

consistent with the voltammetric results, which are indicative of a fairly rapid isomerization process concurrent with reduction; spectroelectrochemical studies indicate that this does *not* involve chloride loss, since chloride loss is seen to be a relatively slow process which wouldn't be observed on the voltammetric time scale.

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## Synthesis, Characterization, and Reactivity of Triphenylsilyl, Triphenylgermyl, and Triphenylstannyl Derivatives of Zirconium and Hafnium

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The crystalline lithium silyl compound  $(\text{THF})_3\text{LiSiPh}_3$  (**1**) was isolated from the reaction of  $\text{Ph}_3\text{SiSiPh}_3$  with lithium in tetrahydrofuran. This compound and tetrahydrofuran solutions of  $\text{LiEPh}_3$  ( $\text{E} = \text{Ge}, \text{Sn}$ ) were used to prepare the complexes  $\text{CpCp}^*\text{Zr}(\text{EPh}_3)\text{Cl}$  (**2**,  $\text{E} = \text{Si}$ ; **3**,  $\text{E} = \text{Ge}$ ),  $\text{CpCp}^*\text{Hf}(\text{EPh}_3)\text{Cl}$  (**5**,  $\text{E} = \text{Si}$ ; **6**,  $\text{E} = \text{Ge}$ ; **7**,  $\text{E} = \text{Sn}$ ),  $\text{Cp}^*_2\text{Zr}(\text{EPh}_3)\text{Cl}$  (**8**,  $\text{E} = \text{Si}$ ; **9**,  $\text{E} = \text{Ge}$ ; **10**,  $\text{E} = \text{Sn}$ ), and  $\text{Cp}^*_2\text{Hf}(\text{SiPh}_3)\text{Cl}$  (**11**). This method did not provide the zirconium stannyl complex  $\text{CpCp}^*\text{Zr}(\text{SnPh}_3)\text{Cl}$  (**4**) but instead gave the phenyl derivative  $\text{CpCp}^*\text{Zr}(\text{Ph})\text{Cl}$  via phenyl transfer. Compound **4** may be obtained via reactions of  $\text{HSnPh}_3$  with **2**, **3**, or  $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ . Reactions of **8** and **11** with  $\text{MeMgBr}$  gave  $\text{Cp}^*_2\text{M}(\text{SiPh}_3)\text{Me}$  (**12**,  $\text{M} = \text{Zr}$ ; **13**,  $\text{M} = \text{Hf}$ ). Hydrogenolysis of **2**, **5**, **8**, and **11** provides routes to the corresponding hydrides  $\text{CpCp}^*\text{MHCl}$  or  $\text{Cp}^*_2\text{MHCl}$ . Likewise, the reactions of **12** and **13** with hydrogen give  $\text{Cp}^*_2\text{ZrH}_2$  and  $\text{Cp}^*_2\text{Hf}(\text{H})\text{Me}$ , respectively. The germyl and stannyl complexes were found to be significantly less reactive toward hydrogen. Reactions of **2**–**11** with  $\text{PhSiH}_3$  gave  $\sigma$ -bond metathesis products in some cases and no reaction in other cases, such that the observed reactivity trends are  $\text{CpCp}^*\text{M} > \text{Cp}^*_2\text{M}$ ;  $\text{Zr} > \text{Hf}$ ;  $\text{M-Si} > \text{M-Ge} > \text{M-Sn}$ . Carbonylation of **8** resulted in formation of  $\text{Cp}^*_2\text{Zr}(\eta^2\text{-COSiPh}_3)\text{Cl}$  (**14**), which reacts with  $\text{HCl}$  to give the thermally stable formylsilane  $\text{Ph}_3\text{SiCHO}$  (**15**) and with  $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}$  to afford the ketenimine  $\text{Cp}^*_2\text{Zr}[\text{OC}(\text{SiPh}_3)(\text{CN-}2,6\text{-Me}_2\text{C}_6\text{H}_3)]\text{Cl}$  (**16**). The silyl complexes **5**, **8**, and **11** react with  $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}$  to give  $\eta^2$ -iminosilaacyl insertion products, as does the germyl **3**. However, no reaction is observed between  $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}$  and stannyl complexes **7** or **10**. These investigations establish the reactivity trends  $\text{M-SiPh}_3 > \text{M-GePh}_3 > \text{M-SnPh}_3$  for  $\sigma$ -bond metathesis processes with hydrogen and phenylsilane and for insertion reactions with carbon monoxide and  $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}$ . It is suggested that, for these analogues  $d^0$  metal silyl, germyl, and stannyl complexes, the energetics of the reactions are influenced primarily by the new E-element bond strengths of the products rather than by the  $d^0$  M-E bond strengths of the starting materials.

### Introduction

Investigations of  $d^0$  metal silyl complexes have revealed a number of interesting reactivity patterns that were unprecedented in transition-metal silicon chemistry.<sup>1</sup> This rich reaction chemistry, which involves migratory insertions of unsaturated substrates into metal-silicon bonds<sup>2</sup>

and  $\sigma$ -bond metathesis processes which can result in new metal-mediated polymerizations,<sup>3</sup> may be attributed to relatively low  $d^0$  M-Si bond dissociation energies. In light of this, it seemed that analogous  $d^0$  germyl and stannyl complexes, which might possess even weaker M-Ge and M-Sn bonds, would be worth investigating. In addition, comparisons of physical and chemical properties for analogous series of silyl, germyl, and stannyl complexes may be of use in developing a better understanding of bonding interactions in these systems.

Here we report results concerning the synthesis, characterization, and reactivity of analogous  $-\text{SiPh}_3$ ,  $-\text{GePh}_3$ , and  $-\text{SnPh}_3$  complexes of zirconium and hafnium. These

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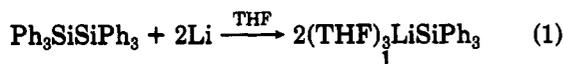
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initial investigations establish reactivity trends for compounds containing bonds between group 4 and group 14 elements. The related complexes Cp<sub>2</sub>M(EPh<sub>3</sub>)Cl (M = Zr, Hf; E = Si, Ge, Sn), synthesized nearly two decades ago by Lappert and Kingston,<sup>4</sup> were described as "difficult to purify" due to their instability in solution at room temperature. Furthermore, their low solubilities in organic solvents precluded thorough reactivity studies. The metallocene derivatives reported here contain at least one pentamethylcyclopentadienyl (Cp\*) group, which results in hydrocarbon-soluble derivatives that are amenable to study.

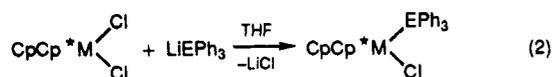
### Results and Discussion

**Isolation of (THF)<sub>3</sub>LiSiPh<sub>3</sub>.** Solutions of (tri-phenylsilyl)lithium have previously been obtained by the reaction of Ph<sub>3</sub>SiSiPh<sub>3</sub><sup>5a</sup> or ClSiPh<sub>3</sub><sup>5b</sup> with lithium in tetrahydrofuran. Although these solutions are fairly stable over extended periods of time at room temperature, a sluggish decomposition to unidentified products has been noted.<sup>5a</sup> We have isolated crystalline (THF)<sub>3</sub>LiSiPh<sub>3</sub> (1) in 82% yield (eq 1), which is stable for months at room

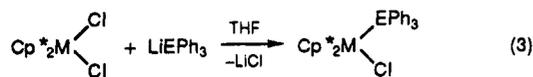


temperature under an inert atmosphere. A stoichiometry of (THF)<sub>2.6</sub>LiSiPh<sub>3</sub> was observed after 12 h under vacuum at room temperature (by <sup>1</sup>H NMR spectroscopy). Compound 1 is reasonably soluble in benzene and diethyl ether but decomposes in these solvents over extended periods of time.

**Zirconocene and Hafnocene Complexes with -SiPh<sub>3</sub>, -GePh<sub>3</sub>, and -SnPh<sub>3</sub> Ligands.** Complexes 2, 3, and 5-11 were prepared by reaction of the metallocene dichlorides with LiEPh<sub>3</sub> in 60-78% isolated yields (eqs 2 and 3). The silyl complexes 2, 5, 8, and 11 were syn-



M = Zr, E = Si (2), Ge (3); M = Hf, E = Si (5), Ge (6), Sn (7)



M = Zr, E = Si (8), Ge (9), Sn (10); M = Hf, E = Si (11)

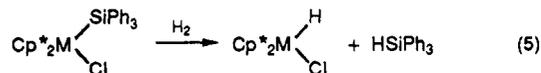
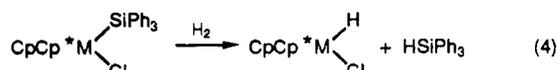
thesized using 1 as the silyl anion reagent. Preparations of the remaining germyl and stannyl complexes employed LiEPh<sub>3</sub> reagents that were generated in tetrahydrofuran via reaction of lithium and ClEPh<sub>3</sub>. This procedure failed to give CpCp\*Zr(SnPh<sub>3</sub>)Cl (4); however, this compound is cleanly produced by the σ-bond metathesis reactions of HSnPh<sub>3</sub> with 2, 3, or CpCp\*Zr[Si(SiMe<sub>3</sub>)<sub>3</sub>]Cl (see Experimental Section). In contrast to the reactions in eq 2, the reaction of CpCp\*ZrCl<sub>2</sub> with LiSnPh<sub>3</sub> in tetrahydrofuran proceeds via phenyl-group transfer to afford only CpCp\*Zr(Ph)Cl, isolated as a pale yellow solid from pentane. This phenyl derivative was prepared independently from CpCp\*ZrCl<sub>2</sub> and PhMgCl. Once isolated, the stannyl derivative 4 is stable at room temperature, but it decomposes thermally (slowly over days at 80 °C) or photolytically in benzene-d<sub>6</sub> solution to a number of products, including CpCp\*Zr(Ph)Cl (ca. 30%).

The above zirconium and hafnium silyl complexes are orange and yellow, respectively, and are soluble in pentane, benzene, and diethyl ether. They are reasonably stable at room temperature under an inert atmosphere but decompose slowly in solution with elimination of HEPPh<sub>3</sub>. Decompositions in solution are accelerated by ambient room light. Trends in stabilities toward photochemical decomposition are observed to be CpCp\*M(EPh<sub>3</sub>)Cl > Cp\*<sub>2</sub>M(EPh<sub>3</sub>)Cl, Hf > Zr, and Sn > Ge > Si.

Steric crowding in the bis(pentamethylcyclopentadienyl) complexes is evidenced by broadening of the phenyl proton resonances in the <sup>1</sup>H NMR spectra. At room temperature, all of the phenyl proton resonances for 8 are broad, whereas only the phenyl ortho proton resonances for 9 are broad, and all the phenyl proton resonances for 10 are sharp and well-resolved. For comparison, the corresponding resonances in the CpCp\*M(EPh<sub>3</sub>)Cl (M = Zr, Hf) series of compounds are sharp under comparable conditions. Variable-temperature <sup>1</sup>H NMR spectra (toluene-d<sub>6</sub>) for 8 reveal that decoalescence of the ortho protons occurs at -50 °C (ΔG<sup>‡</sup> = 10.1 ± 0.2 kcal mol<sup>-1</sup>), and at -80 °C two broad resonances are observed for these protons at δ 7.83 and 8.59. This dynamic behavior may be attributed to restricted rotation about E-C bonds and is consistent with expected steric demands of the EPh<sub>3</sub> groups (SiPh<sub>3</sub> > GePh<sub>3</sub> > SnPh<sub>3</sub>).

Reaction of MeMgBr with the silyl complexes 8 and 11 in diethyl ether produces light orange Cp\*<sub>2</sub>Zr(SiPh<sub>3</sub>)Me (12) and light yellow Cp\*<sub>2</sub>Hf(SiPh<sub>3</sub>)Me (13), respectively. These alkyl silyl complexes are somewhat thermally unstable and thus cannot be stored for long periods at room temperature without contamination by the HSiPh<sub>3</sub> decomposition product. However, freshly prepared samples of ≥99% purity can be isolated (see Experimental Section).

**Reactions with Hydrogen.** Hydrogenolysis of d<sup>0</sup> M-Si bonds is rapid compared to the corresponding reactions of d<sup>0</sup> M-C bonds.<sup>2e,i</sup> For example, whereas Cp<sub>2</sub>ZrMe<sub>2</sub> reacts slowly with 1 atm of H<sub>2</sub> over days,<sup>6</sup> Cp<sub>2</sub>Zr(SiMe<sub>3</sub>)Cl and Cp<sub>2</sub>Zr[Si(SiMe<sub>3</sub>)<sub>3</sub>]SiMe<sub>3</sub> react within a few minutes under comparable conditions.<sup>2i</sup> Thus, hydrogenolyses of d<sup>0</sup> transition-metal silyl derivatives provide convenient routes to the corresponding hydrides. The silyl complexes 2, 5, 8, and 11 react with hydrogen (100 psi) in benzene to afford the hydride species CpCp\*MHCl or Cp\*<sub>2</sub>MHCl (M = Zr, Hf) in 46-77% isolated yields (eqs 4 and 5). The



hydrides CpCp\*MHCl (M = Zr, Hf) have also been prepared by hydrogenolysis of CpCp\*M[Si(SiMe<sub>3</sub>)<sub>3</sub>]Cl (M = Zr, Hf).<sup>7</sup> Previous routes to Cp\*<sub>2</sub>ZrHCl are based on the redistribution of Cp\*<sub>2</sub>ZrH<sub>2</sub> and Cp\*<sub>2</sub>ZrCl<sub>2</sub><sup>8a</sup> and on the hydrogenolysis of Cp\*<sub>2</sub>Zr(CH<sub>2</sub><sup>t</sup>Bu)Cl.<sup>8b</sup> The hydride Cp\*<sub>2</sub>HfHCl was obtained previously by reaction of Cp\*<sub>2</sub>HfH<sub>2</sub> with CH<sub>3</sub>Cl.<sup>8c</sup> A preparative-scale reaction of Cp\*<sub>2</sub>Zr(SiPh<sub>3</sub>)Me with hydrogen (100 psi) cleanly gave the

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hydride  $\text{Cp}^*_2\text{ZrH}_2$ , which was first prepared by addition of  $\text{H}_2$  to  $(\text{Cp}^*_2\text{ZrN}_2)_2\text{N}_2$ .<sup>9a</sup> The less labile  $\text{Cp}^*_2\text{Hf}(\text{SiPh}_3)\text{Me}$  reacts with hydrogen to give the hydrido methyl complex  $\text{Cp}^*_2\text{Hf}(\text{Me})\text{H}$ , which was previously prepared from  $\text{Cp}^*_2\text{HfH}_2$  and  $\text{MeLi}$ .<sup>9b</sup>

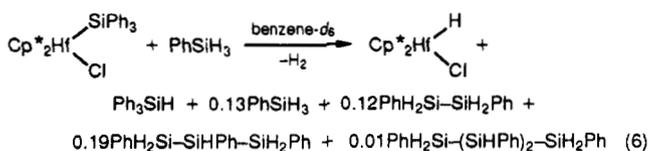
Observed reaction times (to complete reaction, as judged by  $^1\text{H}$  NMR spectroscopy) show that the hydrogenolysis rates decrease in the order  $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$  (5 min) >  $\text{CpCp}^*\text{Hf}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$  (10 min) >  $\text{Cp}^*_2\text{Zr}(\text{SiPh}_3)\text{Me}$  (20 min) >  $\text{Cp}^*_2\text{Zr}(\text{SiPh}_3)\text{Cl}$  (30 min)  $\approx$   $\text{Cp}^*_2\text{Hf}(\text{SiPh}_3)\text{Me}$  (30 min) >  $\text{Cp}^*_2\text{Hf}(\text{SiPh}_3)\text{Cl}$  (2 h)  $\approx$   $\text{CpCp}^*\text{Zr}(\text{SiPh}_3)\text{Cl}$  (2 h) >  $\text{CpCp}^*\text{Hf}(\text{SiPh}_3)\text{Cl}$  (4 h). Therefore reactivity trends for  $d^0$  zirconium and hafnium silyl complexes toward hydrogen may be expressed as the following:  $\text{Cp}^*_2\text{M}(\text{SiR}_3)\text{Cl}$  >  $\text{CpCp}^*\text{M}(\text{SiR}_3)\text{Cl}$ ;  $\text{M}-\text{Si}(\text{SiMe}_3)_3$  >  $\text{M}-\text{SiPh}_3$ ;  $\text{M}(\text{SiR}_3)\text{Me}$  >  $\text{M}(\text{SiR}_3)\text{Cl}$ . Lower hydrogenolysis rates for zirconocene alkyl halide derivatives, as compared to those for zirconocene dialkyl derivatives, have been noted previously by Schwartz and co-workers.<sup>10a</sup> These hydrogenolysis reactions presumably proceed through concerted four-center transition states, as has been proposed previously for hydrogenolysis of  $d^0$  M-C bonds.<sup>10</sup>

The germyl derivatives 3 and 9 also undergo hydrogenolysis reactions but more sluggishly than their triphenylsilyl analogues. Compound 3 reacts under  $\text{H}_2$  (100 psi) over 8 h to give a 65% conversion to  $\text{CpCp}^*\text{ZrHCl}$  and  $\text{HGePh}_3$ . After 5 h under hydrogen (100 psi), 9 gave a 70% conversion to  $\text{Cp}^*_2\text{ZrHCl}$ ,  $\text{HGePh}_3$ , and metal-containing decomposition products. Hydrogenolysis of  $\text{Cp}^*_2\text{Zr}(\text{SnPh}_3)\text{Cl}$  (10) under the same conditions led to a 31% conversion to  $\text{HSnPh}_3$  and metal-containing decomposition products, but resonances corresponding to  $\text{Cp}^*_2\text{ZrHCl}$  were not observed. The latter conversion therefore appears to be due simply to decomposition of 10, and we conclude that no hydrogenolysis occurred. Similarly, complex 7 underwent 67% conversion to  $\text{HSnPh}_3$  and decomposition products after 10 h under hydrogen (100 psi). The hydride  $\text{CpCp}^*\text{HfHCl}$  was not observed as a product. Thus, the trends in hydrogenolysis rates are  $\text{M}-\text{Si}$  >  $\text{M}-\text{Ge}$   $\gg$   $\text{M}-\text{Sn}$ , and  $\text{Zr}$  >  $\text{Hf}$ .

**Reactions with Silanes and Stannanes.** We have previously shown that  $\text{CpCp}^*\text{Hf}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$  reacts with 1 equiv of  $\text{PhSiH}_3$  under illumination by fluorescent room lighting to give quantitative conversion to the  $\sigma$ -bond metathesis products  $\text{CpCp}^*\text{Hf}(\text{SiH}_2\text{Ph})\text{Cl}$  and  $\text{HSi}(\text{SiMe}_3)_3$ .<sup>11</sup> This reaction also proceeds in the dark but is much slower (reaction time 2 days versus 1 h). Reactions of  $\text{CpCp}^*\text{Hf}(\text{SiPh}_3)\text{Cl}$  (5) and  $\text{CpCp}^*\text{Hf}(\text{GePh}_3)\text{Cl}$  (6) with 1 equiv of  $\text{PhSiH}_3$  over 5.5 h in benzene- $d_6$  solution under ambient fluorescent room lighting afford the  $\sigma$ -bond metathesis products  $\text{CpCp}^*\text{Hf}(\text{SiH}_2\text{Ph})\text{Cl}$  (80% conversion for 5 and 30% conversion for 6, as judged by  $^1\text{H}$  NMR), and  $\text{HSiPh}_3$  or  $\text{HGePh}_3$ , respectively. In contrast, no reaction was observed between  $\text{CpCp}^*\text{Hf}(\text{SnPh}_3)\text{Cl}$  (7) and 1 equiv of  $\text{PhSiH}_3$  over 1 day.

The reaction of  $\text{Cp}^*_2\text{Hf}(\text{SiPh}_3)\text{Cl}$  (11) with 1 equiv of  $\text{PhSiH}_3$  under ambient laboratory conditions consumes only 10% of the hafnium starting material after 5.5 h (in benzene- $d_6$ ) and takes 2 days to go to completion. After 2 days, the reaction mixture contained quantitative amounts of  $\text{Cp}^*_2\text{HfHCl}$  and  $\text{HSiPh}_3$ , some unreacted

$\text{PhSiH}_3$ , and silane dehydrocoupling products (by  $^1\text{H}$  NMR spectroscopy; eq 6). Although the dehydrocoupling re-



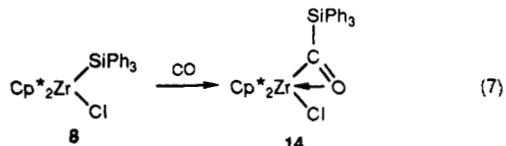
actions probably proceed via the intermediate  $\text{Cp}^*_2\text{Hf}(\text{SiH}_2\text{Ph})\text{Cl}$ , no resonances that could be assigned to this species were observed during the reaction. We suspect that this is because  $\text{Cp}^*_2\text{Hf}(\text{SiH}_2\text{Ph})\text{Cl}$  forms slowly relative to reactions with hydrosilanes that deplete it in the reaction mixture. Consistent with this is the fact that phenylsilane is not completely consumed in the reaction. To test for the possible involvement of migrations to the  $\text{Cp}^*$  ring of 11 in its reaction with  $\text{PhSiH}_3$ ,<sup>12</sup> we monitored the reaction of 11 with  $\text{PhSiD}_3$  by  $^1\text{H}$  and  $^2\text{H}$  NMR spectroscopy. No deuterium incorporation into the  $\text{Cp}^*$  methyl groups was observed, which is consistent with mechanisms involving 4-center transition states.<sup>11</sup> The faster reaction of  $\text{Cp}^*_2\text{Zr}(\text{SiPh}_3)\text{Cl}$  with phenylsilane gave results analogous to those in eq 6.

As noted above,  $\sigma$ -bond metathesis reactions of the silyls 2 and  $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ , or of the germyl 3, with  $\text{Ph}_3\text{SnH}$  give the stannyl complex  $\text{CpCp}^*\text{Zr}(\text{SnPh}_3)\text{Cl}$  (4). Also, the hafnium silyl  $\text{CpCp}^*\text{Hf}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$  reacts cleanly with  $\text{HSnPh}_3$  to give 7.

In summary, the following reactivity trends for  $\sigma$ -bond metathesis reactions of  $d^0$  M-E bonds with E-H  $\sigma$ -bonds have been observed:  $\text{CpCp}^*\text{M}$  >  $\text{Cp}^*_2\text{M}$ ;  $\text{Zr}$  >  $\text{Hf}$ ;  $\text{M}-\text{Si}$  >  $\text{M}-\text{Ge}$  >  $\text{M}-\text{Sn}$  (toward  $\text{PhSiH}_3$ );  $\text{Sn}-\text{H}$  >  $\text{Si}-\text{H}$ . It is of interest to note that the reactivity trend of  $\text{CpCp}^*\text{M}$  >  $\text{Cp}^*_2\text{M}$  for the reactions with  $\text{PhSiH}_3$  is opposite to that found for reactions with hydrogen. For example, 11 is more reactive than 5 toward hydrogen but less reactive than 5 toward  $\text{PhSiH}_3$ . This suggests that the M-E bonds in  $\text{Cp}^*_2\text{M}(\text{EPh}_3)\text{Cl}$  complexes are inherently weaker (and more reactive toward  $\sigma$ -bond metathesis) but protected to a greater degree by steric hindrance.

**Reactions with Carbon Monoxide.** We have previously observed CO-insertion reactions for a number of  $d^0$  M-Si bonds.<sup>2c,e,f,g,i</sup> A solution of  $\text{CpCp}^*\text{Zr}(\text{SiPh}_3)\text{Cl}$  (2) in benzene reacted with CO (100 psi) over 16 h, but a pure compound could not be isolated. No reactions of CO (100 psi) with  $\text{CpCp}^*\text{Zr}(\text{GePh}_3)\text{Cl}$  (3),  $\text{Cp}^*_2\text{Zr}(\text{GePh}_3)\text{Cl}$  (9), or  $\text{Cp}^*_2\text{Zr}(\text{SnPh}_3)\text{Cl}$  (10) were observed after 1 day. Thus, Zr-Si bonds appear to be much more reactive toward CO than comparable Zr-Ge or Zr-Sn bonds.

Orange benzene solutions of 8 react under a pressure of carbon monoxide (100 psi) over 15 h to give the isolable, dark purple silaacyl complex  $\text{Cp}^*_2\text{Zr}(\eta^2\text{-COSiPh}_3)\text{Cl}$  (14), which is soluble in most hydrocarbons and indefinitely stable under an inert atmosphere (eq 7). Spectroscopic



data are clearly consistent with the presence of an  $\eta^2$ -CO-SiPh<sub>3</sub> ligand. The carbonyl stretching frequency for this compound (1470  $\text{cm}^{-1}$ ), like that for  $\text{Cp}_2\text{Zr}(\eta^2\text{-COSiMe}_3)\text{Cl}$  (1489  $\text{cm}^{-1}$ ),<sup>2i</sup> is considerably lower than the  $\nu(\text{CO})$  stretching frequencies found in analogous zirconium acyls

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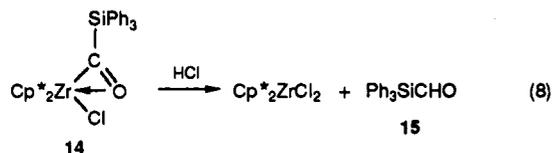
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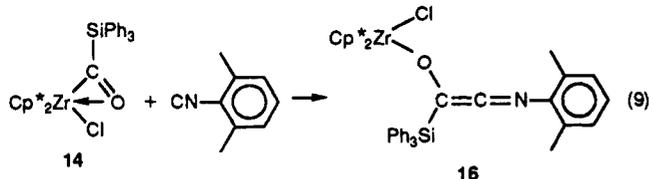
(1500–1550 cm<sup>-1</sup>).<sup>13</sup> The chemical shift for the carbonyl carbon in 14 ( $\delta$  403.8) is slightly higher than that for Cp<sub>2</sub>Zr( $\eta^2$ -COSiMe<sub>3</sub>)Cl ( $\delta$  391.6 ppm), and the <sup>29</sup>Si NMR spectrum of 14 (benzene-*d*<sub>6</sub>) contains a singlet at  $\delta$  -25.82. On the basis of the data presently available, we cannot distinguish between structures exhibiting lateral and central positioning of the silaacyl oxygen atom in the coordination sphere of 14.<sup>20</sup>

Since previous studies of  $\eta^2$ -silaacyl complexes have revealed unusual reactivity trends, we briefly examined the reaction chemistry of 14. Its chemical behavior appears to be quite comparable to that observed for other  $\eta^2$ -silaacyl complexes of zirconocene derivatives. Addition of anhydrous HCl gas (1 equiv) to a benzene-*d*<sub>6</sub> matrix (-196 °C) containing 14, followed by warming to room temperature, produced the formylsilane Ph<sub>3</sub>SiCHO (15, eq 8).



The <sup>1</sup>H NMR spectrum revealed that conversion to Cp\*<sub>2</sub>ZrCl<sub>2</sub> and 15 had occurred. The chemical shift for the aldehydic proton of 15 ( $\delta$  12.15) is comparable to that observed for (Me<sub>3</sub>Si)<sub>3</sub>SiCHO ( $\delta$  12.36),<sup>14</sup> which was obtained by an analogous reaction. The formylsilane Ph<sub>3</sub>SiCHO is distinctly more stable than (Me<sub>3</sub>Si)<sub>3</sub>SiCHO, since no decomposition was observed upon heating the compound to 100 °C for 4 h.

Compound 14 also reacts with the isocyanide 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC, to afford the orange ketenimine complex 16 (eq 9). Crystalline 16 is indefinitely stable under an inert

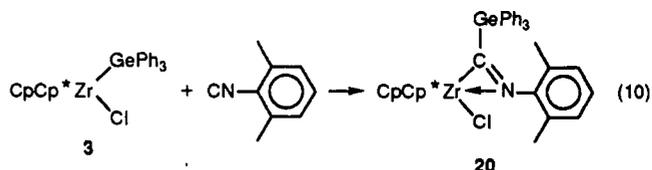


atmosphere. Assignment of the structure of 16 is based on comparisons with spectral data for the known ketenimine Cp<sub>2</sub>Zr[OC(SiMe<sub>3</sub>)(CN-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)]Cl, formed analogously from the silaacyl Cp<sub>2</sub>Zr( $\eta^2$ -COSiMe<sub>3</sub>)Cl and 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC.<sup>21</sup> The Cp\* ligands of 16 are equivalent in the <sup>1</sup>H NMR spectrum down to -80 °C. The <sup>13</sup>C NMR spectrum of 16 contains resonances due to C<sub>α</sub> and C<sub>β</sub> (C<sub>β</sub>=C<sub>α</sub>=N) at  $\delta$  199.3 and 100.4, respectively, which are similar to analogous resonances for Cp<sub>2</sub>Zr[OC(SiMe<sub>3</sub>)(CN-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)]Cl ( $\delta$  202.3 and 109.9). Also in accord with the assigned ketenimine structure, the infrared spectrum of 16 contains a  $\nu$ (CCN) absorption at 1945 cm<sup>-1</sup> (cf. 1977 cm<sup>-1</sup> for Cp<sub>2</sub>Zr[OC(SiMe<sub>3</sub>)(CN-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)]Cl and 2000 cm<sup>-1</sup> for Cp\*<sub>2</sub>Th[OC(CH<sub>2</sub>CMe<sub>3</sub>)(CN-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)]Cl<sup>15</sup>). The <sup>29</sup>Si NMR spectrum of 16 (benzene-*d*<sub>6</sub>) contains a singlet at  $\delta$  -68.28.

**Reactions with 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC.** We have previously shown that d<sup>0</sup> Zr–Si and Hf–Si bonds in a variety of compounds readily insert the isocyanide 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC to

give stable  $\eta^2$ -iminosilaacyl complexes.<sup>2c,e,i</sup> This reactivity is also observed for the triphenylsilyl derivatives described above. The complex CpCp\*Hf[ $\eta^2$ -C(N-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)-SiPh<sub>3</sub>]Cl (17), prepared via addition of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC to 5, was isolated and completely characterized. In addition, the complexes Cp\*<sub>2</sub>M[ $\eta^2$ -C(N-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)-SiPh<sub>3</sub>]Cl (18, M = Zr; 19, M = Hf) were observed to form in solution (by NMR spectroscopy).

Insertion of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC into the M–Ge bond of 3 also occurs readily to give the  $\eta^2$ -iminogermaacyl 20 (eq 10). The yellow, crystalline complex 20 has spectroscopic



characteristics that resemble those for related species such as Cp<sub>2</sub>Zr[ $\eta^2$ -C(N-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)SiMe<sub>3</sub>]Cl<sup>2i</sup> and Cp<sub>3</sub>U[ $\eta^2$ -C(N-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)GePh<sub>3</sub>].<sup>16</sup> The stannyl derivatives are much less reactive toward 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC. For example, CpCp\*Hf(SnPh<sub>3</sub>)Cl (7) and Cp\*<sub>2</sub>Zr(SnPh<sub>3</sub>)Cl (10) do not react with the isocyanide over 1 day (by <sup>1</sup>H NMR spectroscopy).

Addition of 1 equiv of anhydrous HCl to a benzene-*d*<sub>6</sub> matrix (-196 °C) of 20, followed by warming to room temperature, resulted in the clean formation of CpCp\*ZrCl<sub>2</sub> and a compound that we identify as the formimidoylgermane Ph<sub>3</sub>GeCH=N(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (21). The <sup>1</sup>H NMR chemical shift for the formimidoyl proton ( $\delta$  8.76) is comparable to the analogous shift observed for Me<sub>3</sub>SiCH=N(c-C<sub>6</sub>H<sub>11</sub>) ( $\delta$  8.33).<sup>17</sup> Upon heating of this solution of 21 to 100 °C for 8 h, no decomposition was observed.

**Reactions with HCl.** In their early work with group 4 metal silyl derivatives, Kingston and Lappert demonstrated that cleavage of the M–Si bond in Cp<sub>2</sub>Zr(SiPh<sub>3</sub>)Cl by HCl gave Cp<sub>2</sub>ZrCl<sub>2</sub> and the silane HSiPh<sub>3</sub> and that Cp<sub>2</sub>Hf(SiPh<sub>3</sub>)Cl reacted with HBr to give Cp<sub>2</sub>Hf(Cl)Br and HSiPh<sub>3</sub>.<sup>4</sup> Likewise, 8 reacts cleanly with anhydrous HCl (2 equiv,  $\leq$ 30 min) in benzene-*d*<sub>6</sub> to afford Cp\*<sub>2</sub>ZrCl<sub>2</sub> and HSiPh<sub>3</sub>. The corresponding reaction of 9 gave Cp\*<sub>2</sub>ZrCl<sub>2</sub> and HGePh<sub>3</sub> within 1 h. In contrast, the reaction of 1 equiv of 10 with HCl slowly produced Cp\*<sub>2</sub>ZrCl<sub>2</sub>, but HSnPh<sub>3</sub> was not observed as a product. The significant quantity of benzene that is produced by this reaction is apparently due to cleavage of Sn–C(Ph) bonds. Note that treatment of Cp<sub>2</sub>Nb(CO)SnPh<sub>3</sub> in tetrahydrofuran with ethereal HCl resulted in cleavage of the Sn–Ph bonds to produce Cp<sub>2</sub>Nb(CO)SnCl<sub>3</sub>.<sup>18</sup>

**Other Attempted Reactions.** The complexes CpCp\*Zr(EPh<sub>3</sub>)Cl (2, E = Si; 3, E = Ge) and Cp\*<sub>2</sub>Zr(EPh<sub>3</sub>)Cl (8, E = Si; 9, E = Ge; 10, E = Sn) are unreactive toward acetylene (excess, benzene-*d*<sub>6</sub>, 1 day), ethylene (100 psi, benzene, 1 day), phenylacetylene (1 equiv, benzene-*d*<sub>6</sub>, 1 day), carbon disulfide (excess, benzene-*d*<sub>6</sub>, 1 day), and phenyl isocyanate (1 equiv, benzene-*d*<sub>6</sub>, 1 day).

**Comments on Reactivity Trends for d<sup>0</sup> M–E (E = Si, Ge, Sn) Bonds.** The above investigations demonstrate a reactivity trend, M–SiPh<sub>3</sub> > M–GePh<sub>3</sub> >> M–SnPh<sub>3</sub>, for  $\sigma$ -bond metathesis processes with hydrogen and phenyl-

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silane and for insertion reactions with carbon monoxide and 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC. Considering only the influence of ground-state energies for the starting materials, this may seem surprising since established trends in bond energies for group 14 compounds suggest that M-E bond energies should decrease as the atomic number of the group 14 element increases (M-Si > M-Ge > M-Sn). For comparison, estimated Me<sub>3</sub>E-H bond energies (in kcal mol<sup>-1</sup>) decrease in the order Me<sub>3</sub>Si-H (90) > Me<sub>3</sub>Ge-H (82) > Me<sub>3</sub>Sn-H (74).<sup>19</sup>

Thermochemical data for series of transition-metal silyl, germyl, and stannyl complexes are quite limited. On the basis of appearance potential measurements for Cp-(CO)<sub>2</sub>FeEMe<sub>3</sub> (E = Si, Sn),<sup>20</sup> Cp(CO)<sub>3</sub>MEMe<sub>3</sub> (M = Cr, Mo, W; E = Ge, Sn),<sup>21</sup> and (CO)<sub>5</sub>ReEMe<sub>3</sub> (E = Si, Ge, Sn),<sup>22</sup> bond strengths appear to follow the order M-Sn > M-Ge > M-Si. For these low-valent carbonyl derivatives, bond dissociation energies may be significantly influenced by π-interactions between the transition metal and the group 14 atom. However, in d<sup>0</sup> metal silyl, germyl, and stannyl derivatives, such π-bonding cannot exist.

It appears that steric interactions can greatly influence d<sup>0</sup> M-Si distances. Evidence for this is seen, for example, by comparing the Hf-Si distances in CpCp\*Hf[Si(SiMe<sub>3</sub>)<sub>3</sub>]Cl (2.884 (4) Å) and CpCp\*Hf(SiH<sub>2</sub>Ph)Cl (2.729 (3) Å).<sup>7</sup> The influence of ligand-ligand repulsions (stretching or weakening of the M-EPh<sub>3</sub> bonds) should be greater for the -SiPh<sub>3</sub> ligand, which is bulkier due to the shorter bond distances involving silicon. The result is that the least sterically demanding stannyl group should encounter less steric hindrance in its approach to the metal center, resulting in a stronger M-E interaction. This effect is observed by comparing Cp\*Cl<sub>2</sub>HfSi(SiMe<sub>3</sub>)<sub>3</sub>, which has a Hf-Si distance of 2.748 (4) Å, and Cp\*Cl<sub>2</sub>HfGe(SiMe<sub>3</sub>)<sub>3</sub>, with a Hf-Ge distance of 2.740 (1) Å. The surprising similarity in these bond lengths has been attributed to steric interactions between the Cp\* ligand and SiMe<sub>3</sub> groups of the E(SiMe<sub>3</sub>)<sub>3</sub> ligand, which are most severe for E = Si and operate to elongate the Hf-Si bond more.<sup>23</sup> Steric interactions in the CpCp\*M(EPh<sub>3</sub>)Cl and Cp\*<sub>2</sub>M(EPh<sub>3</sub>)Cl series of compounds should be even more severe, and some degree of crowding is clearly evident from the restricted rotations observed for the Cp\*<sub>2</sub>Zr(EPh<sub>3</sub>)Cl complexes.

It is difficult to predict the relative ordering of bond strengths for silyl, germyl, and stannyl complexes of d<sup>0</sup> metals. However, it seems quite possible that changes in d<sup>0</sup> M-E bond strengths as E varies periodically from Si to Sn do not parallel the corresponding changes observed for E-H or E-C bond strengths. Support for this comes from recent thermochemical measurements by Marks et al. on Cp<sub>3</sub>U-EPh<sub>3</sub>, which show that Cp<sub>3</sub>U-EPh<sub>3</sub> bond strengths decrease only slightly along the series E = Si > Ge > Sn.<sup>24</sup> We suggest that the reactivity patterns observed for complexes 2-11 can be rationalized in terms of differences in product stabilities. The energy required to break the M-Si bonds is supplied by formation of relatively strong Si-H or Si-C bonds, but this is true to a lesser degree for the germyl complexes. For the stannyl complexes, breaking a M-Sn bond is not compensated for by

formation of the relatively weak Sn-H or Sn-C bonds that would form.

## Experimental Section

All manipulations were performed under an atmosphere of nitrogen or argon using Schlenk techniques and/or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. Glassware was flame-dried or oven-dried before use. Elemental analyses were performed by Mikroanalytisches Labor Pascher or Schwarzkopf microanalytical laboratories. Infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrometer. NMR spectra were obtained with a GE QE-300 instrument at 300 MHz (<sup>1</sup>H), 75.5 MHz (<sup>13</sup>C), 59.6 MHz (<sup>29</sup>Si), and 46.1 MHz (<sup>2</sup>H). The NMR spectra were recorded at 22 °C, unless stated otherwise. An INEPT sequence was employed to enhance signals in the <sup>29</sup>Si spectra.<sup>25</sup> The compounds CpCp\*ZrCl<sub>2</sub>,<sup>26</sup> CpCp\*HfCl<sub>2</sub>,<sup>27</sup> Cp\*<sub>2</sub>ZrCl<sub>2</sub>,<sup>28</sup> Cp\*<sub>2</sub>HfCl<sub>2</sub>,<sup>28</sup> LiGePh<sub>3</sub>,<sup>29</sup> LiSnPh<sub>3</sub>,<sup>30</sup> and (THF)<sub>3</sub>LiSi(SiMe<sub>3</sub>)<sub>3</sub><sup>31</sup> were prepared by literature methods. Reactions involving elevated pressures of CO or H<sub>2</sub> were conducted in a thick-walled glass pressure bottle, connected via an O-ring seal to a pressure release valve, a pressure gauge, and metal valves used to admit gases and reaction solutions.

(THF)<sub>3</sub>LiSiPh<sub>3</sub> (1). A 500-mL round-bottom flask was charged with hexaphenyldisilane (5.00 g, 9.64 mmol), lithium wire (0.54 g, 77 mmol; cut into ca. 5-mm pieces), and tetrahydrofuran (100 mL) under an argon atmosphere. The mixture was allowed to stir at room temperature for 24 h and was then filtered. The solution was concentrated to 20 mL, pentane (8 mL) was added to the solution, and the solution was cooled to -40 °C to give colorless to yellow crystals (mp 100-102 °C) in 82% yield (7.62 g). Although this compound gave C and H analyses that were variable and somewhat low, spectroscopic data show that it is pure and correctly formulated. The compound can be exhaustively dried to a stoichiometry of (THF)<sub>2.6</sub>LiSiPh<sub>3</sub> after 12 h of pumping at room temperature. Anal. Calcd for C<sub>30</sub>H<sub>36</sub>LiO<sub>3</sub>Si: C, 74.7; H, 8.14. Found: C, 71.7; H, 7.72. IR (Nujol, CsI, cm<sup>-1</sup>): 3040 m, 1573 w, 1420 m, 1291 w, 1250 w, 1177 w, 1108 w, 1080 m, 1043 s, 910 m sh, 890 m, 734 s, 700 s, 675 w, 515 w, 480 w, 460 w, 405 w, 345 m. <sup>1</sup>H NMR (benzene-d<sub>6</sub>): δ 1.19 (br, 12 H, THF), 3.35 (br, 12 H, THF), 7.06 (t, J = 7.2 Hz, 3 H, *p*-H, C<sub>6</sub>H<sub>5</sub>), 7.20 (t, J = 7.2 Hz, 6 H, *m*-H, C<sub>6</sub>H<sub>5</sub>), 7.75 (d, J = 7.2 Hz, 6 H, *o*-H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-d<sub>6</sub>): δ 25.38, 68.43 (THF), 124.86, 127.07, 136.88, 155.32 (C<sub>6</sub>H<sub>5</sub>). <sup>29</sup>Si NMR (benzene-d<sub>6</sub>): δ -46.83.

CpCp\*Zr(SiPh<sub>3</sub>)Cl (2). A solution of CpCp\*ZrCl<sub>2</sub> (0.50 g, 1.38 mmol) and 1 (0.67 g, 1.39 mmol) in tetrahydrofuran (20 mL) was stirred at ambient temperature. After 5 h the solvent was removed by vacuum transfer. The red-brown residue was extracted with pentane (50 mL) and filtered. The solution was concentrated to 15 mL and cooled to -10 °C, resulting in precipitation of an orange solid that was isolated by filtration and dried in vacuo to yield 0.485 g (60%) of 2 (mp 168-170 °C). Anal. Calcd for C<sub>33</sub>H<sub>36</sub>ClSiZr: C, 67.6; H, 6.02. Found: C, 67.5; H, 6.02. IR (Nujol, CsI, cm<sup>-1</sup>): 3040 m, 1581 w, 1426 s, 1305 w, 1260 w, 1188 w, 1155 w, 1110 m, 1090 m, 1065 w sh, 1015 m, 1000 w, 944 m, 810 s, 732 m, 700 s, 500 s, 483 m, 443 w, 400 w, 358 m, 340 w sh. <sup>1</sup>H NMR (benzene-d<sub>6</sub>): δ 1.67 (s, 15 H, C<sub>6</sub>Me<sub>5</sub>), 5.76 (s, 5 H, C<sub>6</sub>H<sub>5</sub>), 7.20 (m, 9 H, *m,p*-H, C<sub>6</sub>H<sub>5</sub>), 7.78 (d, J = 6.6 Hz, 6 H, *o*-H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-d<sub>6</sub>): δ 11.84 (C<sub>5</sub>Me<sub>5</sub>), 112.82 (C<sub>6</sub>H<sub>5</sub>), 121.29 (C<sub>5</sub>Me<sub>5</sub>), 126.64, 127.28, 136.79, 143.36 (C<sub>6</sub>H<sub>5</sub>). <sup>29</sup>Si NMR (benzene-d<sub>6</sub>): δ 42.42.

CpCp\*Zr(GePh<sub>3</sub>)Cl (3). A solution of LiGePh<sub>3</sub> (from ClGePh<sub>3</sub>, 0.492 g, 1.45 mmol, and lithium, 0.040 g, 5.76 mmol) in tetrahydrofuran (25 mL) was slowly added to a stirred sus-

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pension of CpCp\*ZrCl<sub>2</sub> (0.50 g, 1.38 mmol) in tetrahydrofuran (5 mL). After 5 h the solvent was removed in vacuo. The red-brown residue was extracted with pentane (50 mL), and the resulting pentane solution was concentrated to 15 mL and cooled to -10 °C, resulting in precipitation of an orange solid that was isolated by filtration and dried in vacuo to yield 0.556 g (64%) of **3** (mp 198–200 °C). Anal. Calcd for C<sub>33</sub>H<sub>35</sub>ClGeZr: C, 62.8; H, 5.59. Found: C, 61.5; H, 5.88. IR (Nujol, CsI, cm<sup>-1</sup>): 3040 m, 1565 w, 1425 m, 1258 w, 1152 w, 1070 m, 1020 m, 998 w, 815 s, 730 m, 700 s, 660 w sh, 470 m, 365 w. <sup>1</sup>H NMR (benzene-d<sub>6</sub>): δ 1.68 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 5.80 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 7.18 (t, *J* = 7.2 Hz, 3 H, *p*-H, C<sub>6</sub>H<sub>5</sub>), 7.28 (t, *J* = 7.2 Hz, 6 H, *m*-H, C<sub>6</sub>H<sub>5</sub>), 7.80 (d, *J* = 7.2 Hz, 6 H, *o*-H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-d<sub>6</sub>): δ 12.69 (C<sub>5</sub>Me<sub>5</sub>), 113.80 (C<sub>5</sub>H<sub>5</sub>), 122.63 (C<sub>5</sub>Me<sub>5</sub>), 127.25, 128.00, 136.90, 148.63 (C<sub>6</sub>H<sub>5</sub>).

**Reaction of CpCp\*ZrCl<sub>2</sub> with LiSnPh<sub>3</sub>.** A solution of LiSnPh<sub>3</sub> (from ClSnPh<sub>3</sub>, 0.559 g, 1.45 mmol, and lithium, 0.040 g, 5.76 mmol) in tetrahydrofuran (25 mL) was slowly added to a stirred suspension of CpCp\*ZrCl<sub>2</sub> (0.50 g, 1.38 mmol) in tetrahydrofuran (5 mL). After 12 h the solvent was removed in vacuo. Extraction with pentane and cooling to -35 °C provided pale orange, crystalline CpCp\*Zr(Ph)Cl in 80% yield. This light-sensitive complex was independently prepared by the reaction of CpCp\*ZrCl<sub>2</sub> with PhMgCl in tetrahydrofuran. <sup>1</sup>H NMR (benzene-d<sub>6</sub>): δ 1.62 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 5.86 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 7.07 (t, *J* = 7 Hz, 1 H, *p*-H, C<sub>6</sub>H<sub>5</sub>), 7.18 (t, *J* = 7 Hz, 2 H, *m*-H, C<sub>6</sub>H<sub>5</sub>), 7.30 (br, 2 H, *o*-H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-d<sub>6</sub>): δ 12.09 (C<sub>5</sub>Me<sub>5</sub>), 114.39 (C<sub>5</sub>H<sub>5</sub>), 121.96 (C<sub>5</sub>Me<sub>5</sub>), 125.09, 127.30, 137.49, 190.32 (C<sub>6</sub>H<sub>5</sub>).

**CpCp\*Zr(SnPh<sub>3</sub>)Cl (4).** The reaction of **2** (0.020 g, 0.034 mmol; over 13 h in benzene-d<sub>6</sub>) or **3** (0.021 g, 0.033 mmol; over 18 h in benzene-d<sub>6</sub>) with HSnPh<sub>3</sub> (21 mg, 0.06 mmol) gave **4**, along with minor impurities.

CpCp\*Zr[Si(SiMe<sub>3</sub>)<sub>3</sub>]Cl (1.0 g, 1.7 mmol), HSnPh<sub>3</sub> (0.84 g, 3.5 mmol), and toluene (20 mL) were stirred for 12 h. Volatiles were removed by vacuum transfer, and the resulting oily orange residue was washed with pentane (4 × 50 mL) and extracted into diethyl ether (2 × 100 mL). Concentration and cooling of the combined extracts gave thermochroic crystals of **4** (yellow at -40 °C; orange at room temperature) in 60% yield (mp 170–172 °C). Anal. Calcd for C<sub>33</sub>H<sub>35</sub>ClSiZr: C, 58.5; H, 5.22. Found: C, 58.5; H, 5.02. IR (Nujol, CsI, cm<sup>-1</sup>): 3040 w, 1575 w, 1425 m, 1300 w, 1255 w, 1065 m, 1020 m, 990 w, 810 s, 720 s, 700 s, 500 m, 480 m sh, 370 m, 340 w. <sup>1</sup>H NMR (benzene-d<sub>6</sub>): δ 1.71 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 5.87 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 7.20 (t, 3 H, *J* = 7.2 Hz, *p*-H, C<sub>6</sub>H<sub>5</sub>), 7.30 (t, 6 H, *J* = 7.2 Hz, *m*-H, C<sub>6</sub>H<sub>5</sub>), 7.88 (d, 6 H, *J* = 7.2 Hz, *o*-H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-d<sub>6</sub>): δ 12.89 (C<sub>5</sub>Me<sub>5</sub>), 112.75 (C<sub>5</sub>H<sub>5</sub>), 122.39 (C<sub>5</sub>Me<sub>5</sub>), 127.23, 128.67, 138.22, 150.37 (C<sub>6</sub>H<sub>5</sub>).

**CpCp\*Zr(Ph)Cl.** To CpCp\*ZrCl<sub>2</sub> (0.752 g, 2.07 mmol) in tetrahydrofuran (20 mL) was added a tetrahydrofuran solution of PhMgCl (1.04 mL, 2.08 mmol) dropwise over 5 min. The solution was stirred for 12 h, the volatiles were removed by vacuum transfer, and the resulting yellow residue was extracted into pentane (4 × 50 mL). Concentration of this solution to ca. 100 mL and cooling to -10 °C afforded the compound as yellow crystals (mp 170–172 °C) in 54% yield (0.450 g). The yield was not optimized. Anal. Calcd for C<sub>21</sub>H<sub>25</sub>ClZr: C, 62.4; H, 6.24. Found: C, 60.7; H, 5.77. IR (Nujol, CsI, cm<sup>-1</sup>): 3040 w, 1580 w, 1410 w, 1050 m, 1020 m, 1010 m, 990 w, 820 m sh, 810 s, 720 s, 700 s, 450 m, 400 w, 360 m, 330 m, 290 m. <sup>1</sup>H NMR (benzene-d<sub>6</sub>): δ 1.62 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 5.86 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 7.06 (m, 1 H, *p*-H, C<sub>6</sub>H<sub>5</sub>), 7.18 (m, 2 H, *m*-H, C<sub>6</sub>H<sub>5</sub>), 7.29 (br m, 2 H, *o*-H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-d<sub>6</sub>): δ 12.09 (C<sub>5</sub>Me<sub>5</sub>), 114.39 (C<sub>5</sub>H<sub>5</sub>), 121.96 (C<sub>5</sub>Me<sub>5</sub>), 125.09, 127.30, 137.49, 190.32 (C<sub>6</sub>H<sub>5</sub>).

**CpCp\*Hf(SiPh<sub>3</sub>)Cl (5).** A solution of CpCp\*HfCl<sub>2</sub> (0.50 g, 1.11 mmol) and **1** (0.555 g, 1.15 mmol) in tetrahydrofuran (20 mL) was stirred at ambient temperature. After 10 h the solvent was removed by vacuum transfer. The yellow-brown residue was extracted with pentane (50 mL). The resulting pentane solution was concentrated to 15 mL and cooled to -10 °C, resulting in precipitation of a yellow solid that was isolated by filtration and dried in vacuo to yield 0.523 g (70%) of **5** (mp 203–205 °C). Anal. Calcd for C<sub>33</sub>H<sub>35</sub>ClSiHf: C, 58.8; H, 5.24. Found: C, 59.0; H, 5.51. IR (Nujol, CsI, cm<sup>-1</sup>): 3040 m, 1580 w, 1425 s, 1305 w, 1260 w, 1200 w, 1185 w, 1090 m, 1065 w sh, 1023 m, 1011 m, 995 w, 970 w, 820 s, 745 m sh, 735 m, 708 s, 683 m, 670 w, 503 s, 485 m, 445

m, 400 w, 334 w sh, 312 m. <sup>1</sup>H NMR (benzene-d<sub>6</sub>): δ 1.73 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 5.71 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 7.17 (t, *J* = 7.2 Hz, 3 H, *p*-H, C<sub>6</sub>H<sub>5</sub>), 7.78 (t, *J* = 7.2 Hz, 6 H, *m*-H, C<sub>6</sub>H<sub>5</sub>), 7.79 (d, 6 H, *J* = 7.2 Hz, *o*-H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-d<sub>6</sub>): δ 12.51 (C<sub>5</sub>Me<sub>5</sub>), 112.62 (C<sub>5</sub>H<sub>5</sub>), 120.60 (C<sub>5</sub>Me<sub>5</sub>), 127.47, 127.60, 137.83, 145.51 (C<sub>6</sub>H<sub>5</sub>). <sup>29</sup>Si NMR (benzene-d<sub>6</sub>): δ 39.96.

**CpCp\*Hf(GePh<sub>3</sub>)Cl (6).** A solution of LiGePh<sub>3</sub> (from ClGePh<sub>3</sub>, 0.390 g, 1.15 mmol, and lithium, 0.032 g, 4.60 mmol) in tetrahydrofuran (25 mL) was slowly added to a stirred suspension of CpCp\*HfCl<sub>2</sub> (0.50 g, 1.11 mmol) in tetrahydrofuran (5 mL). After 5 h the solvent was removed in vacuo. The dark yellow residue was extracted with pentane (50 mL). The resulting pentane solution was concentrated to 15 mL and cooled to -10 °C, resulting in precipitation of a yellow solid that was isolated by filtration and dried in vacuo to yield 0.544 g (68%) of **6** (mp 202–204 °C). Anal. Calcd for C<sub>33</sub>H<sub>35</sub>ClGeHf: C, 55.2; H, 4.91. Found: C, 55.6; H, 5.61. IR (Nujol, CsI, cm<sup>-1</sup>): 3040 m, 1564 w, 1423 m, 1300 w, 1258 w, 1153 w, 1071 m, 1020 m, 998 w, 816 s, 729 m, 700 s, 660 w sh, 471 m, 365 w. <sup>1</sup>H NMR (benzene-d<sub>6</sub>): δ 1.76 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 5.74 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 7.17 (t, *J* = 7.2 Hz, 3 H, *p*-H, C<sub>6</sub>H<sub>5</sub>), 7.27 (t, *J* = 7.2 Hz, 6 H, *m*-H, C<sub>6</sub>H<sub>5</sub>), 7.78 (d, *J* = 7.2 Hz, 6 H, *o*-H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-d<sub>6</sub>): δ 12.57 (C<sub>5</sub>Me<sub>5</sub>), 112.76 (C<sub>5</sub>H<sub>5</sub>), 121.05 (C<sub>5</sub>Me<sub>5</sub>), 127.26, 128.00, 137.09, 149.87 (C<sub>6</sub>H<sub>5</sub>).

**CpCp\*Hf(SnPh<sub>3</sub>)Cl (7).** A solution of LiSnPh<sub>3</sub> (from ClSnPh<sub>3</sub>, 0.443 g, 1.15 mmol, and lithium, 0.032 g, 4.60 mmol) in tetrahydrofuran (25 mL) was slowly added to a stirred suspension of CpCp\*HfCl<sub>2</sub> (0.50 g, 1.11 mmol) in tetrahydrofuran (5 mL). After 5 h the solvent was removed in vacuo. The dark yellow residue was extracted with pentane (50 mL). The resulting pentane solution was concentrated to 15 mL and cooled to -10 °C, resulting in precipitation of a yellow solid that was isolated by filtration and dried in vacuo to yield 0.594 g (70%) of **7** (mp 166–169 °C). Anal. Calcd for C<sub>33</sub>H<sub>35</sub>ClSnHf: C, 51.9; H, 4.62. Found: C, 53.3; H, 4.73. IR (Nujol, CsI, cm<sup>-1</sup>): 3040 m, 1570 w, 1425 s, 1300 w, 1255 w, 1185 w, 1155 w, 1065 m, 1020 m, 995 m, 822 s, 728 s, 700 s, 646 w, 454 m, 430 m, 340 w, 310 w. <sup>1</sup>H NMR (benzene-d<sub>6</sub>): δ 1.79 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 5.81 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 7.19 (t, *J* = 7.2 Hz, 3 H, *p*-H, C<sub>6</sub>H<sub>5</sub>), 7.30 (t, *J* = 7.2 Hz, 6 H, *m*-H, C<sub>6</sub>H<sub>5</sub>), 7.88 (d, *J* = 7.2 Hz, 6 H, *o*-H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-d<sub>6</sub>): δ 12.74 (C<sub>5</sub>Me<sub>5</sub>), 111.71 (C<sub>5</sub>H<sub>5</sub>), 120.70 (C<sub>5</sub>Me<sub>5</sub>), 127.38, 128.47, 138.32, 151.61 (C<sub>6</sub>H<sub>5</sub>). Compound **7** is also formed by reaction of CpCp\*Hf[Si(SiMe<sub>3</sub>)<sub>3</sub>]Cl (0.02 g, 0.03 mmol) with HSnPh<sub>3</sub> (0.01 g, 0.03 mmol) (benzene-d<sub>6</sub>, 3 h).

**Cp\*<sub>2</sub>Zr(SiPh<sub>3</sub>)Cl (8).** A solution of Cp\*<sub>2</sub>ZrCl<sub>2</sub> (0.50 g, 1.16 mmol) and **1** (0.56 g, 1.16 mmol) in tetrahydrofuran (20 mL) was stirred at ambient temperature. After 5 h the solvent was removed by vacuum transfer. The red-brown residue was extracted with pentane (50 mL), and the pentane solution was concentrated to 15 mL and cooled (-10 °C) to give orange crystals (mp 177–179 °C, dec) in 71% yield (0.54 g). Anal. Calcd for C<sub>38</sub>H<sub>45</sub>ClSiZr: C, 69.5; H, 6.91. Found: C, 69.2; H, 6.98. IR (Nujol, CsI, cm<sup>-1</sup>): 3057 m, 3025 m, 1580 w, 1425 s, 1303 w, 1255 w, 1190 w, 1110 w sh, 1090 m, 1065 w sh, 1025 m, 1000 w, 950 w, 803 w, 742 m sh, 735 m, 710 s, 700 s, 675 w sh, 500 s, 480 m, 455 w, 440 w, 393 w, 351 m, 322 m. <sup>1</sup>H NMR (benzene-d<sub>6</sub>): δ 1.71 (s, 30 H, C<sub>5</sub>Me<sub>5</sub>), 7.21 (br, 9 H, *m*, *p*-H, C<sub>6</sub>H<sub>5</sub>), 8.06 (br, 6 H, *o*-H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-d<sub>6</sub>): δ 12.77 (C<sub>5</sub>Me<sub>5</sub>), 123.09 (C<sub>5</sub>Me<sub>5</sub>), 127.00, 137.38, 140.66, 146.96 (br, C<sub>6</sub>H<sub>5</sub>). <sup>29</sup>Si NMR (benzene-d<sub>6</sub>): δ 47.34.

**Cp\*<sub>2</sub>Zr(GePh<sub>3</sub>)Cl (9).** A solution of LiGePh<sub>3</sub> (from ClGePh<sub>3</sub>, 0.414 g, 1.22 mmol, and lithium, 0.034 g, 4.88 mmol) in tetrahydrofuran (25 mL) was slowly added to a stirred suspension of Cp\*<sub>2</sub>ZrCl<sub>2</sub> (0.50 g, 1.16 mmol) in tetrahydrofuran (5 mL), and after 5 h the solvent was removed by vacuum transfer. Extraction of the orange residue with pentane (50 mL), followed by concentration of the pentane to 15 mL and cooling (-10 °C) gave orange crystals (mp 199–201 °C) in 64% yield (0.517 g). Anal. Calcd for C<sub>38</sub>H<sub>45</sub>ClGeZr: C, 65.1; H, 6.47. Found: C, 65.2; H, 6.56. IR (Nujol, CsI, cm<sup>-1</sup>): 3055 m, 3030 m, 1575 w, 1480 m, 1425 s, 1300 w, 1258 w, 1090 w, 1070 w, 1015 w sh, 1020 m, 994 w, 880 w, 730 s, 706 s, 696 s, 475 m, 352 w, 324 w, 305 w, 275 w. <sup>1</sup>H NMR (benzene-d<sub>6</sub>): δ 1.73 (s, 30 H, C<sub>5</sub>Me<sub>5</sub>), 7.26 (m, 9 H, *m*, *p*-H, C<sub>6</sub>H<sub>5</sub>), 7.88 (br, 6 H, *o*-H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-d<sub>6</sub>): δ 12.65 (C<sub>5</sub>Me<sub>5</sub>), 123.50 (C<sub>5</sub>Me<sub>5</sub>), 127.47, 128.70, 135.95, 137.05 (br) (C<sub>6</sub>H<sub>5</sub>).

**Cp\*<sub>2</sub>Zr(SnPh<sub>3</sub>)Cl (10).** The method for **9** was employed, using LiSnPh<sub>3</sub> (from ClSnPh<sub>3</sub>, 0.470 g, 1.22 mmol, and lithium, 0.034

g, 4.9 mmol) and  $\text{Cp}^*_2\text{ZrCl}_2$  (0.50 g, 1.16 mmol). Crystallization from toluene/pentane (15 mL, 1/9 by volume) at  $-10^\circ\text{C}$  gave orange crystals (mp 218–224  $^\circ\text{C}$  dec) in 68% yield (0.59 g). The crystals were contaminated with small amounts of a material giving rise to  $^1\text{H}$  NMR resonances in the aromatic region ( $\delta$  7.16, m, 0.93 H, 7.66, m, 0.93 H). Anal. Calcd for  $\text{C}_{38}\text{H}_{45}\text{ClSnZr}$ : C, 61.1; H, 6.07. Found: C, 58.6; H, 5.73. IR (Nujol, CsI,  $\text{cm}^{-1}$ ): 3050 m, 3030 m, 1569 m, 1422 s, 1295 w, 1259 w, 1185 w, 1150 w, 1063 m, 1017 m, 995 m, 803 w, 730 s, 700 s, 685 w sh, 675 w, 645 w, 584 w, 458 m, 395 w, 360 w, 325 w.  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  1.79 (s, 30 H,  $\text{C}_5\text{Me}_5$ ), 7.18 (t,  $J = 7.2$  Hz, 3 H,  $p$ -H,  $\text{C}_6\text{H}_5$ ), 7.29 (t,  $J = 7.2$  Hz, 6 H,  $m$ -H,  $\text{C}_6\text{H}_5$ ), 7.92 (d, 6 H,  $o$ -H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (benzene- $d_6$ ):  $\delta$  12.76 ( $\text{C}_5\text{Me}_5$ ), 122.98 ( $\text{C}_5\text{Me}_5$ ), 127.00, 129.14, 138.92, 152.78 ( $\text{C}_6\text{H}_5$ ).

**$\text{Cp}^*_2\text{Hf}(\text{SiPh}_3)\text{Cl}$  (11).** The method used for 8 was employed, with 10 h of stirring. Yellow crystals (mp 214–216  $^\circ\text{C}$  dec) of 11 were obtained in 78% yield (0.56 g). Anal. Calcd for  $\text{C}_{38}\text{H}_{45}\text{ClSiHf}$ : C, 61.4; H, 6.10. Found: C, 61.7; H, 6.20. IR (Nujol, CsI,  $\text{cm}^{-1}$ ): 3060 m, 1580 w, 1427 s, 1305 w, 1260 w, 1090 m, 1025 w, 800 w, 745 w sh, 735 m, 710 s, 700 s, 676 w, 502 s, 482 w, 440 w, 395 w, 325 w, 304 w.  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  1.77 (s, 30 H,  $\text{C}_5\text{Me}_5$ ), 7.22 (m, 9 H,  $m,p$ -H,  $\text{C}_6\text{H}_5$ ), 8.06 (d,  $J = 6.9$  Hz, 6 H,  $o$ -H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (benzene- $d_6$ ):  $\delta$  12.68 ( $\text{C}_5\text{Me}_5$ ), 121.82 ( $\text{C}_5\text{Me}_5$ ), 126.98, 137.56, 140.83, 148.00 (br,  $\text{C}_6\text{H}_5$ ).  $^{29}\text{Si}$  NMR (benzene- $d_6$ ):  $\delta$  42.86.

**$\text{Cp}^*_2\text{Zr}(\text{SiPh}_3)\text{Me}$  (12).** Compound 8 (0.61 g, 0.93 mmol) was dissolved in diethyl ether (30 mL) and cooled to  $-78^\circ\text{C}$ . To this stirred solution was added 0.31 mL of  $\text{MeMgBr}$  (0.93 mmol; 3.0 M in diethyl ether). The reaction mixture was allowed to slowly warm to room temperature over 1.5 h with stirring. The solution was evaporated to dryness, and the product was extracted with pentane ( $3 \times 20$  mL). The combined extracts were concentrated to ca. 30 mL and cooled to  $-35^\circ\text{C}$ , resulting in precipitation of light orange 12 in 62% yield (0.37 g).  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  0.00 (s, 3 H, ZrMe), 1.68 (s, 30 H,  $\text{C}_5\text{Me}_5$ ), 7.21 (m, 9 H,  $m,p$ -H,  $\text{C}_6\text{H}_5$ ), 7.60 (br, 6 H,  $o$ -H,  $\text{C}_6\text{H}_5$ ). The compound decomposes slowly at room temperature, much faster in solution than in the solid state. When the reaction mixture was stirred for 6 h, a mixture of  $\text{Cp}^*_2\text{Zr}(\text{SiPh}_3)\text{Me}$  and  $\text{HSiPh}_3$  (2:1 ratio, as judged by  $^1\text{H}$  NMR) was obtained.

**$\text{Cp}^*_2\text{Hf}(\text{SiPh}_3)\text{Me}$  (13).** Compound 11 (1.00 g, 1.34 mmol) was dissolved in diethyl ether (30 mL), and the solution was cooled to  $-78^\circ\text{C}$ . To this solution was added 1.35 mmol of  $\text{MeMgBr}$  (0.45 mL of a 3.0 M diethyl ether solution). The reaction mixture was allowed to slowly warm to room temperature over 2.5 h with stirring. The solution was evaporated to dryness, and the product was extracted into pentane ( $3 \times 20$  mL). The combined extracts were concentrated to ca. 30 mL and cooled to  $-35^\circ\text{C}$ , resulting in precipitation of a light yellow solid in ca. 76% (0.738 g) yield, which was slightly contaminated with  $\text{HSiPh}_3$ .  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  -0.22 (s, 3 H, HfMe), 1.73 (s, 30 H,  $\text{C}_5\text{Me}_5$ ), 7.22 (m, 9 H,  $m,p$ -H,  $\text{C}_6\text{H}_5$ ), 7.65 (br, 6 H,  $o$ -H,  $\text{C}_6\text{H}_5$ ). When the reaction mixture was stirred for 6 h, a mixture of  $\text{Cp}^*_2\text{Hf}(\text{SiPh}_3)\text{Me}$  and  $\text{HSiPh}_3$  (7:3 ratio, as judged by  $^1\text{H}$  NMR) was obtained. Like 12, this compound decomposes slowly at room temperature.

**$\text{CpCp}^*\text{ZrHCl}$  via Reaction of 2 with  $\text{H}_2$ .** A solution of 2 (0.500 g, 0.853 mmol) in benzene (25 mL) was pressurized with  $\text{H}_2$  (100 psi), resulting in a gradual color change from orange to pale yellow. After 2 h, the  $\text{H}_2$  pressure was released, and the solution was filtered. Volatiles were removed in vacuo, and the residue was dissolved in pentane (5 mL) and cooled ( $-10^\circ\text{C}$ ) to give  $\text{CpCp}^*\text{ZrHCl}$  in 46% yield (0.13 g).  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  1.84 (s, 15 H,  $\text{C}_5\text{Me}_5$ ), 5.85 (s, 5 H,  $\text{C}_6\text{H}_5$ ), 6.59 (s, 1 H, ZrH).

**$\text{CpCp}^*\text{HfHCl}$  via Reaction of 5 with  $\text{H}_2$ .** A solution of 5 (0.500 g, 0.742 mmol) in benzene (25 mL) was pressurized with  $\text{H}_2$  (100 psi), resulting in the gradual development of a colorless solution. After 4 h, the pressure was released, and the solution was filtered. Volatiles were removed in vacuo, the residue was dissolved in pentane (5 mL), and the solution was cooled ( $-10^\circ\text{C}$ ) to give  $\text{CpCp}^*\text{HfHCl}$  in 56% yield (0.17 g).  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  1.89 (s, 15 H,  $\text{C}_5\text{Me}_5$ ), 5.81 (s, 5 H,  $\text{C}_6\text{H}_5$ ), 12.29 (s, 1 H, HfH).

**$\text{Cp}^*_2\text{ZrHCl}$  via Reaction of 8 with  $\text{H}_2$ .** A solution of 8 (0.50 g, 0.76 mmol) in benzene (25 mL) was pressurized with  $\text{H}_2$  (100 psi), resulting in a gradual color change from orange to colorless. After 30 min, the pressure was released, and the solution was

filtered. Volatiles were removed by vacuum distillation, the residue was dissolved in pentane (5 mL), and the resulting solution was cooled to  $-10^\circ\text{C}$  to afford  $\text{Cp}^*_2\text{ZrHCl}$  in 63% yield (0.19 g). Anal. Calcd for  $\text{C}_{20}\text{H}_{31}\text{ClZr}$ : C, 60.3; H, 7.85. Found: C, 59.7; H, 7.15. IR (Nujol, CsI,  $\text{cm}^{-1}$ ): 1585 (ZrH).  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  1.92 (s, 30 H,  $\text{C}_5\text{Me}_5$ ), 6.90 (s, 1 H, ZrH).

**$\text{Cp}^*_2\text{HfHCl}$  via Reaction of 11 with  $\text{H}_2$ .** Hydrogenolysis of 11 for 2 h, according to the procedure for  $\text{Cp}^*_2\text{ZrHCl}$  above, gave  $\text{Cp}^*_2\text{HfHCl}$  in 77% yield (0.25 g). Anal. Calcd for  $\text{C}_{20}\text{H}_{31}\text{ClHf}$ : C, 49.5; H, 6.44. Found: C, 49.4; H, 6.45. IR (Nujol, CsI,  $\text{cm}^{-1}$ ): 1630 (HfH).  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  1.97 (s, 30 H,  $\text{C}_5\text{Me}_5$ ), 12.67 (s, 1 H, HfH).

**Reaction of 12 with  $\text{H}_2$ .** A solution of 12 (0.367 g) in benzene (20 mL) was pressurized with  $\text{H}_2$  (100 psi), resulting in a gradual color change from light yellow to colorless. After 20 min, the  $\text{H}_2$  pressure was released, and the solution was filtered. Volatiles were removed by vacuum transfer. The  $^1\text{H}$  NMR spectrum contained resonances assigned to  $\text{HSiPh}_3$  ( $\delta$  5.69, s, 1 H, SiH, 7.13, m, 9 H,  $m,p$ -H,  $\text{C}_6\text{H}_5$ ), 7.57, d,  $J = 7.5$  Hz, 6 H,  $o$ -H,  $\text{C}_6\text{H}_5$ ) and  $\text{Cp}^*_2\text{ZrH}_2$  ( $\delta$  2.02, s, 30 H,  $\text{C}_5\text{Me}_5$ ), 7.46, s, 2 H, ZrH).

**Reaction of 13 with  $\text{H}_2$ .** The method above was used to show that the reaction proceeds cleanly to  $\text{HSiPh}_3$  and  $\text{Cp}^*_2\text{Hf}(\text{H})\text{Me}$ .<sup>9b</sup>  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  -0.62 (s, 3 H, HfMe), 1.92 (s, 30 H,  $\text{C}_5\text{Me}_5$ ), 13.00 (s, 1 H, HfH).

**Reactions of 3 and 9 with  $\text{H}_2$ .** Reaction of 3 with  $\text{H}_2$  (100 psi) over 8 h resulted in a 65% conversion to  $\text{HGePh}_3$  ( $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  5.85, s, 1 H, GeH, 7.14, m, 9 H,  $m,p$ -H,  $\text{C}_6\text{H}_5$ ), 7.51, m, 6 H,  $o$ -H,  $\text{C}_6\text{H}_5$ ),  $\text{CpCp}^*\text{ZrHCl}$ , and minor amounts of decomposition products. Similarly, reaction of 9 with  $\text{H}_2$  (100 psi) over 5 h gave  $\text{Cp}^*_2\text{ZrHCl}$ ,  $\text{HGePh}_3$ , and decomposition products in 69% conversion (as judged by  $^1\text{H}$  NMR spectroscopy, on the basis of the disappearance of starting material).

**Reactions of 7 and 10 with  $\text{H}_2$ .** Reaction of  $\text{CpCp}^*\text{Hf}(\text{SnPh}_3)\text{Cl}$  with  $\text{H}_2$  (100 psi) over 10 h gave  $\text{HSnPh}_3$  ( $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  6.91, s, 1 H, SnH, 7.14, m, 9 H,  $m,p$ -H,  $\text{C}_6\text{H}_5$ ), 7.51, m, 6 H,  $o$ -H,  $\text{C}_6\text{H}_5$ ) and unidentified hafnium-containing products after 67% conversion of 7. The hydride  $\text{CpCp}^*\text{HfHCl}$  was not observed. Similarly, reaction of  $\text{Cp}^*_2\text{Zr}(\text{SnPh}_3)\text{Cl}$  with  $\text{H}_2$  (100 psi) over 5 h gave  $\text{HSnPh}_3$  and metal-containing decomposition products in 31% conversion.  $\text{Cp}^*_2\text{ZrHCl}$  was not observed as a product.

**Reactions of 5–7 with  $\text{PhSiH}_3$ .** A 5-mm NMR tube was charged with 5 (20 mg, 0.03 mmol),  $\text{PhSiH}_3$  (3 mg, 0.03 mmol), and benzene- $d_6$  (0.4 mL). Two samples were prepared similarly with 6 and 7. After 5.5 h under the same ambient fluorescent room lighting conditions, the  $^1\text{H}$  NMR spectra showed resonances assignable to  $\text{CpCp}^*\text{Hf}(\text{SiH}_2\text{Ph})\text{Cl}$  (80% for 5 and 30% for 6), and  $\text{HSiPh}_3$  or  $\text{HGePh}_3$ , respectively. No reaction of 7 with  $\text{PhSiH}_3$  was observed over the course of 1 day.

**Reactions of 8–11 with  $\text{PhSiH}_3$ .** A 5-mm NMR tube was charged with 8 (20 mg, 0.03 mmol),  $\text{PhSiH}_3$  (3 mg, 0.03 mmol), and benzene- $d_6$  (0.4 mL). Samples were prepared similarly using 9 and 10. The samples were exposed to the same ambient room lighting conditions. After 3 h, 8 had undergone a 91% conversion to a mixture of  $\text{Cp}^*_2\text{ZrHCl}$ ,  $\text{HSiPh}_3$ ,  $\text{PhH}_2\text{SiSiH}_2\text{Ph}$ ,  $\text{PhH}_2\text{SiSiHPhSiH}_2\text{Ph}$ , and  $\text{PhH}_2\text{Si}(\text{SiHPh})_2\text{SiH}_2\text{Ph}$  (as judged by  $^1\text{H}$  NMR spectroscopy). After 3 h, 9 had undergone a 41% conversion to a mixture of  $\text{Cp}^*_2\text{ZrHCl}$ ,  $\text{HGePh}_3$ ,  $\text{PhH}_2\text{SiSiH}_2\text{Ph}$ ,  $\text{PhH}_2\text{SiSiHPhSiH}_2\text{Ph}$ , and  $\text{PhH}_2\text{Si}(\text{SiHPh})_2\text{SiH}_2\text{Ph}$ . No reaction was observed between 10 and  $\text{PhSiH}_3$  over 2 days.

An NMR tube containing 11 (20 mg, 0.03 mmol),  $\text{PhSiH}_3$  (3 mg, 0.03 mmol), and benzene- $d_6$  (0.4 mL) was prepared. After 2 days complete disappearance of 11 had occurred, as judged by  $^1\text{H}$  NMR spectroscopy. The  $^1\text{H}$  NMR spectrum contained resonances assigned to  $\text{PhSiH}_3$ ,  $\text{PhH}_2\text{SiSiH}_2\text{Ph}$ ,  $\text{PhH}_2\text{SiSiHPhSiH}_2\text{Ph}$ ,  $\text{PhH}_2\text{Si}(\text{SiHPh})_2\text{SiH}_2\text{Ph}$ , and  $\text{Cp}^*_2\text{HfHCl}$ , in the proportions given in eq 6.

**$\text{Cp}^*_2\text{Zr}(\eta^2\text{-COSiPh}_3)\text{Cl}$  (14).** A pressure bottle containing 8 (0.40 g, 0.61 mmol) in benzene (15 mL) was pressurized with CO (100 psi), resulting in a slow color change from orange to dark purple. After 15 h, the CO pressure was released, and the solution was filtered. Volatiles were removed in vacuo, the residue was dissolved in pentane, and the solution was cooled ( $-35^\circ\text{C}$ ) to give dark purple crystals (mp 172–174  $^\circ\text{C}$  dec) in 76% yield (0.32 g). Anal. Calcd for  $\text{C}_{39}\text{H}_{45}\text{ClOSiZr}$ : C, 68.4; H, 6.63. Found: C, 68.3; H, 6.78. IR (Nujol, CsI,  $\text{cm}^{-1}$ ): 3042 m, 1588 w, 1470 m ( $\nu_{\text{CO}}$ ,

assigned in a Fluorolube mull spectrum), 1427 s, 1305 w, 1260 w, 1090 m, 1025 w, 800 w, 745 w sh, 735 m, 710 s, 700 s, 676 w, 502 s, 482 w, 440 w, 395 w, 325 w, 304 w. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ 1.61 (s, 30 H, C<sub>5</sub>Me<sub>5</sub>), 7.25 (m, 9 H, *m,p*-H, C<sub>6</sub>H<sub>5</sub>), 8.26 (d, *J* = 7.2 Hz, 6 H, *o*-H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>): δ 11.32 (C<sub>5</sub>Me<sub>5</sub>), 118.29 (C<sub>6</sub>Me<sub>5</sub>), 128.55, 130.52, 131.69, 137.55 (br, C<sub>6</sub>H<sub>5</sub>), 403.78 (ZrCOSi). <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): δ -25.82.

**Reaction of 13 with HCl.** An NMR tube containing 14 (20 mg, 0.03 mmol) and benzene-*d*<sub>6</sub> (0.4 mL) was connected to a vacuum line and cooled to -196 °C. Anhydrous HCl gas (1 equiv) was condensed into the tube, and the tube was sealed with a torch. The tube was warmed to 25 °C, resulting in a rapid color change from dark purple to pale yellow. After 10 min, the <sup>1</sup>H NMR spectrum contained resonances assigned to Cp\*<sub>2</sub>ZrCl<sub>2</sub> and Ph<sub>3</sub>SiCHO (15). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>) for 15: δ 7.12 (m, 9 H, *m,p*-H, C<sub>6</sub>H<sub>5</sub>), 7.52 (d, *J* = 7.5 Hz, 6 H, *o*-H, C<sub>6</sub>H<sub>5</sub>), 12.15 (s, 1 H, CHO).

**Cp\*<sub>2</sub>Zr[OC(SiPh<sub>3</sub>)(CN-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)]Cl (16).** Benzene (20 mL) was added to a flask containing 14 (0.40 g, 0.58 mmol) and 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC (0.08 g, 0.58 mmol). The mixture was stirred for 22 h, resulting in a slow color change from dark purple to orange. Removal of volatiles resulted in a residue which was washed with cold pentane (0 °C, 2 × 5 mL) and then dissolved in 30 mL of pentane. Filtration, concentration, and cooling (-35 °C) of the solution gave orange crystals (mp 172–174 °C dec) in 64% yield (0.30 g). Anal. Calcd for C<sub>48</sub>H<sub>54</sub>ClNOSiZr: C, 70.7; H, 6.67. Found: C, 70.5; H, 6.71. IR (Nujol, CsI, cm<sup>-1</sup>): 3060 m, 3040 m, 1945 s (ν<sub>CCN</sub>), 1584 w, 1480 m, 1423 s, 1308 m, 1285 w sh, 1255 w, 1246 w, 1185 w, 1146 s, 1105 s, 1065 m, 1025 m, 994 w, 915 w, 810 m, 770 m, 755 m, 730 s, 697 s, 675 w, 645 w, 616 w, 560 m, 536 m, 500 s, 472 w, 443 w, 421 w, 400 w, 345 m. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ 1.84 (s, 30 H, C<sub>5</sub>Me<sub>5</sub>), 2.37 (s, 6 H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 6.83 (m, 3 H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 7.19 (m, 9 H, *m,p*-H, C<sub>6</sub>H<sub>5</sub>), 7.88 (d, *J* = 6.9 Hz, 6 H, *o*-H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>): δ 11.70 (C<sub>5</sub>Me<sub>5</sub>), 19.85 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 100.41 (CCN), 121.84 (C<sub>5</sub>Me<sub>5</sub>), 126.13, 128.00, 128.76, 129.87, 132.81, 134.22, 137.30 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>), 199.31 (CCN). <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): δ -68.28.

**CpCp\*Hf[η<sup>2</sup>-C(N-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)SiPh<sub>3</sub>]Cl (17).** A benzene (30 mL) solution containing 5 (0.50 g, 0.74 mmol) and 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC (0.10 g, 0.74 mmol) was stirred at room temperature for 5 h. Volatiles were removed by vacuum transfer, and the yellow residue was washed with cold pentane (0 °C, 2 × 10 mL) and then extracted into pentane. Cooling to -35 °C gave yellow crystals (mp 208–210 °C dec) in 68% yield (0.40 g). Anal. Calcd for C<sub>42</sub>H<sub>44</sub>CINSiHf: C, 62.7; H, 5.51. Found: C, 62.4; H, 5.63. IR (Nujol, CsI, cm<sup>-1</sup>): 3040 w, 1585 w, 1525 w (ν<sub>CN</sub>), 1428 m, 1260 w, 1188 w, 1150 w, 1110 m, 1100 m, 1030 w, 1015 m, 995 w, 805 s, 795 m, 770 w, 740 m, 720 m, 700 s, 675 w, 645 w, 605 w, 500 m, 420 w, 320 w. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ 1.94 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 1.49, 2.04 (s, 6 H, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 5.72 (s, 5 H, C<sub>6</sub>H<sub>5</sub>), 6.68, 6.81 (dd, *J* = 7.2 Hz, 2 H, *m*-H, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 6.93 (t, *J* = 7.2 Hz, 1 H, *p*-H, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 7.13 (m, 9 H, *m,p*-H, C<sub>6</sub>H<sub>5</sub>), 7.70 (d, *J* = 6.9 Hz, 6 H, *o*-H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>): δ 12.89 (C<sub>5</sub>Me<sub>5</sub>), 19.78, 20.79 (C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 110.61 (C<sub>6</sub>H<sub>5</sub>), 117.59 (C<sub>5</sub>Me<sub>5</sub>), 126.16, 128.00, 129.12, 129.30, 129.92, 130.21, 132.41, 134.12, 137.26, 147.64 (C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>), 278.61 (HfCNSi). <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): δ -30.17.

**Reaction of 8 with 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC.** Compound 8 (20 mg, 0.03 mmol), 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC (4 mg, 0.03 mmol), and benzene-*d*<sub>6</sub> (0.4 mL) were combined in an NMR tube. After 4 h, the <sup>1</sup>H NMR spectrum consisted of resonances assigned to the new product

Cp\*<sub>2</sub>Zr[η<sup>2</sup>-C(N-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)SiPh<sub>3</sub>]Cl (18). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ 1.71 (s, 6 H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 1.81 (s, 30 H, C<sub>5</sub>Me<sub>5</sub>), 6.82 (d, *J* = 7.5 Hz, 2 H, *m*-H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 7.02 (t, *J* = 7.5 Hz, 1 H, *p*-H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 7.12 (m, 9 H, *m,p*-H, C<sub>6</sub>H<sub>5</sub>), 7.68 (d, *J* = 7.5 Hz, 6 H, *o*-H, C<sub>6</sub>H<sub>5</sub>).

**Reaction of 11 with 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC.** Via the above method, Cp\*<sub>2</sub>Hf[η<sup>2</sup>-C(N-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)SiPh<sub>3</sub>]Cl (19) was observed. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ 1.72 (s, 6 H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 1.86 (s, 30 H, C<sub>5</sub>Me<sub>5</sub>), 6.81 (d, *J* = 7.5 Hz, 2 H, *m*-H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 7.01 (t, *J* = 7.5 Hz, 1 H, *p*-H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 7.12 (m, 9 H, *m,p*-H, C<sub>6</sub>H<sub>5</sub>), 7.68 (d, *J* = 7.5 Hz, 6 H, *o*-H, C<sub>6</sub>H<sub>5</sub>).

**CpCp\*Zr[η<sup>2</sup>-C(N-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)GePh<sub>3</sub>]Cl (20).** A mixture of 3 (0.40 g, 0.64 mmol), 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC (0.084 g, 0.64 mmol), and benzene (30 mL) was stirred for 5 h. Removal of volatiles by vacuum transfer left a residue which was washed with cold pentane (0 °C, 2 × 10 mL) and then extracted into pentane. Cooling (-35 °C) gave yellow crystals (mp 188–190 °C dec) in 76% yield (0.37 g). Anal. Calcd for C<sub>42</sub>H<sub>44</sub>ClNGeZr: C, 66.2; H, 5.82. Found: C, 66.3; H, 5.91. IR (Nujol, CsI, cm<sup>-1</sup>): 3040 m, 1558 w (ν<sub>CN</sub>), 1430 m, 1260 w, 1185 w, 1155 w, 1693 m, 1084 m, 1027 w, 1015 w, 995 w, 803 s, 793 s, 772 w, 745 m, 735 s, 700 s, 670 w, 462 m, 355 w, 327 w. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ 1.88 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 1.62, 1.99 (s, 6 H, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 5.79 (s, 5 H, C<sub>6</sub>H<sub>5</sub>), 6.73, 6.76 (dd, *J* = 7.5 Hz, 2 H, *m*-H, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 6.93 (t, *J* = 7.5 Hz, 1 H, *p*-H, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 7.12 (m, 9 H, *m,p*-H, C<sub>6</sub>H<sub>5</sub>), 7.62 (d, *J* = 7.2 Hz, 6 H, *o*-H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>): δ 12.92 (C<sub>5</sub>Me<sub>5</sub>), 19.99, 20.52 (C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 111.66 (C<sub>6</sub>H<sub>5</sub>), 118.93 (C<sub>5</sub>Me<sub>5</sub>), 126.14, 128.44, 129.19, 129.38, 129.61, 129.80, 132.29, 136.11, 136.98, 147.23 (C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>), 265.81 (ZrCNGe).

**Reaction of 20 with HCl.** An NMR tube containing 20 (20 mg, 0.026 mmol) and benzene-*d*<sub>6</sub> (0.4 mL) was connected to a vacuum line and cooled to -196 °C. Anhydrous HCl gas (1 equiv) was condensed into the tube, and the tube was sealed with a torch. Warming to 25 °C resulted in a pale yellow solution. After 30 min, the <sup>1</sup>H NMR spectrum contained resonances for CpCp\*ZrCl<sub>2</sub> and Ph<sub>3</sub>GeC(N-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)H (21). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>) for 21: δ 2.04 (s, 6 H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 6.93 (m, 3 H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 7.14 (m, 9 H, *m,p*-H, C<sub>6</sub>H<sub>5</sub>), 7.52 (m, 6 H, *o*-H, C<sub>6</sub>H<sub>5</sub>), 8.76 (s, 1 H, C(N-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)H).

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**Registry No.** 1, 141272-70-0; 2, 141272-71-1; 3, 141272-72-2; 4, 141272-73-3; 5, 141272-74-4; 6, 141272-75-5; 7, 141272-76-6; 8, 141272-77-7; 9, 141272-78-8; 10, 141272-79-9; 11, 141272-80-2; 12, 141272-81-3; 13, 141272-82-4; 14, 141292-00-4; 15, 141272-67-5; 16, 141272-83-5; 17, 141272-84-6; 18, 141272-85-7; 19, 141292-01-5; 20, 141272-86-8; 21, 141272-68-6; CpCp\*HfCl<sub>2</sub>, 87050-25-7; CpCp\*HfMCl, 120578-39-4; CpCp\*ZrCl<sub>2</sub>, 81476-73-5; CpCp\*ZrHCl, 120578-36-1; CpCp\*Zr(Ph)Cl, 141272-87-9; CpCp\*Zr[Si(SiMe<sub>3</sub>)<sub>3</sub>]Cl, 91295-01-1; Cp\*<sub>2</sub>Hf(H)Me, 105930-99-2; Cp\*<sub>2</sub>ZrCl<sub>2</sub>, 54039-38-2; Cp\*<sub>2</sub>ZrHCl, 77299-72-0; Ph<sub>3</sub>SiSiPh<sub>3</sub>, 1450-23-3; PhH<sub>2</sub>SiSiH<sub>2</sub>Ph, 27484-20-4; PhH<sub>2</sub>SiSiHPhSiH<sub>2</sub>Ph, 50518-29-1; PhH<sub>2</sub>Si(SiHPh)<sub>2</sub>SiH<sub>2</sub>Ph, 141272-69-7; LiGePh<sub>3</sub>, 3839-32-5; LiSnPh<sub>3</sub>, 4167-90-2; HSiPh<sub>3</sub>, 789-25-3; HGePh<sub>3</sub>, 2816-43-5; HSnPh<sub>3</sub>, 892-20-6; PhSiH<sub>3</sub>, 694-53-1.

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