Metal Complexes of Benzene Derivatives. 45.1

Dinuclear Bis(η⁶-arene)vanadium and -chromium Complexes Containing 1,3-Disilacyclobutane as a Spacer. An EPR Study of Intermetallic Communication

Christoph Elschenbroich,* Annette Bretschneider-Hurley,1 James Hurley,1 Sigrid Wocadlo,1 and Edward Reijerse*

Andreas Behrendt,* Werner Massa^ 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 R₂Si(CHR)₂CH₃ (n = 1, 2) and R₂SiCH₂SiR₂CH₃ 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 (2.59 Å21) as well as in its derivatives21-25 which are shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-butyldisilane clobutane 1 (2.59 Å2) as well as in its derivatives which are more than 1.5 shorter than the Si—Si bond distance in hexa-f-but...
Inorganic Chemistry, Vol. 34, No. 3, 1995

Notes

Figure 1. Molecular structure and labeling scheme for 4: Thermal ellipsoids are at the 50% probability level. Selected bond distances (Å) and angles (deg): VI—Cl 1 2.119(3), V1—C12 2.153(3), V1—C13 2.200(4), V1—C14 2.216(3), V1—C15 2.216(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), Si 1—C 11 1.874(3), Si 1—C2i 1.836(3), Si 1—Cl 1.845(4), Si 1—C3 1.851(4), VI*—Si 1 2.901(1) Å; Cll—Sil—C21 94.6(1), C l—Sil—C3 81.5(2), Sil—Cl—C2 86.1(2), C1—C2—C3 102.2(3), C2—C3—Sil 185.9(2), C—C—C 116.4(3)–122.4(3).

**Scheme 1**

![Scheme 1](image)

**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 (C, 9). Parameters for 4: \( g \)= 1.9845, \( a(51V) = 5.62 \text{ mT} \), \( g_1 = 1.9770, g_2 = 1.9735, g_3 = 2.0030, A_1 = 8.26, A_2 = 9.0, A_3 = 0.34 \text{ mT} \). Parameters for 2: \( g \)= 1.9845, \( a(51V) = 5.62 \text{ mT} \), \( J = -0.23 \pm 0.02 \text{ cm}^{-1} \). Imperfections in the agreement between experiment and simulation derive from the fact that the simulation program does not incorporate the \( m(51V) \) dependence of the linewidths.

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 (C, 9). Parameters for 4: \( g \)= 1.9845, \( a(51V) = 5.62 \text{ mT} \), \( g_1 = 1.9770, g_2 = 1.9735, g_3 = 2.0030, A_1 = 8.26, A_2 = 9.0, A_3 = 0.34 \text{ mT} \). Parameters for 2: \( g \)= 1.9845, \( a(51V) = 5.62 \text{ mT} \), \( J = -0.23 \pm 0.02 \text{ cm}^{-1} \). Imperfections in the agreement between experiment and simulation derive from the fact that the simulation program does not incorporate the \( m(51V) \) dependence of the linewidths.

The molecular structure of 4 is depicted in Figure 1. The angle of ring tilt in the sandwich unit is 19.9°, which is similar to that found in 6 (20°).

Whereas the bond lengths and bond angles of the silacyclobutane ring in 4 are comparable to those of other silacyclobutane derivates (as determined by electron diffraction), 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 $a(51V)$ is considerably reduced relative to that of parent bis(benzene)vanadium.18 Employing the Si···V separation of 2.90 Å as found in 4 and the Si···Si distance of 2.59 Å in 1,3-disilacyclobutane,2 an approximate V···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 $\chi vs T$ 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 $a(51V) = 2.81$ mT (5.62/2), expected for the limiting case of fast exchange which is defined by the condition $J > a(51V)$. Furthermore, contrary to 6, the $51V$ hyperfine pattern for 2 deviates markedly from a simple binomial 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 [$V\cdots V: 7.60$ 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 Si···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 $^{47,49}$Ti hyperfine pattern in the fluid solution EPR spectrum ($|J| > 10^{-3}$ 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 $-50 \degree C$ and the cyclomotavolymetric 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**

(20) Program MAGRES: Keijzers, C. P.; Reijsjeer, 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 $a(51V)$ 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$^{-1}$.

