR}$ (CDCl_3): δ 0.21 (s, $(\text{CH}_3)_2\text{N-C}_6\text{H}_4\text{-Si(CH}_3)_2$, 6 H), 0.28 (s, $(\text{NC})_2\text{C=CH-C}_6\text{H}_4\text{-Si(CH}_3)_2$, 6 H), 2.89 (s, $\text{N(CH}_3)_2$, 6 H), 6.62–7.12 (AA'BB', $\text{C}_6\text{H}_4\text{-N(CH}_3)_2$, 4 H), 7.45–7.71 (AA'BB', $\text{C}_6\text{H}_4\text{-CH=C(CN)}_2$, 4 H), 7.46 (s, CH=C(CN)_2 , 1 H). $^{29}\text{Si NMR}$ (CDCl_3): δ -22.42 (s, $\text{Si(CH}_3)_2\text{-C}_6\text{H}_4\text{N(CH}_3)_2$), -20.42 (s, $\text{Si(CH}_3)_2\text{-C}_6\text{H}_4\text{-CH=C(CN)}_2$). $^{13}\text{C NMR}$ (CDCl_3): δ 40.1 ($\text{N(CH}_3)_2$), 150.9–112.1, 134.8–122.3 ($\text{C}_6\text{H}_4\text{-N(CH}_3)_2$), -3.7 ($\text{Si(CH}_3)_2\text{-C}_6\text{H}_4\text{-N(CH}_3)_2$), -4.2 ($\text{Si(CH}_3)_2\text{-C}_6\text{H}_4\text{CH=C(CN)}_2$), 150.8, 134.8–129.2, 130.5 ($\text{C}_6\text{H}_4\text{-CH=C(CN)}_2$), 160.0–82.1 ($-\text{CH=C(CN)}_2$), 113.9–112.7 (CN). UV: (CHCl_3) 334 nm ($\epsilon = 25\,680$); (CH_3OH) 328 nm ($\epsilon = 22\,380$); (hexane) 326 nm ($\epsilon = 24\,600$). Anal. Calcd for $\text{C}_{22}\text{H}_{27}\text{N}_3\text{Si}_2$: C, 67.81; H, 6.98; N, 10.78. Found: C, 67.93; H, 7.02; N, 10.66.

Bis(4-bromophenyl)methylchlorosilane (13). The proce-

Table I. Crystal Structure Parameters of Compound 4

empirical formula	C ₂₂ H ₂₇ N ₃ Si ₂	μ , cm ⁻¹	1.619
fw	389.65	λ (Mo K α radiation), Å	0.710 73
cryst syst	monoclinic	temp, °C	≈23
a, Å	25.43 (1)	no. of reflns used $I > 3\sigma(I)$	578
b, Å	13.284 (5)	residuals, R, R _w (F _o)	0.088, 0.099
c, Å	6.697 (3)	F(000)	832
β , deg	90.59 (4)	scan type	$\omega/2\theta$
V, Å ³	2262 (1)	scan range, deg	(1 + 0.35 tan θ)
space group	P2 ₁ /a	data colld	±h, ±k, ±l
Z	4	S	2.458
cryst dimens, mm	0.20 × 0.30 × 0.25	residual density, e/Å ³	0.254
D(calc), g·cm ⁻³	1.144		

cedure followed was that used for 7, with Mg (24.3 g, 1 g-atom), 1,4-dibromobenzene (236 g, 1 mol), and MeSiCl₃ (77 g, 0.51 mol). 13 (yellow oil) was obtained in 35.8% yield (76 g) by distillation under reduced pressure (bp 195 °C/0.25 mmHg). Purity: 94% by GC.

Mass spectrum (CI): m/e 388 (M⁺). FTIR (KBr): 1560–1490 cm⁻¹ (aryl), 1250 cm⁻¹ (ν_{SiCH_3}). ¹H NMR (CDCl₃): δ 0.53 (SiCH₃, 3 H), 7.46–7.42 (AA'BB', Br–C₆H₄, 8 H).

Bis(4-bromophenyl)(4-(dimethylamino)phenyl)methylsilane (14). The procedure followed was that used for 8, with Mg (6.1 g, 0.25 g-atom), 4-bromodimethylaniline (50 g, 0.25 mol), and 13 (97.6 g, 0.24 mol, purity 94% by GC). 14 (yellow oil) was isolated in 77% yield (90 g, purity 98% by GC) by column chromatography (silica gel; ether/hexane, 1/1, v/v).

Mass spectrum (CI): m/e 473 (M⁺). FTIR (KBr): 2860–2820 cm⁻¹ ($\nu_{\text{N(CH}_3)_2}$). ¹H NMR (CDCl₃): δ 0.72 (s, SiCH₃, 3 H), 2.93 (s, N(CH₃)₂, 6 H), 7.28–6.68 (AA'BB', C₆H₄N(CH₃)₂, 4 H), 7.44–7.30 (AA'BB', Br–C₆H₄, 8 H).

Bis(4-formylphenyl)(4-(dimethylamino)phenyl)methylsilane (15). The procedure followed was that used for 9, with Mg (9.72 g, 0.40 g-atom), 14 (90 g, 0.18 mol, purity 98% by GC), and DMF (30 g, 0.41 mol). 15 (yellow oil) was isolated in 32.9% yield (22.6 g, purity 98% by GC) by column chromatography on silica gel (hexane/ether, between 1/1 and 0/1, v/v).

Mass spectrum (CI): m/e 373 (M⁺). FTIR (KBr): 1700 cm⁻¹ (ν_{CHO}). ¹H NMR (CDCl₃): δ 0.90 (s, SiCH₃, 3 H), 2.93 (s, N(CH₃)₂, 6 H), 7.79–7.62 (AA'BB', C₆H₄–CHO, 8 H), 7.28–6.68 (AA'BB', C₆H₄–N(CH₃)₂, 4 H) 9.98 (s, CHO, 2 H).

Bis(4-(2,2-dicyanoethyl)phenyl)(4-(dimethylamino)phenyl)methylsilane (5). The procedure followed was that used for 3, with 15 (10 g, 26.2 mmol, purity 98% by GC) and NCCH₂CN (3.6 g, 54.5 mmol). 5 (orange oil) was isolated in 77% yield (9.5 g) by preparative HPLC on silica gel (hexane/ethyl acetate, 80/20, v/v).

Mass spectrum (CI): m/e 469 (M⁺). FTIR (KBr): 2230 cm⁻¹ (ν_{CN}). ¹H NMR (CDCl₃): δ 0.81 (s, SiCH₃, 3 H), 2.94 (s, N(CH₃)₂, 6 H), 7.28–6.69 (AA'BB', C₆H₄–N(CH₃)₂, 4 H), 7.80–7.61 (AA'BB', C₆H₄–CH=C(CN)₂, 8 H), 7.72 (s, –CH=C(CN)₂, 2 H). ²⁹Si NMR (CDCl₃): δ –10.94. ¹³C NMR (CDCl₃): δ 151.7 (NCH₃)₂, 139.9–112.0, 136.3–116.8 (–C₆H₄–N(CH₃)₂), –3.8 (SiCH₃), 136.1–145.6, 129.5–131.6 (C₆H₄–CH=C(CN)₂), 159.8–83.4 (C–H=C(CN)₂), 112.5–113.7 (CN). UV: (CHCl₃) 317 nm (ϵ = 55 200); (CH₃OH) 311 nm (ϵ = 55 200). Anal. Calcd for C₂₅H₂₃N₅Si: C, 74.16; H, 4.93; N, 14.91; Si, 5.98. Found: C, 74.49; H, 4.80; N, 14.63; Si, 5.90.

(4-Bromophenyl)methyldichlorosilane (16). The procedure followed was that used for 7, with Mg (12.15 g, 0.5 g-atom), 1,4-dibromobenzene (118 g, 0.5 mol), and MeSiCl₃ (224.2 g, 1.5 mol). Compound 16 (colorless oil) was isolated in 61% yield (91 g, purity 90% by GC).

Mass spectrum (CI): m/e 268 (M⁺) and a base peak at m/e 253 (M – CH₃⁺). FTIR (KBr): 1560–1490 cm⁻¹ (aryl), 1250 cm⁻¹ (ν_{SiCH_3}). ¹H NMR: δ 0.54 (s, SiCH₃, 3 H), 7.45–7.40 (AA'BB', C₆H₄Br, 4 H).

Bis(4-(dimethylamino)phenyl)(4-bromophenyl)methylsilane (17). The procedure followed was that used for 8, with Mg (18 g, 0.74 g-atom), 4-bromodimethylaniline (140 g, 0.70 mol), and 16 (80 g, 0.27 mol, purity 90% by GC). 17 (yellow-orange solid) was isolated in 56% yield (66 g) after recrystallization (hexane) (mp 99–100 °C).

Mass spectrum (CI): m/e 438 (M⁺). FTIR (KBr): 2800 cm⁻¹ ($\nu_{\text{N(CH}_3)_2}$). ¹H NMR (CDCl₃): δ 0.67 (s, SiCH₃, 3 H), 2.91 (s,

N(CH₃)₂, 12 H), 7.41–7.32 (AA'BB', C₆H₄Br, 4 H), 7.31–6.67 (AA'BB', C₆H₄–N(CH₃)₂, 8 H).

Bis(4-(dimethylamino)phenyl)(4-formylphenyl)methylsilane (18). The procedure followed was that used for 9, with Mg (4.8 g, 0.20 g-atom), 17 (66 g, 0.15 mol), and DMF (14.6 g, 0.20 mol). Compound 18 (yellow oil) was isolated in 27.1% yield (15.8 g) by chromatography column (silica gel; ether/hexane, 75/25, v/v).

Mass spectrum (CI): m/e 389 (M⁺). FTIR (KBr): 2800 cm⁻¹ ($\nu_{\text{N(CH}_3)_2}$), 1700 cm⁻¹ (ν_{CHO}). ¹H NMR (CDCl₃): δ 0.70 (s, SiCH₃, 3 H) 2.91 (s, N(CH₃)₂, 12 H), 6.66–7.28 (AA'BB', C₆H₄N(CH₃)₂, 8 H), 7.61–7.73 (AA'BB', C₆H₄CHO, 4 H), 9.98 (s, CHO, 1 H).

Bis(4-(dimethylamino)phenyl)(4-(2,2-dicyanoethyl)phenyl)methylsilane (6). To a solution of 18 (15.8 g, 40 mmol) in methanol (100 mL) were added malonodinitrile (2.65 g, 40 mmol) and four drops of piperidine. The mixture was stirred at room temperature for 4 h. After removal of the solvent under vacuum, the crude product was purified by column chromatography (silica gel; ether/hexane, 50/50, v/v). 6 was isolated as a red-orange solid in 80% yield (13.95 g) (mp 158 °C).

Mass spectrum (CI): m/e 436 (M⁺). FTIR (KBr): 2230 cm⁻¹ (ν_{CN}). ¹H NMR (CDCl₃): δ 0.70 (s, SiCH₃, 3 H), 2.91 (s, N(CH₃)₂, 12 H), 6.65–7.28 (AA'BB', C₆H₄N(CH₃)₂, 8 H), 7.62–7.74 (AA'BB', C₆H₄–CH=C(CN)₂, 4 H), 7.68 (s, CH=C(CN)₂, 1 H). ²⁹Si NMR (CDCl₃): δ –11.87. ¹³C NMR (CDCl₃): δ 39.9 (N(CH₃)₂), 151.2–111.9, 136.2–119.9 (–C₆H₄–N(CH₃)₂), –3.3 (SiCH₃), 148.6, 136.0–129.2, 130.9 (–C₆H₄–CH=C(CN)₂), 160.0–82.3 (–CH=C(CN)₂), 113.8–112.7 (CN). UV (CHCl₃): 319 nm (ϵ = 33 600). Anal. Calcd for C₂₇H₂₃N₄Si: C, 74.27; H, 6.46; N, 12.83; Si, 6.43. Found: C, 74.31; H, 6.46; N, 12.68; Si, 6.45.

Crystallography

None of the compounds exhibited any measurable powder second harmonic generation signal (both at 1.06 and 1.34 μm), presumably owing to centrosymmetric or quasi-centrosymmetric crystalline structures.

X-ray Data Collection and Structural Determination of Compound 4. Red-orange prismatic crystals of 4 were grown in hexane solution by cooling to –20 °C. A single prismatic crystal was used to collect data at room temperature on an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromatized Mo K α radiation. Unit-cell parameters were calculated from the setting angles of 25 carefully centered reflections with $1 < \theta < 25^\circ$. Crystal data and intensity collection parameters are given in Table I. Two intensity control reflections (226, 114) monitored every hour showed ca. 10% decay, which was corrected for during the data processing. Examination of the data, which was corrected for Lorentz-polarization effects but not for absorption, reveals the centrosymmetric space group P2₁/a n/a (nonstandard setting of P2₁/c). The structure was determined by direct methods using MULTAN 82⁸ and was refined on F by full-matrix least-squares calculations with isotropic displacement parameters for non-H atoms, due to the limited number of observed data (see Table I). Hydrogen atoms were introduced by their computed coordinates (C–H = 0.95 Å) in structure factor calculations and were

(8) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. *MULTAN 11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data*; Universities of York and Louvain: York, England and Louvain, Belgium, 1982.

Table II. Positional Parameters and $B(\text{eq})$ Values for 4

atom	x	y	z	$B(\text{eq}), \text{\AA}^2$
Si(1)	0.5906 (3)	0.1889 (5)	-0.7574 (9)	5.0 (1)
Si(2)	0.5154 (3)	0.2395 (5)	-0.930 (1)	5.5 (2)
N(1)	0.2617 (6)	0.260 (1)	-0.658 (2)	5.8 (4)
N(2)	0.8061 (8)	-0.062 (2)	-1.806 (3)	9.7 (6)
N(3)	0.3571 (7)	0.328 (1)	-0.276 (2)	6.7 (5)
C(1)	0.5738 (8)	0.088 (2)	-0.574 (3)	5.5 (6)
C(2)	0.6190 (9)	0.297 (2)	-0.632 (3)	7.6 (7)
C(3)	0.6371 (7)	0.137 (1)	-0.946 (3)	4.1 (5)
C(4)	0.6428 (7)	0.035 (1)	-0.976 (3)	4.6 (5)
C(5)	0.6746 (8)	-0.007 (2)	-1.120 (3)	5.7 (6)
C(6)	0.7034 (8)	0.058 (1)	-1.247 (3)	5.3 (5)
C(7)	0.6992 (8)	0.162 (1)	-1.216 (3)	4.7 (5)
C(8)	0.666 (8)	0.196 (2)	-1.064 (3)	5.1 (5)
C(9)	0.7359 (7)	0.013 (2)	-1.400 (3)	4.8 (5)
C(10)	0.7602 (7)	0.055 (1)	-1.560 (3)	4.9 (5)
C(11)	0.2610 (7)	0.339 (1)	-0.608 (3)	4.5 (5)
C(12)	0.7876 (9)	-0.009 (2)	-1.694 (4)	8.1 (7)
C(13)	0.492 (1)	0.139 (2)	-1.092 (4)	8.5 (7)
C(14)	0.532 (1)	0.353 (2)	-1.080 (4)	10.1 (8)
C(15)	0.4640 (7)	0.275 (1)	-0.744 (2)	3.4 (5)
C(16)	0.4331 (6)	0.194 (1)	-0.666 (2)	3.7 (5)
C(17)	0.3975 (7)	0.213 (1)	-0.517 (3)	4.2 (5)
C(18)	0.3923 (7)	0.307 (2)	-0.431 (3)	5.3 (5)
C(19)	0.4226 (8)	0.382 (2)	-0.509 (3)	5.8 (6)
C(20)	0.4585 (9)	0.368 (2)	-0.658 (3)	6.4 (6)
C(21)	0.3368 (9)	0.243 (2)	-0.173 (3)	8.6 (7)
C(22)	0.362 (1)	0.417 (2)	-0.167 (4)	11.9 (9)

Table III. Intramolecular Distances (\AA) for 4

Si(1)-Si(2)	2.325 (7)	C(4)-C(5)	1.39 (2)
Si(1)-C(1)	1.872 (14)	C(5)-C(6)	1.42 (2)
Si(1)-C(2)	1.806 (15)	C(6)-C(7)	1.41 (2)
Si(1)-C(3)	1.872 (13)	C(6)-C(9)	1.46 (2)
Si(2)-C(13)	1.81 (2)	C(7)-C(8)	1.40 (2)
Si(2)-C(14)	1.87 (2)	C(9)-C(10)	1.37 (2)
Si(2)-C(15)	1.875 (13)	C(10)-C(11)	1.45 (3)
N(1)-C(11)	1.10 (2)	C(10)-C(12)	1.42 (2)
N(2)-C(12)	1.14 (2)	C(15)-C(16)	1.432 (15)
N(3)-C(18)	1.40 (2)	C(15)-C(20)	1.37 (2)
N(3)-C(21)	1.43 (2)	C(16)-C(17)	1.380 (15)
N(3)-C(22)	1.39 (2)	C(17)-C(18)	1.38 (2)
C(3)-C(4)	1.366 (15)	C(18)-C(19)	1.36 (2)
C(3)-C(8)	1.351 (15)	C(19)-C(20)	1.37 (2)

assigned isotropic thermal parameters of $B = 5 \text{\AA}^2$. The neutral-atom scattering factors used for all atoms were obtained from standard sources.⁹ For all computations, the Enraf-Nonius SDP package was used.¹⁰

Results

Structure of Compound 4. A perspective view of the molecule with the atom numbering is presented in Figure 3. Bond lengths and selected bond angles are given in Tables III and IV. These are not very accurate, due to the poor quality of the crystal. However, most of them are in the usual range. Thus the bond length Si(1)-Si(2) = 2.325 (7) \AA agrees well with that predicted from covalent radii (Pauling).¹¹ There is a tetrahedral environment about each Si atom.

The two phenyl rings are planar within experimental error and approximately parallel, making an angle of about 11° with each other. The Si(1) and C(9) atoms are respectively situated at -0.15 and -0.07\AA out of the phenyl

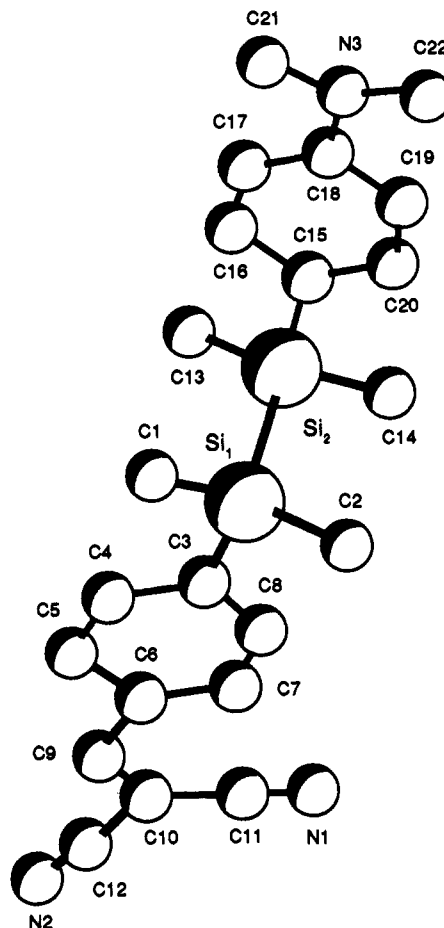


Figure 3. Molecular structure of 4.

Table IV. Intramolecular Bond Angles (deg) for 4

Si(2)-Si(1)-C(1)	110.0 (5)	C(5)-C(6)-C(9)	118 (2)
Si(2)-Si(1)-C(2)	109.0 (5)	C(7)-C(6)-C(9)	124 (2)
Si(2)-Si(1)-C(3)	107.1 (5)	C(6)-C(7)-C(8)	118 (1)
C(1)-Si(1)-C(2)	110.7 (6)	C(3)-C(8)-C(7)	125 (2)
C(1)-Si(1)-C(3)	109.2 (7)	C(6)-C(9)-C(10)	130 (2)
C(2)-Si(1)-C(3)	110.9 (7)	C(9)-C(10)-C(11)	126 (2)
Si(1)-Si(2)-C(13)	110.2 (6)	C(9)-C(10)-C(12)	119 (2)
Si(1)-Si(2)-C(14)	108.0 (6)	C(11)-C(10)-C(12)	116 (1)
Si(1)-Si(2)-C(15)	108.5 (4)	N(1)-C(11)-C(10)	175 (2)
C(13)-Si(2)-C(14)	110.4 (8)	N(2)-C(12)-C(10)	175 (2)
C(13)-Si(2)-C(15)	111.0 (7)	Si(2)-C(15)-C(16)	116 (1)
C(14)-Si(2)-C(15)	108.7 (8)	Si(2)-C(15)-C(20)	126 (1)
C(18)-N(3)-C(21)	116 (2)	C(16)-C(15)-C(20)	117 (1)
C(18)-N(3)-C(22)	120 (2)	C(15)-C(16)-C(17)	120 (1)
C(21)-N(3)-C(22)	117 (2)	C(16)-C(17)-C(18)	122 (1)
Si(1)-C(3)-C(4)	122 (1)	N(3)-C(18)-C(17)	124 (2)
Si(1)-C(3)-C(8)	122 (1)	N(3)-C(18)-C(19)	120 (2)
C(4)-C(3)-C(8)	116 (1)	C(17)-C(18)-C(19)	116 (2)
C(3)-C(4)-C(5)	124 (1)	C(18)-C(19)-C(20)	124 (2)
C(4)-C(5)-C(6)	119 (2)	C(15)-C(20)-C(19)	120 (2)
C(5)-C(6)-C(7)	118 (2)		

ring C(3)-C(8); Si(2) and N(3) atoms, respectively, at 0.16 and 0.05 \AA out of the phenyl ring C(15)-C(20).

The six atoms C(9)/C(10)/C(11)/C(12)/N(1)/N(2) are almost coplanar (the largest deviation is that of the C(10) atom: 0.02 \AA). The dihedral angle between C(10) and the phenyl ring C(3)-C(8) is only 11° . The N(3) atom exists in the pyramidal configuration. Thus the N(3) atom deviates from the plane of the three respective surrounding atoms by -0.207\AA .

The sum of the angles about N(3) is 353° , which also indicates the pyramidal nature of this N atom. The molecules are held together by normal van der Waals forces and are in a head to foot positioning.

(9) International Tables for X-Ray Crystallography; Kynoch Press: Birmingham, U.K., 1974; Vol IV (present distributor Kluwer Academic Publishers, Dordrecht, The Netherlands).

(10) B. A. Frenzt & Associates, Inc. SDP Structure Determination Package; Texas A & M University and Enraf-Nonius; College Station, TX, and The Netherlands; 1985.

(11) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

Nonlinear Optics. The EFISH experiment allows one to explore molecular quadratic hyperpolarizabilities.^{12,13} A Q-switched mode locked YAG:Nd³⁺ laser is used to generate the fundamental radiation at 1.34 μm . The experimental procedure and related data analysis are described extensively in ref 13, the optical nonlinearity being determined from Maker fringes. Translation of a wedge-shaped cell containing the solution and subsequent variation of the interaction length is responsible for this interference pattern.¹⁴ For each compound, dilute solutions of increasing concentrations in acetone are tested, and in all cases absorption is found negligible at both fundamental and harmonic frequencies. Measurements are calibrated with respect to a quartz wedge with a reference value of $d_{11} = 1.2 \times 10^{-9}$ esu at 1.06 μm extrapolated to 1.1×10^{-9} esu at 1.34 μm .

By accounting for environmental effects such as solute-solvent interactions by Lorenz-Lorentz local field corrections, a mean microscopic hyperpolarizability γ^0 of the solute molecule may be derived from the measured macroscopic susceptibility. Its expression is given by

$$\gamma^0 = \gamma^e(-2\omega; \omega, \omega, \omega, 0) + \mu\beta_z(-2\omega; \omega, \omega)/5Kt$$

where the z axis is aligned along the direction of the permanent dipole moment of magnitude μ . The first term is the scalar part of the cubic hyperpolarizability tensor γ_{ijk} , corresponding to purely electronic polarization effects. Assuming Kleinman symmetry, γ^e takes the following expression:

$$\gamma^e = \gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{yyzz} + 2\gamma_{zzxx}$$

The second term originates from the partial Langevin orientation of the permanent dipole moment (μ) along the static field. $\beta_z(2\omega)$, an abbreviation for the standard notation $\beta_z(-2\omega; \omega, \omega, \omega)$ will stand for the z component of the vector part of the susceptibility tensor β_{ijk} , namely

$$\beta_z(2\omega) = \sum \beta_{zjk}(2\omega)$$

The orientation contribution is usually assumed (for the molecular systems considered here) to be predominant over the electronic term γ . The validity of such an approximation has been well established for *p*-nitroaniline derivatives,¹⁵ i.e.

$$\gamma^0 = \bar{\mu} \cdot \bar{\beta}(2\omega)/5KT = \mu\beta_z(2\omega)/5KT = \mu\beta(2\omega) \cos \theta / 5KT$$

β_z is the projection of β on the dipole axis, β the modulus of the tensor (β), and θ the angle between β and μ , as shown in Figure 4. Some molecular dipoles have been known in the literature¹⁶ (1) and measured (3 and 4), and other (2, 5, and 6) have been deduced from geometric considerations starting from simple moieties using an additive vectorial method.¹⁷ It should be noted, though, that dielectric measurements are limited to μ magnitude determination, and we have to rely on modelization for the evaluation of the $\cos \theta$, parameter especially in the case of highly distorted 3-D structures such as 3, 5, or 6 (see Figure 4). The

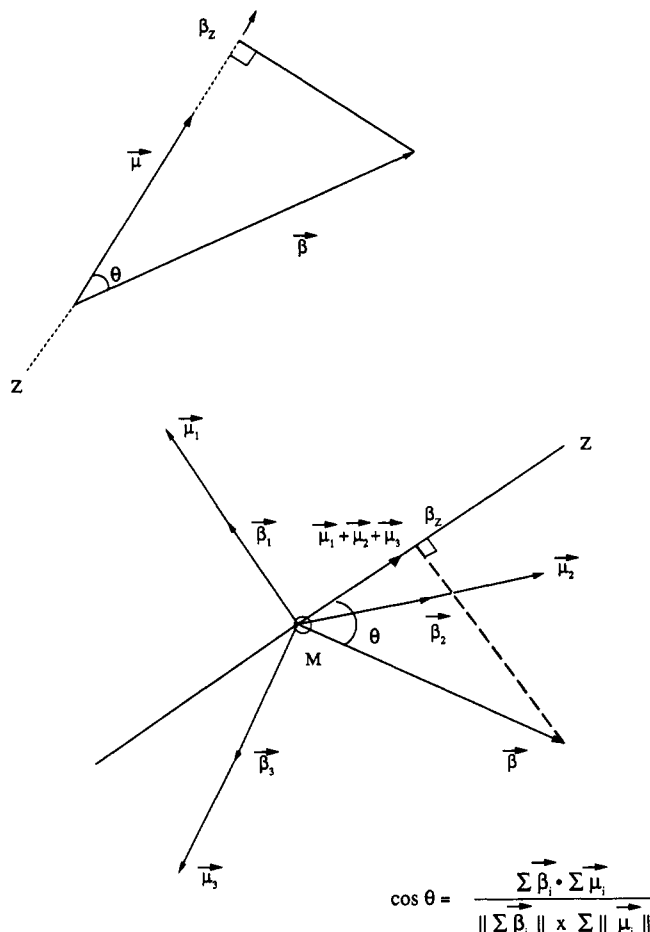


Figure 4. Geometries of the compounds. The upper part displays a general situation where the vector part of the quadratic hyperpolarizability β deviates by an angle θ from the dipole moment. The lower part depicts the geometry corresponding to compounds 5 and 6. The central silicon atom links three subunits which are supposed to contribute in an additive way to the global dipole and hyperpolarizability. Each subunit i ($i = 1-3$) is assumed to be one-dimensional, with μ_i and β_i aligned. However, the vector sum of μ_i 's and β_i 's must not be aligned, and the angle θ between $\bar{\mu}$ and $\bar{\beta}$ for the full molecule is given by the expression at the bottom.

Table V. Experimental Results for Compounds 1-6^a

molecule	λ_{max}	ϵ	μ	$\beta_z(2\omega)$	
				1.17 eV	0 eV
1	264 (MeOH)	17 500	1.76	3.8 ± 1	4
	266 (CHCl ₃)	17 600			
2	316 (MeOH)	26 700	5.0	12 ± 3	9
	322 (CHCl ₃)	27 950			
3	313 (MeOH)	26 650	6.0 ± 0.5	16 ± 4	11
	320 (CHCl ₃)	27 200			
4	328 (MeOH)	22 380	7.0 ± 1	22 ± 5	16
	334 (CHCl ₃)	25 680			
5	311 (MeOH)	55 200	7.1	22.5 ± 5	13
	317 (CHCl ₃)	55 200			
6	(MeOH) ^b		6.6	18 ± 4	16
	319 (CHCl ₃)	33 600			

^a The maximum absorption wavelength (λ_{max}) of the lowest energy transition involved in the intramolecular charge-transfer process (ICT) is determined in two different solvents. The permanent dipole moment is expressed in Debye units. The EFISH experiment was carried out at the fundamental wavelength of 1.34 μm in acetone so as to be in the conditions of a quasi nonresonant regime. $\beta_z(0)$, the static coefficient, was calculated by dividing the measured value by the relevant two-level dispersion factor. All β coefficients are given in 10^{-30} esu. ^b Insoluble in MeOH.

electronic absorptions were recorded in solution for each compound, and the maximum absorption wavelength

(12) Oudar, J. L. *J. Chem. Phys.* 1977, 6, 446.

(13) Ledoux, I.; Zyss, J. *Chem. Phys.* 1982, 26, 2016.

(14) Maker, P. D.; Terhune, R. W.; Nisenoff, M.; Savage, C. M. *Phys. Rev. Lett.* 1962, 8, 21.

(15) Barzoukas, M.; Fremaux, P.; Josse, D.; Kajzar, F.; Zyss, J. *Mater. Res. Soc. Symp. Proc.* 1988, 109, 171.

(16) Gol'oshteyn, I. P.; Traven, V. F.; Kozlov, V. I.; Pyatkina, T. V.; Gur'yanova, N.; Stepanov, B. I. *Zh. Obshch. Khim.* 1976, 46, 2429.

(17) Mc Clellan, A. L. *Tables of Experimental Dipole Moments*; Freeman: San Francisco, 1963; Vol. 1.

(λ_{\max}) of the lowest energy transition corresponding to the intramolecular charge-transfer process (ICT) were determined.

Discussion

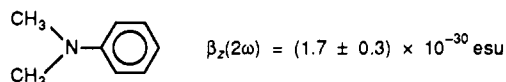
All experimental results are gathered in Table V. The $\beta_z(2\omega)$ values are resonantly enhanced when the second harmonic frequency (2ω) comes close to the molecular absorption frequencies (ω_1). Consequently, the relevant coefficient, for comparing molecules with different molecular absorptions, is the static hyperpolarizability coefficient $\beta(0)$. A dispersion factor, $F(\omega, \omega_1)$, derived from a quantum two-level model, used to frequency-disperse β .¹⁸⁻²⁰

$$F(\omega, \omega_1) = \omega_1^4 / (\omega_1^2 - 4\omega^2)(\omega_1^2 - \omega^2)$$

where $\hbar\omega_1$ is the transition energy to the predominant excited state and ω is the frequency of the fundamental incoming laser.

The $\beta_z(0)$ values, derived from experimental results by use of the appropriate dispersion factor (a λ_{\max} value from solution measurement is used), are listed in Table V.

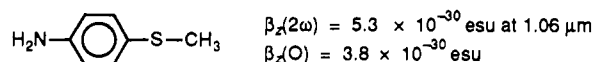
a. $(\text{CH}_3)_3\text{Si}$ as an Electron-Donor or -Acceptor Group. $(\text{CH}_3)_3\text{Si}$ interacts weakly with a donor group such as the dimethylamino group; the value of β_z of 1 is low. The measured β_z of 1 is of the same order of magnitude as that for the *N,N*-dimethylaniline compound²⁰



where the EFISH experiment has been performed at the fundamental wavelength of 1.06 μm .

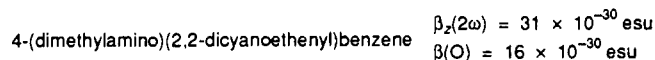
Back-donation, by which part of the electron density of the donor is injected into unfilled Si orbitals, does not appear to be significantly contributing to an efficient intramolecular charge-transfer (ICT) process. The mechanism involved in this interaction is not clearly determined. It could be assigned either to the participation of empty 3d orbitals of Si or to the involvement of low-lying unfilled σ^* orbitals of the $(\text{CH}_3)_3\text{Si}$ group (perhaps mixed with Si 3d orbitals).

It is interesting to note that the measured $\beta_z(2\omega)$ value for compound 1 comes close to the CNDO sum-over-states (CNDO-SOS) estimate for methyl (4-aminophenyl) sulfide (MAS).¹⁵⁻¹⁸



In the case of MAS, all the components of the β_{ijk} tensor have been calculated in an appropriate molecular frame by use of the CNDO-SOS method.¹⁸ It was confirmed that the β_{ijk} tensor is to a good approximation one-dimensional along the CT axis S-NH₂. Some electronic charge is transferred from NH₂ to SMe (donor \rightarrow donor). In the same way, the β_{ijk} tensor corresponding to compound 1 is assumed to be one-dimensional along the ICT axis and lying along the Si \rightarrow N(CH₃)₂ direction (see ref 21).

$(\text{CH}_3)_3\text{Si}$ is markedly more effective as an electron-releasing group. The mechanism involved is interaction between the σ silicon-carbon bond and adjacent π^* orbitals of the benzene ring.^{22,23} The strong degree of polarization of the Si-C bond ensures a high electron density on C and results in an enhanced ability to stabilize an adjacent electron-poor center by orbital overlap. In the same way, the efficiency of the methyl group as a donor has been evaluated, and the participation of -CH₃ in the electron transfer has been associated with hyperconjugation.^{24,25} The nonlinear polarizability results primarily from an electronic ICT between the donor $(\text{CH}_3)_3\text{Si}$ and the acceptor (dicyanovinyl) groups through the conjugated aromatic ring. Thus the β -tensor is expected to be essentially one-dimensional along the ICT axis, and lying along the dicyanovinyl \rightarrow Si direction (see ref 21). Such a result has already been extensively exploited for disubstituted benzene derivatives.^{18,15} The trimethylsilyl group is, however, less effective as a donor than dimethylamino. Experimental results on 4-(dimethylamino)(2,2-dicyanoethenyl)benzene have been reported in ref 26, where the EFISH measurement was carried-out at 1.3 μm using dimethyl sulfoxide (DMSO) as solvent



The maximum absorption wavelength of 2 is remarkably hypsochromic (322 nm in acetone) as compared to that of (dimethylamino)(2,2-dicyanoethenyl)benzene located at 440 nm (DMSO). However, the magnitude of σ - π interaction involved in the ICT process is reduced as compared to π - π conjugation. The polarizable electron density being more mobile in the latter case, it can therefore be more readily transferred from the donor to the acceptor group.

b. Si as Part of the Conjugation Path. The Si atom also has been tested as an electron bridge connecting separate phenyl rings. The conjugation path of compounds 3 (respectively 4) is made up of two phenyl rings linked by one (respectively two) $-(\text{CH}_3)_2\text{Si}-$ moieties. A donor (D = dimethylamino) and an acceptor (A = dicyanovinyl) group are attached at opposite ends of the conjugation path. In compounds 5 and 6 three phenyl rings are grafted on the same Si atom. The effect on β of a di-donor/acceptor (DD/A) or di-acceptor/donor (AA/D) interaction through this system can then be investigated.

In order to get a better understanding of the microscopic processes contributing to the quadratic nonlinearity, we rely strongly on the following geometric consideration. In organosilicon compounds such as 3 the Si atom tends to establish tetrahedral bonds via sp^3 hybridization. Both

(21) The electronic ICT in the ground state goes from the donor to the acceptor group. The corresponding dipole moment is oriented from the acceptor to donor group. For compounds 1 and 2, the sign of the scalar product $\vec{\mu} \cdot \vec{\beta}$ (given by the EFISH experiment) is found to be positive, so that $\vec{\beta}$ is pointing along $\vec{\mu}$. To explain the meaning of this sign, it is interesting to describe the molecule as a two-level system.^{19,20,27} This model takes into account only the predominating one-dimensional ICT process occurring between a donor and an acceptor group through a conjugated system. β is found proportional to $\Delta\mu$ (the difference of dipole moments between the excited and the ground states), which thus defines its sign and direction. Accordingly, a positive sign of $\vec{\mu} \cdot \vec{\beta}$ indicates that $\Delta\mu$ is oriented in the same direction as μ , meaning that there is an increase of the value of the dipole moment in the excited state. The effect of the electronic ICT from the donor to the acceptor group is then enhanced in the excited state as compared to the ground state.

(22) Berwin, H. J. *J. Chem. Soc., Chem. Commun.* 1972, 237.

(23) Eaborn, C. *J. Chem. Soc., Chem. Commun.* 1972, 1255.

(24) Dulicic, A.; Sauteret, C. *J. Chem. Phys.* 1978, 69, 3453.

(25) Dulicic, A.; Flytzanis, C. *Opt. Commun.* 1978, 25, 402.

(26) Katz, H. E.; Singer, K. D.; Sohn, J. E.; Dirk, C. W.; King, L. A.; Gordon, H. M. *J. Am. Chem. Soc.* 1987, 109, 6561.

(27) Oudar, J. L.; Le Person, H. *Opt. Commun.* 1976, 15, 258.

(18) Barzoukas, M.; Josse, D.; Zyss, J.; Gordon, P.; Morley, J. O. *Chem. Phys.* 1989, 139, 359.

(19) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* 1977, 66, 2664.

(20) Oudar, J. L.; Zyss, J. *Phys. Rev. A.* 1982, 26, 2016.

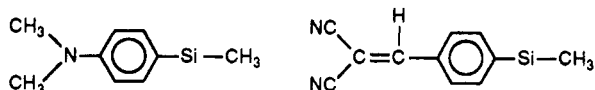
phenyl rings are tilted out of the N-Si-C plane, thus diminishing orbital overlap. Direct conjugation between a strong donor and a strong acceptor attached at each end of the phenyl-Si-phenyl system will then strongly decrease. The molecular structure of compound 4, as reported in the previous section, confirms the sp^3 hybridization of the Si atoms, the angles (at Si) being approximately $107^\circ 1$ and $108^\circ 5$ min. The out-of-plane twist of the phenyl rings and the trans geometry result from steric hindrance.

The structures of compounds 5 and 6 can be easily inferred from the above descriptions, and the three phenyl rings are not likely to be coplanar, thus limiting the possibility of charge transfer via the bridging Si atom. This reduced polarizability is confirmed by comparison of static $\beta_z(0)$ coefficients of compounds 3-6 with that of 4-nitro-4'-aminostilbene. Most noteworthy are the off-resonant efficiencies of compound 4 and of 4-nitro-4'-aminostilbene, which differ by as much as 1 order of magnitude, although the nitro group is less effective as an electron-acceptor than the dicyanovinyl group.²⁶ The following values for 4-nitro-4'-aminostilbene have been reported:¹² $\beta_z(2\omega) = 450 \times 10^{-30}$ esu and $\beta_z(0) = 140 \times 10^{-30}$ esu, where the EFISH experiments have been performed at $1.06 \mu\text{m}$ in acetone.

The maximum absorption wavelength of the compound 4 exhibits a strong hypsochromic shift with respect to that of 4-nitro-4'-aminostilbene (respectively, 334 and 405 nm in acetone).

We conclude that a strong donor and a strong acceptor interact weakly when linked through a silicon-containing conjugation path. It is interesting to note that the off-resonance $\beta_z(0)$ hyperpolarizability of compound 4 is larger than that of compound 3, although two Si atoms are included in the conjugation path of compound 4, the two phenyl rings being then further apart in 4 than in 3. The enhancement of the quadratic nonlinearity cannot then originate from an increased conjugation between the dimethylamino and the dicyanovinyl group and may be ascribed to purely geometrical factors. There is also a small increase in the nonlinear response of compounds 5 and 6, as compared to compound 3, whereas the values of the maximum absorption wavelength λ_{max} of compounds 3, 5, and 6 are very similar. These results rule out any significant strengthening of the D/A interaction, while the additional D or A substituents present in compounds 5 and 6 do not increase significantly the electronic ICT. The slight increase can also be largely ascribed to the geometric factors in agreement with an additive vectorial model of the β hyperpolarizability.¹²

Such a description has been successfully applied to β 's of sulfur-containing systems¹⁸ and is justified by the weak mutual interaction of the substituents through the conjugation path. Accordingly, compounds 3-6 are assumed to be built from the following noninteracting subunits:



The additive behavior is tested by comparing the sum of the hyperpolarizabilities ascribed to each subunit with the hyperpolarizability of the resulting compound. Each of these moieties (a or b) is made up of a donor and an acceptor group interacting through the phenyl ring. It will be assumed that the quadratic hyperpolarizability tensor β_{ijk} associated with the submoiety is essentially one-dimensional along the ICT axis (see Figure 3). This approximation is in fact justified by the previously developed analysis on compounds 1 and 2 stating that the quadratic

Table VI. β_{add} Results from a Combination of the Quadratic Hyperpolarizabilities of the Subunits Making Up the Molecule^a

a		$\beta_a = 3.52 \times 10^{-30}$ esu
		$\mu_a = 1.76 \text{ D}$
b		$\beta_b = 9 \times 10^{-30}$ esu
		$\mu_b = 5 \text{ D}$

molecule	β_{add}^b	$\beta_z(0)^b$
3	11	11
4	13	16
5	12	13
6	13	16

^aThe β nonlinearity of each contributing moiety is derived from experimental results on compounds 1 and 2. ^b β is projected consistently along μ_{add} to allow for comparison with the static coefficient $\beta_z(0)$, where dispersion has been factored out by use of a two-level model. All β coefficients are expressed in 10^{-30} esu.

hyperpolarizability tensor amounts to a vector lying along the ICT axes and oriented from the acceptor to the donor substituent (Figure 1). The magnitude of β_a and β_b is easily derived from the static $\beta_z(0)$ coefficient of compounds 1 and 2, where the additional methyl group is not expected to contribute significantly. Static coefficients are preferably used so as to divide-out dispersion enhancement as already pointed out. β_{add} is then calculated as the vector sum of the quadratic hyperpolarizabilities of each moiety. For instance in the axis of compound 3

$$\vec{\beta}_{\text{add}} = \vec{\beta}_a + \vec{\beta}_b$$

The angle between the two vectors is approximately 109° , due to sp^3 hybridization of Si. The structure of each compound must be taken into account in the numeration (Figure 1). The increase of $\beta_z(0)$, when a second Si atom is added between the two phenyl rings, may now be straightforwardly explained. The trans geometry of compound 4 leads to a more favorable configuration, the directions of β_a and β_b being now approximately parallel as compared to the sp^3 distortion and ensuing cosine projection factor in 3.

To allow for comparison with experimental results, β_{add} is projected along the permanent dipole moment μ_{add} , which is consistently defined as the vector sum of the dipole moments ascribed to each subunit of the molecule, as shown in Figure 4. Results are summarized in Table VI. There is good agreement between calculated and experimental results, which confirms the low level of interaction between the substituent groups attached at each end of the Si-containing system. In view of the validity of this additive model, Si is not to be considered as a polarizable electron connection between the phenyl rings. The ICT processes involved are mainly localized within each moiety. The contributing transitions are Si \leftarrow dimethylamino (Si \rightarrow D) and Si \leftarrow dicyanovinyl (Si \leftarrow A). It must be noted that although the Si \leftarrow A contribution is predominant, the Si \rightarrow D contribution is not negligible. However, these transitions cannot be distinguished in room-temperature vis-UV solution spectra owing to a probably large band overlap. Solvatochromic effects are weak, i.e. of the order of 5 nm or less, in Table V in the case of two usual, protic (methanol) and aprotic (chloroform) solvents. This points out the difficulty of relating in general, nonlinear susceptibilities with the magnitude of solvatochromic displacements. It is seen, in fact, to partially account for the rise in the quadratic hyperpolarizability of compound 4 as compared to that of compound 3. In the same way, the β hyperpolarizability of

compounds 5 and 6 can be traced down to donor/acceptor interactions that take place in each moiety.

Conclusion

β measurements, using the EFISH technique, provide evidence that the trimethylsilyl group can behave both as a donor and as an acceptor group but more efficiently as a donor group. The back-donation process involved in the Si/donor interaction does not contribute to a significant enhancement of β . The efficiency of the trimethylsilyl group as an electron-releasing group is ascribed to σ - π interaction. It is found, however, to be less effective than a donor group containing a filled p orbital.

Silicon has also been investigated as part of a conjunction path connecting phenyl rings. The nonplanar geom-

etry of the phenyl-Si-phenyl system prevents silicon from behaving as an efficient transmitter. The additive behavior of β indicates that silicon must not be viewed as an electron bridge connecting conjugated systems. The charge-transfer interactions contributing to the β nonlinearity are confined within each moiety, and the overall nonlinearity can be accordingly accounted for by a vectorially additive model.

Registry No. 1, 16087-24-4; 2, 136155-28-7; 3, 129620-60-6; 4, 129620-64-0; 5, 130104-06-2; 6, 130104-05-1; 7, 18236-77-6; 8, 129620-58-2; 9, 129620-59-3; 10, 129620-61-7; 11, 129620-62-8; 12, 129620-63-9; 13, 18089-97-9; 14, 136155-29-8; 15, 136155-30-1; 16, 18141-19-0; 17, 136155-31-2; 18, 136155-32-3.

Supplementary Material Available: A listing of structure factors (4 pages). Ordering information is given on any current masthead page.

Metal to Ligand Charge-Transfer Photochemistry of Metal-Metal-Bonded Complexes. 10.[†] Photochemical and Electrochemical Study of the Electron-Transfer Reactions of $\text{Mn}(\text{CO})_3(\alpha\text{-diimine})(\text{L})^{\cdot}$ (L = N-, P-Donor) Radicals Formed by Irradiation of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\alpha\text{-diimine})$ Complexes in the Presence of L

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This article describes the catalytic properties of $\text{Mn}(\text{CO})_3(\alpha\text{-diimine})(\text{L})^{\cdot}$ radicals, formed by irradiation with visible light of the complexes $(\text{CO})_5\text{MnMn}(\text{CO})_3(\alpha\text{-diimine})$ (1) in the presence of L (L = N-, P-donor). The radicals initiate the catalytic disproportionation of complexes 1 in an electron transfer chain (ETC) reaction to give $\text{Mn}(\text{CO})_5^{\cdot}$ and $[\text{Mn}(\text{CO})_3(\alpha\text{-diimine})(\text{L})]^+$. The efficiency of this reaction is low if L is a hard base; it increases for ligands having smaller cone angles and, for phosphines, higher basicities. The $\text{Mn}(\text{CO})_3(\alpha\text{-diimine})(\text{L})^{\cdot}$ radicals also reduce several of the cluster compounds $\text{M}_3(\text{CO})_{12-x}(\text{PR}_3)_x$ (M = Fe, Ru; x = 0-2) and catalyze the substitution of CO by PR_3 . In that case the efficiency of the reaction is mainly determined by the reduction potentials of the $[\text{Mn}(\text{CO})_3(\alpha\text{-diimine})(\text{PR}_3)]^+$ cation and the cluster. These potentials have been measured with cyclic voltammetry and differential pulse voltammetry.

Introduction

Many mechanistic studies have been carried out on ligand substitution reactions of metal carbonyls, complexes which play an important role in various catalytic processes.¹ For many years such reactions have been assumed to proceed exclusively via intermediates with 16 or 18 valence electrons. Recently, however, several substitution reactions have been found to proceed much more rapidly via 17- or 19-valence-electron intermediates. Kochi² was the first who recognized the important role played by

radicals in organometallic chemistry. Since his first publications on this subject many review articles have appeared in which the generation and the structural, spectroscopic, and chemical properties of such radicals are discussed.³ Odd-electron organometallic species can be

(1) (a) *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1968; Vol. 2. (b) Sheldon, R. A. *Chemicals from Synthesis Gas*; Reidel: Dordrecht, The Netherlands, 1983. (c) *Photocatalysis, Fundamentals and Applications*; Serpone, N. Pelizzetti, E., Eds.; Wiley: New York, 1989.

(2) (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978. (b) Kochi, J. K. *J. Organomet. Chem.* 1986, 300, 139.

[†]Part 9: ref 50.

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