Table I. Selected Interatomic Distances in $Cs^+(18C6)\cdot e^{-}$ [a]

Cs⁺ to oxygen, Å		electron[b] to surrounding atoms, Å	
Cs^+–O_1	3.453 (8)	e^-–H_{6a}[c]	3.29
Cs^+–O_4	3.296 (8)	e^-–H_{15b}[d]	3.64
Cs^+–O_7	3.305 (7)	e^-–H_{2a}[e]	3.76
Cs^+–O_{10}	3.457 (8)	e^-–H_{17a}[d]	4.09
Cs^+–O_{13}	3.296 (9)	e^-–H_{15a}[d]	4.17
Cs^+–O_{16}	3.304 (8)	e^-–C_6[c]	4.19
		e^-–H_{3a}[e]	4.24
		e^-–H_{8b}[c]	4.29

[a] Mean C–C in crown, 1.49Å; mean C–O in crown, 1.42 Å. [b] Distances from e^- are calculated from the inversion center at 0, $^1/_2$, 0. [c] Indicates atom at $^1/_2 - x, y + {}^1/_2, {}^1/_2 - z$. [d] At $-x - {}^1/_2, {}^1/_2 + y, {}^1/_2 - z$. [e] At $-x, y, {}^1/_2 - z$.

determined at −57 °C in the monoclinic space group $C2/c$ with a = 13.075 (5) Å, b = 15.840 (7) Å, c = 17.359 (8) Å, β = 92.30 (3)°, and Z = 4. The refinement began with the non-sodium parameters of the isostructural Cs^+(18-crown-6)$_2$ Na^- structure.[12] Final agreement factors of R = 0.058 and R_w = 0.070 were obtained for 1306 observed unique reflections. An ORTEP stereo packing diagram is shown in Figure 1. The ions pack in alternate planes of cations and anionic holes perpendicular to the c axis with closest in-plane separation of 10.27 Å. The anionic holes are separated by 8.68 Å along the c axis. The cations, lying alternately ±0.42 Å from the c axis along the b direction, are separated by 8.72 Å. The size of the anionic hole, which lies at an inversion center, may be estimated by subtracting the van der Waal's radius for hydrogen from the distances to the surrounding hydrogen atoms from this center. The shortest hydrogen–hole center distances are listed in Table I and give a minimum hole radius of 2.1 Å and a mean hole radius of ~2.4 Å. A stereoview of the anionic hole down the b axis is shown in Figure 2. The hole appears to be nearly spherical with a slight elongation along the c axis toward the nearest-neighbor trapped electrons. The average calculated electron density throughout the anionic hole is only 0.026 $e^-/Å^3$, which is below the noise level on the final difference electron density map, thus precluding direct observation of the electride ion. That the cesium is a cation is shown by the Cs–O distances, which are nearly identical with those in the $Cs^+(18C6)_2{\cdot}Na^-$ structure and only about 0.2 Å longer than those in the Cs^+-(18C6)·SCN^- structure.[13]

Since the structure consists of only a complexed cation and noise level electron density at the usual anionic site, it supports the picture of a localized electride as a salt with electrons as the anions. This study is the first direct determination of the local structure around a trapped electron.

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Supplementary Material Available: Tables of data collection and refinement summaries, positional parameters, thermal parameters, bond distances and angles, least-squares planes, and F_{obsd} and F_{calcd} and stereoviews of the anionic hole along the a and c axes (29 pages). Ordering information is given on any current masthead page.

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Silox Hydrides (silox = t-Bu_3SiO^-) of Group 5: Do $[(silox)_2MH_2]_2$ (M = Nb, Ta) Complexes Contain Unbridged M–M Bonds?

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Complexes containing M–H bonds are widely recognized as being important intermediates in numerous catalytic processes.[1] Investigations of early metal hydride reactivity have resulted in reagents[2] useful in organic synthesis and modeling studies[3-5] relevant to the Fischer–Tropsch process.[6]

A variety of group 5 hydrides have been described; the majority contain ancillary phosphine[7,8] and/or cyclopentadienyl ligands[9-11] that tend to electronically and sterically saturate the early metal center. By introducing an ancillary ligand system with electronic

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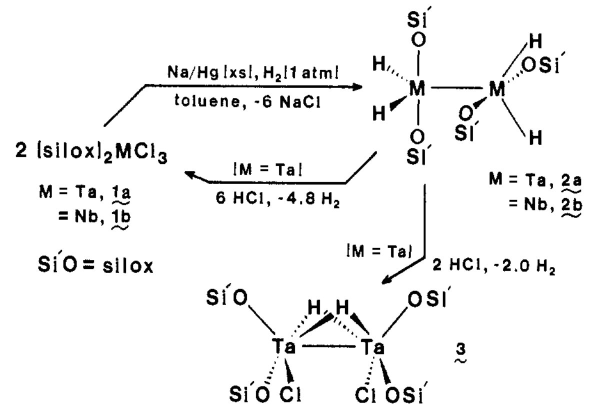
Table I. NMR, IR, and Molecular Weight Data for silox ($((CH_3)_3C')_3SiO$) Bridges

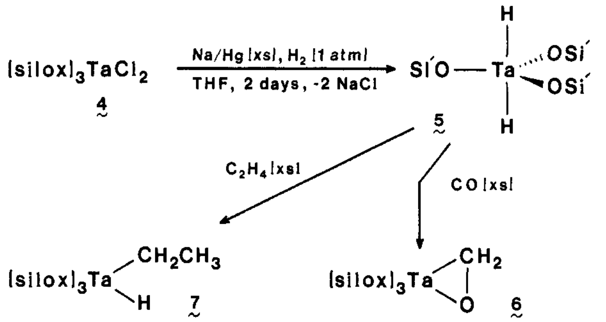
	^1H, δ^a		^{13}C, $\delta^{b,c}$		^{29}Si, $\delta^{a,c}$	IR, $cm^{-1\,d}$	M_r^e	
	CH_3	Ta–H	C	C′	Si	ν(Ta–H/D)	Calcd	Found
$[(silox)_2TaH_2]_2$ (**2a**)	1.26	12.13	30.34	23.37	$14.14^{f,g}$	1760/1270	1228	1240
$[(silox)_2NbH_2]_2$ (**2b**)	1.31	7.3	30.34	23.27	14.50^g	1720/1230	*h*	*h*
$[(silox)_2TaCl]_2(\mu\text{-}H)_2$ (**3**)	1.27	9.35	30.78	24.25 23.81	19.32 16.75	1595/1240	*h*	*h*
$(silox)_3TaH_2$ (**5**)	1.26	21.99	30.49	23.37	15.29^f	1725/1250 δ 750/570^i	829	900

^{a}Benzene-d_6, referenced to Me_4Si (δ 0.00), all singlets. ^{b}Referenced to benzene-d_6 (δ 128.0). ^{c}^1H-decoupled spectra. ^{d}Nujol; M–H,D stretches (m,w) were all broad (spectra taken in cyclohexane exhibited slight band shifts as did thin films of **2a** and **2b**). ^{e}Benzene freezing point depression. ^{f}Selective decoupling experiments indicated $J_{SiH(Ta)} \simeq 0$. ^{g}Toluene-d_8, −70 °C: **2a** δ 12.11; **2b** δ 12.30. ^{h}Traces of lattice-solvated THF precluded accurate measurement. ^{i}Assigned as scissoring; very strong.

Scheme I



Scheme II



properties dissimilar[12] to the aforementioned strong σ-donors, the reactivity and structural properties common to these metal hydrides may be altered. Reported herein are syntheses and selected reactions of group 5 hydrides ligated by tri-*tert*-butylsiloxide ($t\text{-}Bu_3SiO^-$, silox),[13] which has been shown to sterically saturate metal centers while leaving them electron deficient.[14]

As Scheme I indicates, dimeric Ta and Nb(IV) silox hydrides were obtained upon Na/Hg reduction of $(silox)_2MCl_3$ (M = Ta, **1a**;[14] Nb, **1b**[15]) for 15 and 2 days, respectively, in the presence of H_2. Both dimers, $[(silox)_2MH_2]_2$ (M = Ta, **2a**; Nb, **2b**),[16] could be isolated as dark orange crystals in good yield (**2a**, 60%; **2b**, 40%). Treatment of **2a** with 2 equiv of HCl afforded a purple, tantalum hydrochloride dimer, $[(silox)_2TaCl]_2(\mu\text{-}H)_2$ (**3**),[16] in 88% yield, while 6 equiv of HCl quantitatively regenerated **1a**, concomitant with 4.8 equiv of H_2.

The spectroscopic features (Table I) of these dimers provide strong evidence for unusual geometries. A single silox ligand is observed for both **2a** and **2b** in the ^1H, ^{13}C, and ^{29}Si NMR spectra. The hydride resonances (toluene-d_8: **2a**, δ 12.06; **2b**, δ 7.2) remained unchanged from 25 to −80 °C,[17] although the quadrupolar-broadened Nb–H peak sharpened considerably. Infrared spectra of **2a** and **2b** were distinctly similar, implicating an isostructural relationship; only broad, terminal hydrides (**2a**, 1760 cm^{-1}; **2b**, 1720 cm^{-1}) were observed. A D_{2d} structure consisting of two interlocked tbp Ta centers, with axial silox and equatorial H ligands, or an alternative H(axial), silox(equatorial) arrangement is therefore proposed.[18] A $[(silox)MH_2]_2(\mu\text{-}silox)_2$ geometry is credible, provided terminal/bridge exchange is fast. The ^{13}C NMR spectrum of **3** manifests two inner-carbon silox resonances while the IR indicates bridging hydrides (1590 cm^{-1}), leading to a structure with square pyramids linked by basal μ-H's and a Ta–Ta bond, reminiscent of $(\eta^5\text{-}C_5R_5)_2Ta_2Cl_3R'(\mu\text{-}H)_2$ (R′ = alkyl, Cl) species prepared by Schrock et al.[9]

When a similar reduction of $(silox)_3TaCl_2$ (**4**)[19] was conducted, monomeric $(silox)_3TaH_2$ (**5**)[16] was prepared in 52% yield (Scheme II). A tbp geometry for **5** seems most plausible, given the size of the silox ligands, a terminal Ta–H stretch (1725 cm^{-1}), and an extremely intense scissoring ($\delta(TaH_2)$) band at 750 cm^{-1}. The electrophilic character of **5** is manifested by its rapid reduction of CO (25 °C) to quantitatively provide $(silox)_3Ta(\eta^2\text{-}CH_2O)$ (**6**).[20-22] By exposing a ~1:1 mixture of **5** and $(silox)_3TaD_2$ (**5**-d_2) to 2 equiv of CO, some (~15%) crossover product, $(silox)_3Ta(\eta^2\text{-}CHDO)$ (**6**-d_1),[23] was generated. However, at CO pressures > 5 atm only **6** and **6**-d_2 are formed, suggesting that both mono-

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(16) Anal. Calcd for **2a**, $Ta_2Si_4O_4C_{48}H_{112}$: C, 46.96; H, 9.20. Found: C, 46.72; H, 9.03. Anal. Calcd for **2b**, $Nb_2Si_4O_4C_{48}H_{112}$: C, 54.83; H, 10.73. Found: C, 54.60; H, 10.55. Anal. Calcd for **3**, $Ta_2Cl_2Si_4O_4C_{48}H_{110}$: C, 44.47; H, 8.55; Cl, 5.47. Found: C, 44.63; H, 8.41; Cl, 5.49. Anal. Calcd for **5**, $TaSi_3O_3C_{36}H_{83}$: C, 52.14; H, 10.09. Found: C, 51.90; H, 10.05.

(17) As expected (see ref 14), broadening of ^1H and ^{13}C silox resonances due to stoppage of *tert*-butyl or silox rotations obfuscated their VT NMR analysis.

(18) The absence of a δ vibration, as observed for **5**, slightly favors the former description.

(19) Anal. Calcd for **4**, $TaCl_2Si_3O_3C_{36}H_{81}$: C, 48.14; H, 9.09. Found: C, 47.99; H, 8.93. ^1H NMR (C_6D_6) δ 1.34; $^{13}C\{^1H\}$ NMR δ 30.63 (CH_3), 24.93 (SiC).

(20) Anal. Calcd for **6**, $TaSi_3O_4C_{37}H_{83}$: C, 51.84; H, 9.76. Found: C, 51.92; H, 9.66. ^1H NMR (C_6D_6) δ 1.25 (s, CH_3, 81 H), 4.06 (s, CH_2O, 2 H); $^{13}C\{^1H\}$ NMR δ 93.87 (CH_2O, J_{CH} = 159 Hz), 30.58 (CH_3), 23.56 (SiC). IR (**6**/**6**-d_2/**6**-^{13}C, cyclohexane) ν ($H_2CO/D_2CO/H_2{}^{13}CO$) 932, 932, 914 cm^{-1}; ($CH_2/CD_2/{}^{13}CH_2$ wag) 552, 502, 543 cm^{-1}; ($H_2CO/D_2CO/H_2{}^{13}CO$ rock (tentative)) 600, 588, 600 cm^{-1}. M_r found 830 (calcd 856).

(21) A similar carbonylation of $(\eta^5\text{-}C_5Me_5)TaMe_4$ affords an η^2-acetone complex. See: Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421.

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(23) Neither **5** and **5**-d_2 ($(silox)_3TaHD$ (**5**-d_1): ^1H NMR (C_6D_6) δ 21.97 (TaH)) nor **6** and **6**-d_2 ($(silox)_3Ta(\eta^2\text{-}CHDO)$ (**6**-d_1): ^1H NMR (C_6D_6) δ 4.03 (CHDO)) undergo H/D exchange under similar conditions.

and bimetallic reduction processes play roles, the former prevailing at higher pressures.[23] When treated with ~2 equiv of C_2H_4 in a sealed NMR tube, **5** is quantitatively converted to the ethyl hydride, $(silox)_3Ta(Et)H$ (**7**);[24] presumably the steric properties of **7** preclude further ethylene insertion.

Species **2a**,**2b**, **3**, **5**, and **7** represent a class of unusual metal hydrides that possess "hard" ancillary ligands.[12] The absence of bridging ligands in the postulated **2a**,**b** structure is surprising in view of the propensity of hydride and alkoxide ligands to span two early metal centers.[8,9,25] Perhaps the structure reflects the dominance of silox steric influences; alternatively, plausible μ-H units may ineffectively compete for orbitals utilized in strong silox $p\pi \gg d\pi$ donation. Clarification of such explanations must await an ongoing X-ray structure determination. Studies pertaining to the CO reduction products of **2a** and **3** and the reductive elimination pathways available to the hydride and alkyl hydride derivatives are future endeavors.

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[24] $(silox)_3Ta(CH_2CH_3)H$ (7): ^1H NMR (C_6D_6) δ 1.29 (s, silox, 81 H), 1.82 (dq, CH_2, 2 H, J = 3.2, 7.8 Hz), 2.18 (t, CH_3, 3 H, J = 7.8 Hz), 22.30 (t, TaH, 1 H, J = 3.2 Hz).

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Can Nucleophiles Attack Radical Cations Directly? "Allowed" and "Forbidden" Polar Reactions[1]

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As a result of Woodward and Hoffmann's pioneering work on pericyclic reactions,[2] the concept of "allowed" and "forbidden" reactions has become part of the language of organic chemistry. Till now, however, the terms have been restricted to just this class of reactions. Polar reactions, which constitute a large majority of organic reaction types, have never been classified in this way. In this paper we wish to demonstrate that the terms allowed and forbidden may be usefully applied to polar reactions as well. Within a family of polar reactions, e.g., nucleophilic addition, certain cases may be demonstrated to be intrinsically high-energy ones, i.e., forbidden, while in contrast others are low-energy reactions, i.e., allowed. The concept is illustrated by considering the reaction of radical cations and regular cations with nucleophiles, and a general rule enabling classification of polar reactions as either allowed or forbidden is provided.[3]

The reaction of nucleophiles with radical cations has been extensively studied over recent years[4,5] and their low reactivity noted by Eberson.[5a] One of the key mechanisms that has been proposed for these reactions, termed the half-regeneration mechanism,[4] involves as a first step, direct attack of the nucleophile on the radical cation (eq 1). Such a process is consistent with

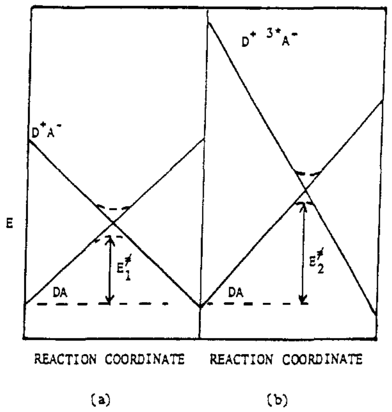

Figure 1. (a) Schematic energy diagram illustrating the way in which the reaction profile for nucleophilic attack on a normal cation may be built up from the avoided crossing of DA and D^+A^- configurations. (b) Corresponding diagram for nucleophilic attack on a radical cation, in which the product configuration is now $D^+\ {}^{3*}A^-$. Since $D^+\ {}^{3*}A^-$ is doubly excited with respect to DA, while D^+A^- is just singly excited, $E_2^{\ddagger} > E_1^{\ddagger}$.

$$A^{+\cdot} + Nu \rightleftharpoons (A\text{-}Nu)^{+\cdot} \qquad (1)$$

conventional organic chemical thinking and is readily represented by curly arrows. However, Parker[4a,b] has recently reassessed existing data and concluded that in certain cases the half-regeneration pathway is not operative, as was initially thought. Alternative routes appear to be followed. It appears that disproportionation of the radical cation to the dication and the neutral *precedes* nucleophilic attack.[4a,b,6] This is quite unexpected since the equilibrium constant for disproportionation is ca. 10^{-9}. The questions arise: *What inhibits direct nucleophilic attack on the radical cation? Why is it the dication and not the radical cation that reacts with the nucleophile?* We now demonstrate, using elements of the configuration mixing (CM) model,[7,8] that direct nucleophilic attack on a regular carbocation is an allowed polar process while the corresponding attack on a radical cation is a high-energy pathway and hence a forbidden process.

All nucleophilic addition reactions may be thought of in terms of a DA-D^+A^- avoided crossing. This is consistent with our recent discussion suggesting that much of organic reactivity may be

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[1] Presented in part at the ACS Symposium on "Nucleophilicity", Chicago, Sept, 1985.

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[3] The terms "allowed" and "forbidden", as employed in this paper, have the same practical consequences as in Woodward and Hoffmann's original treatment.[2] However, the theoretical roots are different. For pericyclic reactions the allowedness is based on symmetry considerations, while for polar reactions the selection is governed by just energetic considerations.

[4] For recent reviews, see: (a) Parker, V. D. *Acc. Chem. Res.* **1984**, *17*, 243. (b) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55. (c) Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *13*, 156.

[5] For a selection of papers on the reaction of radical cations with nucleophiles, see: (a) Eberson, L.; Blum, Z.; Helgée, B.; Nyberg, K. *Tetrahedron* **1978**, *34*, 731. (b) Manning, G.; Parker, V. D.; Adams, R. N. *J. Am. Chem. Soc.* **1969**, *91*, 4584. (c) Shine, H. J.; Murata, Y. *Ibid.* **1969**, *91*, 1872. (d) Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368. (e) Parker, V. D.; Eberson, L. *J. Am. Chem. Soc.* **1970**, *92*, 7488. (f) Marcoux, L. *Ibid.* **1971**, *93*, 537. (b) Svanholm, U.; Hammerich, O.; Parker, V. D. *Ibid.* **1975**, *97*, 101. (h) Svanholm, U.; Parker, V. D. *Ibid.* **1976**, *98*, 997, 2942. (i) Kim, K.; Hull, V. J.; Shine, H. J. *J. Org. Chem.* **1974**, *39*, 2534. (j) Evans, J. F.; Blount, H. N. *Ibid.* **1977**, *42*, 976. (k) Evans, J. F.; Blount, H. N. *J. Am. Chem. Soc.* **1978**, *100*, 4191. (l) Evans, J. F.; Blount, H. N. *J. Phys. Chem.* **1979**, *83*, 1970. (m) Hammerich, O.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1981**, *35*, 341. (n) Cheng, H. Y.; Sackett, P. H.; McCreery, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 962. For a more extensive list of references, see ref 4.

[6] If the free radical cation undergoes disproportionation the mechanism is termed the disproportionation mechanism, while if the radical cation is first complexed to the nucleophile then the pathway is termed the complexation mechanism.[4]

[7] For recent reviews of the CM model, see: (a) Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363. (b) Pross, A. *Adv. Phys. Org. Chem.* **1985**, *21*, 99. (c) Shaik, S. S. *Prog. Phys. Org. Chem.* **1985**, *15*, 197.

[8] (a) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 187. (b) Shaik, S. S.; Pross, A. *Ibid.* **1982**, *104*, 2708. (c) Pross, A.; Shaik, S. S. *Tetrahedron Lett.* **1982**, 5467. (d) McLennan, D. J.; Pross, A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 981. (e) Shaik, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 4359. (f) Pross, A.; Shaik, S. S. *Ibid.* **1982**, *104*, 1129.

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