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Silyl Substitution Effects on Metal−Pentadienyl Bonding: Synthesis, Structure, Photoelectron Spectroscopy, and Electronic Structure of a High-Valent Half-Open Zirconocene

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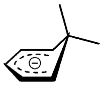
The molecule Cp(3-Me_3Si-6,6-dmch)ZrI_2 (Cp = η^5-cyclopentadienyl; 3-Me_3Si-6,6-dmch = η^5-3-trimethylsilyl-6,6-dimethylcyclohexadienyl) has been synthesized, and the molecular and electronic structures have been investigated. Photoelectron spectroscopy shows that substitution of a trimethylsilyl group in place of a hydrogen atom on the 6,6-dmch ligand destabilizes all of the ionizations of Cp(3-Me_3Si-6,6-dmch)ZrI_2 by ca. 0.1−0.2 eV compared to those of Cp(6,6-dmch)ZrI_2. Density functional calculations accurately reproduce the experimental structure of the molecule and agree with the observed shift of all ionizations to lower energies. Interestingly, the ionizations are calculated to shift to lower energies without the expected increase in electron density at the metal center. This apparent contradiction is understood from analysis of one-center and two-center charge effects in the molecule. As a consequence of these charge effects, the silyl substitution makes the 3-Me_3Si-6,6-dmch ligand a slightly better donor and, surprisingly, also a better acceptor ligand than the 6,6-dmch ligand.

Introduction

The utilization of pentadienyl ligands in transition metal complexes has almost entirely been limited to low-valent metal centers, apparently due to difficulties in bringing about effective orbital overlap between the wide pentadienyl ligands and the contracted orbitals of higher valent metal ions, and because of the ability of low-valent metal centers to back-bond to the strongly δ-acidic pentadienyl ligand.[1] Higher valent complexes that are known generally possess strong π-donating ligands,[2−5] which could serve to reduce the metal positive charge and perhaps even provide some electron density to the metal center for back-bonding to the pentadienyl ligand. Recently, however, some Zr(IV) pentadienyl complexes have been reported both with[6,7] and without[8−11] π-donating ligands. In the latter category can be included the first general classes of higher valent metal pentadienyl compounds, (6,6-dmch)$_2$ZrX_2[10] and Cp(6,6-dmch)ZrX_2,[12] for X = Cl, Br, and I; Cp = η^5-C_5H_5 and 6,6-dmch = η^5-6,6-$Me_2C_6H_5$ (**1**). In this work, it was of interest to explore the utilization of 3-Me_3Si-6,6-dmch (**2**) as a ligand, which could be especially useful for higher valent metal−pentadienyl chemistry due to the sterics of the Me_3Si group and the changes in electronic structure that this substitution induces. The incorporation of Me_3Si substituents into both pentadienyl[13] and allyl ligands[14,15] has already been shown to lead to remarkable stabilizations of otherwise highly unstable species.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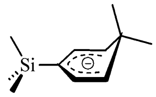

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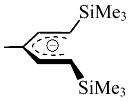
The 3-Me_3Si-6,6-dmch ligand affords some steric protection of the dienyl ligand's 1, 3, and 5 positions: those that can undergo coupling reactions leading to their expulsion as decatetraenes, thus bringing about the formal reduction of the metal center. Indeed, the 3-Me-1,5-$(Me_3Si)_2C_5H_4$ ligand (**3**), which in essence has an inverted substitution pattern relative



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Scheme 1 [a]

$$CpZrCl_2Br \xrightarrow[x\ PMe_3]{3\ KPdl} Cp(Pdl)Zr(PMe_3)_x \xrightarrow{1,2\text{-}C_2H_4I_2} Cp(Pdl)ZrI_2$$

[a] Pdl = 3-Me_3Si-6,6-dmch.

to 3-Me_3Si-6,6-dmch, has allowed for the isolation of a Mn(II) pentadienyl complex,[16] while less substituted pentadienyl ligands brought about at least some reduction of Mn(II).[17] Further, while low-valent pentadienyl complexes have been prepared with a variety of substituents,[12,18−24] the chemistry of the higher valent analogues is only just beginning to be studied. This, then, provides an opportunity to examine the influences of a silyl substituent in a higher valent metal pentadienyl compound.

The electronic effects of silyl substitution on a given system and its chemistry are not straightforward to anticipate.[25] The electropositive nature of the silicon atom could easily lead to a dominance in the inductive electron donor ability of the $SiMe_3$ group.[26,27] However, assessments of the electronegativity of the $SiMe_3$ group in the literature differ widely. Depending on the criteria or the chemical system, the $SiMe_3$ group might be considered to be either more electronegative or less electronegative than H.[28] In contrast, several gas-phase photoelectron studies on silyl-substituted ligands consistently show lower ionization energies compared to the unsubstituted analogues, indicating a greater electron donor ability of the $SiMe_3$ group.[29,30] The silicon beta effect, which involves the overlap between the p orbital on a β carbon atom and the Si−Cα σ bond orbital, could be another factor to be considered, as well as an alpha effect, which leads to stabilization of negative charge on an attached carbon atom.[31,32] Photoelectron spectroscopy provides a well-defined experimental energy measure of the magnitude of the electronic effects of a silyl group, and computations in combination with the experimental measurements provide an assessment of the electronic interactions.

Experimental Section

All reactions were carried out under an atmosphere of prepurified nitrogen gas using Schlenk apparatus and techniques. THF was dried by distillation from sodium benzophenone ketyl under a nitrogen atmosphere, while hexane was dried by passing it through a column of activated alumina under a nitrogen atmosphere. 3-Trimethylsilyl-6,6-dimethylcyclohexa-(1,3 or 1,4)-diene can be prepared either through reported procedures[33] or by the reaction of Me_3SiCl (3.7 g, 3.4 mmol) with K(6,6-dmch) (5.0 g, 3.4 mmol).[34] In a variation of this approach, the dropwise addition of Me_3SiCl to the anion in 70 mL of ether at 0 °C, followed by slow warming to room temperature, overnight stirring, extraction with 100−120 mL of ether, and removal of the ether under vacuum, led to a 5.0 g yield (82%) of product. The diene may then be deprotonated to the desired anion in 91% yield with *n*-C_4H_9Li/KO(*t*-C_4H_9) in hexane according to standard procedures.[32,35] Elemental analyses were obtained from Desert Analytics.

Diiodo(η^5-cyclopentadienyl)(η^5-3-trimethylsilyl-6,6-dimethylcyclohexadienyl)zirconium, Cp(3-Me_3Si-6,6-dmch)ZrI_2. To a slurry of $CpZrCl_2Br$ (1.90 g, 6.19 mmol) in 20 mL of THF at −78 °C was added PMe_3 (1.30 mL, 12.4 mmol), and the mixture was allowed to stir for 5 min. K(3-Me_3Si-6,6-dmch) (1.00 g, 18.6 mmol) in 30 mL of THF was added dropwise via a pressure-equalizing addition funnel. The reaction mixture turned dark red and then purple and was slowly warmed to room temperature, and thereafter allowed to stir for 2 h. The solvent was removed in vacuo to give a dark red solid. Extraction of the solid with ca. 220 mL of hexanes and filtration through a Celite pad on a medium frit gave a purple filtrate. The filtrate was concentrated to ca. 20 mL. Next, 1,2-diiodoethane (1.05 g, 3.72 mmol) was dissolved in 20 mL of hexanes, then added to the purple solution, which immediately turned bright red. The reaction mixture was stirred for 45 min. The solvent was then removed in vacuo to give a red solid. Extraction of the solid with 40 mL of toluene and filtration through a Celite pad on a medium frit gave a red filtrate. Concentration in vacuo of the filtrate to ca. 6 mL and cooling to −30 °C overnight gave 0.73 g (∼40%) of red solid.

^{1}H NMR (benzene-d_6, ambient): δ 0.19 (s, 9H, $SiMe_3$), 0.56 (s, 3H, exo CH_3), 1.29 (s, 3H, endo CH_3), 5.07 (d, $2H_{1,5}$, $J = 7.8$ Hz), 6.11 (d, $2H_{2,4}$, $J = 7.5$ Hz), 6.17 (s, 5H, Cp). ^{13}C NMR (benzene-d_6, ambient): δ 0.2 (q, 3C, $J = 119.4$ Hz, $SiMe_3$), 30.0 (q, 1C, $J = 121.6$ Hz, exo CH_3), 31.4 (s, $1C_6$), 35.2 (q, 1C, $J = 127.1$ Hz, endo CH_3), 106.0 (s, C_3), 112.8 (d, $2C_{1,5}$, $J = 166.9$ Hz), 115.6 (d of quintets, 5C, $J = 176.3$, 6.7 Hz), 126.8 (dd, $2C_{2,4}$, $J = 135.6$ Hz). Anal. Calcd for $C_{16}H_{24}SiI_2Zr$: C, 32.60; H, 4.10. Found: C, 32.34; H, 3.90.

Details of the crystal structure determination, photoelectron data collection, and computational methodology are provided in the Supporting Information.

Results and Discussion

Preparation. The reaction of $CpZrCl_2Br$ with PMe_3 and 3 equiv of the 3-Me_3Si-6,6-dmch anion yielded a purple solution, presumed to contain a Cp(3-Me_3Si-6,6-dmch)Zr$(PMe_3)_x$ ($x = 1$ or 2) complex. A value of $x = 2$ would be reasonable based on the existence of Cp(6,6-dmch)Zr$(PMe_3)_2$,[36] although the presence of the bulky Me_3Si substituent could favor formation of a mono(phosphine) complex, analogous to Cp(6,6-dmch)Ti(PMe_3).[37] Treatment of the purple solution with 1,2-diiodoethane led to the formation of the desired Cp(3-Me_3Si-6,6-dmch)ZrI_2 complex (Scheme 1), which could be isolated routinely in at least 40% yield. Room-temperature ^{1}H and ^{13}C NMR spectra revealed a

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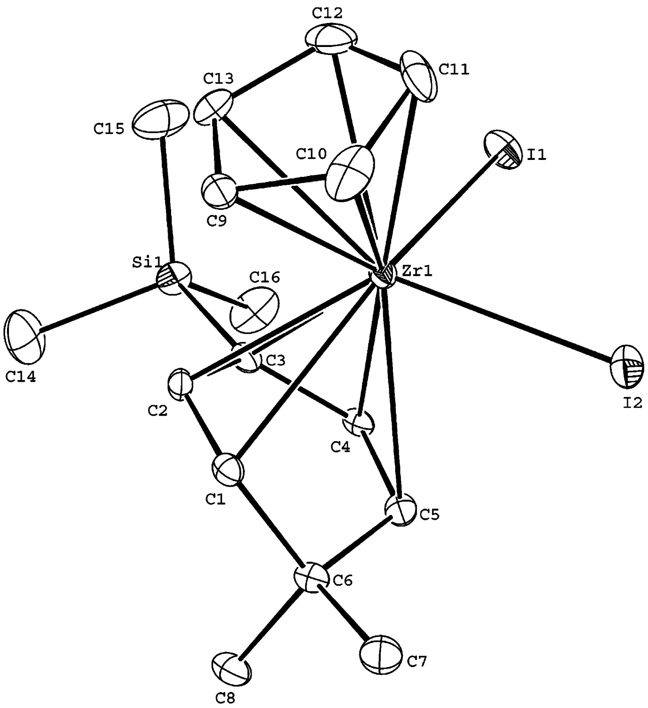


Figure 1. Structure of Cp(3-Me_3Si-6,6-dmch)ZrI_2.

symmetric pattern for the 3-Me_3Si-6,6-dmch ligand, such that one side of the ligand would be symmetric to the other on the NMR time scale (i.e., C1, C5; C2, C4).

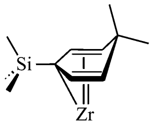
Structure. The structure of Cp(3-Me_3Si-6,6-dmch)ZrI_2 is presented in Figure 1, and pertinent geometric parameters are summarized in Table 1. Note that the approximate mirror plane of the 3-Me_3Si-6,6-dmch ligand is close to perpendicular to the approximate mirror plane of the $CpZrI_2$ portion of the molecule, rather than aligning the mirror planes for overall C_s symmetry of the molecule. The dihedral angle from the Si atom to the centroid of the pentadienyl carbon atoms to the Zr atom to the centroid of the Cp ring (Si–Pdl_c–Zr–Cp_c angle) is 77.8°. This reduces the symmetry of the 3-Me_3Si-6,6-dmch ligand such that one side is not equivalent to the other side in the solid state. The calculations indicate that this orientation also is a geometry minimum for the molecule in the gas phase. The calculated potential energy for rotation of the pentadienyl about the pentadienyl–Zr bond is shown in the Supporting Information. Two energy minima are found: one with the dihedral angle at 77.6° is essentially identical to the value from the crystal structure, and another with a dihedral angle near 170° is close to C_s symmetry. The calculated free energy barrier to rotation is on the order of 5–6 kcal/mol, and the free energies of the two minima are essentially identical (calculated the same within 0.1 kcal/mol at room temperature). The low energy for rotation of the 3-Me_3Si-6,6-dmch ligand in the molecule is consistent with the averaging of the symmetrically related positions of the pentadienyl ligand on the NMR time scale.

Table 1. Experimental Pertinent Bonding Parameters [calculated][a] for Cp(3-Me_3Si-6,6-dmch)ZrI_2

Bond Distances (Å)			
Zr–I1	2.8755(4) [2.86]	Zr–I2	2.8480(4) [2.83]
Zr–C1	2.609(4) [2.58]	Zr–C9	2.495(4) [2.52]
Zr–C2	2.503(3) [2.51]	Zr–C10	2.484(4) [2.53]
Zr–C3	2.496(4) [2.51]	Zr–C11	2.497(4) [2.51]
Zr–C4	2.562(4) [2.55]	Zr–C12	2.515(4) [2.54]
Zr–C5	2.759(4) [2.72]	Zr–C13	2.506(4) [2.53]
C1–C2	1.388(5) [1.40]	C3–C4	1.447(5) [1.44]
C2–C3	1.425(5) [1.42]	C4–C5	1.361(5) [1.38]
Bond Angles (deg)			
I1–Zr–I2	93.854(13) [96.5]	C2–C3–C4	113.6(3) [115.7]
C2–C1–C6	119.0(3) [118.8]	C3–C4–C5	122.8(3) [121.4]
C1–C2–C3	121.9(3) [120.1]	C4–C5–C6	120.7(3) [118.8]

[a] The structural values calculated from ADF.

The general atomic arrangement is very similar to that of Cp(6,6-dmch)ZrI_2,[11] with some relatively minor differences. The average Zr–C distance for the C_5H_5 ligand is essentially unchanged, 2.499(5) vs 2.502(8) Å, while for the electronically open dienyl ligands one observes a slight lengthening, 2.586 vs 2.572 Å, due to the silyl substituent. The lengthening arises almost entirely from the Zr–C1 and Zr–C3 bonds. As in other examples of higher valent metal pentadienyl complexes, the Zr–C3 distance is shortest, while the distances for the subsequent atoms get progressively longer. This should provide a good structural model for the facile reductions that typically occur, via loss of pentadienyl ligands, during the attempted preparations of higher valent complexes, and thus nicely explains the dramatic preference that pentadienyl ligands display for bonding to metals in low (≤+2) oxidation states. Consistent with this is the fact that while (Ti or Zr)–C bond lengths for pentadienyl ligands in the low-valent half-open metallocenes may be as much as 0.2 Å shorter than the accompanying distances for their C_5H_5 ligands,[38] one sees a dramatic reversal in this preference for higher valent species, in this case the Zr–C(pentadienyl) lengths being 0.087 Å longer. A significant contribution of resonance hybrid **4** is consistent with the structural trends.



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Furthermore, the generation of significant σ-bonding character between Zr and C3 should impart more sp^3 character to the bonds to C3, leading to a deviation of the silicon atom out of the dmch ligand plane by 11.8° compared to 2.0° for H3 in the dmch analogue, away from the metal atom. One final structural effect of the silyl substituent is that it brings about a reduction in the C2–C3–C4 bond angle, analogous to general observations for alkyl and aryl substituents, but opposite of observations for siloxy and possibly CF_3 substituents.

The calculated bond lengths and angles for the optimized geometry of the Cp(3-Me_3Si-6,6-dmch)ZrI_2 molecule are compared to the experimental values in Table 1. The calculated Zr–C bond lengths are close to the crystallographic values, and they follow trends similar to those observed in the crystal structure. Overall, the structure determined by X-ray crystallography appears to be a good representation of the structure of the molecule in the gas phase.

Ionization Energies and Electronic Structure. To demonstrate the electronic effects of silyl substitution on the pentadienyl ligand, the valence photoelectron spectrum of Cp(Si-6,6-dmch)ZrI_2 is compared to that of Cp(6,6-dmch)ZrI_2 in Figure 2.[11] The vertical ionization energies for the valence ionizations are given in Table 2. The ionization features of these two molecules are very similar, with the valence ionizations of Cp(3-Me_3Si-6,6-dmch)ZrI_2 shifted to lower ionization energy relative to those of the 6,6-dmch analogue by about 0.1 to 0.2 eV. On the basis of the previous band assignments of the Cp(6,6-dmch)ZrI_2 spectrum, the first ionization band at 7.42 eV

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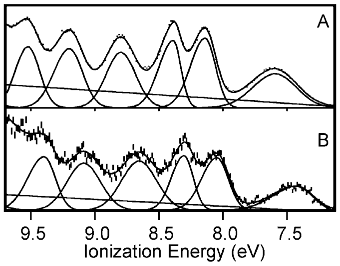

Figure 2. He I photoelectron spectra of (A) Cp(6,6-dmch)ZrI_2 and (B) Cp(3-Me_3Si-6,6-dmch)ZrI_2.

Table 2. Experimental and Calculated Vertical Ionization Energies (eV) of Cp(3-Me_3Si-6,6-dmch)ZrI_2 and Shifts to Lower Energies from Those of Cp(6,6-dmch)ZrI_2 (in brackets)

label[a]	exptl	DFT
Pdl π	7.42 [0.17]	7.57 [0.16]
I π	8.04 [0.10]	7.73 [0.14]
I π	8.30 [0.09]	8.02 [0.17]
I π	8.66 [0.14]	8.62 [0.26]
I π	9.09 [0.11]	8.88 [0.13]
Pdl π	9.41 [0.11]	9.21 [0.37]

[a] Pdl is the 3-Me_3Si-6,6-dmch pentadienyl.

in the spectrum of Cp(3-Me_3Si-6,6-dmch)ZrI_2 is predominantly the first π ionization of the 3-Me_3Si-6,6-dmch ligand with some mixing of iodine pπ character. The next four ionizations are primarily iodine pπ orbital based. The ionization at 9.41 eV in the present spectrum of Cp(3-Me_3Si-6,6-dmch)ZrI_2 is assigned to the second 3-Me_3Si-6,6-dmch π ionization, as was the similar ionization in the spectrum of Cp(6,6-dmch)ZrI_2. The Cp π and Zr−I σ bond ionizations appear above 9.5 eV.

The vertical ionization energies calculated using the ΔE(SCF) energy for the first ionization and the TDDFT method for the higher positive ion states are compared to the experimental ionization energies in Table 2. The vertical ionization energies were calculated for both the 77° and the 170° orientations of the pentadienyl because, according to the calculations, these geometries are similar in energy and both are likely significantly populated in the gas phase at the temperature of the photoelectron experiment. The orientation of the pentadienyl makes little difference to the calculated ionization energies, and only those obtained at the 77° orientation are listed in Table 2. The calculated ionization energies and Kohn−Sham orbital energies for both conformations are listed in the Supporting Information. The calculated characters of the orbitals are consistent with the assignments of the experimental ionizations. Orbital surface plots for the 10 highest occupied molecular orbitals and the lowest unoccupied molecular orbital of Cp(3-Me_3Si-6,6-dmch)ZrI_2 also are provided in the Supporting Information.

The calculated shift of the first ionization to lower ionization energy from Cp(6,6-dmch)ZrI_2 to Cp(3-Me_3Si-6,6-dmch)ZrI_2 is essentially the same as the experimental first ionization shift (0.16 vs 0.17 eV). The shifts of all the ionizations to lower energies might, at first thought, be interpreted simply in terms of the low electronegativity of the silyl group contributing electron charge density throughout the molecule, including the CpZrI_2 portion of the molecule. According to the calculations, this explanation is only partly correct. Voronoi[39−41] analysis of the charge density distribution in Cp(6,6-dmch)ZrI_2 compared to Cp(3-Me_3Si-6,6-dmch)ZrI_2 indicates that the carbon (C3) to which the silyl group is attached has the highest increase in negative charge density (−0.07 charge), as is expected. However, there is little change in total charge density in the vicinity of Zr, the iodine atoms, and the cyclopentadienyl ring nor on the other atoms of the open pentadienyl upon silyl substitution. If anything, the charge on the Zr atom becomes slightly more positive (+0.01 charge), completely counter to the simple expectation based on the electronegativity of the silyl group. A complete list of Mulliken and Voronoi atomic charges is available in the Supporting Information. The greater charge potential felt at the Zr atom in the Cp(3-Me_3Si-6,6-dmch)ZrI_2 molecule is directly due to the increased negative charge on C3 through two-center Coulomb repulsion interaction with the Zr center. Similarly, the shifts of iodine pπ ionizations to lower energy in the Cp(3-Me_3Si-6,6-dmch)ZrI_2 molecule are caused by the two-center charge repulsion between C3 and the iodine atoms.

This charge distribution has interesting consequences on the relative bonding of the pentadienyl ligands with the Zr center. The calculated donor/acceptor capabilities of these two ligand types, 3-Me_3Si-6,6-dmch and 6,6-dmch, and their Mayer bond orders with the Zr(IV) center are compared with those of the Cp ligand in Table 3. The 3-Me_3Si-6,6-dmch ligand is calculated to be a better donor from its occupied orbitals to the CpZrI_2 portion of the molecule than the 6,6-dmch ligand, as was expected, but only slightly. Interestingly, the 3-Me_3Si-6,6-dmch ligand is calculated also to be a better acceptor from the Zr center into its π^* orbitals than the 6,6-dmch ligand. Better acceptor ability for a more electron-rich ligand is not normally expected. This is made possible because the increased electron charge from the silyl substitution resides primarily on the C3 carbon atom, which becomes a slightly better donor, and the dienyl bonding, which involves the π^* orbitals primarily on the C1−C2 and C4−C5 carbon atoms as depicted in valence bond structure **4**, remain energetically available for accepting electron density from the metal center. The increased charge potential at the Zr atom due to repulsion of the electron density on the metal by the electron density on C3 destabilizes the Zr electrons and increases their donation to the dienyl π^* orbitals.

The result is that both donation and acceptance bonding modes tend to strengthen the bonding of the Me_3Si-6,6-dmch ligand relative to the 6,6-dmch ligand to the higher valent Zr center, and there is little net change in charge at the metal center. As an additional consequence of the small net change in charge at the metal center, there is little change in bonding to the cyclopentadienyl ring, as indicated by the similar calculated donor and acceptor properties of the Cp ring in the two molecules, similar calculated Mayer bond orders[42] for the Cp rings with the metal (both shown in Table 3), and similar observed bond distances in the crystal structures. Both pentadienyl ligands bond more strongly to the metal center than the cyclopentadienyl ligand, which is in agreement with the results obtained for the (6,6-dmch) ligand versus the Cp ligand in a previous study.[11]

Also shown in Table 3 are the donor/acceptor abilities and Mayer bond orders of 6,6-dmch and Cp to the Zr(II) center in Cp(6,6-dmch)Zr(PMe_3)$_2$. The difference in Mayer bond orders of the Cp and the pentadienyl ligand with the d^2 Zr(II) center is quite substantial compared to those with the d^0 Zr(IV) center, indicating a higher favorability of Zr−(dienyl) bonding compared to the Zr−Cp bonding. This underscores the importance

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Table 3. Calculated Total Donor and Acceptor Abilities for (Cp)$^-$ and Pentadienyl Ligands (Pdl)$^-$ and the Mayer Zr−L Bond Orders

	molecule					
	(3-Me_3Si-6,6-dmch)-CpZrI_2		(6,6-dmch)-CpZrI_2		(6,6-dmch)-CpZr(PMe_3)$_2$	
	(Cp)$^-$	(Pdl)$^-$	(Cp)$^-$	(Pdl)$^-$	(Cp)$^-$	(Pdl)$^-$
total donor ability	1.01	1.07	1.01	1.05	0.74	0.89
total acceptor ability	0.09	0.17	0.08	0.13	0.18	0.69
Mayer Zr−L bond order	1.48	1.55	1.49	1.53	1.26	2.04

of back-bonding from the metal to the pentadienyl ligand in accounting for the extra stability of low-valent metal−pentadienyl complexes.

Overall, the electronic features of the Cp(3-Me_3Si-6,6-dmch)-ZrI_2 molecule are very similar to those of Cp(6,6-dmch)ZrI_2, but there are also some significant perturbations. It was not anticipated that the change in charge distribution with silyl substitution would be largely confined to the C3 atom with little net change at the Zr atom and that the silylated pentadienyl ligand would become a better acceptor ligand. Because these effects are due to largely localized charge distributions, solvent effects are expected to play a role in refining their effect on the molecular behavior in solution. In this case the negative charge on the C3 carbon atom can be stabilized by solvent, and the influence of this charge on the electronic structure of the rest of molecule can be diminished. When calculations include acetonitrile solvation, the ionization energy shifts with silyl substitution are calculated to be negligible (see Supporting Information). Solvation effects likely play a role in the apparent contradictions in the literature concerning the electronic effects of silyl substitutions in other systems.[26,28] Additionally, the Mayer bond orders for Cp and pentadienyl ligands reveal opposite preferences, the Cp ligand indices being greater for higher oxidation states, with the reverse being true for pentadienyls. The combination of structural, dynamic, and bonding properties of these molecules and the electronic structure perturbations with substitution suggest that a rich chemistry remains to be explored.

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Supporting Information Available: Information on the crystal structure determination, photoelectron data collection and analysis, and computational methodology with additional tables and figures, and a CIF file giving crystal data for Cp(3-Me_3Si-6,6-dmch)ZrI_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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