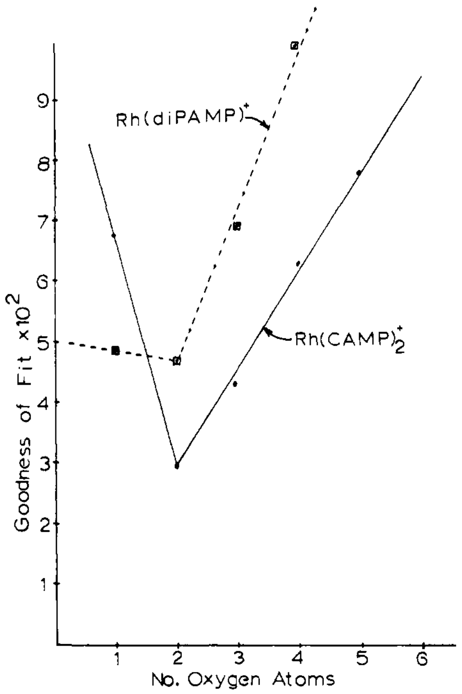
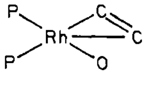


Figure 3. Plots of the goodness of fit from a two unique atom least-squares fit vs. the number of oxygen atoms in the fit. For all fits two phosphorus atom contributions were included.

caption. Plots showing the goodness of fit (derived from the data shown in Figure 2) vs. the number of oxygen atoms are presented in Figure 3. Both Figures 2 and 3 show that force fitting the data with different numbers of oxygen atoms resulted in the best fit when two oxygen atoms and two phosphorus are bonded to the rhodium.

Our final analysis used fixed integral values for the coordination numbers of the different ligands. Although an attempt to simultaneously vary N and σ resulted in similar results, these parameters may be highly correlated in the nonlinear least-squares procedure, and the effect of this coupling leaves undetermined the accuracy of the values acquired by general parameter variation.

The derived coordination distances for the Rh(diPAMP)-$(CH_3OH)_2^+$ species are Rh–P = 2.34 and Rh–O = 2.34 Å, and for Rh(CAMP)$_2$$(CH_3OH)_2^+$ the distances are Rh–P = 2.35 and Rh–O = 2.36 Å. Data have been obtained and analyzed for species C in Figure 1 where the phosphorous ligand was diPAMP. When the substrate [α-(acylamino)cinnamic acid, Ac] was added to the methanol solvated species, Rh(diPAMP)$(CH_3OH)_2^+$, the following structural parameters were obtained: Rh–P_1 = 2.36, Rh–P_2 = 2.29, Rh–C = 2.26, and Rh–O = 1.86 Å. There are two distinct Rh–P distances, one being trans to an oxygen and one trans to the olefin. This square-planar arrangement is supported by the X-ray structural analysis of Halpern et al.[14] The coordination environment about the rhodium is



The Rh–C and Rh–P distances derived from the EXAFS data for the in situ prepared catalyst–substrate complex agree favorably with the values for the crystalline Rh(diPAMP)Ac$^+$ compound in Table I. The short Rh–O distance of 1.86 Å compared to 2.0 Å for the crystalline compounds is surprising and may not be valid. However, recent experimental observations[15] indicate differences between the crystalline Rh(diPAMP)Ac$^+$ and the in situ active catalytic species in solution. More EXAFS data for other rhodium–phosphine–substrate complexes is needed to verify the short Rh–O distance.

The sensitivity of EXAFS data to different species in solution is illustrated in the following experiment. When the catalyst substrate was added to the disolvated species, Rh(CAMP)$_2$-$(CH_3OH)_2^+$ (CAMP is a monodentate ligand), no reasonable information pertaining to the catalyst–substrate complex was obtained. Attempts to fit the data as either the disolvated species or some reasonable catalyst–substrate complex resulted in diverging least-squares refinements. Numerous attempts to refine these data were unsuccessful. In hindsight, this was to be expected. From NMR experiments we now know that when the phosphine ligands are monodentate, as for CAMP, rapid isomerization occurs in solution. This isomerization is not possible for bidentate ligands such as diPAMP. At best we would expect a mixture of three or four different species in solution after the substance was added. The fact that we were unable to force fit this data is important in illustrating the sensitivity of EXAFS data to different species in solution.

In summary, our work with the asymmetric rhodium catalysts has shown EXAFS to be a valuable tool for studying homogeneous catalysis. We obtained good agreement between the structural parameters determined by EXAFS and X-ray crystallography. Our work demonstrates that useful information pertaining to the identity and structural parameters for solutions may be obtained from EXAFS. A word of caution to be stressed is that one needs to have very good model compounds whose structures are known in order to distinguish subtle differences between species by using EXAFS.

Our continued work in this area emphasizes obtaining data on other catalyst intermediates for complexes with several different phosphine ligand systems (Figure 1). Amelioration of the facilities at Stanford Synchrotron Radiation Laboratory through expansion and improvements hopefully will increase access for these data collection in the near future.

Acknowledgment. Some of the material incorporated in this work was developed at the Stanford Synchrotron Radiation Laboratory which is supported by the National Science Foundation (under Contract DMR-27489), in cooperation with SLAC and the Department of Energy.

---

[14] Chan, A. S. C.; Pluth, J. J.; Halpern, J. *Inorg. Chem. Acta.* **1979**, *37*, 477.

[15] (a) Chan, A. S. C.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 839. (b) Chan, A. S. C.; Pluth, J. J.; Halpern, J. *Ibid.* **1980**, *102*, 5952.

Tetraanion of 1,1-Dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene

Daniel H. O'Brien* and David L. Breeden

Department of Chemistry, Texas A&M University
College Station, Texas 77843

Received February 26, 1981

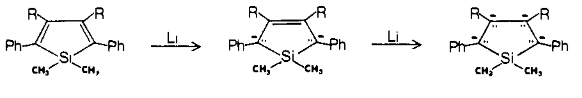
The alkali metal reduction of phenyl-substituted silacyclopentadienes **1** and **2** have been followed with electron spin resonance spectroscopy.[1] Monitoring the reactions with ultraviolet spectroscopy showed that further reduction leads to the disappearance of the anion radical spectrum and the appearance of a new UV spectrum attributed to the dianion. The presence of the dianion of **2** was also shown by aqueous quenching and the isolation of *cis*-dibenzylstilbene and poly(dimethylsiloxane).[2] The reduction of **2** showed the formation of another anionic species past the dianion stage, but this new species could not be identified from the UV evidence.[1] We report here the carbon-13 characterization of this species as the highly charged tetraanion $\mathbf{2}^{4-}$ (eq 1).

---

[1] Janzen, E. G.; Pickett, J. B.; Atwell, W. H. *J. Organomet. Chem.* **1967**, *10*, P6–P8.

[2] Balasubramanian, R.; George, M. V. *J. Organomet. Chem.* **1975**, *85*, 311-316.

0002-7863/81/1503-3237$01.25/0


(1)

1, R = H $1^{=}$ $2^{\equiv}$

2, R = Ph $2^{=}$

Reduction of **1** with lithium metal in THF at ambient temperature leads to the dianion $\mathbf{1}^{2-}$, characterized by large upfield chemical shift changes at the electron-rich carbons (C_α, C_β, C_4, and $C_{2,6}$) compared to its precursor (Table I).[3] However, the shifts of C_α and C_4 are not as shielded as the same carbons in the nonsilicon analogue, the lithium dianion of 1,4-diphenylbutadiene $(\mathbf{3})^{2-}$. The deshielding of C_α and C_4 in $\mathbf{1}^{2-}$ compared to $\mathbf{3}^{2-}$ qualitatively measures silicon's ability to delocalize a small amount of the negative charge. The lithium dianion of **1** in THF and other ethereal solvents (MeTHF and DME) and the sodium and potassium dianions of **1** in THF are all remarkably stable *even in the presence of excess alkali metal.* For example, no spectral changes are observed for the lithium dianion in THF even after 2 weeks at ambient temperature.

Reduction of **2** first leads to the dianion $\mathbf{2}^{2-}$. However, the 11 resonances due to $\mathbf{2}^{2-}$ disappear over a period of approximately 3 h and are replaced by 15 new resonances (Table II). This reaction occurs only in the presence of excess lithium metal. If the metal is removed after the formation of $\mathbf{2}^{2-}$, the spectrum remains unchanged for long periods. Addition of metal to a solution of $\mathbf{2}^{2-}$ results in the resumption of the reaction and the appearance of the new species.

Carbon-13 chemical shift changes provide the strongest evidence that this new species is the tetraanion $\mathbf{2}^{4-}$. The empirical relationship between carbon-13 shifts and π-electron density predicts a shift change of approximately 320 ppm for the addition or removal of two electrons from a completely conjugated hydrocarbon.[4] The carbon-13 chemical shift changes ($\Delta\delta$) for the lithium dianions of 1,4-diphenylbutadiene ($\mathbf{3}^{2-}$), stilbene ($\mathbf{4}^{2-}$), and tetraphenylethylene ($\mathbf{5}^{2-}$) will be used as suitable estimates of the $\Delta\delta$ expected in adding electrons to the conjugated hydrocarbon portion of the silacyclopentadienes. All three react readily with lithium in THF to give good dianion spectra. Their resonances are easily assigned when compared to previously reported carbon-13 carbanion spectra (Table I).[5] These model hydrocarbons and their dianions are similar in structure to **1** and **2** and their anions: $\mathbf{3}^{2-}$ is the nonsilicon analogue of $\mathbf{1}^{2-}$; the reduction of $\mathbf{2}^{2-}$ to $\mathbf{2}^{4-}$ can be viewed as the addition of two electrons to the stilbene moiety of $\mathbf{2}^{2-}$; tetraphenylethylene is similar to **2**, having four phenyls attached to an alkene unit.[6,7]

Table I. Carbon-13 Chemical Shifts for 1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene, Its Dianion (1^{2-}) and Model Dianions[a]

	1	1^{2-}	$\mathbf{3}^{2-}$	4^{2-}	5^{2-}
C_α	144.6	74.0	65.2	58.9	85.6
C_β	137.9	104.9	104.8		
C_1	138.8	150.5	146.3	140.3	146.2
$C_{2,6}$	126.2	119.5	118.5 110.6	117.4 102.5	118.1
$C_{3,5}$	128.7	128.0	128.7	131.2 127.3	128.2
C_4	126.8	109.8	96.9	97.5	107.9
SiMe	−2.9	3.0			

[a] Reference 3.

Table II. Carbon-13 Chemical Shifts for 1,1-Dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene, Its Dianion ($\mathbf{2}^{2-}$) and Tetraanion $\mathbf{2}^{4-}$ [a]

	2		$\mathbf{2}^{2-}$		2^{4-}	
C_α	141.7		77.4		75.3	
C_β	153.7		128.5		89.4	
	α Ph	β Ph	α Ph	β Ph	α Ph	β Ph
C_1	139.7	138.6	150.6	147.1	146.4	136.1
$C_{2,6}$	129.1	128.6	123.3	125.8	112.7 110.4	119.7 113.2
$C_{3,5}$	129.8	129.4	126.5	132.4	128.8 125.8	130.6 129.7
C_4	126.0	125.4	107.8	120.5	94.7	99.3
SiMe	−4.0		3.2		2.0	

[a] Reference 3.

Table III. Carbon-13 Chemical Shift Changes, $\Delta\delta$

hydrocarbon	→	carbanion	$\Delta\delta$
$Ph\bar{C}H{=}CH{-}CH{=}CHPh$ (**3**)		$Ph\bar{C}HCH{=}CH\bar{C}HPh$ ($\mathbf{3}^{2-}$)	−272.8
cis-$PhCH{=}CHPh$ (4)		$Ph\bar{C}H{-}\bar{C}HPh$ (4^{2-})	−270.4
$Ph_2C{=}C{-}Ph_2$ (5)		$Ph_2\bar{C}{-}\bar{C}{-}Ph_2$ (5^{2-})	−276.0
1		1^{2-}	−247.4
2		$\mathbf{2}^{2-}$	−222.0
$\mathbf{2}^{2-}$		$\mathbf{2}^{4-}$	−271.6

The chemical shift changes for the three model systems are smaller than the predicted 320 ppm/2 electrons, but the variation among them is quite small (Table III).[8,9] Addition of two electrons to **1** and **2** results in a smaller upfield shift change than the average change (−273 ppm) for formation of $\mathbf{3}^{2-}$, $\mathbf{4}^{2-}$, and $\mathbf{5}^{2-}$. This decreased shielding in forming dianions $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ qualitatively measures silicon's ability to delocalize some of the electron density. Most importantly, in reducing $\mathbf{2}^{2-}$ to the new species, an additional upfield shift change of −271.6 ppm is observed. This is exactly the upfield change expected if the reduction of $\mathbf{2}^{2-}$ to $\mathbf{2}^{4-}$ is viewed as the addition of two electrons to the *cis*-stilbene moiety of $\mathbf{2}^{2-}$.

Other carbon-13 evidence also suggests that the product of the reduction of $\mathbf{2}^{2-}$ is the tetraanion $\mathbf{2}^{4-}$. Delocalization of the charge into the phenyls in the tetraanion would be expected to increase the barrier to rotation about the ring carbon–phenyl C_1 bonds compared to $\mathbf{2}^{2-}$. Thus, the spectrum of $\mathbf{2}^{4-}$ displays nonequivalent ortho and meta carbons for both the α and β phenyls. Proton-coupled spectra show that the α-carbon resonance at δ 75.3 is a singlet. This excludes anions of 1-(dimethylsilyl)tetraphenylbutadiene and tetraphenylbutadiene which might form through

---

(3) All anions were prepared in septum-capped, argon-flushed, 10-mm tubes by adding a solution of the precursor dissolved in dry THF to an excess of lithium metal wire. Carbon-13 spectra were obtained with a JEOL PFT 100/Nicolet 1080 Fourier transform spectrometer. Typical anion solutions were approximately 0.3 M and required about 2000 average transients for satisfactory signal-to-noise ratios. All chemical shifts are referenced to tetramethylsilane by using a small amount of cyclohexane in the carbanion solutions as an internal reference and the relationship $\delta_{Me_4Si} = \delta$cyclohexane + 27.5 ppm. Negative chemical shifts are upfield of Me_4Si and negative chemical shift changes are upfield changes. Carbon-13 chemical shift assignments for the silacyclopentadiene anions were based upon one-bond proton–carbon couplings, relative peak intensities, and comparison to shifts of model carbanions. Proton–carbon couplings distinguish the C_α, C_β, α–C_1, and β–C_1 singlets from the phenyl doublets. The phenyl C_4 carbons can be distinguished from the $C_{2,6}$ and $C_{3,5}$ carbons by comparing their relative intensities and/or by comparing their chemical shifts to shifts of model carbanions. For the tetraanionic species, proton-coupled spectra showed four singlets assigned to α C_1, β C_1, C_β, and C_α, two doublets assigned to the phenyl C_4 carbons because of their high field chemical shifts, and eight doublets for the $C_{2,6}$ and $C_{3,5}$ carbons. Specific assignments of these eight resonances could not be made. However, it is important to note that as long as the resonances can be separated into three groups (singlets, C_4 doublets, and $C_{2,6}$ $C_{3,5}$ doublets), the calculation of $\Delta\delta$ does *not* require specific assignments within each group.

(4) (a) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468–472. (b) Lauterbur, P. C. *Tetrahedron Lett.* **1961**, 274–279. (c) Lauterbur, P. C. *J. Am. Chem. Soc.* **1961**, *83*, 1838–1846.

(5) O'Brien, D. H. In "Comprehensive Carbanion Chemistry"; Buncel, E., Durst, T., Eds.; Elsevier: New York, 1980; pp 271–322.

(6) It would be desirable to compare the carbon-13 spectra of $\mathbf{2}^{2-}$ and $\mathbf{2}^{4-}$ to the spectra of their nonsilicon analogues, the dianion and tetraanion of 1,2,3,4-tetraphenylbutadiene. Although the presence of these two anions in solution has been indicated in quenching experiments,[7] several attempts to observe lithium or sodium anions resulted only in broad, ill-defined spectra.

(7) Sandel, V. R.; Belinky, B.; Stefaniak, T.; Kreil, D. *J. Org. Chem.* **1975**, *40*, 2116–2120.

(8) A similar chemical shift change argument has been used effectively to describe the *decrease* in π-electron density in going from aromatic hydrocarbons to arene dications.[9]

(9) Forsyth, D. A.; Olah, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 4086–4090.

cleavage of the silicon-ring carbon bonds, solvent protonation, and further reduction. In such anions the electron-rich α carbons would be doublets. Aqueous quenching of the anion solutions has been less definitive than the spectral evidence. A complex mixture is obtained which contains at least six silicon-containing compounds in addition to three silacyclopentenes. The proton NMR of this complex mixture displays a broad benzylic region ($\delta \sim 2.9$–4.1). This indicates that protonation is occurring on the ring phenyls as well as on the central silacyclopentane ring.

Much work with silacyclopentadienes has undoubtedly been undertaken with the hope that cleavage of a silicon-substituent bond would lead to a silacyclopentadienide ion.[10,11] In the case of **2**, after the addition of two electrons, loss of methyllithium would result in 1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienide ion. No evidence for the formation of methyllithium was found, and the very large upfield shift change (−493.6 ppm) argues strongly against this pathway for **2**. Although silacyclopentadienide ion formation might occur in silicon systems similar to **2**, particularly when silicon bears a better leaving group than methyl, the possibility of tetraanion formation should also be considered.

Acknowledgment. Support of this work by the Robert A. Welch Foundation (Grant A-331) is gratefully acknowledged.

---

(10) Attempted formation of pentaphenylsilacyclopentadienide ion by removal of a proton from silicon with *n*-butyllithium: (a) Curtis M. D. *J. Am. Chem. Soc.* **1967**, *89*, 424–425. (b) *Ibid.* **1969**, *91*, 6011–6018.

(11) Proposed formation of a silacyclopentadienide ion in the potassium reduction of 5,5-diphenyldibenzosilole: Janzen, E. G.; Harrison, W. B.; Pickett, J. B. *J. Organomet. Chem.* **1969**, *16*, 48–50.

Book Reviews

Preparation and Properties of Stereoregular Polymers. Edited by W. Lenz (University of Massachusetts) and F. Ciardelli (University of Pisa). D. Reidel Publishing Company, Dordrecht, Holland. 1980. XVII + 472 pp. U.S. $44.75.

This book contains the texts of the main lectures presented at the NATO Advanced Studies Institute on Advances in Preparation and Properties of Stereoregular Polymers held at Tirrenia near Pisa, Italy, from October 3 to 14, 1978. Also, a few contributed papers that were concerned with topics not included in the main lectures have been included. Because of the nature of the subject, the topics covered are rather specialized.

There is a rapidly increasing activity in the study of stereoregular polymerization and the preparation of structurally ordered polymers as a means of achieving improvements in existing polymeric materials through new developments in synthesis and properties as well as in discovering new polymeric structures.

Continued progress is needed in areas such as the improvement of existing polymerization processes, through the discovery of new catalytic systems with much higher activity and stereospecificity, and in the improvement of mechanical and stability properties of existing polymeric materials. Increasing attention is also being directed toward the custom synthesis of polymers with highly defined molecular and morphological structure for use in a wide variety of new applications such as catalysis, drug-delivery systems, electronics, super-high tenacity fibers, processed foods, metal recovery, secondary recovery of oil, ecological and environmental control applications, and many others. Indeed, the field of custom designed macromolecules is destined to make an increasingly important contribution to mankind in the future.

The subjects treated are organized in a classical manner under the two general areas as follows: Section I—Synthesis of Stereoregular Polymers and the Mechanism of Stereospecific Polymerization, and Section II—Structure and Properties of Stereoregular Polymers.

Section I includes an excellent introduction of the basic concepts of stereoregularity in polymers, recent developments, kinetic consideration, new catalysts, diolefin selective polymerization, stereoregulation in metathesis reactions, homogeneous free radical, cationic and anionic polymerization, active species in anionic polymerization, ion pair effects on anionic oligomerization, stereoregulation of polyisocyanides, stereospecific polymerization of cyclic monomers, both three-membered and large rings, and stereoregular polymers from β-lactones and β-lactams.

Section II includes properties of optically active polylactones, NMR analysis of stereoregular polymers and copolymers, configurational and conformational analysis, application of chiroptical properties to conformational analysis, vibrational spectroscopy, crystalline structure, viscoelastic and mechanical properties, and effect of stereoregularity on bulk properties.

The editors have endeavored to maintain an integration of subject matter, among all aspects of the science of stereoregular polymers. This integration has quite adequately been achieved by treating synthetic procedures and mechanisms of stereospecific and stereoselective (or stereoelective) polymerization with chemical transformations and the physical properties of stereoregular polymers (with particular emphasis on characterization, solution, and solid-state properties) and mechanical properties. By this approach, a continuous spectrum of research activities extending from synthesis to structure, structure to properties, and properties to application has been attained. It is anticipated that polymer scientists will recognize this spectrum as the characteristic which makes polymer science unique among the sciences, and will have an appreciation for their place and their interdependence within the spectrum.

Also, the book should provide the reader with the basic knowledge and the inspiration necessary for the continuing development of the science of stereoregular and structurally ordered polymers, and promote cooperative research programs and interdisciplinary approaches to defined problems.

It is anticipated that those readers who will benefit most from this publication are those professional scientists who have as their objective the attainment of one or another of the above-defined goals rather than the casual reader of scientific publications.

George B. Butler, *University of Florida*

Organic Chemistry. Topics in Current Chemistry. Volume 92. Managing Editor: F. L. Boschke. Springer-Verlag, Berlin. 1980. iv + 178 pp. $54.00.

Although titled "Organic Chemistry", this book will appeal to a broader audience, particularly organometallic chemists. The 92nd in a series designed to "present critical reviews of the present position and future trends in modern chemical research", it includes several thought-provoking, but difficult, chapters.

Two-Step Reversible Redox Systems of the Weitz Type, by S. H. Hünig and H. Berneth, considers polymethines in which the terminal groups exhibit quinoid character in the reduced form (e.g., "Viologenes" such as Paraquat). The emphasis is on correlations of chemical and physical properties, in particular redox potentials (and potential differences), disproportionation equilibria, and spectral properties, with structure. The remarkable variety of redox systems of this type, combined with the predictive ability derived from the correlations, suggest that redox systems can be tailored to meet special purposes.

Controlling Factors in Homogeneous Transition-Metal Catalysis, by P. Heimbach and H. Schenkluhn, is an ambitious attempt to apply the methods and formalisms of inorganic chemistry and of enzyme chemistry to the study of metal-catalyzed coupling reactions. The basic empirical concept is that "chemical systems coupled via a metal atom behave like fragments joined with one another by σ-bonds". Starting from that point the authors examine variations in the metal, ligands, and reacting groups in order to derive a model for the analysis of the structural and dynamic features of complex chemical systems. Although this is a potentially important paper (even if, as the authors note, it is somewhat risky), it is incredibly difficult to read. A combination of unusual English, vast amounts of unique terminology, and complicated diagrams make it hard to follow the authors' arguments.

In Search of New Organometallic Reagents for Organic Synthesis, by T. Kauffmann, was originally presented as a meeting lecture. Consequently, it is basically a review of the author's own work and that of his students, primarily in the field of lithium chemistry.