

PDF hosted at the Radboud Repository of the Radboud University Nijmegen

The following full text is a publisher's version.

For additional information about this publication click this link.

<http://hdl.handle.net/2066/29332>

Please be advised that this information was generated on 2017-12-05 and may be subject to change.

Notes

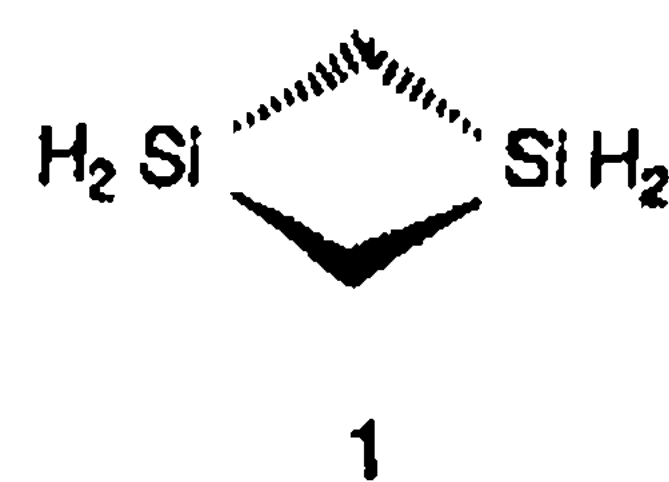
**Metal Complexes of Benzene Derivatives. 45.¹
Dinuclear Bis(η^6 -arene)vanadium and -chromium
Complexes Containing 1,3-Disilacyclobutane as a
Spacer. An EPR Study of Intermetallic
Communication[§]**

Christoph Elschenbroich,^{*,†}
Annette Bretschneider-Hurley,[†] James Hurley,[†]
Andreas Behrendt,[†] Werner Massa,[†]
Sigrid Wocadlo,[†] and Edward Reijerse[‡]

Fachbereich Chemie, Philipps-Universität, D-35032 Marburg,
Germany, and Department of Molecular Spectroscopy,
University of Nijmegen, 6525 ED,
Nijmegen, The Netherlands

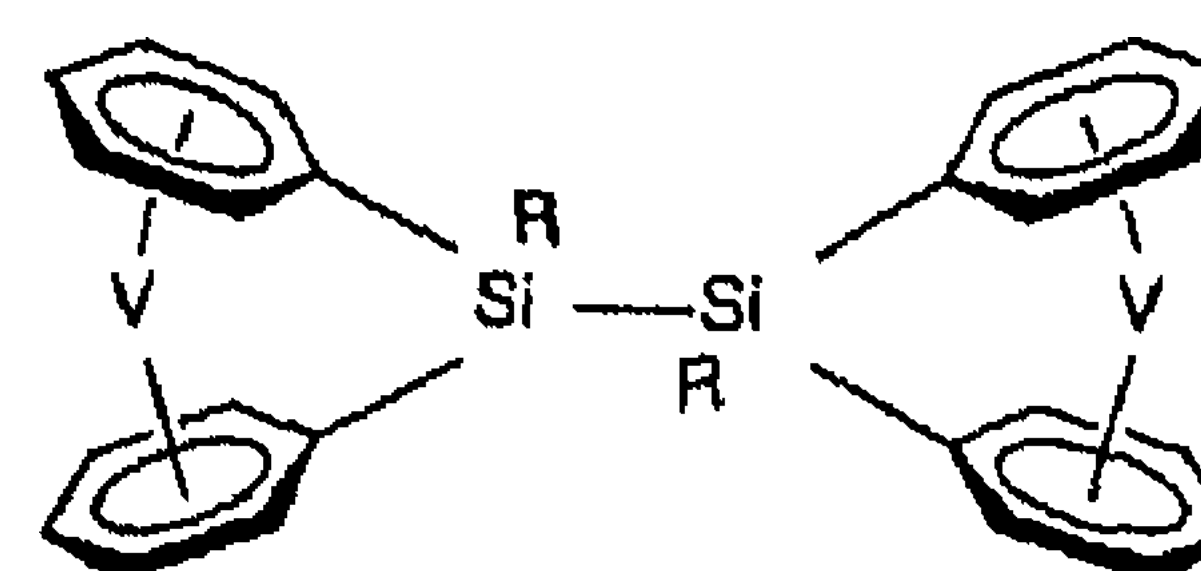
Received August 24, 1994

Structure and bonding in small cyclocarbosilanes of the types $R_2Si(CH_2)_nCH_2$ ($n = 1, 2$) and $R_2SiCH_2SiR_2CH_2$ currently receives considerable attention. Questions of interest include the nature and extent of transannular electronic interaction and of strain-induced distortion like ring folding. In particular, the conspicuously short Si...Si distances in parent 1,3-disilacyclobutane **1** (2.59 Å^{2a}) as well as in its derivatives^{2b} which are shorter than the Si–Si bond distance in hexa-*t*-butyldisilane (2.70 Å³) has triggered a discussion concerning the presence or absence of a silicon–silicon bond. There now appears to be consensus that in **1** and in the related 1,3-cyclodisiloxanes



such a bond is either absent^{2,4–9} or very weak.^{9,10} In fact, ab initio SCF MO calculations on **1** have led to the conclusion, that the Mulliken overlap population across the ring is large and negative; i.e., the interaction is strongly antibonding.⁵ It therefore appeared attractive to us, to investigate the ability of the 1,3-disilacyclobutane unit to transmit electron–electron

exchange interaction.¹¹ Toward this goal, we have attached two paramagnetic units of bis(η^6 -benzene)vanadium to the silicon atoms of **1** to form the binuclear complex **2**. We also report on the synthesis of the analogous chromium complex **3** and on the heterometalocyclophanes **4** and **5**, which are intended to serve as mononuclear reference molecules. The biradical **2** complements our study of [μ -1,2-diphenyl-1,1,2,2-tetrakis(η^6 -phenyl)disilane]divanadium (**6**) which *does* contain a Si–Si



6 R = 4*n*-propylphenyl

bond in the spacer and which, although formally nonconjugated, was shown to promote electron exchange coupling.¹²

The silacyclobutane- and 1,3-disilacyclobutane derivatives of bis(benzene)vanadium and bis(benzene)chromium were syn-

- (11) Magnetic exchange interaction propagated by multiatom bridges is of continuing interest; see: Hendrickson, D. N. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willet, R. D., Gatteschi, D., Kahn, O., Eds.; NATO ASI Series; Reidel: Dordrecht; The Netherlands, 1985, pp 523–554 and leading references in ref 1.
- (12) Part 42: Elschenbroich, Ch.; Bretschneider-Hurley, A.; Hurley, J.; Massa, W.; Wocadlo, S.; Pebler, J.; Reijerse, E. *Inorg. Chem.* **1993**, *32*, 5421.
- (13) Procedures and data for compounds **2–5** are as follows. **2**: Bis(benzene)vanadium (1.21 g, 5.8 mmol) in cyclohexane (75 mL) is metalated with *n*-BuLi (14.3 mmol, 8.9 mL of 1.6 M solution in hexane) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 2.15 mL, 14.0 mmol) at 85 °C (1 h). After this was cooled to ambient temperature, cyclohexane is decanted and replaced by 85 mL of petroleum ether 40/60. To this is added at –15 °C during 3 h 1,1,3,3-tetrachloro-1,3-disilacyclobutane¹⁴ (0.66 g, 2.9 mmol) in 100 mL of petroleum ether. After this was stirred for 12 h at room temperature, the solvent is removed in vacuo and the orange red residue dissolved in toluene and filtered over silica gel. Concentration and cooling (–78 °C) affords **2** (220 mg, 15%) as a red powder. Anal. Calcd for C₂₆H₂₄Si₂V₂: C, 63.15; H, 4.89. Found: C, 55.63; H, 3.76. In our experience notoriously low C and H values in microanalyses of Si- and V-containing organometallics are quite common. MS (EI, 70 eV): *m/z* (relative intensity): 443 (M⁺ – V, 39.9%), 314 (Ph₂Si(CH₂)₂SiPh⁺, 47.3), 301 (Ph₂CH₂SiPh⁺, 53.5), 105 (PhSi⁺, 19.0), 78 (PhH⁺, 100), 51 (V⁺, 22.3), 28 (Si⁺, 60.0). FD-MS: 392 (M⁺ – 2V, 100%). **3**: Preparation in analogy to that of **2** gave **3** (230 mg, 16%) as a greenish-brown microcrystalline material. MS (EI, 70 eV): *m/z* 444 (M⁺ – Cr, 100), 314 (Ph₂Si(CH₂)₂SiC₆H₄⁺, 49.0), 301 (Ph₂SiCH₂SiPh⁺, 58.3), 105 (PhSi⁺, 43.9), 78 (PhH⁺, 49.8), 52 (Cr⁺, 74.2), 28 (Si⁺, 15.6). ¹H NMR (C₆D₆, 30 °C): 1.46 (d, 2 H, CH₂), 3.62 (m, 4 H, ortho-H), 4.41 – 4.56 (m, 6 H, meta-, para-H). ¹³C NMR (C₆D₆, 30 °C): 27.8 (2 C, CH₂), 69.8, 76.8, 77.6 (aryl C). **4**: Bis(benzene)vanadium (1.46 g, 7.0 mmol) was lithiated as described in the preparation of **2**. Then, 1,1-dichloro-1-silacyclobutane¹⁵ (1.09 g, 7.7 mmol) in petroleum ether (80 mL) was added during 2 h at –15 °C. After this was stirred for 12 h at 30 °C, filtered over silica gel and cooled to –25 °C, **4** (0.87 g, 46%) is obtained as brown-black needles. Anal. Calcd for C₁₅H₁₆SiV: C, 65.44; H, 5.86. Found: C, 62.05; H, 4.21. MS (high resolution): calcd, 275.04613; found, 275.04611. MS (EI, 70 eV): *m/z* 275 (M⁺, 100), 247 (M⁺ – C₂H₄, 40.2), 196 (PhSi=CH₂⁺, 67.7), 181 (Ph₂Si⁺ – H, 39.6), 105 (PhSi⁺, 51.1), 51 (V⁺, 28.1), 28 (Si⁺, 35.8). **5**: Using procedures identical to those described for **4** above afforded **5** (0.67 g, 52%) as brown needles. MS (EI, 70 eV): *m/z* 276 (M⁺, 100), 248 (M⁺ – C₂H₄, 32.6), 52 (Cr⁺, 89.6). ¹H NMR (C₆D₆, 30 °C): 1.5 (t, ³J = 8.0 Hz, 4 H, CH₂), 2.42 (quint, ³J = 8.0 Hz, 2 H, CH₂), 3.98 (d, ³J = 5.0 Hz, 4 H, ortho-H), 4.54 (t, ³J = 5.0 Hz, 4 H, meta-H), 4.72 (t, ³J = 5.0 Hz, 2 H, para-H). ¹³C NMR (C₆D₆, 30 °C): 16.41 (2 C, CH₂), 17.79 (1 C, CH₂), 39.30 (2 C, ipso-C), 74.83 (4 C, ortho-C), 79.93 (2 C, para-C), 82.96 (2 C, meta-C) ²⁹Si NMR (C₆D₆, 30 °C): 29.49.

[§] Dedicated to Professor Peter Paetzold on the occasion of his 60th birthday.

[†] Philipps-Universität.

[‡] University of Nijmegen.

- (1) Part 44: Elschenbroich, Ch.; Metz, B.; Neumüller, B.; Reijerse, E. *Organometallics* **1994**, *13*, 5072. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.
- (2) (a) Rempfer, B.; Pfafferot, G.; Oberhammer, H.; Auner, N.; Boggs, J. E. *Acta Chem. Scand. Ser. A* **1988**, *42*, 352. (b) Peters, K.; Peters, E.-M.; von Schnering, H.-G. *Z. Anorg. Allg. Chem.* **1983**, *502*, 61. Baines, K. M.; Brook, A. G.; Lickiss, P. D.; Sawyer, J. F. *Organometallics* **1989**, *8*, 709. Braddock-Wilking, J.; Chiang, M. Y.; Gaspar, P. P. *Organometallics* **1993**, *12*, 197.
- (3) Wiberg, N.; Schuster, H.; Simon, A.; Peters, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 79.
- (4) Savin, A.; Flad, H.-J.; Flad, J.; Preuß, H.; v. Schnering, H.-G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 185.
- (5) O'Keeffe, M.; Gibbs, G. V. *J. Phys. Chem.* **1985**, *89*, 4574.
- (6) Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 823.
- (7) Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589.
- (8) Jemmis, E. D.; Pavan Kumar, P. N. V.; Sreenivas Kumar, N. R. *J. Chem. Soc., Dalton Trans.* **1987**, 271.
- (9) Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 1186.
- (10) Grev, R. S.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1987**, *109*, 6577.

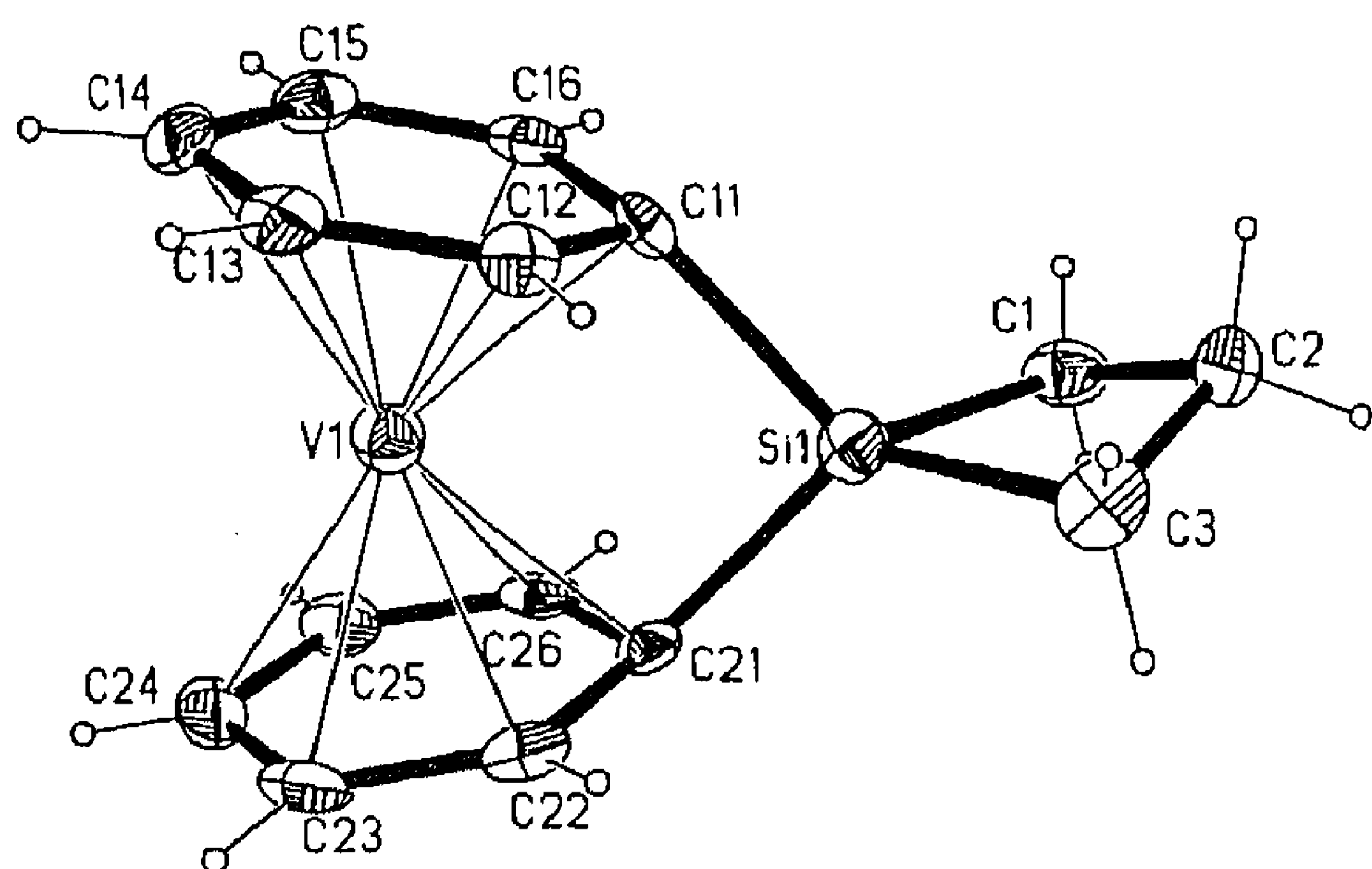
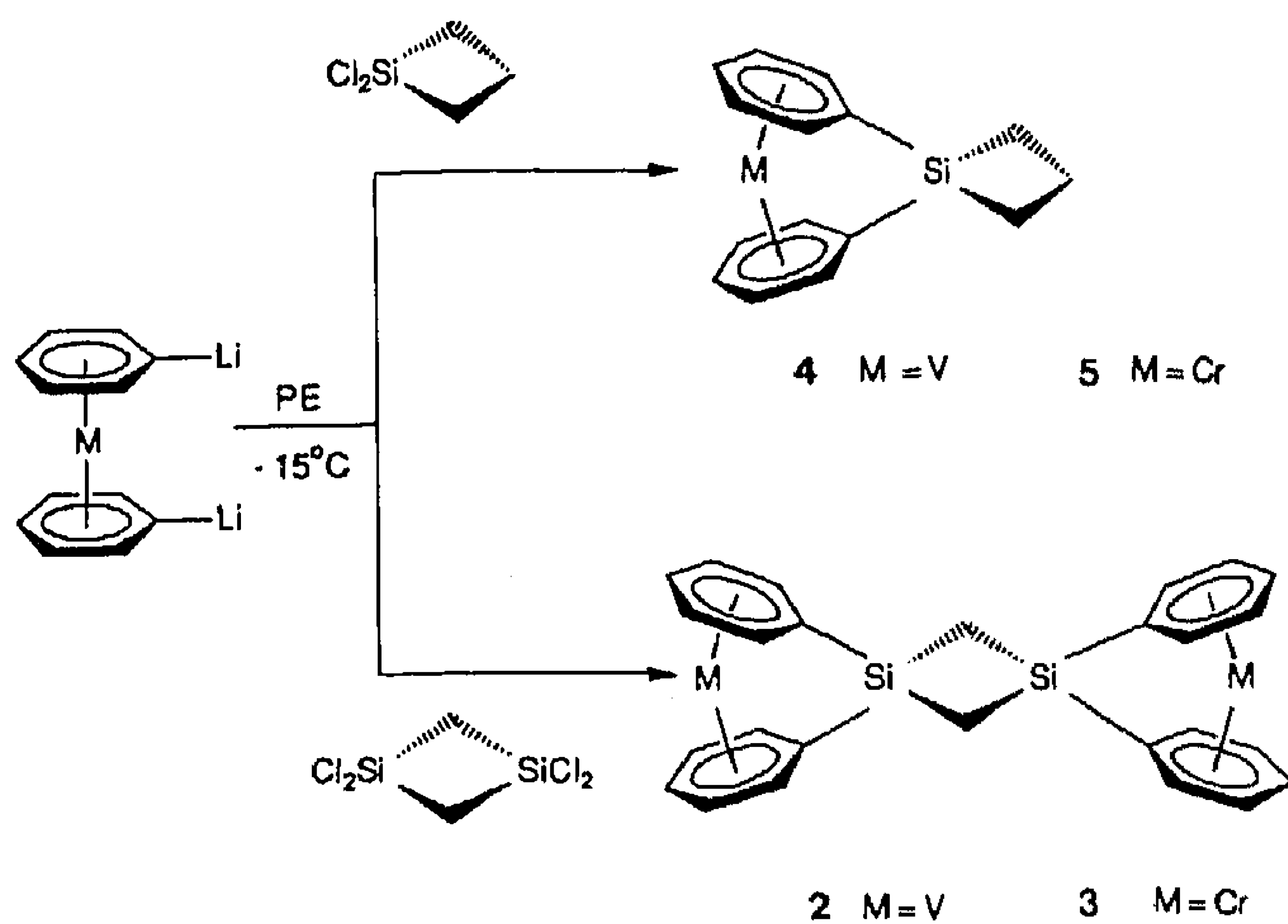


Figure 1. Molecular structure and labeling scheme for **4**: Thermal ellipsoids are at the 50% probability level. Selected bond distances (Å) and angles (deg): V1–C11 2.119(3), V1–C12 2.153(3), V1–C13 2.200(4), V1–C14 2.216(3), V1–C15 2.197(3), V1–C16 2.134(3), V1–C21 2.153(3), V1–C22 2.155(3), V1–C23 2.181(3), V1–C24 2.188(3), V1–C25 2.196(4), V1–C26 2.170(3), C–C 1.399(5)–1.434(5), Si1–C11 1.874(3), Si1–C21 1.836(3), Si1–C1 1.845(4), Si1–C3 1.851(4), V1···Si1 2.901(1) Å; C11–Si1–C21 94.6(1), C1–Si1–C3 81.5(2), Si1–C1–C2 86.1(2), C1–C2–C3 102.2(3), C2–C3–Si1 185.9(2), C–C–C 116.4(3)–122.4(3).

Scheme 1



thesized as shown in Scheme 1.¹³ As opposed to the dinuclear complexes **2** and **3** the mononuclear species **4** yielded crystals suitable for X-ray structural analysis.¹⁶ The molecular structure of **4** is depicted in Figure 1. The angle of ring tilt in the

(14) Auner, N.; Grobe, J. *J. Organomet. Chem.* **1980**, *188*, 151.

(15) Laane, J. *J. Am. Chem. Soc.* **1967**, *89*, 1144. Damrauer, R.; Davis, R. A.; Burke, M. T.; Karn, R. A.; Goodman, G. T. *J. Organomet. Chem.* **1972**, *43*, 124.

(16) The X-ray structure determination for **4** was as follows. A dark brown needle-shaped single crystal (size 0.06 × 0.15 × 0.08 mm) of **4** (C₁₅H₁₆SiV) was investigated at 193 K on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo K α radiation. The monoclinic space group *P2₁/n* (*Z* = 4) was found, the lattice constants were refined from 25 high-angle reflections to *a* = 13.367(4) Å, *b* = 6.235(1) Å, *c* = 14.412(4) Å, β = 93.09(2)°. A total of 1967 reflections (2θ range 4–45°; $\pm h, \pm k, -l$) were collected by ω -scans over (0.8 + 0.35 tan θ)° and an additional 25% before and after each reflection for background measurement. A total of 1697 independent reflections were left after merging (*R*_{int} = 0.021), from which 1388 with *F*_o > 3 σ (*F*) were used. No absorption corrections were applied (μ = 8.98 cm⁻¹). The structure was solved by Patterson methods and refined with anisotropic temperature factors for all non-H atoms to *R* = 0.033 and *R*_w = 0.024 (weights *w* = 1/ σ^2 (*F*_o)) (SHELXTL-*plus*, Sheldrick, G. M. Release 4.2 for Siemens R3 Crystallographic Research Systems. Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1990; scattering factors, $\Delta f'$ and $\Delta f''$ from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV). All hydrogen atoms could be located and were refined with isotropic temperature factors common by groups. The complete results have been deposited.

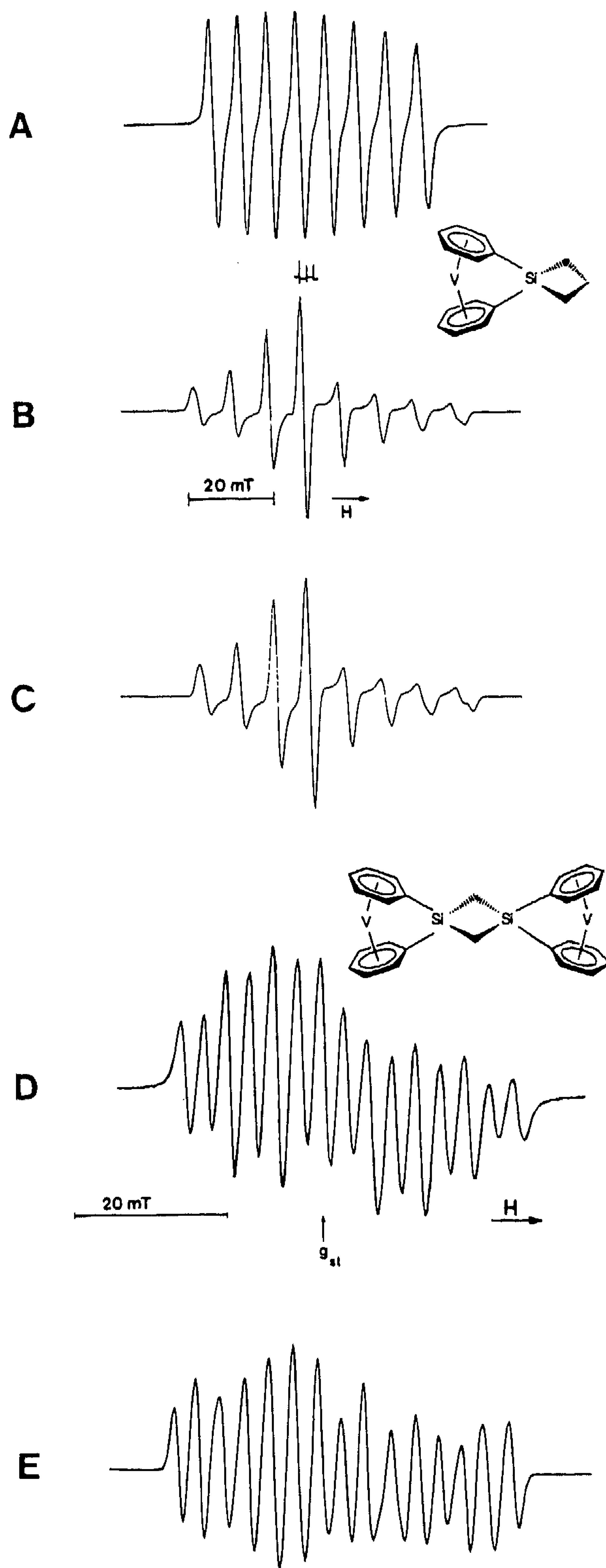
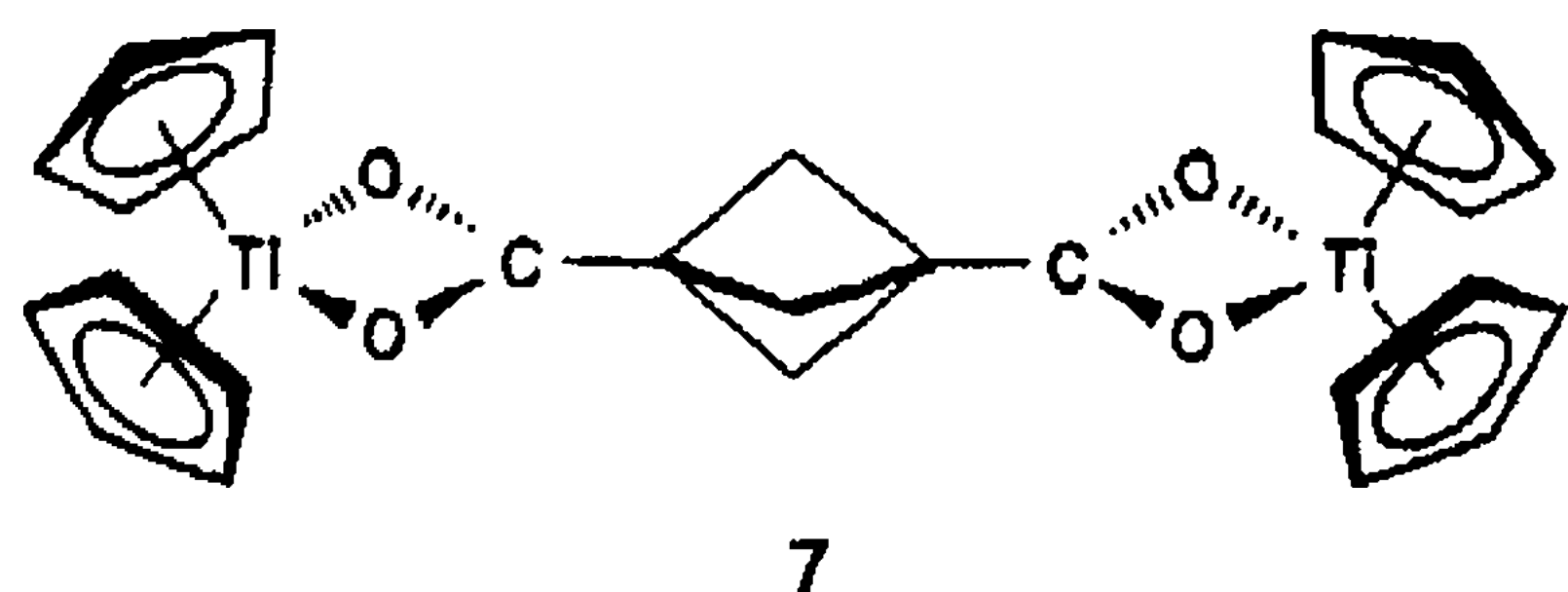


Figure 2. EPR spectra of mononuclear **4** and of dinuclear **2** in toluene at 298 K (A, D) and 103 K (B) and the respective computer simulated traces (C¹⁹, E²⁰). Parameters for **4**: $\langle g \rangle$ = 1.9845, $a(^{51}\text{V})$ = 5.62 mT, g_1 = 1.9770, g_2 = 1.9735, g_3 = 2.0030, A_1 = 8.26, A_2 = 9.0, A_3 = 0.34 mT. Parameters for **2**: $\langle g \rangle$ = 1.9845, $a(^{51}\text{V})$ = 5.62 mT, J = -0.23 ± 0.02 cm⁻¹. Imperfections in the agreement between experiment and simulation derive from the fact that the simulation program²⁰ does not incorporate the $m_l(^{51}\text{V})$ dependence of the linewidths.

sandwich unit is 19.9°, which is similar to that found in **6** (20°).¹² Whereas the bond lengths and bond angles of the silacyclobutane ring in **4** are comparable to those of other silacyclobutane derivatives (as determined by electron diffraction¹⁷), the degree

of ring folding is considerably attenuated (compare: **4** = 23°, 1,1'-dimethylsilacyclobutane = 30°).



In solution, rapid inversion of the four-membered ring leads to magnetic equivalence of the respective axial and equatorial methylene protons. However, the rigid tilt of the sandwich units in **3** and **5** causes large shielding differences between the ortho, meta, and para positions resulting in first-order ^1H NMR spectra. The bending of the sandwich axis also affects the EPR parameters of the radical **4** (Figure 2): the loss of axial symmetry generates an orthorhombic g tensor, the three components being clearly resolved, and the hyperfine coupling constant $a(^{51}\text{V})$ is considerably reduced relative to that of parent bis(benzene)vanadium.¹⁸ Employing the $\text{Si}\cdots\text{V}$ separation of 2.90 Å as found in **4** and the $\text{Si}\cdots\text{Si}$ distance of 2.59 Å in 1,3-disilacyclobutane,² an approximate $\text{V}\cdots\text{V}$ separation of 8.39 Å is inferred for the binuclear complex **2**. As in the case of **6**,¹² magnetic susceptibility data taken down to 4.2 K for **2** yield a linear χ^{-1} vs T plot with a negative intercept thereby indicating very weak antiferromagnetic exchange. In order to gauge the magnitude of this interaction, we have recorded the EPR spectrum of the biradical **2** (Figure 2).

In fluid solution the EPR spectrum of dinuclear **2** displays 15 lines which are separated by 3.16 mT. This value is slightly larger than the coupling constant $a(^{51}\text{V}) = 2.81$ mT (5.62/2), expected for the limiting case of fast exchange which is defined by the condition $J \gg a(^{51}\text{V})$. Furthermore, contrary to **6**, the ^{51}V hyperfine pattern for **2** deviates markedly from a simple binominal distribution. Spectral simulation²⁰ for **2** yielded the exchange coupling constant $J = -0.23 \pm 0.02$ cm $^{-1}$ which falls short of the value $J = -0.48$ cm $^{-1}$ determined for **6**.¹² While,

qualitatively, this gradation is the one expected from a naive distance argument [$\text{V}\cdots\text{V}$: 7.60 Å (**6**), 8.39 Å (**2**)], the magnitude of J for **2** is remarkable in view of the fact that there appears to be no transannular silicon-silicon σ bond in the spacer 1,3-disilacyclobutane (vide supra). Possibly, exchange coupling in **2** is transmitted by an "unsupported π -bond" which has been proposed to be responsible for the surprisingly low $\text{Si}\cdots\text{Si}$ distance in 1,3-disilacyclobutanes.¹⁰ An observation which in the present context warrants mentioning is the magnetic exchange interaction propagated by a bicyclo[1.1.1]pentane-1,3-dicarboxylate spacer in the binuclear dicyclopentadienyltitanium(III) complex **7**.²¹ Here, despite the large intermetallic distance of 9.85 Å and the presence of a saturated bridge, intramolecular spin exchange also manifests itself in the $^{47,49}\text{Ti}$ hyperfine pattern in the fluid solution EPR spectrum ($|J| \gg 10^{-3}$ cm $^{-1}$).²² From magnetic susceptibility data the parameter $J = -1.3$ cm $^{-1}$ was derived which may, however, contain intermolecular contributions.

Information concerning intermetallic communication may in principle also be gleaned from electrochemical behavior in that the observation of disparate first and second redox potentials for a binuclear complex indicates stabilization of the mixed valence state.²³ Unfortunately, in the case of the binuclear complexes **2** and **3** this technique is inapplicable since oxidation as well as reduction of the mononuclear species **4** and **5** turned out to be irreversible even at -50 °C and the cyclic voltammetric traces for **2** and **3** were ill-defined. Presumably, opening of the interannular link occurs subsequently to electron transfer, the ease of desilylation of silylarene complexes being well documented.¹⁸

Supplementary Material Available: Tables of bond lengths (Table S1), angles (Table S2), best planes (Table S3), and atomic fractional coordinates and anisotropic temperature factors (Table S4) (5 pages). Ordering information is given on any current masthead page.

IC9409975

- (17) (a) Krapivin, A. M.; Mägi, M.; Svergun, V. I.; Zaharjan, R. Z.; Babich, E. O.; Ushakov, N. V. *J. Organomet. Chem.* **1980**, *190*, 9. (b) Mastryukov, V. S.; Dorefeeva, O. V.; Vilkov, L. V.; Cyvin, S. J.; Cyvin, B. N. *J. Struct. Chem. (Engl. Transl.)* **1975**, *16*, 438. (c) Cyvin, B. N.; Cyvin, S. J.; Strelkow, S. A.; Mastryukov, V. S.; Vilkov, L. V.; Golubinskii, A. V. *J. Mol. Struct.* **1986**, *144*, 385.
- (18) Elschenbroich, Ch.; Hurley, J.; Metz, B.; Massa, W.; Baum, G. *Organometallics* **1990**, *9*, 889.
- (19) Daul, C.; Mohos, B.; Schläpfer, C. W. EPR-simulation program POWDER, Univ. Fribourg. Möckel, R. Refined version, Univ. Marburg, 1980.

- (20) Program MAGRES: Keijzers, C. P.; Reijerse, E. J.; Stam, P.; Dumont, M. F.; Gribnau, M. C. M., *J. Chem. Soc. (Faraday Trans.)* **1987**, *83*, 3613. The visual fit between the experimental and the simulated traces suffers from the nonincorporation of the $m_l(^{51}\text{V})$ dependence of the linewidth. Variation in the range $|0.100| < J < |0.4000|$ cm $^{-1}$ reveals, however, that optimal agreement is obtained for the value $J = -0.23$ cm $^{-1}$.
- (21) Kramer, L. S.; Clauss, A. W.; Francesconi, L. C.; Corbin, D. R.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1981**, *20*, 2070. Clauss, A. W.; Wilson, S. R.; Buchanan, R. M.; Pierpont, C. G.; Hendrickson, D. N. *Inorg. Chem.* **1983**, *22*, 628.
- (22) The electronic idiosyncrasies of the bicyclo[1.1.1]pentane unit have been studied extensively: Gleiter, R.; Pfeifer, K. H.; Szeimies, G.; Bunz, U. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 413.
- (23) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107.