J. Am. Chem. Soc. **1980**, *102*, 7241-7244

Importance of (p–d)π Bonding in the Siloxane Bond

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Abstract: The participation of silicon d orbitals in the siloxane bonds in H_3COSiH_3, $H_3SiOSiH_3$, and $H_3SiO{-}OSiH_3$ has been investigated by ab initio termination of geometric and electronic structures of these molecules. (p–d)π bonding in the Si–O bond was found to be of minor importance, while the ionic character of the bond is much higher than that estimated from electronegativities.

Introduction

The nature of the siloxane bond has attracted great interest for many years. One of the most striking properties is its shortness when compared with the prediction from the Schomaker–Stevenson rule,[1] i.e., the sum of the covalent radii of silicon and oxygen corrected for differences in the electronegativities. For a large variety of organic silicon compounds, Si–O bond lengths of 1.64 ± 0.03 Å have been obtained from experiments,[2] while the Schomaker–Stevenson rule predicts an Si–O bond length of 1.77 Å. The longest Si–O bond distance (1.681 ± 0.008 Å) for any molecule studied in the gas phase has been determined for bis(trimethylsilyl) peroxide, $Me_3SiO{-}OSiMe_3$.[3] Figure 1 demonstrates that this "failure" of the Schomaker–Stevenson rule is not restricted to the Si–O bond but is observed also for other bonds to silicon.[4-8] The difference between predicted and experimental Si–X bond lengths increases with increasing electronegativity of the X atom. Another unusual structural feature of molecules containing the Si–O bond is an increase in the oxygen bond angle in ether-type molecules upon substitution of methyl groups by silyl groups. The oxygen bond angle in dimethyl ether (111.5 ± 1.5°)[9] increases to 120.6 ± 1.0° in methyl silyl ether[10] (CH_3OSiH_3) and to 144.1 ± 0.9° in disiloxane.[7] Only a small increase of the oxygen bond angle of the entity –O–O–Si has been observed between $Me_3C{-}O{-}O{-}CMe_3$ and $Me_3Si{-}O{-}O{-}SiMe_3$.[3]

The two unusual structural features of disiloxane, i.e., the short Si–O bond length and the large oxygen bond angle, have been explained qualitatively by the concept of (p–d)π back-bonding.[2,11-13] In this widely held view, silicon with its unoccupied 3d orbitals functions as acceptor in the donor–acceptor (p–d)π bond. According to this concept the partial π bond in addition to the σ bond shortens the Si–O distance, and partial delocalization of the oxygen lone pairs allows an increase of the SiOSi bond angle. The large oxygen bond angle can also be accounted for by the concept of "one angle nonbonded radii"[14] which is based on minimum distances between nonbonded atoms. This concept accounts for the large bond angle as a consequence of the short Si–O bond, without explaining this shortening.

Recent semiempirical MO calculations in the CNDO/2 approximation[15] for a series of compounds containing the Si–O bond demonstrated that the experimental oxygen bond angles in these compounds are reproduced reasonably well by these calculations without the use of Si (3d) functions. Thus, it is concluded that the increase in the oxygen bond angles in siloxanes does not require the assumption of a (p–d)π contribution. In all these calculations the bond lengths were fixed at their experimental values. The attempt to optimize the Si–O bond length in disiloxane with the CNDO/2 method, however, failed. For SiOSi bond angles between 110 and 150° the total energy decreases with increasing Si–O bond lengths up to Si–O = 2.00 Å. For Si–O = 2.05 Å or greater, the SCF procedure in the CNDO/2 approximation diverges. When Si (3d) functions are included in the basis set, similar results are obtained. The total energy decreases for increasing Si–O bond lengths up to Si–O = 1.75 Å, and the SCF procedure diverges for Si–O = 1.80 Å or greater. Since the CNDO/2 approximation with or without Si (3d) functions does not reproduce the experimental Si–O bond distances at all, no final conclusions concerning the electronic structure of this bond can be drawn from these calculations. The aim of this investigation is to study the importance of Si (3d) functions in siloxanes and the contribution of (p–d)π bonding in the Si–O bond.

Method

The geometries of H_3COSiH_3, $H_3SiOSiH_3$, and $H_3SiO{-}OSiH_3$ were fully optimized with the ab initio gradient program TEXAS,[16] using 21 and 4-21 basis sets for hydrogen and second-row elements.[17] For silicon, the 3-3-21 basis set derived earlier[18] and tested for some molecules containing Si–C bonds was supplemented by d functions. As suggested by Pulay,[16] these d functions have been constructed from p functions with an orbital exponent $\eta = 0.8$ with one of the six diagonal, i.e., angle-dependent, functions replaced by a special 3s combination. In agreement with other calculations using the 4-21 basis set,[19] we observe that in many molecules experimental oxygen bond angles are reproduced satisfactorily only when polarization functions are added (4-21* basis set). These polarization functions are constructed in the same way as the Si (d) functions. Without polarization functions the optimized COSi bond angle in H_3COSiH_3 is larger by 8.2° than the experimental value, and the SiOSi skeleton in disiloxane comes out to be linear. In disilyl peroxide the oxygen polarization functions do not change the OOSi bond angle very much but have a large effect on the SiOOSi dihedral angle. Without polarization

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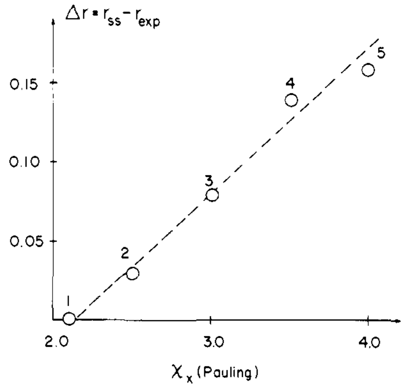

Figure 1. Differences of Si–X bond lengths between Schomaker–Stevenson prediction[7] (r_{ss}) and experimental values for some X atoms with different electronegativities, χ_X: 1, X = P ($P(SiH_3)_3$);[4] 2, X = C (H_3C-SiH_3);[5] 3, X = N ($N(SiH_3)_3$);[6] 4, X = O ($O(SiH_3)_2$).[7] 5, X = F (SiF_4).[8]

Table I. Calculated and Experimental Geometric Parameters (Å and deg) and Dipole Moments for H_3COSiH_3[a]

	ab initio	expt[b]
Si–O	1.627	1.640 (3)
∠SiOC	120.4	120.6 (1.0)
C–O	1.426	1.418 (9)
Si–H_1	1.462	(1.485)[c]
Si–H_2	1.468	
C–H_4	1.081	1.080 (9)
C–H_5	1.086	
∠$OSiH_1$	108.0	109.0 (3.0)
∠$OSiH_2$	111.8	
∠H_1SiH_2	109.1	110.0 (3.0)
∠H_2SiH_3	107.0	
∠OCH_4	107.9	111.0 (2.0)
∠OCH_5	111.5	
∠H_4CH_5	108.6	108.0 (2.0)
∠H_5CH_6	108.6	
μ (Debye)	1.40[d]	1.17[e]

[a] See Figure 2 for numbering of atoms. [b] Reference 10. [c] Not refined in the experiment. [d] See Figure 2 for direction of dipole moment. [e] Reference 21.

functions the optimized dihedral angle is 180°, i.e., a planar trans configuration of the SiOOSi skeleton. The same result was obtained earlier for hydrogen peroxide[20] with much larger s,p basis sets, where the experimental dihedral angle could be reproduced only by adding polarization functions to the oxygen basis set.

Geometric parameters were optimized until changes were less than 0.002 Å for bond distances and 0.2° for bond angles and dihedral angles. It has been pointed out[19] that the objective of ab initio calculations should be to operate at a level where the offset from the true value is constant and known rather than to obtain the best absolute value of a structural parameter which may result from chance cancellation of errors. Previous calculations[17,18] indicate that calculations at the double-ζ level using the 4-21 basis set for first-row elements and the 3-3-21* basis set for silicon result in bond distances which are systematically too long or too short by a certain amount, so that trends in bond lengths should be more accurate than absolute values. For bond angles, calculations at the 4-21 level agree with experiment within the experimental uncertainties, provided polarization functions are added in the case of oxygen.[19]

Table II. Calculated and Experimental Geometric Parameters (Å and deg) and Dipole Moments for $H_3SiOSiH_3$[a]

	ab initio	expt[b]
Si–O	1.617	1.634 (2)
∠SiOSi	143.3	144.1 (0.9)
Si–H_1	1.462	1.486 (10)
Si–H_2	1.466	
∠$OSiH_1$	109.4	109.8 (1.3)
∠$OSiH_2$	111.3	
∠H_1SiH_2	108.6	109.1 (1.3)
∠H_2SiH_3	107.7	
μ (Debye)	0.33[c]	0.24[d]

[a] See Figure 3 for numbering of the atoms. [b] Reference 7. [c] See Figure 3 for direction of dipole moment. [d] Reference 21.

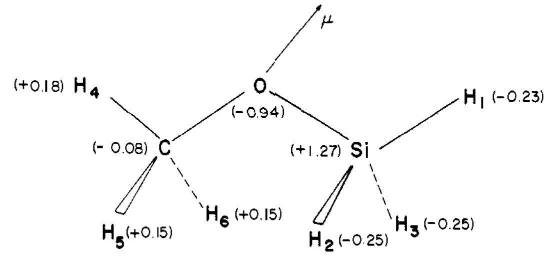

Figure 2. Atom numbering and atomic net charges (au) for H_3COSiH_3.

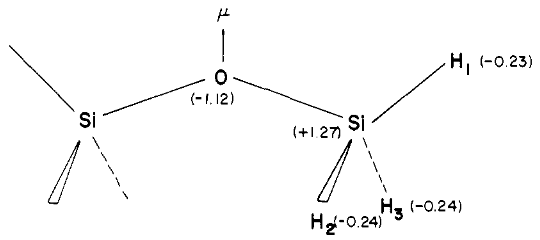

Figure 3. Atom numbering and atomic net charges (au) for $H_3SiOSiH_3$.

Results: Bond Lengths and Angles and Dipole Moments

The agreement between experimental values and our ab initio calculations with d functions for silicon and polarization functions for oxygen is generally very good; see Tables I–III. Our Si–O and C–H bond lengths are perhaps 0.01 Å shorter than the experimental would be if corrected to r_e (equilibrium) basis. In this respect our C–O value (Table I) is exceptional. The C–O–Si and Si–O–Si angles agree well within the experimental uncertainties, perfectly confirming the increase in oxygen bond angle on substituting SiH_3 for CH_3.

Lacking experimental values for disilyl peroxide, we compare our Si–O and Si–O–O results with the experimental values[3] for Me_3SiO–$OSiMe_3$. The effects of replacing silyl by trimethylsilyl we take from $Me_3SiOSiMe_3$:[22] no significant change in Si–O (1.634 (2) Å vs. 1.631 (3) Å) and a 4° increase in Si–O–Si (144.1 (9)° vs. 148.0 (30)°). For H_3SiO–$OSiH_3$ as compared to Me_3SiO–$OSiMe_3$ we accordingly expect a nearly equal bond length and a somewhat smaller Si–O–O angle similar to the C–O–O angle in dimethyl peroxide[23] (105 (3)°, incomplete study). The long Si–O in the silyl peroxides is thus doubly confirmed and the seeming discrepancy in Si–O–O, in Table III, explained. Our O–O length, 0.03 Å less than the experimental for Me_3SiO–$OSiMe_3$, attracts attention. Calculations without the oxygen polarization functions gave better absolute agreement for both Si–O and O–O but, as pointed out above, led to serious disagreement for bond and dihedral angles. The present dihedral agreement (Table III) is tolerable.

The angular distortion of the SiH_3 groups from C_{3v} symmetry is primarily a tilt of the C_3 axis with respect to the Si–O direction toward the oxygen lone pairs. It is largest for the peroxide, causing OSiH angle differences as big as 7°. The SiH_3 group in the peroxide is very nearly staggered to the O–O bond. Because these "ab initio" differences in bond lengths and angles are usually both more reliable than the absolute values and difficult or impossible

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Table III. Calculated Geometric Parameters (Å and deg) for $H_3SiO–OSiH_3$ and Experimental Values for the SiO–OSi Skeleton of $Me_3SiO–OSiMe_3$

	ab initio	expt[a]
Si–O	1.667	1.681 (3)
O–O	1.447	1.480 (8)
∠OOSi	101.2	106.6 (1.4)
δ (SiOOSi)	136.5	143.5 (6.0)
$Si–H_1$	1.463	
$Si–H_2$	1.458	
$Si–H_3$	1.460	
$∠OSiH_1$	104.7	
$∠OSiH_2$	111.6	
$∠OSiH_3$	111.0	
$∠H_1SiH_2$	110.0	
$∠H_1SiH_3$	109.7	
$∠H_2SiH_3$	109.8	
$\partial(OOSiH_1)$	179.3	
$\delta(OOSiH_2)$	60.4	
$\delta(OOSiH_3)$	−62.4	
μ (Debye)	0.88[b]	

[a] Reference 3. [b] See Figure 4 for direction of dipole moment.

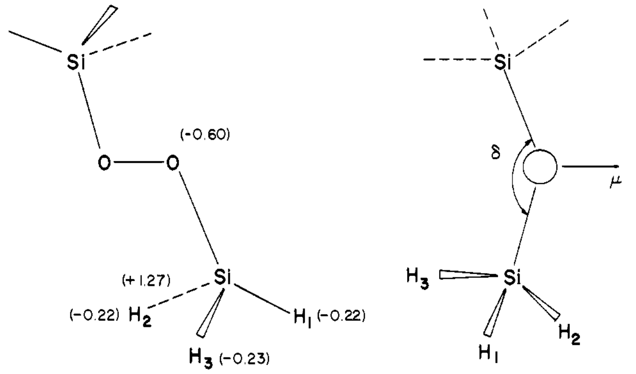

Figure 4. Atom numbering and atomic net charges (au) for $H_3SiO–O–SiH_3$.

to determine experimentally, they should be taken into account in any future structure determination or redetermination of these molecules.

A further test for the quality of the wave functions is the fair agreement between calculated and experimental dipole moments for the ether-type compounds; see Tables I and II.

Mulliken Population Analysis

The "nature"—i.e., the electronic structure—of the siloxane bond may be discussed on the basis of a Mulliken population analysis.[24] The atomic net charges are given in Figures 2–4. The most surprising result of this analysis is the very high positive value of +1.27 au for silicon in all three molecules. More than half of this positive charge results from donation to the hydrogen atoms, and the overall charges of the SiH_3 groups are only 0.54–0.60 au. In H_3COSiH_3 there is no drastic difference between the overall charges of SiH_3 and CH_3 (0.54 and 0.40 au), but the net charge on silicon is high and positive in contrast to the small negative net charge on carbon. The CH_3 charge distributions in H_3COSiH_3 and dimethyl ether[29] are closely similar (0.38 au overall charge and −0.07 au carbon net charge). The negative net charge of oxygen is similar for H_3COSiH_3 and $H_3SiOSiH_3$ (−0.94 and −1.12 au) but considerably smaller for the peroxide (−0.60 au). The oxygen net charge would of course be only half as large in the peroxide as in disiloxane, if the overall charge of the two silyl groups were constant. This estimate is in close agreement with the charges obtained from the Mulliken population analysis. A consequence of this charge distribution is a very high polarity of the siloxane bond in the silyl ethers and a reduced, but still high, polarity in the peroxide.

Table IV. Atomic Net Charges q (au), Ionic Characters I (%), and Overlap Populations p (au) for the Si–O Bonds in H_3COSiH_3, $H_3SiOSiH_3$, and $H_3SiO–OSiH_3$

	H_3COSiH_3	$H_3SiOSiH_3$	$H_3SiO–OSiH_3$
$r(Si–O)$[a]	1.640 (3)	1.634 (2)	1.681 (3)
q_{Si}	+1.27	+1.27	+1.27
q_O	−0.94	−1.12	−0.60
I_{SiO}[b]	50	50	50
I_{SiO}[c]	110	120	93
$p(Si–O)$ total	0.256	0.236	0.199
(p–d)π	0.014	0.017	0.010

[a] Experimental Si–O bond lengths. [b] $I_{AB} = 100[1 - \exp(-0.25|\chi_A - \chi_B|^2)]$. [c] $I_{AB} = 50(p_A - p_B)$.

The polarity of a bond is usually measured by the ionic character which was originally introduced by Pauling.[1] The ionic character of a bond can be estimated either from dipole moments or from nuclear quadrupole coupling constants if one of the nuclei has a nuclear quadrupole moment. On the basis of such experimental data, various empirical relations between the ionic character of a bond and the difference in electronegativities of the two atoms involved have been proposed by Pauling,[1] Hannay and Smith,[25] Gordy,[26] and Dailey and Townes.[27] For an isolated siloxane bond, an ionic character of about 50% is estimated from Pauling's relation. All these considerations, however, are restricted to diatomic molecules. If we follow the suggestion of Klessinger[28] and derive the ionic character for a bond A–B from the Mulliken population analysis, $I_{AB} = 50(p_A - p_B)$, p_A and p_B being the atomic net charges, we obtain values of 110%, 120%, and 93% for the siloxane bonds in H_3COSiH_3, $H_3SiOSiH_3$, and $H_3SiO–OSiH_3$, respectively. Although this definition of ionic character is also limited to diatomic molecules, the atomic net charges p_A and p_B reflect the effects of various substituents on atoms A and B. Such effects are ignored completely in the electronegativity concept.

When ionic characters are based on atomic net charges, they parallel qualitatively the Si–O bond lengths. The covalent bond strength, in addition to the ionic character, determines the Si–O bond length. The decreasing trend of Mulliken overlap populations (Table IV) from H_3COSiH_3 to $H_3SiOSiH_3$ opposes the trend of ionic characters, and both are small. The net effect is a slight decrease in Si–O bond lengths. Continuing to the peroxide, however, the trend in overlap population steepens while the trend in the ionic character strongly reverses, hence the unusually long Si–O bond. The (O (p)–Si (d))π contribution to these Si–O overlap populations, always small, is at 7% largest for the disiloxane. The small involvement of the Si (d) functions also follows from the small population of the diagonal Si (d) functions (about 0.10 au for all three molecules).

For disiloxane the s part of the d functions is populated more strongly (0.17 au) than all five diagonal functions together. To test the effect of the diagonal functions alone, we optimized the geometry by including the s part but not the diagonal parts of the d functions, resulting in Si–O bond lengths of 1.649 Å and an SiOSi bond angle of 138°. Thus, we conclude from all this that the Si (d) functions to some extent only compensate for the rather small and not quite adequate s,p basis set and do not account for the unusual structural features of disiloxane.

Conclusion

Since our ab initio calculations reproduce the geometry and dipole moments of the three molecules very well, conclusions concerning the electronic structure of the siloxane bond derived from these calculations should be at least qualitatively correct. (1) (p–d)π bonding is of minor importance for explaining the unusual properties of the siloxane bond. These findings are in contrast to the widely held view that (p–d)π bonding is important

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for this bond. A (p–d)π bond order of 0.4 has been deduced from experimental bond lengths.[2] (2) The small value of the Si–O bond length is rather a consequence of its ionic character which is considerably higher than that estimated from electronegativity differences.

These conclusions should be qualitatively correct, even if we concede some arbitrariness of the Mulliken population analysis in distributing the electronic charges among the atoms and some dependence on the basis set. A similar result has been obtained previously for Si–C bonds[18] where the net charges for Si and C are about +1.0 and −0.6 au. We may assume that considerably larger ionic characters as estimated from electronegativity differences can also explain the "failure" of the Schomaker–Stevenson rule for other Si–X bonds, as demonstrated in Figure 1.

It is more difficult to correlate the increase in the bond angles upon CH_3/SiH_3 substitution in the ether-type molecules with the electronic structure. Intuitively we expect increased steric interactions due to the Si–O bond shortening. This intuition has been formulated in the "one angle nonbonded radii" concept. In disiloxane, electronic repulsions between the strongly positive silicon atoms will cause a further increase of the SiOSi angle. Such electrostatic interactions may also explain why no increase of the oxygen bond angle is observed for the peroxide, where the O···Si interaction is attractive.

Acknowledgment. This work has been supported by a grant from the Robert A. Welch Foundation. H.O. would like to express his appreciation to the North Atlantic Treaty Organization for a travel grant which has made this cooperative research possible. We thank Floyd R. Cordell for assistance with some of the calculations. Furthermore, we are grateful to the reviewers whose suggestions helped to make this paper easier to understand.

Low-Temperature Infrared Study of d^0 Carbonyl Complexes

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Abstract: Low-temperature (−70 °C) infrared measurements have established that the carbonyl stretching frequencies of $(C_5Me_5)_2Zr(H)_2CO$ and $(C_5Me_5)_2Hf(H)_2CO$ are 2044 and 2036 cm^{-1}, respectively. The perdeuteriated complex $(C_5(CD_3)_5)_2ZrD_2CO$ exhibits a CO stretch at 2044 cm^{-1}. The unanticipated reduction of this frequency upon coordination to a d^0 metal center is rationalized in terms of back-bonding from a filled MH_2 bonding orbital of appropriate symmetry. $(C_5H_5)_2ZrCl_2$ is not carbonylated under 500 psi CO, a characteristic which is attributed to competitive π-donation by the chloro ligands. The significance of these results is discussed in relation to the hydrogenation of bound CO which ensues when $(C_5Me_5)_2M(H)_2CO$ (M = Zr, Hf) are warmed above −50 and −10 °C, respectively.

Introduction

The quest for stoichiometric or catalytic reduction of carbon monoxide by H_2 is currently proceeding in a variety of directions. One successful proposal[1] holds that transfer of a hydride ligand to coordinated CO will be favored if that hydride ligand is particularly electron rich; this characteristic has been claimed for hydrides of zirconium on the basis of both ^1H NMR[1] and reactivity criteria.[2] An extension of this strategy suggests that the opposite polarization of the "donor" ($MH^{\delta-}$) and the "acceptor" ($MC^{\delta+}O$) should be maximized. Thus, carbonyl complexes with minimal back-bonding to CO are appealing substrates for (intra- or intermolecular) hydrogen transfer.[3] This might be achieved in carbonyl complexes of metals in high oxidation states or those with a limited number of d electrons.

In the course of studying the homogeneous reduction of CO with $Cp^*_2ZrH_2$ (**1**) ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$), Bercaw et al. observed the transient intermediate $Cp^*_2ZrH_2(CO)$ (**2**) by low-temperature NMR.[1a] In addition to the obvious mechanistic implications, the observance of this adduct is of considerable theoretical interest, since zirconium in **2** is in the +4 oxidation state and hence formally d^0. This formal absence of d electrons indicates that conventional $d \rightarrow \pi^*$ back-bonding from the metal to carbon monoxide cannot be operative and that the adduct should possess only simple Lewis acid–base bonding, as is the case for $BH_3{\cdot}CO$ ($\nu(CO) = 2165\ cm^{-1}$ compared to 2143 cm^{-1} for gaseous CO). In light of these considerations, we have measured the low-temperature infrared spectra of $Cp^*_2ZrH_2(CO)$ and $Cp^*_2HfH_2(CO)$, another d^0 carbonyl which subsequently undergoes CO reduction.[4] These represent the first reported infrared data for d^0 carbonyl complexes.[5]

Experimental Section

Syntheses. $Cp^*_2ZrH_2$ was prepared as described earlier.[1b] $(Cp^*\text{-}d_{15})_2ZrD_2$ was obtained by treatment of 2 mmol of $Cp^*_2ZrH_2$ with five 82-mmol portions of D_2 at 72 °C over a period of 40 h.[6] A greater than 95% D incorporation was confirmed by ^1H and ^2H NMR spectrometries. $Cp^*_2HfH_2$ was obtained via treatment of $Cp^*_2HfCl_2$ with *n*-BuLi under H_2 by a procedure to be published.[4]

Spectra. A mixture of hexanes was dried over NaK alloy and vacuum distilled. IR spectra were obtained with a Perkin-Elmer 283 spectrometer. Gaseous CO was used for calibration above 2000 cm^{-1} and polystyrene for calibration below 2000 cm^{-1}.

In a typical experiment, 25 mg of the dihydride was dissolved in 1 mL of hexanes and the solution placed in a low-temperature IR cell of local design.[7] The cell is vacuum-jacketed and employs indium wire to achieve a vacuum-tight seal of the cell windows at variable temperatures. Flow-through access to the cell contents is available at all temperatures via two stainless-steel tubes which pass through the coolant well. These tubes are closed with rubber septa. The brass body of the spectral cell incorporates a chamber of 1-cm^3 volume to facilitate mixing. The solution of the dihydride was placed in this cell under N_2 in a glovebox. The cell was then cooled to −78 °C (−35 °C in the case of $Cp^*_2HfH_2$), and

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