Acetone and Acetophenone Adducts of the Zwitterionic Zirconocene Cp*[η^5-C$_5$Me$_4$CH$_2$B(C$_6$F$_5$)$_3$]ZrC$_6$H$_5$

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The recently reported zwitterionic complex Cp*[η^5-C$_5$Me$_4$CH$_2$B(C$_6$F$_5$)$_3$]ZrC$_6$H$_5$, **1**, reacts rapidly with 1 equiv of acetone or acetophenone to form the adducts Cp*[η^5-C$_5$Me$_4$CH$_2$B(C$_6$F$_5$)$_3$]Zr(C$_6$H$_5$)[O=C(CH$_3$)R] (R = CH$_3$, **2a**; C$_6$H$_5$, **2b**) in ~85% yield. Spectroscopic evidence in favor of this assignment is presented; the adduct nature of the complexes was also confirmed in each case via an X-ray structural analysis. The ketone ligands are bound in an η^1 end-on fashion (the Zr−O=C angles are near linear at 174.2° and 166.1° for **2a** and **2b**, respectively), allowing for a π-component to the Zr−O bonding. Unlike other fleetingly observed ketone adducts of nonzwitterionic cationic metallocenes, the ketone ligands in compounds **2** do not undergo insertion into the Zr−C bond neither upon thermolysis nor in the presence of excess ketone.

Introduction

The body of knowledge concerning the chemistry of cationic group 4 metallocenes[1] has grown rapidly in the last decade, primarily due to the role these complexes play in the homogeneous polymerization of olefins.[2] Efforts have also been directed toward finding use for this family of compounds in other arenas, such as other types of polymerizations[3] and synthetic organic chemistry.[4] In both of these areas, the behavior of cationic metallocenes in the presence of carbonyl functions has been of interest. Since the cations are strong Lewis acids, adduct formation with a carbonyl group is facile (eq 1). When the X ligand in the metallocene wedge is
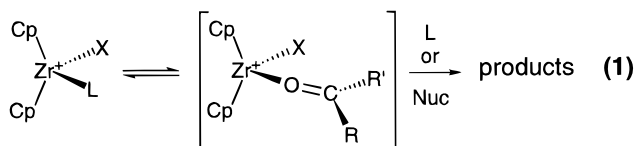
L = labile Lewis base

an alkyl group, the adducts are unstable toward an insertion reaction which yields a cationic alkoxide complex, usually stabilized by a second equivalent of carbonyl compound, L in eq 1.[5] On the other hand, when X is a heteroatom-based donor (such as an alkoxide), the metallocene behaves simply as a strong

Lewis acid capable of activating carbonyl functions through adduct formation. Collins *et al.* have shown that such adducts are key participants in Diels−Alder additions,[6] Mukaiyama aldol reactions,[7] and the group transfer polymerization of methacrylates.[8] For both X = R and OR', the metallocene/carbonyl compound adducts have been observed spectroscopically but not isolated.

Recently, we prepared a family of zwitterionic zirconocenes via reaction of "tuck-in" complexes with the highly electrophilic boranes XB(C$_6$F$_5$)$_2$ (X = H,[9] C$_6$F$_5$[10]) and examined their effectiveness as olefin polymerization catalysts.[11] Apart from the olefin chemistry of these zwitterions, we observed that reaction of Cp*[η^5-C$_5$Me$_4$CH$_2$B(C$_6$F$_5$)$_3$]ZrC$_6$H$_5$, derived from the tuck-in phenyl complex Cp*(η^5-η^1-C$_5$Me$_4$CH$_2$)ZrC$_6$H$_5$[12] and B(C$_6$F$_5$)$_3$, with simple ketones CH$_3$C(O)R (R = CH$_3$, C$_6$H$_5$) yielded stable 1:1 adducts resistant to insertion. Herein, we report the details concerning the preparation of these adducts and their full characterization, including their crystal structures.

Experimental Section

General Considerations. Routine procedures have been described in detail elsewhere.[11] Acetone and acetophenone

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were dried by distillation from activated molecular sieves or calcium hydride. Isotopically labeled ketones employed herein were purchased from Cambridge Isotopes and dried in a similar fashion to unlabeled reagents prior to use. $B(C_6F_5)_3$ was purchased from Boulder Scientific and dried by treatment of a toluene suspension with excess BCl_3 followed by sublimation.

Synthesis of Cp*[η^5-C$_5$Me$_4$CH$_2$B(C$_6$F$_5$)$_3$]Zr(C$_6$H$_5$)[O=C-(CH$_3$)$_2$], 2a. Benzene (15 mL) was condensed into an evacuated flask containing Cp*[η^5-C$_5$Me$_4$CH$_2$B(C$_6$F$_5$)$_3$]ZrC$_6$H$_5$, **1**, (108 mg, 0.114 mmol) at -78 °C. Dry acetone (8.3 μL, 0.113 mmol) was added via syringe; an immediate orange to yellow color change was observed. The reaction was stirred for 1 h at -78 °C and warmed to room temperature. Benzene was removed *in vacuo*, and the residue was recrystallized from benzene (2 mL). The yellow crystals were isolated by filtration and washed once with a portion of cold hexanes. Yield of **2a**: 96 mg, 0.095 mmol, 84%. Once crystallized out of solution, compound **2a** was found to be only sparingly soluble in benzene and toluene. Anal. Calcd for $C_{47}H_{40}F_{15}OBZr$: C, 55.97; H, 4.00. Found: C, 56.37; H, 2.35.

Synthesis of Cp*[η^5-C$_5$Me$_4$CH$_2$B(C$_6$F$_5$)$_3$]Zr(C$_6$H$_5$)[O=C-(CH$_3$)(C$_6$H$_5$)], 2b. An analogous procedure to that employed above for **2a**, using toluene (15 mL), **1** (104 mg, 0.110 mmol), and dry acetophenone (13.6 μL, 0.117 mmol), was employed. Yield of orange **2b**: 100 mg, 0.093 mmol, 85%. Once crystallized out of solution, compound **2b** was found to be only sparingly soluble in benzene and toluene. Anal. Calcd for $C_{52}H_{42}F_{15}OBZr$: C, 58.38; H, 3.96. Found: C, 58.69; H, 2.81.

Reaction of 2a with Acetone. Acetone (0.9 μL, 1.26 $\times$ 10^{-5} mol) was injected into an NMR tube containing **1** (12 mg, 1.26 $\times$ 10^{-5} mol) in C_6D_6. After the acetone and **1** were mixed, a color change from orange to yellow was observed and the ^{1}H NMR spectrum showed the clean formation of **2a**. A second equivalent of acetone was injected via syringe and resulted in an immediate precipitation of adduct **2a**. The ^{1}H NMR spectrum was recorded and showed only the resonances for free acetone and **2a**; no evidence of insertion of acetone into the Zr–C$_6$H$_5$ bond was observed. The sample was heated at 50 °C for 0.5 h without a significant change; when heated at 80 °C, decomposition to a variety of products ensued.

Reaction of 2a with Acetone-d_6. An NMR sample of **2a** was generated as described above. Acetone-d_6 (1 equiv) was injected via syringe, and the ^{1}H NMR spectrum was recorded. The spectrum indicated the presence of free acetone, while the signal for coordinated acetone was diminished in intensity accordingly (ratio of coordinated:free $\approx$ 1:1).

Reaction of 2b with Acetone. Acetophenone (2.3 μL, 2.0 $\times$ 10^{-5} mol) was injected into an NMR tube containing **1** (19 mg, 2 $\times$ 10^{-5} mol) in C_6D_6. After the acetophenone and **1** were mixed, a color change from orange to red was observed and the ^{1}H NMR spectrum showed the clean formation of **2b**. Acetone (1.5 μL, 2.0 $\times$ 10^{-5} mol) was added to this sample via syringe, inducing a color change from red to yellow. Formation of **2a** and free acetophenone was confirmed by ^{1}H NMR spectroscopy. There is no evidence of insertion of acetone or acetophenone into the Zr–C$_6$H$_5$ bond. The sample was heated at 50 °C for 0.5 h without a significant change; when heated at 80 °C, decomposition to a variety of products ensued.

X-ray Crystallography. General Considerations. The structures were solved from data collected on the Siemens SMART system on crystals loaded into sealed glass capillaries; the crystal data is summarized in Table 1. In each case, unit-cell parameters were calculated from reflections obtained from 60 data frames collected at different sections of the Ewald sphere. The structures were solved by direct methods, completed by subsequent Fourier syntheses, and refined with full-matrix least-squares methods. All scattering factors and anomalous dispersion coefficients are contained in the SHELX-TL 5.03 program library. **2a**: Crystals were obtained from benzene solutions of *in situ* generated **2a**. The diffraction data

Table 1. Summary of Data Collection and Structure Refinement Details for 2a and 2b

	2a	2b
formula	$C_{50}H_{43}BF_{15}OZr$	$C_{64}H_{54}BF_{15}OZr$
fw	1046.87	1226.10
cryst syst	orthorhombic	triclinic
a, Å	18.1795(4)	10.9823(2)
b, Å	26.1871(4)	14.4223(2)
c, Å	19.2613(4)	20.7910(3)
α, deg	90	98.523(1)
β, deg	90	102.039(1)
γ, deg	90	100.744(1)
V, Å^3	9169.7(3)	3103.64(8)
space group	*Aba*2	*P$\bar{1}$*
Z	8	2
$F(000)$	4248	1252
d_{calc}, mg m^{-3}	1.517	1.312
μ, mm^{-1}	0.339	0.261
R1	0.0762	0.0804
wR2	0.2479	0.204
gof of F^2	1.135	1.495

and unit-cell parameters were consistent with the space groups *Aba2* and *Acam* (*Cmca*). The absence of a molecular inversion point, mirror plane, or a 2-fold axis and $Z = 8$ strongly suggested the acentric option, which yielded chemically reasonable and computationally stable results. A trial application of a semi-empirical absorption correction based on redundant data at varying effective azimuthal angles yielded T_{max}/T_{min} at unity and was ignored. A molecule of cocrystallized benzene solvent was located disordered at a 2-fold axis with a 50% site occupancy distribution. Non-hydrogen atoms were refined with anisotropic displacement coefficients; hydrogen atoms were treated as idealized contributions. **2b**: Crystals were grown by slow diffusion of hexanes into a benzene solution of *in situ* generated **2b**. The diffraction data and unit cell parameters indicated no symmetry higher than triclinic was present. The E stastistics strongly suggested the centric option, and solution in $P\bar{1}$ yielded chemically reasonable and computationally stable results. A semi-empirical absorption correction based on redundant data at varying effective azimuthal angles was applied to the data set. Two molecules of cocrystallized benzene were located in the asymmetric unit. Non-hydrogen and hydrogen atoms were treated as above.
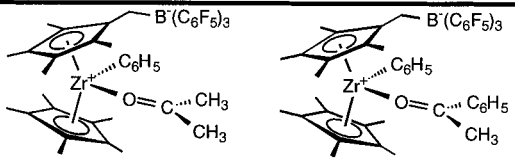
Results and Discussion

When benzene solutions of zwitterion **1** were treated with 1 equiv of acetone or acetophenone, an immediate orange to yellow or red color change was observed, signaling the formation of the adducts Cp*[η^5-C$_5$Me$_4$CH$_2$B-(C$_6$F$_5$)$_3$]Zr(C$_6$H$_5$)[O=C(CH$_3$)R] (R = CH$_3$, **2a**; C$_6$H$_5$, **2b**), eq 2. In more concentrated solutions, the ketone ad-

(2)

1   R = CH$_3$, **2a**
           R = C$_6$H$_5$, **2b**
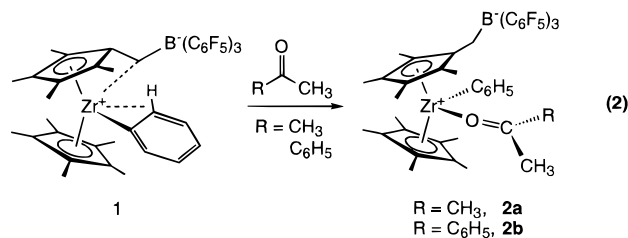
ducts crystallized out of the medium with one (**2a**) or two (**2b**) molecules of benzene; the products were isolated in 80–85% yield. Spectroscopic data for the new compounds is presented in Table 2.

We have observed phenyl zwitterion **1** to react rapidly with PMe$_3$ to regenerate the neutral tuck-in phenyl complex with concomitant formation of Me$_3$P·

Table 2. NMR and IR Spectral Data for Zwitterionic Ketone Adducts 2a and 2b[a]

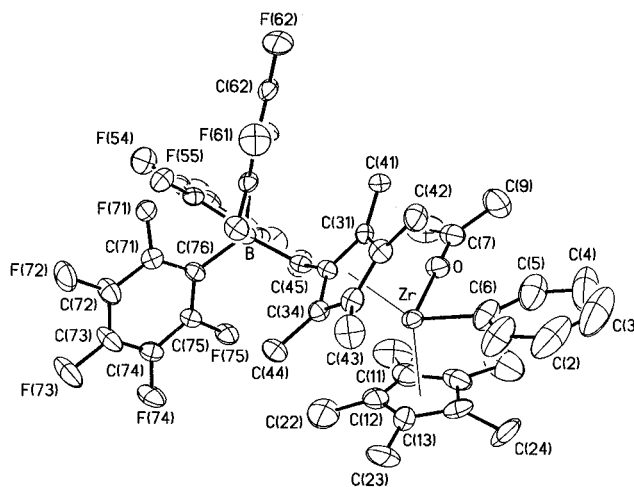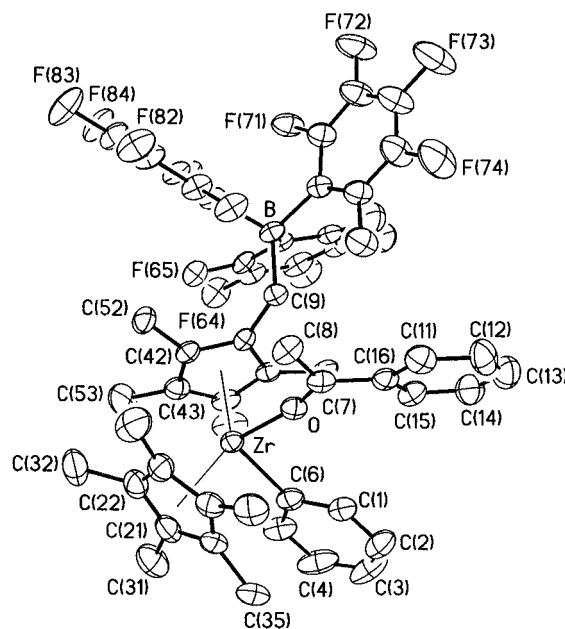| Data	2a		2b[b]	
¹H	6.4, 6.6 (d, 2H)	o-C₆H₅	7.59 (d, 2H)	o-C₆H₅CO
	7.1 (m, 3H)	m, p-C₆H₅	7.07 (m, 6H)	m, p-C₆H₅
	2.2, 2.3 (d, 2H)	CH₂B	6.81, 6.68 (d, 2H)	o-C₆H₅
	1.88 (s, 6H)	O=C(CH₃)₂	2.63, 2.39 (d,2H)	CH₂B
	1.91, 1.75[c]	O=C(CH₃)₂	2.49 (br, 3H)	O=C(CH₃)
	1.57, 1.34 (s, 6H)	C₅(CH₃)₄	1.62, 1.40 (s, 6H)	C₅(CH₃)₄
	1.30, 0.69 (s, 6H)	C₅(CH₃)₄	1.36, 0.90 (s, 6H)	C₅(CH₃)₄
	1.23 (s, 15H)	C₅(CH₃)₅	1.30 (s, 15H)	C₅(CH₃)₅
¹³C	---[d]	O=C(CH₃)₂	220.4	O=C
	136.2, 129.9	o-C₆H₅	136.4, 131.5	o-C₆H₅
	127.9[e]	m,p-C₆H₅	131.3	o-C₆H₅CO
	32.6	O=C(CH₃)₂	138.9, 129.5,	m,p-C₆H₅
	23.8	BCH₂	128.8, 127.7,	m,p-C₆H₅
	12.5, 12.0,	C₅(CH₃)₄	126.0	m,p-C₆H₅
	11.1, 11.0	C₅(CH₃)₄	31.3	O=C(CH₃)
	11.4	C₅(CH₃)₅	24.2	BCH₂
			12.9, 12.2	C₅(CH₃)₄
			11.4, 10.9	C₅(CH₃)₄
			11.6	C₅(CH₃)₅
¹⁹F	-129.2 (br)	o-F	-129.8 (br)	o-F
	-162.0 (br)	p-F	-162.2 (br)	p-F
	-166.3 (br)	m-F	-166.4 (br)	m-F
¹¹B	-11.67		-11.70	
IR	2978, 2917, 2869		2902	
	1660 (vCO)		1639, 1513, 1457, 1286, 1082,	
	1636, 1514, 1457, 1382, 1273,		977	
	1083, 979			

[a] All NMR spectra were recorded in C₆D₆; IR spectra were obtained in KBr pellets. [b] Room temperature spectra reflect the average spectra of the **2b**-endo and **2b**-exo isomers. [c] Chemical shifts at 216 K; other peaks are essentially unchanged in the low-temperature spectra. [d] Not detected. [e] Other resonances are obscured by the solvent peak in the 2-D spectra.

Figure 1. ORTEP diagram for acetone adduct **2a**.

Figure 2. ORTEP diagram for acetophenone adduct **2b**.

B(C₆F₅)₃.[11] This reaction path was, thus, also a possibility for reactions of **1** with ketones; however, we have previously prepared the acetophenone adduct of B(C₆F₅)₃[13] and it was not observed in this reaction. Furthermore, the ¹¹B chemical shifts are characteristic of anionic borate centers,[14] witnessing that complexes **2** remain zwitterionic. Other data are consistent with ketone adduct formation as opposed to insertion to form cationic alkoxide derivatives. In the ¹H NMR spectra, signals for protons of the same connectivity in the borate-substituted Cp* ring are inequivalent, indicative of two different ligands in the metallocene wedge. Although similar patterns might be obtained if an insertion product was stabilized by a strong chelating interaction between the pendant borate counterion and the zirconium center, ¹³C and IR spectroscopic data further support an uninserted adduct product structure. For complex **2a**, a strong band in the IR at 1660 cm⁻¹ was observed for the C=O stretch of the coordinated acetone, shifted 40 cm⁻¹ to lower energy compared to free acetone.[15] The analogous band in the IR spectrum of **2b** was obscured by absorbances for the Cp* ligands;

however, the ¹³C NMR spectrum of **2b** prepared from **1** and C₆H₅¹³C(O)CH₃ showed a peak at 220.4 ppm for the carbonyl carbon and proved conclusively that **2b** was also an adduct. This peak is shifted downfield by 23.6 ppm from that of free acetophenone (196.8 ppm), deshielded as a consequence of coordination to the Lewis acid.

The tendency of these compounds to crystallize out of benzene allowed us to characterize them crystallographically. ORTEP drawings of the two molecules are shown in Figures 1 and 2, while selected bond lengths and angles are given in Tables 3 and 4, respectively. The structures share similar gross features. Coordination of the ketones supplant the phenyl agostic interaction and the donation from the borate carbon to zirconium which stabilize phenyl zwitterion **1**,[11] and the distortions in the phenyl group and the metallated Cp* ring these interactions engender are not observed in adducts **2**. The borate moiety is, thus, completely swung away from the metal center toward the side of the equatorial bonding region in compounds **2a** and **2b**, and no close contacts between zirconium and any atoms of the CH₂B(C₆F₅)₃ unit exist.

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Table 3. Selected Bond Lengths (Å) for 2a and 2b

2a		2b	
Zr–O	2.132(5)	Zr–O	2.134(5)
Zr–C(6)	2.231(11)	Zr–C(6)	2.288(7)
Zr–C(35)	2.499(7)	Zr–C(41)	2.593(6)
Zr–C(31)	2.518(7)	Zr–C(42)	2.496(6)
Zr–C(34)	2.519(8)	Zr–C(43)	2.532(7)
Zr–C(33)	2.554(8)	Zr–C(44)	2.570(7)
Zr–C(32)	2.571(7)	Zr–C(45)	2.577(6)
B–C(45)	1.658(11)	B–C(9)	1.674(9)
O–C(7)	1.241(10)	O–C(7)	1.252(7)
C(7)–C(8)	1.461(14)	C(7)–C(16)	1.466(9)
C(7)–C(9)	1.494(14)	C(7)–C(8)	1.490(9)
C(31)–C(32)	1.419(10)	C(41)–C(42)	1.412(8)
C(31)–C(35)	1.421(10)	C(41)–C(45)	1.423(8)
C(32)–C(33)	1.405(11)	C(42)–C(43)	1.435(9)
C(33)–C(34)	1.420(10)	C(43)–C(44)	1.415(10)
C(34)–C(35)	1.429(9)	C(44)–C(45)	1.418(9)
C(31)–C(41)	1.501(10)	C(42)–C(52)	1.503(9)
C(32)–C(42)	1.483(11)	C(43)–C(53)	1.526(10)
C(33)–C(43)	1.501(11)	C(44)–C(54)	1.520(9)
C(34)–C(44)	1.485(10)	C(45)–C(55)	1.492(9)
C(35)–C(45)	1.510(9)	C(41)–C(9)	1.500(8)
Zr–Cp*$_{cent}$	2.250	Zr–Cp*$_{cent}$	2.262
Zr–Cp*B$_{cent}$	2.227	Zr–Cp*B$_{cent}$	2.250

Table 4. Selected Bond Angles (deg) for 2a and 2b

2a		2b	
O–Zr–C(6)	97.2(4)	O–Zr–C(6)	97.4(2)
C(7)–O–Zr	174.2(6)	C(7)–O–Zr	166.1(4)
C(1)–C(6)–C(5)	110.6(12)	C(1)–C(6)–C(5)	115.1(7)
C(5)–C(6)–Zr	118.9(9)	C(1)–C(6)–Zr	114.8(5)
C(1)–C(6)–Zr	130.3(10)	C(5)–C(6)–Zr	129.8(6)
O–C(7)–C(8)	119.2(9)	O–C(7)–C(16)	119.0(6)
O–C(7)–C(9)	120.5(10)	O–C(7)–C(8)	119.8(6)
C(8)–C(7)–C(9)	120.3(10)	C(16)–C(7)–C(8)	121.2(6)
C(32)–C(31)–C(35)	108.9(6)	C(42)–C(41)–C(45)	108.9(5)
C(33)–C(32)–C(31)	107.6(7)	C(41)–C(42)–C(43)	106.9(5)
C(32)–C(33)–C(34)	108.7(6)	C(42)–C(43)–C(44)	108.2(6)
C(33)–C(34)–C(35)	108.0(6)	C(45)–C(44)–C(43)	108.3(5)
C(31)–C(35)–C(34)	106.8(6)	C(44)–C(45)–C(41)	107.4(5)
C(32)–C(31)–C(41)	124.3(7)	C(42)–C(41)–C(9)	127.3(5)
C(35)–C(31)–C(41)	126.2(7)	C(45)–C(41)–C(9)	123.6(5)
C(33)–C(32)–C(42)	127.4(8)	C(41)–C(42)–C(52)	125.5(6)
C(31)–C(32)–C(42)	124.3(8)	C(43)–C(42)–C(52)	125.7(6)
C(32)–C(33)–C(43)	125.4(8)	C(44)–C(43)–C(53)	123.7(7)
C(34)–C(33)–C(43)	124.8(8)	C(42)–C(43)–C(53)	126.3(7)
C(33)–C(34)–C(44)	124.4(7)	C(45)–C(44)–C(54)	125.5(7)
C(35)–C(34)–C(44)	125.9(7)	C(43)–C(44)–C(54)	124.5(7)
C(31)–C(35)–C(45)	126.3(6)	C(44)–C(45)–C(55)	124.0(6)
C(34)–C(35)–C(45)	126.8(6)	C(41)–C(45)–C(55)	128.2(6)
C(35)–C(45)–B	119.3(5)	C(41)–C(9)–B	116.4(5)
		C(15)–C(16)–C(11)	118.9(7)
		C(15)–C(16)–C(7)	121.1(6)
		C(11)–C(16)–C(7)	120.0(6)
Cp$_{cent}$–Zr–Cp$_{cent}$	137.3	Cp$_{cent}$–Zr–Cp$_{cent}$	139.0

The phenyl ligands are twisted out of the plane bisecting the two Cp* donors away from the *endo* group of the ketone ligands by about 12–14°. The ketone ligands of compounds **2** reside in the other metallocene coordination site and are also twisted out of the aforementioned bisecting plane. Steric interactions between the phenyl ligand and the *endo* ketone substitutent are also minimized as a consequence of the end-on coordination mode of the ketone ligands. The Zr–O–C(7) angles are near linear at 174.2° and 166.1° for **2a** and **2b**, respectively. While there is a significant amount of latitude in the M–O–C angles for carbonyl compounds bonded to Lewis acids, usually η^1-bound ketone or aldehyde ligands are bent at oxygen.[16] In addition to the steric considerations already mentioned, linear, end-on coordination allows for π-donation from the ketone (**I**) to the empty $1a_1$ frontier orbital of the metallocene.[17] The dihedral angles between the planes

I
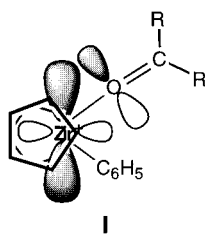
defined by C(6), Zr, and O and the four coplanar atoms of the ketone ligands are ~12° and ~18° for **2a** and **2b**, respectively, deviating only slightly from the coplanarity expected for such a σ-π bonding mode. The near linearity also allows for optimal alignment of the C=O dipole toward the positively charged zirconium center.

Direct comparison data are unavailable, but the Zr–O bond distances of 2.132(5) and 2.134(5) Å in **2a** and **2b** are more comparable to the Zr–O bond lengths of ~2.12 Å found in cationic zirconocenes with σ–π bound THF

ligands[1b] than those wherein the π component is attenuated.[1b,18] The Zr–O bonds in adducts **2** are also closer in length to the covalent Zr–O bonds found in η^2-bound ketone and aldehyde complexes of zirconium (which fall in the range of 2.11–2.18 Å[19]) than the dative Zr–O linkages in neutral (2.20–2.29 Å[20]) and cationic (2.242(7) Å in Cp*$_2$Zr(η^2-COCH$_3$)CO[21]) η^2-acyl complexes. These observations suggest that the distances in compounds **2** may be viewed as being short for a dative interaction, because of the π component depicted in **I**. Since both the σ and π donation from the ketone ligands to zirconium occurs from orbitals which are nonbonding with respect to C(7)–O, these bonds are only slightly elongated to 1.241(10) and 1.252(7) Å from a typical C=O distance of 1.210Å.[22]

Evidence of a dynamic behavior associated with the ketone ligands is apparent in the ^{1}H NMR data (Table 2). For example, at room temperature, only one singlet is observed for the methyl groups of the acetone ligand in **2a**; the solid state structures, if static, would give rise to two singlets for inequivalent methyl groups. Furthermore, the proton resonance for the acetophenone methyl group in **2b** is considerably broadened at room temperature. These observations suggest a process which exchanges the two ketone substituent sites. In the case of **2a**, this process was frozen out at low temperature, giving two signals at 1.91 and 1.75 ppm for the now inequivalent *exo* and *endo* methyl groups

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in the low-temperature limit. For **2b**, the single set of peaks for the various ligands observed in the room temperature ^{1}H NMR spectra transformed into two sets of peaks as the temperature was lowered. The isomers of **2b** were present in a 4.8:1 ratio at 247 K; a NOESY experiment confirmed that the isomer with the C_6H_5 group in the *endo* position (*i.e.*, that found in the solidstate, **2b**-*endo*) is the major isomer in solution under these conditions.

We propose that the exchange of *exo* and *endo* ketone substitutents occurs by the process shown in Scheme 1. In this process, the $\sigma-\pi$ bonding that the solid state structures indicate relaxes to a "σ-only" Zr−O bond, which allows for rotation of the ketone ligand and exchange of the *exo* and *endo* sites in the ligand. The difference of over 8° in the observed Zr−O−C(7) angles for adducts **2** suggests that the linear σ-π to bent σ-only transformation has a rather shallow potential surface. The barrier found for the process exchanging the methyl groups in **2a** (by analysis of the coalescence behavior of the signals[23]) was 11.1(4) kcal mol^{-1}.

Although fluxional, the acetone and acetophenone ligands in adducts **2** are not prone to insertion into the Zr−C_6H_5 bond. Gentle heating (50−80 °C) of solutions of either complex resulted in decomposition to a variety of products; similar observations were made even in the presence of an excess of ketone. While insertion may be occurring to a limited degree, competitive processes involving dissociation of the ketone and decomposition of phenyl zwitterion **1**, which was observed to be thermally unstable in solution,[11] are dominant. The lability of the ketone ligands was demonstrated by exchange experiments, such as those shown in eq 3.

$$R^1 = CH_3; R^2 = R^3 = CD_3 \quad \mathbf{K_{eq}} \approx \mathbf{1}$$
$$R^1 = C_6H_5; R^2 = R^3 = CH_3 \quad \mathbf{K_{eq} > 95}$$
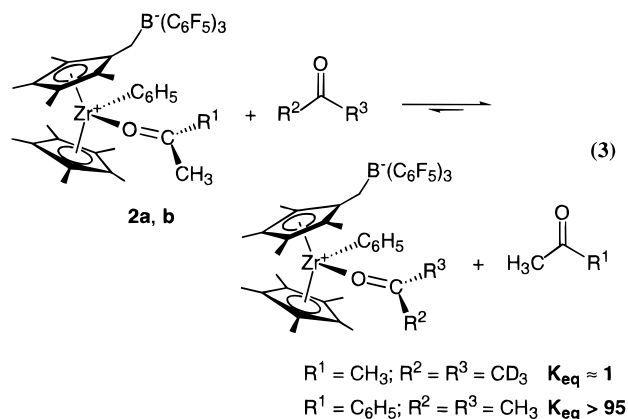
Treatment with acetone-d_6 resulted in a ~1:1 mixture of **2a** and **2a**-d_6, and the more basic acetone displaces acetophenone rapidly to generate **2a** from **2b** ($K_{eq} > 95$ by ^{1}H NMR spectroscopy). Alternatively, the presence of significant amounts of benzene in the thermalized samples of **2a** and **2b** suggests that enolization of the ketone may also be occurring to some extent. It is entirely likely that the barrier to ketone insertion is higher than the barriers to these other processes since the ketone is unable to assume the η^2-bonding mode

Scheme 1

$\sigma-\pi$ bonding σ bonding

2b-*endo*:**2b**-*exo* = 4.8:1
at 247 ° K
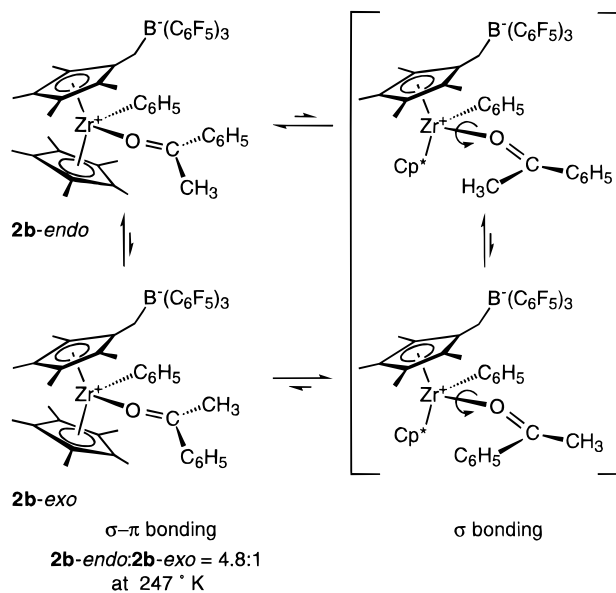
necessary for insertion due to severe steric interactions with the bulky Cp donors, as depicted in **II**.[24]

II
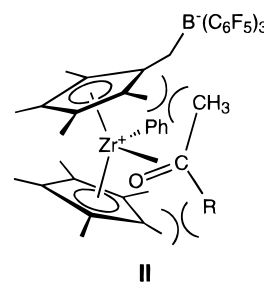
In conclusion, we have prepared acetone and acetophenone adducts of a zwitterionic zirconocene complex. Such adducts have been observed spectroscopically in nonzwitterionic zirconocene alkyl cations prior to ketone insertion into the Zr−C bond; the adducts described herein are unable to undergo insertion due to steric destabilization of the insertion transition state. The structures of these adducts and their dynamic behavior in solution give some insight into how carbonyl functions interact with these Lewis acids.

Supporting Information Available: Tables of crystallographic data, atomic parameters, hydrogen parameters, atomic coordinates, anisotropic thermal parameters, and complete bond distances and angles for **2a** and **2b** (24 pages). Ordering information is given on any current masthead page.

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(24) It should be noted that the phenyl ligand would also be required to rotate perpendicular to the metallocene plane, also a sterically problematic proposition.