Octa- and Nonamethylfluorenyl Complexes of Zr(II), Zr(IV), and Hf(IV). Investigation of Steric and Electronic Effects

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The lithium salts of 1,2,3,4,5,6,7,8-octamethylfluorenyl (Flu″) and 1,2,3,4,5,6,7,8,9-nonamethylfluorenyl (Flu*) were reacted with Zr and Hf half-sandwich complexes to generate mixed-ligand-metallocenes Cp″Flu″ZrCl$_2$ (**1**), Cp″Flu*ZrCl$_2$ (**2**), and Cp*Flu*HfCl$_2$ (**3**) (Cp″ = 1,3-(SiMe$_3$)$_2$C$_5$H$_3$, Cp* = C$_5$Me$_5$). Reaction of the metallocene dichlorides with MeLi yielded the dimethyl derivatives Cp″Flu*ZrMe$_2$ (**4**) and Cp*Flu*HfMe$_2$ (**5**). Reduction of the zirconocene dichlorides in the presence of CO gas yielded the dicarbonyl derivatives Cp″Flu″Zr(CO)$_2$ (**6**) and Cp″Flu*Zr(CO)$_2$ (**7**), which represent the first examples of zirconocene dicarbonyls containing a fluorenyl ligand derivative. Structural characterization of the zirconocene dichloride **2** and the dicarbonyls **6** and **7** revealed that the methylated fluorenyl ligands adopt an η^5-coordination and display a twisted tricyclic core in each case. A spectroscopic study of a small series of zirconocene dicarbonyl analogues indicates that the methylated fluorenyl ligands are strong electron donors and similar in this regard to heptamethylindenyl (Ind*) and Cp*.

Introduction

The usefulness of group 4 metallocene complexes in a wide array of chemical transformations, and particularly as catalysts for olefin polymerization,[1,2] has made them the subject of intense research efforts. At the center of this research activity is the search for ancillary ligands that impart the metal complex with the desired physical properties and chemical reactivity.[3] Popular variations on the simple cyclopentadienyl ligand (Cp, C$_5$H$_5$) include the peralkylated species pentamethylcyclopentadienyl (Cp*, C$_5$Me$_5$) and fused-ring derivatives such as indenyl (Ind, C$_9$H$_7$) and fluorenyl (Flu, C$_{13}$H$_9$).

Application of the fluorenyl ligand in group 4 metallocene chemistry has distinctly lagged behind that of Cp and Ind derivatives.[4] This is partly due to the decreased stability of Flu complexes with respect to their Cp or Ind analogues. For example, Flu$_2$ZrCl$_2$ is known to decompose in the presence of donor solvents.[5] The Flu ligand's ability to undergo a change in hapticity from η^5 to η^3 or η^1 may account for the difficulty in isolating fluorenyl compounds and their susceptibility toward decomposition. Elimination of strong donor solvents from the reaction mixtures and development of *ansa*-bridged fluorenyl ligands helped fuel the progress of group 4 fluorenyl chemistry.[4] Complementary to Brintzinger's discovery of *ansa*-bridged

bis(indenyl) complexes[6] and their application toward the isospecific polymerization of α-olefins, *ansa*-bridged fluorenyl ligands have been particularly useful in the preparation of syndiospecific C_s-symmetric catalysts of the general type Me$_2$C(C$_5$H$_4$)(C$_{13}$H$_8$)MCl$_2$ (M = Zr, Hf).[7]

Interestingly, considering the widespread use of the Cp* ligand in main group, transition metal, and f-block chemistry, the completely methylated analogues of Ind and Flu have received far less attention. The heptamethylindenyl ligand (Ind*, C$_9$Me$_7$), first synthesized in 1981,[8] represents a potentially useful ligand that has received limited attention; for example, very few complexes of Ind* with group 4 complexes are known.[9] The nonamethylfluorenyl ligand (Flu*, C$_{13}$Me$_9$) was only recently reported, and its coordination chemistry is limited to late transition metals (Ru, Fe, Mn).[10,11] Studies on the few known Ind*- and Flu*-containing complexes suggest that these ligands are highly electron-donating.[10,12]

The highly donating and sterically demanding properties of the Flu* ligand suggest that it may support highly reactive early

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(9) Compounds Ind*TiCl$_3$, Ind*ZrCl$_3$, Ind*$_2$ZrCl$_2$, Ind*HfCl$_3$, Ind*$_2$HfCl$_2$, and Ind*$_2$HfMe$_2$ were reported in: O'Hare, D.; Murphy, V. J.; Diamond, G. M.; Arnold, P.; Mountford, P. *Organometallics* **1994**, *13*, 4689.

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Scheme 1
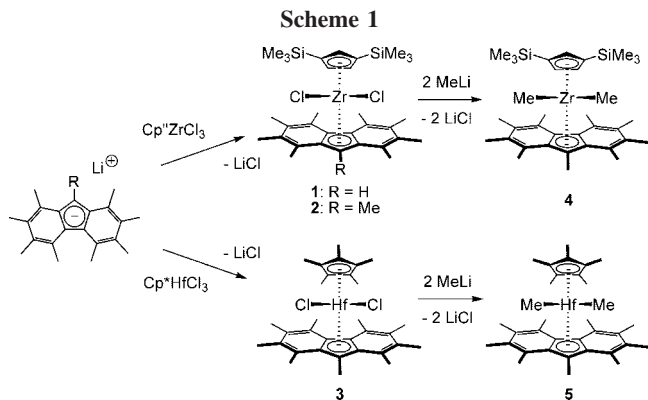
transition metal centers. Thus, it is important to investigate its viability as an ancillary ligand for such metals and probe the structural and electronic properties of Flu*−early metal complexes. Here, the synthesis and characterization of several mixed-ligand group 4 metallocene derivatives containing the octa- or nonamethylfluorenyl ligand are reported. A series of zirconocene dicarbonyl complexes, and their spectroscopic properties, are also described. The results of these studies highlight the strongly donating nature of the methylated fluorenyl ligands.

Results and Discussion

Synthesis of Metallocene Dichlorides. To access group 4 metallocene complexes containing a highly methylated fluorenyl ligand, synthetic studies began with an appropriate half-sandwich compound that would undergo salt metathesis with alkali metal salts of the fluorenyl ligand derivatives to generate mixed-ligand metallocenes.[13] Reaction of the lithium salts of 1,2,3,4,5,6,7,8-octamethylfluorenyl (Flu″, $C_{13}Me_8H$) or 1,2,3,4,5,6,7,8,9-non-amethylfluorenyl (Flu*, $C_{13}Me_9$) with 1,3-bis(trimethylsilyl)cyclopentadienylzirconium trichloride (Cp″ZrCl$_3$, where Cp″ = 1,3-(SiMe$_3$)$_2$C$_5$H$_3$) gave the desired zirconocene dichlorides Cp″Flu*ZrCl$_2$ (**1**) and Cp″Flu*ZrCl$_2$ (**2**) in good and moderate yields, respectively (Scheme 1). Compounds **1** and **2** were isolated as red crystalline solids from aromatic solvents, and their spectroscopic features are consistent with the expected metallocene structures.

The ^{1}H NMR spectrum of **1** contains a total of eight signals, and the presence of the Flu″ ligand is supported by the appearance of five singlets for the ring proton and the methyl groups, in a 1:6:6:6:6 ratio. The peak assigned to the aromatic proton at the 9-position of the ligand appears at 6.10 ppm, and the other four signals assigned to the fluorenyl methyl groups appear between 2.64 and 2.13 ppm. On the basis of the previously reported solid-state structure of Flu″H,[10] the ligand is expected to possess a significantly twisted structure due to steric repulsion between the methyl groups at the 4- and 5-positions, which would render the eight methyl groups chemically inequivalent. The NMR data, however, suggest that the predicted twisted conformation of the Flu″ ligand is rapidly interconverting. This is consistent with spectroscopic results obtained for previously reported metal complexes containing Flu″ or Flu*.[11a] Low-temperature NMR

spectroscopic measurements performed on the related Cp*Flu*Ru complex indicated a very low energy barrier for interconversion in the Flu* ligand.[10]

The characteristic features of compound **1** in the ^{13}C{^{1}H} NMR spectrum are a peak at 80.8 ppm for the carbon at the 9-position of the Flu″ ligand and a set of four signals for the fluorenyl methyl groups (23.7, 17.7, 17.2, and 16.7 ppm), which is consistent with the ^{1}H NMR spectrum. It is worth noting that the chemical shift of the ring carbon at the 9-position of the Flu″ ligand is rather upfield and suggests that the ligand may adopt an η^3-coordination mode.[14] The fluorenyl ligand in the related, mixed-ligand metallocene Cp(2,7-Me$_2$-Flu)ZrCl$_2$ is bound to the metal center in an η^3 fashion and exhibits a peak in the ^{13}C NMR spectrum at 84.3 ppm.[13a]

The ^{1}H NMR spectrum of **2** is very similar to that of **1** in that it also contains only eight signals and the Flu* ligand appears as five singlets. The fluorenyl methyl group at the 9-position appears as a singlet at 3.05 ppm, integrating to three protons, and the remaining eight methyl groups appear as four singlets between 2.60 and 2.14 ppm, each integrating to six protons. Once again, the NMR data suggest that the expected twisted structure of the Flu* ligand in **2** is rapidly interconverting. The ^{13}C{^{1}H} NMR spectrum reveals characteristic peaks expected for the Flu* ligand, such as a peak at 95.0 ppm for the carbon at the 9-position and a set of five peaks for the fluorenyl methyl groups (24.0, 19.9, 19.2, 17.2, and 17.0 ppm). Interestingly, the additional methyl group in Flu* causes the signal for the carbon at the 9-position to appear more downfield compared to the respective signal in **1** and falls in the expected range for an η^5-coordinated fluorenyl ligand.[14] Similar downfield shifts have been observed for other 9-alkylated fluorenyl ligands, which also tend to exhibit η^5-coordination more often than their nonalkylated analogues. For example, the related compound Cp(9-Me-Flu)ZrCl$_2$ gives rise to a corresponding peak in the ^{13}C NMR spectrum at 99.0 ppm.[13c]

Extending this synthetic approach to hafnium, the lithium salt of Flu* was combined with Cp*HfCl$_3$ to generate the desired mixed-ligand hafnocene Cp*Flu*HfCl$_2$ (**3**) (Scheme 1). Compound **3** was isolated as a red-orange crystalline solid in moderate yield. The spectroscopic signatures of compound **3** are consistent with the anticipated metallocene structure. The ^{1}H NMR spectrum contains only six singlets, with the Flu* ligand giving rise to five signals for the methyl groups in a 3:6:6:6:6 ratio, at chemical shifts ranging from 2.92 to 2.13 ppm. This suggests that the Flu* ligand is rapidly interconverting between twisted conformations. The ^{13}C{^{1}H} NMR spectrum contains characteristic signals for Flu*, a peak at 93.9 ppm for the carbon at the 9-position, and a set of five peaks for the five fluorenyl methyl groups (23.6, 19.3, 18.4, 17.0, and 16.8 ppm). Overall, the NMR characteristics for the Flu* ligand in compounds **2** and **3** are very similar.

Structure Determination of Cp″Flu*ZrCl$_2$. To investigate the preferred coordination mode for the Flu* ligand in zirconium complexes, a single-crystal X-ray diffraction study of **2** was performed. The molecular structure obtained is illustrated in Figure 1, and selected metrical parameters are listed in Table 1. The structure of compound **2** can be broadly described as a bent metallocene and resembles that of other mixed-ligand zirconocene dichlorides possessing a 9-alkylated fluorenyl ligand (e.g., Cp(9-^{i}Pr-Flu)ZrCl$_2$).[13c] The Cp-type ligands adopt a staggered conformation and exhibit a centroid−Zr−centroid

(13) (a) For examples of unbridged cyclopentadienyl fluorenyl zirconocene derivatives see: Schmid, M. A.; Alt, H. G.; Milius, W. *J. Organomet. Chem.* **1995**, *501*, 101. (b) Schmid, M. A.; Alt, H. G.; Milius, W. *J. Organomet. Chem.* **1996**, *525*, 9. (c) Schmid, M. A.; Alt, H. G.; Milius, W. *J. Organomet. Chem.* **1996**, *525*, 15. (d) Tian, G.; Wang, B.; Xu, S.; Zhou, X. *Transition Met. Chem.* **2000**, *25*, 568. (e) Severn, J. R.; Duchateau, R.; van Santen, R. A.; Ellis, D. D.; Spek, A. L. *Organometallics* **2002**, *21*, 4. (f) Severn, J. R.; Duchateau, R.; van Santen, R. A.; Ellis, D. D.; Spek, A. L.; Yap, G. P. A. *Dalton Trans.* **2003**, 2293.

(14) A chemical shift of approximately 78 ppm is expected for an η^3-coordinated, and 100 ppm for an η^5-coordinated fluorenyl ligand; see ref 4.
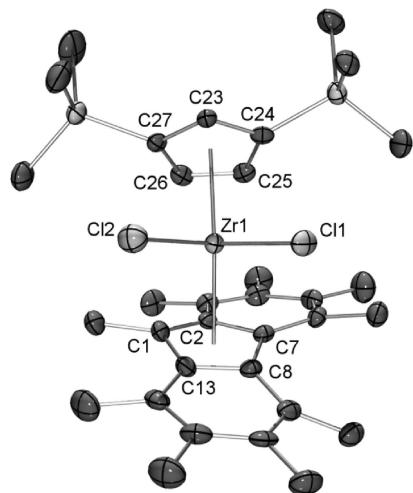
Figure 1. Thermal ellipsoid plot for compound **2**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Table 1. Selected Bond Distances and Angles for Cp″Flu*ZrCl₂ (2)

Distances (Å)			
Zr(1)−Cl(1)	2.4320(14)	Zr(1)−Cl(2)	2.4268(16)
Zr(1)−C(1)	2.444(5)	Zr(1)−C(23)	2.552(5)
Zr(1)−C(2)	2.617(5)	Zr(1)−C(24)	2.572(5)
Zr(1)−C(7)	2.593(5)	Zr(1)−C(25)	2.472(5)
Zr(1)−C(8)	2.677(5)	Zr(1)−C(26)	2.491(5)
Zr(1)−C(13)	2.580(5)	Zr(1)−C(27)	2.565(5)
Flu*$_{cent}$−Zr	2.27	Cp″$_{cent}$−Zr	2.23

Angles (deg)			
Flu*$_{cent}$−Zr−Cp″$_{cent}$	128.8	Cl(2)−Zr(1)−Cl(1)	95.05(5)
C(6)−C(7)−C(8)−C(9)	−14.4(9)		

angle of 128.8°, which is in line with related values for unbridged zirconocenes such as Cp₂ZrCl₂ (129.3°)[15] and Cp*₂ZrCl₂ (130.9°).[16] The molecular structure of compound **2** clearly showcases the unique framework of the Flu* ligand. As expected, the tricyclic core of the fluorenyl ligand is markedly twisted due to steric repulsion between the two methyl groups at the 4- and 5-positions (C(18)−C(19) = 2.98 Å). This twist, which can be quantified using the dihedral angle formed by the four carbons atoms at the 4-, 4a-, 5a-, and 5-positions (14.4(9)°), is somewhat smaller than the respective dihedral angle in Flu*H (22.7(6)°). Such a reduction in the dihedral angle upon coordination to a metal center has also been seen in the ruthenocene complex Cp*Flu*Ru[10] and is presumably due to added steric pressure from the metal center. The twisted fluorenyl core has a significant effect on metal–ligand bonding. The Zr−Flu*$_{cent}$ distance of 2.27 Å is in line with other reported Zr−Flu$_{cent}$ lengths;[13] however there is substantial variation in the individual Zr−C bond lengths. Like most fluorenyl complexes, the shortest Zr−C$_{Flu*}$ bond is that between the metal and the carbon at the 9-position (Zr(1)−C(1) = 2.444(5) Å), but in this case because of the twisted configuration there is considerable variation in the other four Zr−C$_{Flu*}$ bond lengths. Three of the bonds are intermediate in distance, ranging from 2.580(5) to 2.617(5) Å, and one bond (Zr(1)−C(8)) is particularly long at 2.677(5) Å. In comparison, all five of the Zr−C$_{Cp″}$ bond lengths in **2** fall in a narrow range from 2.472(5) to 2.572(5) Å.

Synthesis of Metallocene Dimethyl Derivatives. The widespread use of group 4 metallocene complexes is in large part due to their ability to support a varied assortment of functional groups. Metallocene alkyl derivatives, and in particular cationic alkyl complexes, are extremely important in the field of olefin polymerization.[3a,17] Thus, alkyl derivatives of Flu*-containing Zr and Hf complexes were targeted. Reaction of the dichloride **2** with 2 equiv of MeLi generated the dimethyl derivative Cp″Flu*ZrMe₂ (**4**), which was obtained as orange crystals in a 69% yield (Scheme 1). Using similar conditions, the dimethyl hafnocene derivative Cp*Flu*HfMe₂ (**5**) was obtained as orange crystals in 57% yield from the reaction of compound **3** with MeLi (Scheme 1).

The ¹H NMR spectrum of **4** contains signals for both the Cp″ and Flu* ligand and also contains a signal due to the zirconium methyl groups, at −0.75 ppm. The ¹³C{¹H} NMR spectrum is also consistent with the proposed structure. The characteristic signals for the Flu* are clearly present, with a peak at 91.4 ppm for the carbon at the 9-position and a set of five signals for the fluorenyl methyl groups. The Zr-bound methyl groups give rise to a signal at 36.8 ppm, which is similar to values obtained for other metallocene dimethyl derivatives.[18]

The hafnocene dimethyl derivative **5** also gives rise to NMR spectra that are consistent with the expected metallocene product. The ¹H NMR spectrum contains appropriate signals for the Cp* and Flu* ligands, and the presence of the Hf-bound methyl groups is confirmed by a peak at −0.88 ppm, which integrates to six protons.

Synthesis of Zirconocene Dicarbonyl Derivatives. The highly methylated fluorenyl ligands Flu″ and Flu* were designed to have, in addition to their unique structural features, strongly donating electronic properties. Electrochemical studies on mixed-ligand ruthenocenes containing Flu″ or Flu* examined the effect the ligands had on the oxidation potentials of the Ru complexes and demonstrated that these highly methylated ligands were considerably more electron-donating than Cp* and Flu.[10] It was therefore of interest to determine whether the strongly donating nature of these ligands would also be apparent in early transition metal complexes.

The electronic influence of Cp-type ligands of group 4 metallocene complexes has been previously investigated by examining the effect of the ancillary ligand set on both the reduction potential of dichloride derivatives and the CO stretching frequency of Zr(II) dicarbonyl analogues.[19] Infrared spectroscopy was judged to be a more reliable measure of relative ligand electronic properties, since electrochemical measurements were shown to depend on additional factors such as polarization and solvation of the anionic complex produced after reduction.[19] Assessing a ligand's electronic influence can also be complicated by the difficulty in separating electronic from steric effects, which can affect both physicochemical properties and chemical reactivity.[20,27]

Comparison of a wide variety of bridged and unbridged zirconocene dicarbonyls provides a fairly good understanding of how substituents on a Cp ligand will influence its electronic

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(17) (a) Kaminsky, W. *Catal. Today* **1994**, *20*, 257. (b) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57.

(18) For instance Cp(Flu)ZrMe₂ exhibits a peak in the ¹³C{¹H} NMR spectrum at 35.2 ppm for the Zr-Me goups; see ref 14a.

(19) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525.

(20) (a) Gassman, P. G.; Winter, C. H. *Organometallics* **1991**, *10*, 1592. (b) Gassman, P. G.; Deck, P. A.; Winter, C. H.; Dobbs, D. A.; Cao, D. H. *Organometallics* **1992**, *11*, 959. (c) Deck, P. A. *Coord. Chem. Rev.* **2006**, *250*, 1032.

properties. However, due to the scarcity of Zr(II) dicarbonyls containing fused-ring Cp derivatives, there is little information pertaining to the effect annelation has on the ligand's donation ability. The few data points available seem to indicate that Ind is significantly less donating than Cp. For instance, the average ν_{CO} value for $Ind_2Zr(CO)_2$[21] of 1942 cm^{-1} is significantly higher than the value obtained for $Cp_2Zr(CO)_2$[22] (1931.5 cm^{-1}) and is more in line with the *ansa*-bridged compound $Me_2Si(C_5H_4)_2Zr(CO)_2$ (1939.5 cm^{-1}).[19,23] On the basis of the values obtained for $Ind_2Zr(CO)_2$, it might be expected that Flu derivatives are even less donating than Ind ligands. However there are no reported zirconocene dicarbonyls containing a Flu ligand derivative, and therefore no experimental values available for comparison. Therefore, zirconocene dicarbonyl derivatives possessing the Flu″ and Flu* ligands were targeted.

Reduction of compounds **1** and **2** with Mg powder activated by $HgCl_2$ in the presence carbon monoxide generated the desired dicarbonyls $Cp″Flu″Zr(CO)_2$ (**6**) and $Cp″Flu*Zr(CO)_2$ (**7**) as dark green crystalline products (eq 1). This procedure was successful either with an atmosphere of CO or at higher pressures (60 psi). The color of the compounds obtained and their high solubility in aliphatic solvents, such as pentane, are consistent with other reported Zr(II) dicarbonyls.[24] Compounds **6** and **7** can also be identified as the desired dicarbonyls using spectroscopic methods. The ^1H NMR spectrum of compound **6**, although similar to that of **1** (total of 8 peaks), displays notable differences such as a substantial upfield shift of the resonances for the ring hydrogens of the Cp″ ligand. The signals that appear at 6.63 and 5.86 ppm for **1** now appear at 4.26 and 5.19 ppm, respectively, in **6**. The presence of the carbonyl ligands in **6** is confirmed by the appearance of a peak in the $^{13}C\{^1H\}$ NMR spectrum at 273.1 ppm and by the presence of two very strong absorption bands at 1955 and 1871 cm^{-1} in the infrared (IR) spectrum due to the symmetric and asymmetric stretching modes of the carbonyl ligands.

The key spectroscopic characteristics for compound **7** are very similar to those of **6**. The ring protons of the Cp″ ligand appear significantly upfield in the ^1H NMR spectrum of **7** compared to that of the dichloride precursor **2**. Also, the $^{13}C\{^1H\}$ NMR spectrum contains a peak at 274.5 ppm due to the CO ligands and the IR spectrum exhibits strong absorption bands for the *cis*-carbonyl ligands at 1950 and 1864 cm^{-1}.

(1)
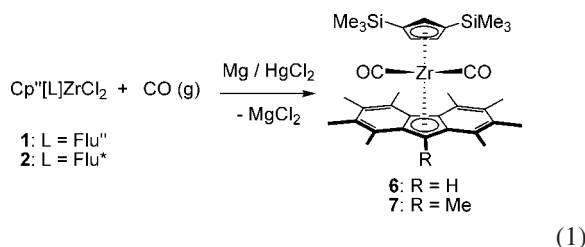
Structural Determinations of Zirconium Dicarbonyl Derivatives. Compounds **6** and **7** represent the first reported examples of fluorenyl-supported zirconocene dicarbonyl complexes. Therefore, single-crystal X-ray diffraction studies of

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(24) For example Cp″₂Zr(CO)₂ is described as a dark green crystalline compound; see: Antiñolo, A.; Lappert, M. F.; Winterborn, D. J. W. *J. Organomet. Chem.* **1984**, *272*, C37.
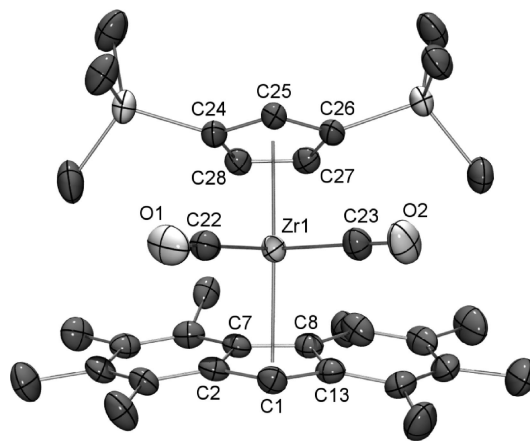
Figure 2. Thermal ellipsoid plot for compound **6**. Hydrogen atoms and one set of disordered atoms (C17B and C18B) have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability.
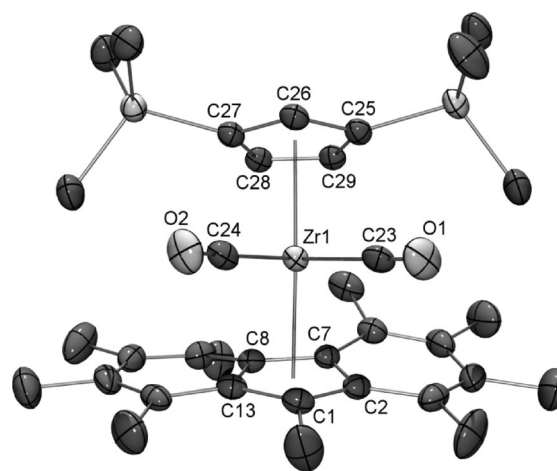
Figure 3. Thermal ellipsoid plot for compound **7**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Table 2. Selected Bond Distances and Angles for Cp″Flu″Zr(CO)₂ (6)

Distances (Å)			
Zr(1)−C(22)	2.178(4)	Zr(1)−C(23)	2.169(4)
O(1)−C(22)	1.149(4)	O(2)−C(23)	1.145(4)
Zr(1)−C(1)	2.464(3)	Zr(1)−C(24)	2.482(3)
Zr(1)−C(2)	2.547(3)	Zr(1)−C(25)	2.463(3)
Zr(1)−C(7)	2.563(3)	Zr(1)−C(26)	2.510(3)
Zr(1)−C(8)	2.543(3)	Zr(1)−C(27)	2.498(3)
Zr(1)−C(13)	2.548(3)	Zr(1)−C(28)	2.479(3)
Flu*$_{cent}$−Zr	2.22	Cp″$_{cent}$−Zr	2.17
Angles (deg)			
O(1)−C(22)−Zr(1)	177.0(3)	O(2)−C(23)−Zr(1)	179.4(4)
Flu*$_{cent}$−Zr−Cp″$_{cent}$	143.0	C(23)−Zr(1)−C(22)	83.22(13)
C(6)−C(7)−C(8)−C(9)	5.6(7)		

compounds **6** and **7** were performed. The molecular structures of **6** and **7** are illustrated in Figures 2 and 3, respectively, and selected structural parameters are listed in Tables 2 and 3. The assignment of compound **6** as the expected mixed-ligand zirconocene dicarbonyl species is clearly confirmed by the solid-state structure. The compound displays a bent metallocene structure with the Cp″ and Flu″ ligands bound to the Zr center via their five-membered rings, and these rings adopt an eclipsed conformation (C(25)−Cp″$_{cent}$−Flu″$_{cent}$−C(1) = 1.18°). The CO ligands demonstrate typical bonding motifs, with Zr−C$_{CO}$

Table 3. Selected Bond Distances and Angles for Cp″Flu*Zr(CO)$_2$ (7)

Distances (Å)			
Zr(1)−C(23)	2.169(4)	Zr(1)−C(24)	2.177(4)
O(1)−C(23)	1.160(4)	O(2)−C(24)	1.152(4)
Zr(1)−C(1)	2.476(3)	Zr(1)−C(25)	2.508(3)
Zr(1)−C(2)	2.553(3)	Zr(1)−C(26)	2.458(3)
Zr(1)−C(7)	2.531(3)	Zr(1)−C(27)	2.486(3)
Zr(1)−C(8)	2.599(3)	Zr(1)−C(28)	2.486(3)
Zr(1)−C(13)	2.538(3)	Zr(1)−C(29)	2.508(3)
Flu*$_{cent}$−Zr	2.22	Cp″$_{cent}$−Zr	2.18

Angles (deg)			
O(1)−C(23)−Zr(1)	175.2(3)	O(2)−C(24)−Zr(1)	175.4(3)
Flu*$_{cent}$−Zr−Cp″$_{cent}$	144.0	C(23)−Zr(1)−C(24)	77.81(14)
C(6)−C(7)−C(8)−C(9)	15.6(7)		

distances of 2.178(4) and 2.169(4) Å and Zr−C−O angles of 177.0(3)° and 179.4(425)°.[25] The Cp″ ligand clearly displays η^5-bonding to the Zr atom with rather homogeneous Zr−C$_{Cp''}$ distances ranging from 2.463(3) to 2.510(3) Å. The Flu″ ligand also displays η^5-bonding to the metal center but, as expected, exhibits greater variability in its Zr−C$_{Flu''}$ distances, with the shortest distances being observed for the carbon at the 9-position. Interestingly, the twisted structure of the Flu″ is disordered in the crystal lattice and the two methyl groups at the 4- and 5-positions were refined into two distinct positions with an occupancy ratio of approximately 60:40. However, the associated disorder in the other carbon positions could not be refined. The disordered structure causes the expected twist in the fluorenyl core to appear much less pronounced in the refined molecular structure (dihedral angle = 5.6(7)°).

The solid-state structure of **7** exhibits features similar to those of compound **6**. Both the Cp″ and Flu* ligands are bonded to the Zr center via their five-membered rings and adopt an eclipsed configuration (C(25)−Cp″$_{cent}$−Flu″$_{cent}$−C(1) = 5.4°). The Zr−C$_{CO}$ distances are 2.169(4) and 2.177(4) Å and the Zr−C−O angles are 175.2(3)° and 175.4(3)°. Again, the Cp″ ligand is bound in a typical η^5-coordination mode (av Zr−C$_{Cp''}$ = 2.18 Å) with all Zr−C$_{Cp''}$ distances having similar values (from 2.458(3) to 2.508(3) Å). However, the Flu* exhibits a distorted η^5-coordination due to the ligand's twisted conformation. No disorder of the type found in **6** was observed. The twisted fluorenyl core (dihedral angle = 15.6(7) Å) causes large variations in the Zr−C$_{Flu*}$ distances, which range from 2.476(3) Å for the C atom at the 9-position to 2.599(3) Å for the C atom twisted furthest away from the metal center. It is worth noting that the difference between the shortest and longest Zr−C$_{Flu*}$ bond in **7** is roughly half of that observed for the corresponding value in the dichloride **2** (0.12 vs 0.23 Å).

Spectroscopic Study of Ligand Effects in Zirconocene Dicarbonyl Derivatives. With Flu″- and Flu*-containing dicarbonyl complexes in hand, it was of interest to obtain related compounds that would allow direct comparisons and a meaningful analysis of electronic properties of Flu″ and Flu* relative to those of similar Cp-type ligands such as Cp*, Ind, Ind*, and Flu. To access such a series, appropriate mixed-ligand zirconocene dichlorides (**8–11**) were targeted (eq 2). The Cp* derivative **8** has previously been reported,[26] and compounds

(25) For reference see the structure of Cp$_2$Zr(CO)$_2$: Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Floriani, C.; Fachinetti, G.; Chiesi-Villa, A. *Inorg. Chem.* **1980**, *19*, 3812.

(26) Pool, J. A.; Bradley, C. A.; Chirik, P. J. *Organometallics* **2002**, *21*, 1271.

(27) Cp″Cp*Zr(CO)$_2$ has appeared in the literature; however no experimental details were given, see: Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 2241.

Table 4. Carbonyl Stretching Frequencies of Zirconocene Dicarbonyl Complexes

	ν_{CO} (cm^{-1}) (pentane)		
compound	sym. ν_{CO}	asym. ν_{CO}	av ν_{CO}
Ind$_2$Zr(CO)$_2$	1985[a]	1899[a]	1942[a]
Cp$_2$Zr(CO)$_2$	1976[b]	1887[b]	1931.5[b]
Cp″CpZr(CO)$_2$	1973[c]	1888[c]	1930.5[c]
Cp″IndZr(CO)$_2$ **13**	1972	1888	1930
Cp″Flu″Zr(CO)$_2$ **6**	1955	1871	1913
Cp″Cp*Zr(CO)$_2$ **12**	1954	1865	1909.5
Cp″Ind*Zr(CO)$_2$ **14**	1953	1865	1909
Cp″Flu*Zr(CO)$_2$ **7**	1950	1864	1907
Cp″$_2$Zr(CO)$_2$	1945[d]	1852[d]	1898.5[d]

[a] Reference 20. [b] (a) Reference 21, (b) ref 24. [c] Reference 19. [d] Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1265.

9–11 were synthesized in a manner similar to that used for the preparations of **1** and **2**. Details pertaining to their synthesis and full characterization are included in the Supporting Information.

$$Cp''[L]ZrCl_2 \ + \ CO \ (g) \ \xrightarrow[- \ MgCl_2]{Mg \ / \ HgCl_2} \ Cp''[L]Zr(CO)_2$$

8: L = Cp*   **12**: L = Cp*
9: L = Ind   **13**: L = Ind
10: L = Ind*   **14**: L = Ind*
11: L = Flu

(2)

The dichlorides **8–11** were reduced in the presence of CO to yield the expected mixed-ligand zirconium(II) dicarbonyls Cp″Cp*Zr(CO)$_2$ (**12**),[27] Cp″IndZr(CO)$_2$ (**13**), and Cp″Ind*Zr(CO)$_2$ (**14**) (eq 2). However, all attempts to prepare the corresponding Flu derivative Cp″FluZr(CO)$_2$ failed. This result is noteworthy considering the ease with which the Flu″ or Flu* derivatives were obtained. Compounds **12–14** were all fully characterized using NMR and IR spectroscopy along with elemental analysis, and all of the data are consistent with the proposed structures (eq 2). Specifically, all of the compounds contain a peak for the CO ligands in their $^{13}C\{^1H\}$ NMR spectra and also display characteristic absorptions in their IR spectra.

The solution IR spectra of the five Zr(II) dicarbonyls (**6**, **7**, **12–14**) all display two very strong absorption bands due to the symmetric and asymmetric stretching modes of the carbonyl ligands. The energies of these stretching modes are sensitive to the amount of π back-bonding from the metal to the CO ligand, which depends on the electronic density at the metal center and will therefore vary with the donating ability of the ligand set. Table 4 contains the solution IR data obtained for compounds **6**, **7**, and **12–14**, along with values for related, previously reported compounds.

Comparison of the average ν_{CO} values listed in Table 4 allows estimation of the relative electronic influence of the various Cp-type ligands. For example, the permethylated derivative Cp* is expected to be a much stronger donor than Cp, and this is in fact reflected in a much lower average ν_{CO} value for the Cp* derivative Cp″Cp*Zr(CO)$_2$ (**12**) compared to that reported for Cp″CpZr(CO)$_2$[19] (1909.5 vs 1930.5 cm^{-1}).

As mentioned, the IR data for Ind$_2$Zr(CO)$_2$ suggest that Ind is less donating than Cp. However, a recent study of a series of bis(indenyl)zirconocene dicarbonyls showed that 1,3-disubstituted Ind ligands can either be more or less donating than similarly 1,3-disubstituted Cp analogues.[28] It therefore remains

(28) Bradley, C. A.; Flores-Torres, S.; Lobkovsky, E.; Abruña, H. D.; Chirik, P. J. *Organometallics* **2004**, *23*, 5332.

unclear as to the relative electronics of Ind ligands versus their Cp analogues. The stretching frequencies obtained for the mixed-ligand Ind derivative Cp″IndZr(CO)$_2$ (**13**) are almost identical to those reported for Cp″CpZr(CO)$_2$ and suggest that Ind and Cp are fairly similar in electronic properties. As with Cp/Cp*, permethylation of the Ind ligand is expected to drastically increase its electron-donating ability, and indeed this is reflected in the values obtained for Cp″Ind*Zr(CO)$_2$ (**14**) and **13** (1909 vs 1930 cm^{-1}). In fact, the value obtained for **14** is essentially identical to that obtained for the Cp* analogue **12**, suggesting that Ind* and Cp* have similar electronic properties.

There are no literature examples of group 4 metallocene dicarbonyls containing a Flu ligand that can be used for comparisons. However, the average v_{CO} obtained for compound **6** (1913 cm^{-1}) suggests that Flu″ is less donating than both Cp* and Ind*. On the other hand, the value obtained for **7** (1907 cm^{-1}) indicates a substantial influence for one extra methyl group at the 9-position and suggests that Flu* possesses electron-donating properties similar to, or even greater than, those of Cp* and Ind*.

Concluding Remarks. The results presented here demonstrate the viability of the highly methylated fluorenyl derivatives Flu″ and Flu* as ancillary ligands for early transition metals and represent the first examples of their use in the preparation of group 4 metallocene derivatives. The reagents LiFlu″ and LiFlu* were used to prepare well-defined mixed-ligand Zr and Hf metallocene dichlorides. The structure of the zirconocene dichloride Cp″Flu*ZrCl$_2$ (**2**) confirms the expected η^5-coordination mode and highlights the unique twisted tricyclic core of the ligand. The NMR spectra, however, indicate that the torsional conformation of the ligand is highly fluxional in solution. The ability of this class of ligand to further support metal-based chemistry is supported by the successful alkylation of both the Zr and Hf metallocene dichlorides **2** and **3** to generate dimethyl derivatives (**4** and **5**).

In an attempt to evaluate the relative electronic properties of the unique Flu″ and Flu* ligands, the dichloride derivatives **1** and **2** were reduced in the presence of carbon monoxide gas to generate the zirconocene dicarbonyl compounds **6** and **7**, which consist of the only reported group 4 metallocene dicarbonyls containing a fluorenyl derivative as a ligand. Structural studies of both Cp″Flu″Zr(CO)$_2$ and Cp″Flu*Zr(CO)$_2$ confirmed their identity and revealed that the fluorenyl ligand derivatives again adopt an η^5-coordination mode and exhibit a twisted tricyclic core. Comparison of the carbonyl stretching frequencies of **6** and **7** to those of other mixed-ligand analogues **12–14** indicates that the highly methylated fluorenyl ligands are strong donors and that Flu* possesses donating properties that are equal to, or slightly greater than, those of Ind* and Cp*. Continuing efforts are focused on further establishing the early transition metal chemistry of the Flu″ and Flu* ligands and determining how their unique structural and electronic properties might promote new chemical reactions.

Experimental Section

General Procedures. All air-sensitive manipulations were performed under an atmosphere of nitrogen using Schlenk techniques and/or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed for all air-sensitive manipulations. Removal of thiophenes from benzene and toluene was accomplished by washing each with H$_2$SO$_4$ and saturated NaHCO$_3$ followed by drying over MgSO$_4$. All dried solvents were distilled from sodium benzophenone ketyl, with the exception of benzene-d_6, which was obtained by vacuum distillation from Na/K alloy, and dichlo-

Table 5. Selected Crystal Data and Data Collection Parameters for 2, 6, and 7

		2	6	7
formula		C$_{33}$H$_{48}$Cl$_2$Si$_2$Zr	C$_{34}$H$_{46}$O$_2$Si$_2$Zr	C$_{35}$H$_{48}$O$_2$Si$_2$Zr
fw		663.01	634.11	648.13
T (K)		145(2)	150(2)	153(2)
wavelength (Å)		0.71073	0.71073	0.71073
cryst syst		monoclinic	monoclinic	monoclinic
space group		*C2/c*	*P2$_1$/n*	*P2$_1$/n*
a (Å)		15.7039(16)	11.8741(9)	13.5735(19)
b (Å)		13.2091(14)	15.1861(11)	16.060(2)
c (Å)		32.361(3)	18.4029(14)	15.706(2)
α (deg)		90	90	90
β (deg)		101.991(2)	103.3300(10)	100.134(2)
γ (deg)		90	90	90
V (Å^3)		6566.3(12)	3229.0(4)	3370.3(8)
Z		8	4	4
abs coeff (mm^{-1})		0.592	0.443	0.426
final R indices	R1	0.0524	0.0364	0.0428
	wR2	0.1254	0.0981	0.1043
R indices (all)	R1	0.0761	0.0434	0.0524
	wR2	0.1363	0.1026	0.1086

romethane-d_2, which was obtained from vacuum distillation from CaH$_2$. The compounds Cp″ZrCl$_3$,[29] Cp*HfCl$_3$,[30] Flu″H,[10] and Flu*H[10] were prepared according to literature procedures. All other chemicals, MeLi (1.6 M in ether), BuLi (1.6 M in hexane), Mg, HgCl$_2$, (Aldrich), and CO (g) (Air Gas), were purchased and used as received. Elemental analyses were performed by the microanalytical laboratory at the University of California at Berkeley. All NMR spectra were recorded at room temperature unless otherwise noted, using either a Bruker AM-400, AMX-400, or AMX-300 instrument. Infrared spectroscopy (FT-IR) were recorded using pentane solutions of the compounds in a solution cell (KBr).

Cp″Flu″ZrCl$_2$ (1). A suspension of Li(TMEDA)Flu″ (prepared by reaction of Flu″H with BuLi in toluene in the presence of TMEDA (1.2 equiv), followed by filtration; the presence of coordinated TMEDA was determined by ^{1}H NMR spectroscopy in pyridine-d_5) (0.850 g, 2.13 mmol) in toluene (10 mL) was added to a toluene solution (8 mL) of Cp″ZrCl$_3$ (0.865 g, 2.13 mmol) at room temperature. The reaction mixture turned deep red and was stirred for an additional 16 h. All volatiles were removed under vacuum, and the product was extracted using dichloromethane (20 mL). The extracts were filtered through Celite, and all volatiles were removed under vacuum to yield the product as a red solid (1.32 g, 96%). The product was further purified by crystallization from a concentrated dichloromethane solution at −35 °C. Two crystal crops were obtained (total 1.02 g, 74%). ^{1}H NMR (benzene-d_6, 300 MHz, 25 °C): δ 6.63 (t, 1H, CH), 6.10 (s, 1, CH), 5.86 (d, 2H, CH), 2.64 (s, 6H, CH_3), 2.37 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 2.13 (s, 6H, CH_3), 0.23 (s, 18H, CH_3). ^{13}C{^{1}H} NMR (benzene-d_6, 75 MHz, 25 °C): δ 131.2 (*C*), 135.2 (*C*), 134.4 (*C*), 131.1 (*C*), 130.8 (*C*), 127.6 (*C*), 127.4 (*C*H) 125.5 (*C*), 119.4 (2 *C*H), 80.8 (*C*H), 23.7 (2 *C*H$_3$), 17.7 (2 *C*H$_3$), 17.2 (2 *C*H$_3$), 16.7 (2 *C*H$_3$), 0.1 (6 *C*H$_3$). Anal. Calcd for C$_{32}$H$_{46}$Cl$_2$Si$_2$Zr: C, 59.22; H, 7.14. Found: C, 59.27; H, 7.23.

Cp″Flu*ZrCl$_2$ (2). A suspension of Li(DME)Flu* (prepared by reaction of Flu*H with BuLi in THF, followed by crystallization from DME; the presence of coordinated DME was determined by ^{1}H NMR spectroscopy in pyridine-d_5) (0.300 g, 0.77 mmol) in toluene (8 mL) was added to a toluene solution (8 mL) of Cp″ZrCl$_3$ (0.315 g, 0.77 mmol) at room temperature. The reaction mixture quickly turned dark red and was allowed to stir for 15 h. All volatiles were removed under vacuum, and the product was extracted into toluene (10 mL). The extracts were filtered through

(29) Winter, C. H.; Zhou, X.-X.; Dobbs, D. A.; Heeg, M. J. *Organometallics* **1991**, *10*, 210.

(30) Blenkers, J.; de Liefde Meijer, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *218*, 383.

Celite and concentrated under vacuum. The concentrated solution was cooled to −35 °C to yield red crystals of the product (0.342 g, 67%). ^{1}H NMR (benzene-d_6, 300 MHz, 25 °C): δ 6.61 (t, 1H, C*H*), 5.71 (d, 2H, C*H*), 3.05 (s, 3H, C*H*$_3$), 2.60 (s, 6H, C*H*$_3$), 2.52 (s, 6H, C*H*$_3$), 2.22 (s, 6H, C*H*$_3$), 2.14 (s, 6H, C*H*$_3$), 0.23 (s, 18H, C*H*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 75 MHz, 25 °C): δ 137.8 (*C*), 136.3 (*C*), 134.3 (*C*), 130.0 (*C*), 129.7 (*C*), 129.0 (*C*), 128.3 (*C*H) (determined via DEPT-135), 124,5 (*C*), 120.7 (*C*H), 95.0 (*C*), 24.0 (2 *C*H$_3$), 19.9 (*C*H$_3$), 19.2 (2 *C*H$_3$), 17.2 (2 *C*H$_3$), 17.0 (2 *C*H$_3$), 0.27 (6 *C*H$_3$). Anal. Calcd for C$_{33}$H$_{48}$Cl$_2$Si$_2$Zr: C, 59.78; H, 7.30. Found: C, 60.17; H, 7.55.

Cp*Flu*HfCl₂ (3). A suspension of Li(DME)Flu* (0.220 g, 0.57 mmol) in benzene (10 mL) was added to a benzene solution (15 mL) of Cp*HfCl₃ (0.238 g, 0.57 mmol). The reaction mixture was stirred for 4 h at room temperature, and then all volatiles were removed under vacuum. The compound was extracted by washing the solid residue with toluene (20 mL) and dichloromethane (30 mL). The extracts were combined and then filtered through Celite. All volatiles were removed under vacuum. The crude product was purified by crystallization from a concentrated toluene solution at −35 °C to give red-orange crystals (0.243 g, 63%). ^{1}H NMR (benzene-d_6, 400 MHz, 25 °C): δ 2.92 (s, 3H, C*H*$_3$), 2.53 (s, 6H, C*H*$_3$), 2.44 (s, 6H, C*H*$_3$), 2.15 (s, 6H, C*H*$_3$), 2.13 (s, 6H, C*H*$_3$), 1.70 (s, 15H, C*H*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 100 MHz, 25 °C): δ 135.8 (*C*), 133.3 (*C*), 132.1 (*C*), 128.9 (*C*), 128.7 (*C*), 122.8 (5 *C*), 119.1 (*C*), 93.9 (*C*), 23.6 (2 *C*H$_3$), 19.3 (2 *C*H$_3$), 18.4 (1 *C*H$_3$), 17.0 (2 *C*H$_3$), 16.8 (2 *C*H$_3$), 11.5 (5 *C*H$_3$). Anal. Calcd for C$_{32}$H$_{42}$Cl$_2$Hf: C, 56.85; H, 6.26. Found: C, 57.04; H, 6.41.

Cp″Flu*ZrMe₂ (4). The dichloride Cp″Flu*ZrCl₂ (0.150 g, 0.23 mmol) was dissolved in a 1:1 mixture of toluene and ether (total volume 10 mL). To this solution was added MeLi (0.30 mL, 0.48 mmol). The reaction mixture turned to a yellow color and was stirred for 12 h at room temperature. All volatiles were removed under vacuum, and the product was extracted into hexanes (2 × 5 mL). The extracts were combined and filtered through Celite. All volatiles were removed under vacuum, the product was dissolved in pentane (4 mL), and the resulting solution was cooled to −35 °C to give orange crystals (0.97 g, 69%). ^{1}H NMR (benzene-d_6, 300 MHz, 25 °C): δ 6.61 (t, 1H, C*H*), 5.28 (d, 2H, C*H*), 2.94 (s, 3H, C*H*$_3$), 2.53 (s, 6H, C*H*$_3$), 2.50 (s, 6H, C*H*$_3$), 2.23 (s, 6H, C*H*$_3$), 2.16 (s, 6H, C*H*$_3$), 0.19 (s, 18H, C*H*$_3$), −0.75 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 75 MHz, 25 °C): δ 134.2, 131.2, 129.1, 128.3, 127.9, 127.4, 126.4, 120.6, 117.1, 91.4, 36.8 (Zr-*C*H$_3$), 24.4 (2 *C*H$_3$), 19.4 (2 *C*H$_3$), 18.5 (1 *C*H$_3$), 17.1 (*C*H$_3$), 16.9 (2 *C*H$_3$) 0.5 (6 *C*H$_3$). Anal. Calcd for C$_{35}$H$_{54}$Si$_2$Zr: C, 67.56; H, 8.75. Found: C, 67.66; H, 8.79.

Cp*Flu*HfMe₂ (5). The dichloride Cp*Flu*HfCl₂ (0.340 g, 0.50 mmol) was dissolved in a mixture of toluene (20 mL) and THF (4 mL). To this solution was added an ether solution of MeLi (0.66 mL, 1.05 mmol). The reaction mixture slowly turned from orange to yellow and was stirred for a total of 20 h at room temperature. All volatiles were removed under vacuum, and the product was extracted into toluene (15 mL). The extracts were filtered through Celite and then concentrated under vacuum. The saturated solution was cooled to −35 °C to yield the product as orange crystals (0.183 g, 57%). ^{1}H NMR (benzene-d_6, 300 MHz, 25 °C): δ 2.91 (s, 3H, C*H*$_3$), 2.40 (s, 6H, C*H*$_3$), 2.35 (s, 6H, C*H*$_3$), 2.15 (s, 6H, C*H*$_3$), 2.14 (s, 6H, C*H*$_3$), 1.54 (s, 15H, C*H*$_3$), −0.88 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 75 MHz, 25 °C): δ 134.1 (*C*), 129.7 (*C*), 129.5 (*C*), 128.7 (*C*), 127.1 (*C*), 117.2 (Cp*-*C*), 115.9 (*C*), 98.4 (*C*), 44.7 (Hf-*C*H$_3$), 23.8 (2 *C*H$_3$), 19.2 (2 *C*H$_3$), 17.0 (2 *C*H$_3$), 16.9 (1 *C*H$_3$), 16.7 (2 *C*H$_3$), 10.9 (5 *C*H$_3$). Anal. Calcd for C$_{34}$H$_{48}$Hf: C, 64.29; H, 7.62. Found: C, 64.51; H, 7.89.

Cp″Flu″Zr(CO)₂ (6). A Fischer-Porter bottle charged with Cp″Flu″ZrCl₂ (0.342 g, 0.53 mmol), Mg (0.063 g, 2.6 mmol), and HgCl₂ (0.143 g, 0.53 mmol) was immersed in a cold bath at −78 °C. The flask was evacuated and refilled with CO gas. Under a slight counterflow of CO gas, THF solvent (20 mL) was slowly added via syringe through the outlet valve. The outlet valve was then closed, and the flask was pressurized to 60 psi of CO gas. The reaction mixture was allowed to warm to room temperature over the course of 2 h and stirred for an additional 16 h. All volatiles were removed under vacuum. The product was extracted into hexanes (10 mL). The extracts were filtered through Celite and concentrated under vacuum (1–2 mL). The solution was cooled to −35 °C to yield green crystals of the product (0.255 g, 76%). ^{1}H NMR (benzene-d_6, 400 MHz, 25 °C): δ 5.47 (s, 1H, C*H*), 5.19 (d, 2H, C*H*), 4.26 (t, 1H, C*H*), 2.52 (s, 6H, C*H*$_3$), 2.30 (s, 6H, C*H*$_3$), 2.11 (s, 6H, C*H*$_3$), 2.10 (s, 6H, C*H*$_3$), −0.05 (s, 18H, C*H*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 100 MHz, 25 °C): δ 273.1 (*C*O), 131.1 (*C*), 130.4 (*C*), 127.9 (*C*), 125.7 (*C*), 121.6 (*C*), 111.2 (*C*H), 111.1 (*C*), 105.2 (*C*), 99.2 (*C*H), 71.8 (*C*H), 24.1 (2 *C*H$_3$), 17.3 (2 *C*H$_3$), 16.53 (2 *C*H$_3$), 16.46 (2 *C*H$_3$), −0.04 (6 *C*H$_3$). Anal. Calcd for C$_{34}$H$_{46}$O$_2$Si$_2$Zr: C, 64.40; H, 7.31. Found: C, 64.66; H, 7.33.

Cp″Flu*Zr(CO)₂ (7). This complex was synthesized in a manner identical to that for compound **6**. A Fischer-Porter bottle charged with Cp″Flu*ZrCl₂ (0.307 g, 0.46 mmol), Mg (0.063 g, 2.3 mmol), and HgCl₂ (0.125 g, 0.46 mmol) was immersed in a cold bath at −78 °C. The flask was evacuated and refilled with CO gas. Under a slight counterflow of CO gas, THF solvent (20 mL) was slowly added via syringe through the outlet valve. The outlet valve was then closed and the flask was pressurized to 60 psi of CO gas. The reaction mixture was allowed to warm to room temperature over the course of 2 h and stirred for an additional 16 h. All volatiles were removed under vacuum. The product was extracted into hexanes (10 mL). The extracts were filtered through Celite and concentrated under vacuum (1 mL). The solution was cooled to −35 °C to yield green crystals of the product (0.189 g, 63%). ^{1}H NMR (benzene-d_6, 400 MHz, 25 °C): δ 5.10 (d, 2H, C*H*), 4.25 (t, 1H, C*H*), 2.94 (s, 3H, C*H*$_3$), 2.58 (s, 6H, C*H*$_3$), 2.44 (s, 6H, C*H*$_3$), 2.12 (s, 6H, C*H*$_3$), 2.10 (s, 6H, C*H*$_3$), −0.01 (s, 18H, C*H*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 100 MHz, 25 °C): δ 274.5 (*C*O), 131.7 (*C*), 130.8 (*C*), 129.0 (*C*), 125.5 (*C*), 121.5 (*C*), 111.4 (*C*H), 111.2 (*C*), 105.9 (*C*), 99.5 (*C*H), 86.5 (*C*), 24.6 (2 *C*H$_3$), 18.8 (2 *C*H$_3$), 18.1 (*C*H$_3$), 17.3 (2 *C*H$_3$), 16.8 (2 *C*H$_3$), 0.01 (6 *C*H$_3$). Anal. Calcd for C$_{35}$H$_{48}$O$_2$Si$_2$Zr: C, 64.86; H, 7.46. Found: C, 64.98; H, 7.48.

Cp″Cp*Zr(CO)₂ (12). A 150 mL Teflon-stoppered Schlenk flask was charged with Cp″Cp*ZrCl₂ (0.300 g, 0.59 mmol), Mg (0.071 g, 3.0 mmol) and HgCl₂ (0.160 g, 0.59 mmol). The flask was then evacuated and THF (ca. 20 mL) was vacuum transferred into the flask at −78 °C. The flask was backfilled with CO gas and closed. The cold bath was then removed, and the reaction was allowed to warm to room temperature and was then stirred for 14 h. All volatiles were then removed under vacuum. The product was extracted into hexanes (10 mL). The extracts were filtered through Celite, and then all volatiles were removed under vacuum to yield the product (0.262 g, 90%). The product can be further purified by crystallization from a concentrated hexanes solution at −35 °C. ^{1}H NMR (benzene-d_6, 400 MHz, 25 °C): δ 4.97 (d, 2H, C*H*), 4.78 (t, 1H, C*H*), 1.74 (s, 15H, C*H*$_3$), 0.25 (s, 18H, C*H*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 100 MHz, 25 °C): δ 271.0 (2 *C*O), 112.2 (*C*H), 107.9 (*C*H), 106.3 (*C*), 98.8 (*C*), 11.7 (5 *C*H$_3$), 0.6 (6 *C*H$_3$). Anal. Calcd for C$_{23}$H$_{36}$O$_2$Si$_2$Zr: C, 56.16; H, 7.38. Found: C, 56.11; H, 7.49.

Cp″IndZr(CO)₂ (13). This complex was synthesized in a manner similar to that for compound **6**. A Fischer-Porter bottle charged with Mg (0.074 g, 3.1 mmol), and HgCl₂ (0.167 g, 0.62 mmol) was immersed in a cold bath at −78 °C. The flask was evacuated and refilled with CO gas. Under a slight counterflow of CO gas, a THF solution (20 mL) of Cp″IndZrCl₂ (0.300 g, 0.62 mmol) was added via syringe through the outlet valve. The outlet valve was then closed, and the flask was pressurized to 60 psi of CO gas. The reaction mixture was stirred for 30 min, then the cold bath was removed and the reaction was allowed to slowly warm to room temperature and stirred for an additional 1 h. All volatiles were

removed under vacuum. The product was extracted into hexanes (10 mL). The extracts were filtered through Celite, and all volatiles were removed under vacuum. The product was crystallized from a pentane solution (2 mL) at −35 °C to yield green crystals of the product (0.098 g, 34%). ^{1}H NMR (benzene-d_6, 400 MHz, 25 °C): δ 7.07 (dd, 2H, CH), 6.75 (dd, 2H, CH), 5.54 (t, 1H, CH), 5.24 (d, 2H, CH), 4.99 (t, 1H, CH), 4.95 (d, 2H, CH), 0.08 (s, 18H, CH_3). ^{13}C{^{1}H} NMR (benzene-d_6, 100 MHz, 25 °C): δ 264.3, 124.7 (2 CH), 123.4 (2 CH), 116.7 (C), 106.9 (CH), 105.0 (CH), 95.0 (CH), 83.6 (2 CH and C (determined by HMBC experiments)), 0.38 (6 CH_3). Anal. Calcd for $C_{22}H_{28}O_2Si_2Zr$: C, 56.00; H, 5.98. Found: C, 55.88; H, 5.83.

Cp″Ind*Zr(CO)$_2$ (14). This complex was synthesized in a manner similar to that for compound **12**. A 250 mL Teflon-stoppered Schlenk flask was charged with Cp″Ind*ZrCl$_2$ (0.120 g, 0.21 mmol), Mg (0.025 g, 1.0 mmol), and HgCl$_2$ (0.056 g, 0.21 mmol). The flask was then evacuated, and THF (ca. 25 mL) was vacuum transferred into the flask at −78 °C. The flask was backfilled with CO gas and closed. The cold bath was then removed, and the reaction was allowed to warm to room temperature and was then stirred for 14 h. All volatiles were then removed under vacuum. The product was extracted into toluene (10 mL). The extracts were filtered through Celite, and all volatiles were removed to yield the product as a green solid (0.092 g). The product was further purified by crystallization from a concentrated toluene solution at −35 °C (0.089 g, 76%). ^{1}H NMR (benzene-d_6, 400 MHz, 25 °C): δ 5.03 (d, 2H, CH), 4.51 (t, 1H, CH), 2.39 (s, 6H, CH_3), 2.23 (s, 6H, CH_3), 2.03 (s, 6H, CH_3), 1.94 (s, 3H, CH_3), 0.12 (s, 18H, CH_3). ^{13}C{^{1}H} NMR (benzene-d_6, 100 MHz, 25 °C): δ 273.0 (2 CO), 129.6 (C), 127.3 (C), 116.7 (C), 115.2 (C), 112.9 (CH), 106.2 (CH), 98.0 (C), 96.0 (C), 17.3 (2 CH_3), 16.5 (2 CH_3), 14.9 (2 CH_3), 12.4 (CH_3), 0.3 (6 CH_3). Anal. Calcd for $C_{29}H_{42}O_2Si_2Zr$: C, 61.10; H, 7.43. Found: C, 61.28; H, 7.47.

Crystallographic Structure Determinations. Crystallographic data for all compounds are summarized in Table 5. All crystals were mounted on a glass fiber using Paratone-N oil. The Laue symmetry of each was photographically determined, and the space groups were assigned unambiguously for **2**, **6**, and **7** from systematic absences. All structures were solved by direct methods, refined with anisotropic thermal parameters, and include idealized hydrogen atom contributions. All computations were performed using SHELXTL software (version 5.1, G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

Supporting Information Available: Crystallographic data (tables and CIF files) for **2**, **6**, and **7** are available free of charge via the Internet at http://pubs.acs.org.

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