(40 mL) was added by syringe to a stirred solution of 4^+-Ru (20 mg, 0.037 mmol) in acetonitrile (40 mL) during a 2-4-min period. The reaction was over immediately, and the mixture of products was isolated following the same workup procedure as for the preparative electrolysis experiments. Reductions of concentrated (40 mM) substrate solutions were carried out analogously, except that the cobaltocene, dissolved in a minimum amount of acetonitrile, was added all at once. Relative and absolute product yields from these reactions are summarized in Table II.

Acknowledgment. We gratefully acknowledge generous support from Statoil under the VISTA program, administered by the Norwegian Academy of Science and Letters.

Communications

Electron Spin Distribution in Cyclotetrasilane Radical Anions

Rudolf Janoschek*[,1a] **and Burkhard Kirste**[1b]

Institut für Theoretische Chemie, Universität Graz
A-8010 Graz, Austria
and the Institut für Organische Chemie
Freie Universität Berlin
D-1000 Berlin 33, West Germany

Received December 7, 1988

Summary: Ab initio PUHF calculations of hyperfine coupling constants of the octamethylcyclotetrasilane radical anion $(Me_2Si)_4^{\bullet-}$ have been performed. A satisfactory agreement with EPR and ENDOR studies could be achieved. The singly occupied MO is composed of Rydberg-like Si-Si pπ and Si-C σ^* contributions.

Cyclopolysilanes are interesting compounds because of their thermal and chemical stability and their unique bonding properties.[2,3] In some respect these saturated compounds resemble aromatic hydrocarbons; evidence of electron delocalization is found in their ultraviolet[4,5] and photoelectron spectra.[5,6] Moreover, peralkylcyclotetra- and peralkylcyclopentasilanes can be reduced to radical anions in which the unpaired electron is delocalized over the ring. These systems have been investigated extensively by EPR[4,7-11] and ENDOR[12] (electron nuclear double resonance) spectroscopy, yielding sets of ^{1}H, ^{13}C, and ^{29}Si hyperfine coupling constants and hence information about the electron spin distribution.

Table I. Spin Density Population (SD), Fermi Contact Analysis (FC in au), and Hyperfine Coupling Constants (a in MHz) of Peralkylcyclotetrasilane Radical Anions

	$(Me_2Si)_4^{\bullet-}$				$(t\text{-}BuMeSi)_4^{\bullet-}$
	SD	FC	a_{calcd}[a]	a_{exptl}[b]	a_{exptl}[c]
^{29}Si	0.2618	−0.019 584	+17.39		+15.15
^{13}C	0.0045	0.067 420	+75.78	58.8	+59.07
^{1}H	−0.0035	−0.000 343	−1.53	1.88	+1.45

[a] Calculated with the following proportionality constants (in MHz/au): 4469 (^{1}H), 1124 (^{13}C), and −888 (^{29}Si). [b] From ref 9 and 11. [c] From ref 12.

However, a rigorous quantum-mechanical treatment of cyclosilane radical anions has been lacking so far. A simple perturbation approach was proposed to rationalize the EPR spectra of substituted cyclopentasilane radical anions, leading to a model in which the SOMO (singly occupied molecular orbital) has major contributions from Si-Si σ^* and Si-C σ^* antibonding orbitals involving silicon 3p$_x$, 3p$_y$, and 3p$_z$ and carbon 2s, 2p$_x$, 2p$_y$, and 2p$_z$ atomic orbitals.[11] This model predicts a negative sign for the ^{29}Si hyperfine coupling constant, which is in conflict with the positive sign determined experimentally by TRIPLE resonance.[12] Recently, an ab initio HF-DZP calculation for the hypothetic unsubstituted neutral cyclotetrasilane, $(H_2Si)_4$, has been performed where the LUMO is considered as a model for the SOMO of the radical anion.[13] In the present paper dealing with ab initio PUHF-STO-3G+ calculations[14] for the parent cyclotetrasilane radical anion, $(H_2Si)_4^{\bullet-}$, as well as for the octamethylcyclotetrasilane radical anion, $(Me_2Si)_4^{\bullet-}$, it will be shown that for both systems the SOMO is a Rydberg-like orbital composed of Si-Si π and Si-C/Si-H σ^* contributions (A_{2u} in D_{4h} symmetry).

In Table I a comparison of calculated hyperfine coupling constants of the octamethylcyclotetrasilane radical anion with experimental data for this radical and the related *trans*-1,2,3,4-tetra-*tert*-butyltetramethylcyclotetrasilane radical anion is given. Whereas only an incomplete set of

---

(1) (a) Universität Graz. (b) Freie Universität Berlin.

(2) West, R.; Carberry, E. *Science* **1975**, *189*, 179.

(3) West, R. *Pure Appl. Chem.* **1982**, *54*, 1041.

(4) Carberry, E.; West, R.; Glass, G. E. *J. Am. Chem. Soc.* **1969**, *91*, 5446.

(5) Stüger, H.; Hengge, E.; Janoschek, R. *Phosphorus, Sulfur, Silicon*, submitted for publication.

(6) Bock, H.; Ensslin, W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 404.

(7) Kira, M.; Bock, H.; Hengge, E. *J. Organomet. Chem.* **1979**, *164*, 277.

(8) Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 1458.

(9) Wadsworth, C. L.; West, R.; Nagai, Y.; Watanabe, H.; Muraoka, T. *Organometallics* **1985**, *4*, 1659.

(10) Wadsworth, C. L.; West, R. *Organometallics* **1985**, *4*, 1664.

(11) Wadsworth, C. L. Ph.D. Thesis, University of Wisconsin, Madison, WI, 1984. Wadsworth, C. L.; Carlson, C. W.; West, R., private communication.

(12) Kirste, B.; West, R.; Kurreck, H. *J. Am. Chem. Soc.* **1985**, *107*, 3013.

(13) Grev, R. S.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 6569.

(14) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Krishnan, R.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN 82, Carnegie-Mellon University, Pittsburgh, PA, 1982. The STO-3G basis set is augmented by a diffuse silicon sp set (0.0331) and a diffuse carbon s set (0.0438). D_{4h} symmetry and standard geometry data (pm, deg) have been used: SiSi = 236, SiC = 187, CSiC = 109.

0276-7333/89/2308-1563$01.50/0

Table II. Functions of the Augmented STO-3G+ and 3-21+G Basis Sets of Silicon and MO Expansion Coefficients of the Highest Doubly Occupied MO (B_{2g}) and the SOMO (A_{2u}) in $Si_4H_8^{\bullet -}$

	STO-3G+		3-21+G		
basis functions (exponents)	3p 1.479 0.412 0.161	p 0.033	3pI 1.079 0.302	3pO 0.093	p 0.033
B_{2g}	0.386	0.125	0.248	0.212	−0.006
A_{2u}	0.174	−0.336	0.091	0.565	−0.169

coupling constants has been determined for the former radical by EPR (the ^{29}Si hyperfine coupling constant is not known),[9,11] accurate data for the latter radical have been measured by ENDOR spectroscopy.[12] Moreover, relative signs of the hyperfine couplings were determined by general TRIPLE resonance.[12] Since it seems to be reasonable to assume a positive sign for the large methyl ^{13}C coupling constant, this choice of signs has been adopted in Table I.

A comparison with the calculated data reveals an unexpected good agreement. The important general features are reproduced correctly, namely, a large (positive) ^{13}C coupling constant, a fairly small (positive) ^{29}Si coupling constant, and a small proton coupling constant. Perhaps more importantly, the calculation predicts that the electron spin density is located mainly in diffuse orbitals, particularly in Rydberg-type Si pπ orbitals which contribute almost 100% to the total Si value. This result is in excellent agreement with the conclusions drawn from ENDOR relaxation studies for the various nuclei, demonstrating that anisotropic hyperfine interactions are negligibly small [$\mathrm{Tr}(A'_{Si}{}^2) \approx 30$–$100\ \mathrm{MHz}^2$], implying essentially isotropic electron spin distributions around the ^{29}Si and ^{13}C nuclei.

The diffuse character of the SOMO is not an artefact of the limited valence basis (STO-3G) where electron density could be forced into the diffuse orbitals. An improved basis set (3-21G) for the unsubstituted species $Si_4H_8^{\bullet -}$ also rules out a valencelike SOMO. Additional diffuse functions on silicon, labeled as s and p, exhibit only small contributions to valence orbitals such as the highest doubly occupied MO (B_{2g}). In contrast, the expansion coefficients of the diffuse functions are increased by a factor of 30 in the SOMO (A_{2u}) of $Si_4H_8^{\bullet -}$. According to Table II the MO expansion coefficients of the inner (3pI) and the outer (3pO) basis functions also indicate unequivocally an increased size of the SOMO compared with valencelike orbitals. The sizes of the inner and the outer "valence" basis functions, i.e. the orbital radii, differ by a factor of 2. The importance of Rydberg orbitals especially for the photochemistry of polysilanes is extensively described in the literature.[15]

Thus, the experiment as well as the calculations would rule out a SOMO constructed from valence-type Si 3pπ atomic orbitals. The present calculations provide a satisfactory picture of the electron spin density distribution in cyclopolysilane radical anions, rendering obsolete any previous speculations invoking the participation of hybrid orbitals or of Si 3d orbitals.

---

[15] Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press: New York, 1975; Vols. 1–3. Bock, H.; Wittel, K.; Veith, M.; Wiberg, N. *J. Am. Chem. Soc.* **1976**, *98*, 109. Halevi, E. A.; Winkelhofer, G.; Meisl, M.; Janoschek, R. *J. Organomet. Chem.* **1985**, *294*, 151. Experimental and calculated electronic transitions of Si_4Me_8 are reported in ref 5.

Migration of the Phosphorus Ligand from Iron to the Cyclopentadienyl Ring in Complexes of the Type $(\eta^5\text{-}C_5H_5)(CO)LFe\{P(O)YZ\}$

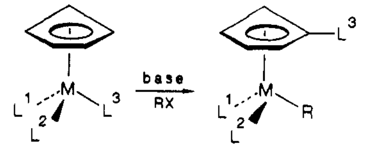
Hiroshi Nakazawa,* Makoto Sone, and Katsuhiko Miyoshi*

Department of Chemistry, Faculty of Science
Hiroshima University, Hiroshima 730, Japan

Received December 29, 1988

Summary: Reaction of $(\eta^5\text{-}C_5H_5)(CO)LFe\{P(O)YZ\}$ (L = CO, Y = Z = OEt; L = CO, Y = OMe, Z = NEt_2; L = $P(OMe)Ph_2$, Y = Z = Ph) with lithium diisopropylamide (LDA) results in a migration of the P(O)YZ group from iron to the cyclopentadienyl ring. The resulting $(\eta^5\text{-}C_5H_4\{P(O)YZ\})(CO)LFe^-$ anion reacts with MeI to give $(\eta^5\text{-}C_5H_4\{P(O)YZ\})(CO)LFeMe$.

Transition-metal complexes containing a η^5-cyclopentadienyl group (Cp) and three monodentate ligands, which are referred to as piano-stool complexes because of their molecular shape, are well-known. Recently reactions of cyclopentadienyl complexes have been reported in which one of the monodentate ligands on the transition metal undergoes base-induced migration to the Cp ring: silyl from iron[1] and rhenium,[2] acyl from iron[3] and rhenium,[4] alkoxycarbonyl from iron,[3c] formyl from rhenium,[4b] hydride from rhenium,[5] and germyl from molybdenum and tungsten.[6] Some related reactions also have been reported.[7] However, migration of a phosphorus substituent on a transition metal to a Cp ring bonded to the same metal atom has not been reported thus far. We report here the first example of such phosphorus substituent migration from a transition metal to the Cp ring (eq 2).



(1)

In a typical reaction, 298 mg (0.95 mmol) of $(\eta^5\text{-}C_5H_5)(CO)_2Fe\{P(O)(OEt)_2\}$ in 10 mL of THF was treated with 2 equiv of freshly prepared lithium diisopropylamide (LDA) in THF at −78 °C. The initially yellow solution immediately became dark brown. After the mixture had been stirred for 10 min at −78 °C, 118 μL (269 mg, 1.90 mmol) of MeI was added, and the mixture was allowed to warm gradually to room temperature. The solvent was

---

[1] (a) Berryhill, S. R.; Sharenow, B. *J. Organomet. Chem.* **1981**, *221*, 143. (b) Thum, G.; Ries, W.; Greissinger, D.; Malisch, W. *J. Organomet. Chem.* **1983**, *252*, C67. (c) Berryhill, S. R.; Clevenger, G. L.; Burdurlu, F. Y. *Organometallics* **1985**, *4*, 1509. (d) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5*, 1056.

[2] (a) Pasman, P.; Snel, J. J. M. *J. Organomet. Chem.* **1986**, *301*, 329. (b) Crocco, G. L.; Young, C. S.; Lee, K. E.; Gladysz, J. A. *Organometallics* **1988**, *7*, 2158.

[3] (a) Liebeskind, L. S.; Welker, M. E. *Organometallics* **1983**, *2*, 194. (b) Brinkman, K.; Helquist, P. *Tetrahedron Lett.* **1985**, *26*, 2845. (c) Abbott, S.; Baird, G. J.; Davies, S. G.; Dordor-Hedgecock, I. M.; Maberly, T. R.; Walker, J. C.; Warner, P. *J. Organomet. Chem.* **1985**, *289*, C13.

[4] (a) Heah, P. C.; Gladysz, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 7636. (b) Heah, P. C.; Patton, A. T.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1185.

[5] (a) Crocco, G. L.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 283. (b) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6110.

[6] Dean, W. K.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1061.

[7] (a) Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1974**, 516. (b) Werner, H.; Hofmann, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 464. (c) Hubbard, J. L.; McVicar, W. K. *J. Am. Chem. Soc.* **1986**, *108*, 6422. (d) Pannell, K. H.; Vincenti, S. P.; Scott III, R. C. *Organometallics* **1987**, *6*, 1593.

0276-7333/89/2308-1564$01.50/0