75-05-8; $\operatorname{Ru}_{3}(\operatorname{CO})_{10}(\operatorname{MeCN})_{2}$, 103257-53-0; $[\operatorname{HRu}_{3}(\operatorname{CO})_{9}(\mu_{3}-\eta^{2}\cdot\sigma;\eta^{2}\cdot\operatorname{C}_{6}\operatorname{H}_{7})]$, 128363-70-2; $[\operatorname{HRu}_{3}(\operatorname{CO})_{9}(\mu_{3}-\eta^{2}:\eta^{2}\cdot\eta^{2}\cdot\operatorname{C}_{6}\operatorname{H}_{6})][\operatorname{BF}_{4}]$, 128391-81-1; 1,3-cyclohexadiene, 592-57-4.

Supplementary Material Available: Complete listings of

positional and thermal parameters, atomic coordinates, and bond distances and bond angles for LTf and LTh (22 pages); listings of calculated and observed structure factors for LTf and LTh (49 pages). Ordering information is given on any current masthead page.

Synthesis and Chemistry of Cp₂Zr(Ph)(THF)⁺. Selectivity of Protolytic and Oxidative Zr-R Bond-Cleavage Reactions

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The neutral complexes $Cp_2Zr(R)_2$ (R = CH₃ (1), CH₂Ph (2)) react with $[Cp'_2Fe][BPh_4]$ in THF via oxidative Zr-R bond cleavage to yield $[Cp_2Zr(R)(THF)][BPh_4]$ (R = CH₃ (3), R = CH₂Ph (4)). No reaction is observed with $Cp_2Zr(Ph)_2$ (5). The mixed phenyl-alkyl complexes $Cp_2Zr(Ph)(R)$ (R = CH₃ (9), CH₂Ph (10)) react with Cp'_2Fe^+ in THF to yield 3 and $Cp_2Zr(Ph)(THF)^+$ (6), respectively. The susceptibility of Zr-CH₂Ph bonds to oxidative cleavage is ascribed to the low bond energy. Reaction of 5 with $[HN(CH_3)_2Ph][BPh_4]$ in THF also produces 6 in good yield. Complexes 1, 2, and 5 react with $[HN(CH_3)_3][BPh_4]$ to yield $[Cp_2Zr(R)(OCH_2CH_2CH_2N(CH_3)_3][BPh_4]$ (R = CH₃ (15), CH₂Ph (13), and Ph (12)) via Zr-R bond protonolysis and subsequent nucleophilic THF ring opening. Reactions of 10 and 9 with $[HN(CH_3)_3][BPh_4]$ in THF yield 13 and 15 via initial selective Zr-Ph protonolysis. Complex 1 reacts with $[HN(^{B}u)_{3}][BPh_{4}]$ in THF to yield 3 whereas neither 2 nor 5 react. The selectivity and qualitative rates of these reactions indicate that ease of Zr-R bond protonolysis varies in the order Zr-Ph > Zr-CH₃ > Zr-CH₂Ph and that steric effects also strongly influence reactivity. Complex 6 reacts rapidly with 2 equiv of PMe₃ in THF solvent to yield $Cp_2Zr(Ph)(PMe_3)_2^+$ (16) and with 2-methylpyridine (α -picoline) in CD_2Cl_2 solvent to yield $Cp_2Zr(\eta^2(N, C))$ -picolyl)(THF)⁺ (17). Complex 6 initiates the ring-opening polymerization of THF and does not react with 2-butyne in CD_2Cl_2 .

Current interest in the chemistry of $Cp_2M(R)(L)^+$ (M = Ti, Zr, Hf) complexes¹⁻³ is motivated by the proposed role of closely related 14-electron $Cp_2M(R)^+$ ions in Cp₂MX₂-based Ziegler-Natta olefin polymerization catalyst systems⁴ and by the potential utility of these complexes in catalytic C-H activation/C-C coupling chemis-

try.⁵ Cationic zirconium alkyl complexes of this type have been prepared by oxidative cleavage (with Ag^+ , Cp_2Fe^+ , or Cp'_2Fe^+ ($Cp' = C_5H_4Me$)) or protonolysis (with HNR_3^+) of Zr-R bonds of neutral Cp₂ZrR₂ complexes.^{2,3} Related Ti cations have also been prepared by halide displacement reactions of Cp₂Ti(CH₃)X in coordinating solvents, protonolysis of Cp*₂TiR₂ and by one-electron oxidation of $Cp*_{2}Ti(R)$.¹ In all these cases noncoordinating anions such as BPh_4^- are required for the isolation of stable salts.⁶

This paper describes the reactions of several symmetric Cp_2ZrR_2 and mixed $Cp_2Zr(R)(R')$ complexes with Cp_2Fe^+ and HNR_3^+ reagents. The principal objective of this study was to develop a simple synthesis of cationic phenyl complexes $Cp_2Zr(Ph)(L)^+$, which are of interest for structural and reactivity comparisons to other Cp₂Zr(R)(L)⁺ complexes. Additionally, we were interested in elucidating the general reactivity and selectivity trends of these reactions with the ultimate objective of developing efficient methods for in situ generation of $Cp_2Zr(R)(L)^+$ catalysts.^{5a} Several nucleophilic THF ring-opening reactions of Cp₂Zr(R)-(THF)⁺ complexes that we discovered during the course of these studies are also described.

Results

Reaction of $Cp_2Zr(Ph)(R)$ Complexes with Cp_2Fe^+ Reagents. Synthesis of $Cp_2Zr(Ph)(THF)^+$ from

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 $Cp_2Zr(Ph)(CH_2Ph)$. The neutral complexes $Cp_2Zr(CH_3)_2$ (1) and $Cp_2Zr(CH_2Ph)_2$ (2) react with $[Cp'_2Fe][BPh_4]$ at room temperature in THF to yield $Cp_2Zr(CH_3)(THF)^+$ (3) and $Cp_2Zr(CH_2Ph)(THF)^+$ (4), respectively (eq 1).^{2e,k} The



latter reaction (minutes) is considerably faster than the former (hours). Analogous reactions occur with $[Cp_2Fe][BPh_4]$ and $Ag[BPh_4]$ in CH_3CN to yield Cp_2Zr -(R)(CH₃CN)_n⁺ complexes. However, the phenyl complex $Cp_2Zr(Ph)_2$ (5) is not converted to $Cp_2Zr(Ph)(THF)^+$ (6) by analogous reactions in THF. In this solvent, neither [Cp₂Fe][BPh₄] nor Ag[BPh₄] induces Zr-Ph bond cleavage of 5, and the former salt decomposes. Also, no reaction is observed in THF between these reagents and Cp'₂ZrPh₂, which should be more easily oxidized due to increased electron donation from the Cp' rings.⁷ In contrast, both Ag[BPh₄] and [Cp₂Fe][BPh₄] react rapidly with 5 in CH₃CN to yield Cp₂Zr(Ph)(CH₃CN)_n⁺ (7), but this species rapidly rearranges to the CH₃CN insertion product 8 (eq 2).⁸ It is not clear why 5 reacts with these reagents in



 CH_3CN but not in THF. Note that both $Ag[BPh_4]$ and $[Cp_2Fe][BPh_4]$ are insoluble in both solvents. It is possible that CH_3CN promotes the reaction of 5 with the oxidant via weak coordination and/or that solvent polarity is important.

The reactions of a series of mixed alkyls $Cp_2Zr(Ph)(R)$ with Cp_2Fe^+ oxidants in THF were explored with the expectation that the more weakly bonded R ligand would undergo oxidative cleavage yielding $Cp_2Zr(Ph)(THF)^+$. On the basis of the Zr-R bond strength trend⁹ Zr-Ph > Zr- $CH_3 > Zr-CH_2Ph$, we anticipated that selective cleavage of the Me group of $Cp_2Zr(Ph)(CH_3)$ (9) and the benzyl group of $Cp_2Zr(Ph)(CH_2Ph)$ (10) would be favored. Surprisingly however, the reaction of 9 with $[Cp_2Fe][BPh_4]$ in THF yields 3 as the major product (87% NMR yield); i.e., net cleavage of the Zr-Ph bond is favored (eq 3). A



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minor product (13% NMR yield, $\delta(Cp) = 6.09$; vide infra) is also observed. Mixed phenyl benzyl complex 10 is prepared by the reaction of 4 with PhLi at -78 °C (eq 4).



On a 1-2-g scale in THF at -78 °C this reaction yields a mixture of 10 (ca. 80%), $Cp_2Zr(Ph)_2$ (5, 10%), and $Cp_2Zr(CH_2Ph)_2$ (2, 10%), from which 10 is isolated by crystallization. Increased amounts of the latter two products are obtained when the reaction is performed at higher temperatures or on a larger scale. However, this route is superior to others that we investigated.¹⁰ The reaction of 10 with excess [Cp'₂Fe][BPh₄] in THF yields selectively the cationic Ph complex 6 (36% isolated yield, eq 4). The low yield is due in part to decomposition of the oxidant under the reaction conditions and to decomposition of 6 to $Cp_2Zr(Ph)\{(-OCH_2CH_2CH_2CH_2-)_n\}$ (11; vide infra).¹¹ There is no evidence for the formation of 4 via Zr-Ph bond cleavage under these conditions.

Synthesis of $Cp_2Zr(Ph)(THF)^+$ by Protonolysis of Cp₂ZrPh₂. The reaction of 5 with [HNBu₃][BPh₄]^{1e,2a,1,m,3} in THF proceeds sluggishly at 50 °C (60% conversion after 14 h) to yield a complex mixture of products. In contrast, 5 reacts rapidly with the less crowded ammonium reagent [HNMe₃][BPh₄] at 23 °C (THF, 3 h) to yield [Cp₂Zr-(Ph)(OCH₂CH₂CH₂CH₂CH₂NMe₃)][BPh₄] (12) via Zr-Ph bond protonolysis followed by nucleophilic THF ring-opening (eq 5). This product is formed in 50% NMR yield along



with several unidentified Cp_2Zr compounds, from which it could not be obtained analytically pure, and has been characterized by ¹H and ¹³C NMR spectroscopy only. In a control experiment, the reaction of 6 with 1.5 equiv of NMe_3 in THF- d_8 was monitored by ¹H NMR spectroscopy at 23 °C. Rapid conversion to $[Cp_2Zr(Ph) (OCD_2CD_2CD_2CD_2NMe_3)$ [BPh₄] (12-d₈, 75% complete after 30 min) without detectable intermediates was observed. The THF ring-opening reaction is avoided by using the more acidic ammonium reagent HNMe₂Ph⁺, the conjugate base of which is less nucleophilic than NMe₃. The reaction of 5 with 2 equiv of [HNMe₂Ph][BPh₄] in THF proceeds rapidly (<10 min) to yield 6 cleanly (>90% NMR yield, 62% isolated; eq 6). This reaction provides the most

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⁽¹¹⁾ An NMR scale reaction of Cp₂Zr(Ph)(CH₂Ph) with 3 equiv of $[Cp'_{2}Fe][BPh_{4}]$ (THF-d₈, 23 °C, 1 h) yielded only $Cp_{2}Zr(Ph)(THF)^{+}$ (48%) along with 52% unreacted $Cp_{2}Zr(CH_{2}Ph)(Ph)$.

convenient synthesis of 6. The excess [HNMe₂Ph][BPh₄] is required because this salt decomposes under the reaction conditions.

Reactions of $Cp_2Zr(R)(R')$ Complexes with HNR_3^+ **Reagents.** The reactions of several $Cp_2Zr(R)(R')$ complexes with HNR₃⁺ reagents were investigated to compare selectivity trends with those observed in the Cp₂Fe⁺ reactions described above. The reaction of phenyl benzyl complex 10 with [HNⁿBu₂][BPh₄] in THF proceeds sluggishly at 50 °C to yield a mixture of unidentified Cp_2Zr products.¹² However, the reaction with $[HNMe_3][BPh_4]$ proceeds at 23 °C to yield $[Cp_2Zr(CH_2Ph)-$ (OCH₂CH₂CH₂CH₂NMe₃)][BPh₄] (13, 90% NMR yield) and 1 equiv of benzene in 24 h (eq 7). Complex 13 is



formed by selective Zr-Ph bond protonolysis to yield 4, followed by nucleophilic THF ring opening. A similar ring opening occurs at elevated temperature in the reaction of 4 with PMe_2Ph , which yields $[Cp_2Zr(CH_2Ph)-$ (OCH₂CH₂CH₂CH₂PMe₂Ph)][BPh₄] (14, eq 8) as noted in



a preliminary communication.^{2e} The selectivity for Zr–Ph bond cleavage in the reaction of 10 with $HNMe_3^+$ parallels the relative reactivities of $Cp_2Zr(CH_2Ph)_2$ (2) and $Cp_2Zr(Ph)_2$ (5) with this reagent. The reaction of $HNMe_3^+$ and 2 proceeds slowly in THF at 50 °C (ca. 60% complete by ¹H NMR after 13 h) to yield the ring-opened product 13; no reaction of 2 is observed at 23 °C. In contrast and as noted above, 5 reacts rapidly with HNMe₃⁺ at 23 °C.

The reaction of $Cp_2Zr(Ph)(CH_3)$ (9) with $HNMe_3^+$ also results in selective Zr-Ph bond protonolysis. This reaction proceeds at 23 °C to yield $Cp_2Zr(CH_3)$ -(OCH₂CH₂CH₂CH₂NMe₃)⁺ (15) via nucleophilic THF ring opening of initially formed 3 (eq 7). When this reaction is monitored by ¹H NMR spectroscopy in THF- d_8 , rapid formation of $Cp_2Zr(CH_3)(THF-d_8)^+$ (3-d₈, 70%), benzene, and free NMe₃ is observed, followed by slower conversion to $Cp_2Zr(CH_3)(OCD_2CD_2CD_2CD_2NMe_3)^+$ (15-d₈). Small amounts of 12-d₈ (10%) derived from Zr-CH₃ protonolysis, $Cp_2Zr(CH_3)_2$ (1, 10%), and several unidentified Cp_2Zr products are also observed. Complex 15 is also formed by reaction of 1 and $HNMe_3^+$ in THF (eq 9).



Several mechanisms are possible for these THF ringopening reactions. When the reaction of 3 and NMe₃ is monitored by ¹H NMR spectroscopy, transient Cp resonances for 1 and another Cp_2Zr compound (δ 6.37, Cp) in a 1:1 ratio are observed. Associated with the δ 6.37 resonance (10 H) is a resonance for coordinated NMe₃ at δ 2.08 (9 H).¹³ The resonances for both 1 and the unknown Cp_2Zr compound disappear by the end of the reaction, leaving only resonances for 15- d_8 . We propose that the new transient Cp₂Zr species is the dication Cp₂Zr(NMe₃)- $(THF)_n^{2+}$ (n = 1 or 2) formed by disproportionation of $Cp_2Zr(CH_3)(NMe_3)^+$, which is in equilibrium with 3 and free NMe₃ (eq 10). Similar disproportionation reactions



+ THE + NMe-

are observed for $Cp_2Zr(X)(CH_3CN)_2^+$ (X = halide)^{2d} and $Cp_2Hf(CH_3)(CH_3CN)_2^{+.14}$ Complex 15 thus may be derived from direct reaction of 3 and NMe₃ as in eq 9 or by intramolecular ring opening of Cp₂Zr(NMe₃)(THF)²⁺ followed by ligand redistribution.

The importance of steric effects in these protonolysis and ring-opening reactions is illustrated by the reactions of HNBu₃⁺. While this ammonium reagent does not react readily with 2 or 5, even at 50 °C, it reacts rapidly with 1 at 23 °C to yield 3. No subsequent THF ring opening to yield an N("Bu)₃ analogue of 15 is observed. This is the most convenient synthesis of 3.

Characterization and Chemistry of Cp₂Zr(Ph)-(THF)⁺ (6). Cationic Zr-Ph complex 6 is characterized by NMR spectroscopy (Table I) and analysis. The lowtemperature ¹H NMR spectrum in CD₂Cl₂ (-90 °C) exhibits a single Cp resonance, resonances for coordinated THF shifted significantly upfield from those of free THF,¹⁵ and a single set of ortho, meta, and para H resonances for the Zr-Ph ligand. These results establish that the sides of the Ph group are equivalent, which is consistent with either (i) a static structure in which the phenyl group lies in a perpendicular orientation relative to the plane between the Cp ligands, or (ii) rapid rotation about the Zr-Ph bond.¹⁶ At higher temperatures (>10 °C) 6 decomposes

⁽¹²⁾ At 50 °C, ca 50% Cp₂Zr(Ph)(CH₂Ph) is converted to a mixture of products with Cp₂Zr resonances at δ 6.39 (10%), 6.25 (10%), 5.96 (10%), 5.94 (3%), and 5.92 (3%) and additional resonances in smaller amounts.

⁽¹³⁾ The transient δ 6.37 and 2.08 resonances are also observed when the reaction of 1 and HNMe₃⁺ is monitored by ¹H NMR spectroscopy. (14) R. F. Jordan and G. D. Hinch, unpublished results. (15) ¹H NMR of free THF (-90 °C, CD₂Cl₂): δ 3.62, 1.74.

	INMIN ADD "U NMK DA	190 NEW Compound	
<u>'H NMR</u>	assgnt	¹³ C NMR	assgnt
	[Cp ₂ Zr(Ph)(THF)][BPh4] (6)	
7.19 (t, $J = 6.8, 2 \text{ H})^{b,e}$	<i>m</i> -phenyl	184.9	i-phenyl
7.11 (t, $J = 6.6, 1$ H)	<i>p</i> -phenyl	133.7	o-phenyl
7.09 (d, $J = 7.1, 2$ H)	o-phenyl	128.2	<i>m</i> -phenyl
6.29 (s, 10 H)	C_5H_5	127.8	<i>p</i> -pnenyl
3.27 (or m, 4 m) 1.71 (br m. 4 H)	1 NF Tur	116.6	$C_5 H_5$
1.71 (br iii, 4 fi)	INF		
	[Cp ₂ Zr(Ph)(THF)][BPh ₄] (6)	
7.30-1.18 (br m, 5 H) ⁴	aryl		
0.40 (S, 10 H)	$C_5 n_5$		
	Cp ₂ Zr(CH ₂ Ph)	(Ph) (10)	
7.11 (d, of d, $J = 7.8, 1.3, 2 \text{ H})^{cf}$	o-phenyl	183.3	i-phenyl
7.03 (t, $J = 7.3, 2$ H)	m-benzyl	152.5	i-benzyl
7.01 (t, $J = 7.3, 2$ H)	<i>m</i> -pnenyl	136.0	aryl
6.90 (t of t, $J = 7.3, 1.4, 1$ H) 6.96 (d of d $I = 7.7, 1.16, 9$ H)	p-pnenyi	128.3	aryl
6.00 (u of u, J = 7.3, 1.10, 2 H)	p-benzyl	127.0	aryl
6.10 (s. 10 H)	C.H.	125.3	n-phenyl
2.11 (s, 2 H)	CHoPh	121.0	p-benzyl
	2	112.7	CaHa
		62.6	ZrCH ₂
IC.		H.NMe.)][BPh.] (12)	-
7.4-6.8 (m. obscured by BPh. ⁻)	$p_2 21 (1 1) (0 0 11_2 0 11_$	179 d ^h	i-phenyl
6.13 (s. 10 H) ^{c,h}	Č.H.	139.7	o-phenyl
4.02 (t, $J = 6.1, 2$ H)	ŹrÔĊ <i>H</i> ,	127.4	<i>m</i> -phenyl
3.18-3.07 (m, 2 H)	NCH ₂	125.0	<i>p</i> -phenyl
2.89 (s, 9 H)	$N(C\tilde{H}_3)_3$	112.5	C_5H_5
1.75–1.60 (m, 2 H)	$ZrOCH_2CH_2$	73.2	OCH ₂
1.53-1.38 (m, 2 H)	NCH_2CH_2	67.6 (br s)	NCH ₂
		53.8 (t, $J_{\rm CN} = 4$)	$N(CH_3)_3$
		30.9	OCH ₂ CH ₂
[Cp ₂	2r(CH ₂ Ph)(OCH ₂ CH ₂ CH	[₂ CH ₂ NMe ₃)][BPh ₄] (13)	
7.12 (t, $J = 7.6, 2 \text{ H})^{b,h}$	<i>m</i> -phenyl	154.8^{h}	i-benzyl
6.86 (2 H, obscured by BPh_4^{-})	o-benzyl	128.4	aryl
6.76 (t, $J = 7.3, 1$ H)	<i>p</i> -benzyl	127.4	aryl
5.96 (s, 10 H)	C ₅ H ₅	120.8	<i>p</i> -benzyl
3.90 (t, J = 0.1, 2 H)		73.1	
3.14 - 3.09 (m, 2 m)	N(CH)	$52.8 (t, J_{CN} = 3)$	NCH
2.52 (s, 511) 2.25 (s, 2 H)	$CH_{2}Ph$	46.5	CH_Ph
1.68-1.59 (m, 2 H)	OCH CH	30.9	OCH CH
1.44-1.36 (m, 2 H)	NCH ₂ CH ₂	20.4	NCH ₂ CH ₂
78-67 (m 20 H)dd	$2\Gamma(C\Pi_2\Gamma\Pi)(OC\Pi_2C\Pi_2C\Pi_2C\Pi_2C\Pi_2C\Pi_2C\Pi_2C\Pi_2C\Pi_2C\Pi_2$	$_{2}Cn_{2}PNie_{2}Pn_{1}[BPn_{4}]$ (14)	i hongul
5.83 (n 10 H)	$C_{-}H_{-}$	$135.3 (d J_{} = 4)$	n-DMe.Ph
3.79 (t. $J = 6.0, 2$ H)	ZrOCH	$131.8 (d, J_{PC} = 10)$	o-PMe.Ph
2.16 (s, 2 H)	ZrCH _o Ph	$130.9 (d, J_{PC} = 13)$	<i>m</i> -PMe ₂ Ph
1.6-1.0 (m, 6 H)	PCH,CH,CH,	128.2	o- or <i>m</i> -benzyl
1.26 (d, $J_{\rm PH} = 13, 6$ H)	$P(C\tilde{H}_3)_2$	127.2	o- or m-benzyl
		120.7	<i>p</i> -benzyl
		111.9	C_5H_5
		73.0	ZrOCH ₂
		46.8	ZrCH ₂ Ph
		24.3 (d, $J_{PC} = 51$)	$2rUCH_2CH_2CH_2CH_2$
		$23.3 (d, J_{PC} = 16)$	
		$19.1 (0, J_{PC} = 4)$ 6.8 (d. I. = 55)	D(CH) Dh
		$0.0 (0, 0 p_{\rm C} - 0.0)$	1 (0113/21 11
	$p_2 Zr(CH_3)(OCH_2CH_2CH_3)$	$_{2}CH_{2}NMe_{3}[BPh_{4}]$ (15)	<u>CH</u>
5.00 (s, 10 H) ^{5,7}		111.5"	
$3.00 (0, \sigma = 0.3, 4 \Pi)$ 3.08-3.03 (m - 9.14)	NCH	(2.0) 67 A (br a)	NCH.
2.88 (s. 9 H)	$N(CH_{a})_{a}$	53.7 (br s)	N(CH _a)
1.66 - 1.53 (m. 2 H)	OCH ₃ CH ₅	31.1	$Zr(CH_{2})$
1.41 - 1.28 (m, 2 H)	NCH ₃ CH ₃	20.3	OCH ₂ ČH ₂
-0.06 (s, 3 H)	$Zr(CH_3)$	18.2	NCH ₂ CH ₂
., ,	[('n-7.(Dh)/Dh/A)-][BPb.] (16)	
7.46-7.38 (m. 2 H)	m-nhenvi	$140.9^{j,k}$	a-nhenvl
7.02–6.95 (m. 3 H)	o- and p-phenyl	127.3	<i>m</i> - or <i>p</i> -phenvl
6.07 (t, $J_{\rm PH} = 1.9, 10$ H)	C_5H_5	126.5	m- or p-phenyl
1.03 (d, $J_{\rm PH} = 7.4, 18$ H)	P(CH̃ ₃) ₃	108.6	C_5H_5
		15.5 (d, $J_{\rm PC}$ = 20)	$P(CH_3)_3$

^aSpectra of cationic complexes also contain normal BPh₄⁻ resonances; see ref 2. J values in Hz. ^b360 MHz. ^c300 MHz. ^d200 MHz. ^cCD₂Cl₂, -90 °C. ^fTHF-d₈, ambient T. ^dCD₂Cl₂, ambient T. ^hCD₃CN, ambient T. ⁱipso-C of P-Ph ring not observed. ^jTHF-d₈, -43 °C. ^kipso-C of Zr-Ph not observed.

after several hours in this solvent.¹⁷

Complex 6 decomposes slowly in THF- d_8 solution (33%) in 5 days at 23 °C) to yield a product with a Cp resonance at δ 6.09. When this reaction is performed in THF and the solvent removed under vacuum, and the residue subsequently dissolved in THF- d_8 and analyzed by ¹H NMR spectroscopy, resonances assignable to poly(tetrahydrofuran) (δ 3.37 br s, 1.58 br s) are observed.¹⁸ These results establish that 6 initiates the ring-opening polymerization of THF (eq 11). The resonance at δ 6.09 is identical with



that for $Cp_2Zr(Ph)(OCH_2CH_2CH_2CH_3)$, generated in THF- d_8 by reaction of 2 with 1 equiv of ⁿBuOH,¹⁹ and is assigned to zirconium alkoxy species 11 in eq 11. The Cp resonance for 12 also appears in this region. Associated with the Cp singlet at δ 6.09 is a triplet at δ 4.02 assigned to the $ZrOCH_2$ - group of 11. The minor Cp resonance at δ 6.09 in the NMR spectrum of the product mixture of the reaction in eq 3 is assigned to 11 and indicates that a small amount of Zr-CH₃ bond cleavage occurs in this reaction.

Complex 6 reacts with 2 equiv of PMe₃ in THF or CH_2Cl_2 solvent to yield $Cp_2Zr(Ph)(PMe_3)_2^+$ (16, eq 12).



The ¹H NMR spectrum of 16 at room temperature in THF- d_8 contains a sharp Cp resonance at δ 6.02, which splits to a 1:2:1 triplet $(J_{H-P} = 1.7 \text{ Hz})$ at -43 °C. However, the Cp resonance of 16 shifts only slightly upon addition of excess (6 equiv total) PMe₃ or upon lowering the temperature. These observations establish that 16 adopts a symmetric structure with the Zr-Ph ligand in the central coordination site at low temperature and undergoes rapid PMe₃ exchange at ambient temperature, though the extent of PMe_3 dissociation is minor. The analogous methyl complex, $Cp_2Zr(CH_3)(PMe_3)_2^+$, exhibits similar properties.^{2f} Interestingly, 6 does not form a mono(trimethylphosphine) complex. The ¹H NMR spectrum of a THF- d_8 solution of 6 containing 1 equiv of PMe₃ exhibits a broad Cp resonance at δ 6.16 at ambient temperature characteristic of rapid exchange. Upon cooling of the solution to -43 °C, only resonances for 6 and 16 are observed.

Complex 6 reacts with 2-methylpyridine (α -picoline) in CD_2Cl_2 to yield benzene and $Cp_2Zr(\eta^2(N,C)-picolyl)(THF)^+$ (17) as a 1:1 mixture of isomers (eq 13). This reaction is rapid at room temperature ($t_{1/2} < 10$ min). The same



products are obtained from the reaction of 3 and α -picoline at a comparable rate $(t_{1/2} \text{ ca. } 6 \text{ min}).^{5b}$

Complex 6 reacts rapidly in CH₃CN via ligand substitution and CH₃CN insertion (eq 2) to yield azomethine product 8.8 However this high insertion reactivity does not extend to hydrocarbon substrates. For example, the reaction of 6 with excess 2-butyne (>30 equiv) in CD_2Cl_2 yields only Cp₂Zr(Ph)(Cl) (derived from reaction with solvent)¹⁷ and several minor unidentified Cp products. In contrast 3 reacts rapidly with 2-butyne to yield the insertion product Cp₂Zr(CMe=CMe₂)(THF)^{+.20} Similarly, only traces of polyethylene are formed when a CD₂Cl₂ solution of 6 is charged with 1 atm of ethylene.

Discussion

Oxidation Chemistry. Neutral Cp₂ZrR₂ complexes react with Cp_2Fe^+ or Cp'_2Fe^+ in THF to yield the cationic complexes $Cp_2Zr(R)(THF)^+$ via oxidative cleavage of a Zr-R bond. The qualitative rates of reactions of Cp_2ZrR_2 complexes, and the selectivity observed in reactions of mixed complexes $Cp_2Zr(R)(R')$, indicate that the ease of Zr-R bond oxidative cleavage varies in the order Zr-CH₂Ph > Zr-Ph, Zr-CH₃. Thus, $Cp_2Zr(CH_2Ph)_2$ (2) reacts with Cp'₂Fe⁺ rapidly at room temperature and below, Cp₂Zr- $(CH_3)_2$ (1) reacts slowly at room temperature, and Cp_2ZrPh_2 (5) and Cp'_2ZrPh_2 do not react. The mixed phenyl benzyl complex 10 reacts with Cp'₂Fe⁺ via Zr- CH_2Ph cleavage. In contrast, the methyl phenyl complex 9 reacts with Cp'₂Fe⁺ to yield principally 3 via Zr-Ph cleavage and only minor amounts of 11 derived from Zr- CH_3 cleavage. While the mechanistic details of these oxidative cleavages are not fully understood, available evidence suggests that these reactions proceed by initial one-electron oxidation from a Zr-R bonding orbital²¹ followed by R[•] extrusion and trapping of the resulting Zr cation by solvent.^{2e,22} The facile cleavages of weak Zr-CH₂Ph bonds,⁹ and the lack of reaction of Cp₂ZrPh₂, which contains strong Zr-Ph bonds and exhibits a relatively high (irreversible) $E_{1/2}(\text{oxid})$,²² are consistent with this mechanism. At present we have no explanation for the selective cleavage of the Zr-Ph bond of 9 (which is presumably stronger than the $Zr-CH_3$ bond).

Protonolysis Chemistry. Neutral Cp₂ZrR₂ complexes react with HNR₃⁺ in THF via Zr-R bond protonolysis to yield $Cp_2Zr(R)(THF)^+$ complexes as initial products. This general reaction has been developed by Hlatky and Turner^{2a,1,m} and by Marks³ for the synthesis of Cp*₂ZrCH₃+ and Cp*2ThCH3⁺ complexes. In the case of the HNMe3⁺, the unhindered amine NMe3 released in the protonolysis step undergoes nucleophilic THF ring-opening reactions $Cp_2Zr(R)(THF)^+$ with yielding $Cp_2Zr(R)$ -(OCH₂CH₂CH₂CH₂NMe₃)⁺ complexes as ultimate products. These Zr-promoted THF ring-opening reactions are

⁽¹⁶⁾ Under these conditions exchange of free and coordinated THF is slow on the NMR time scale.

⁽¹⁷⁾ The initial Cp₂Zr decomposition product exhibits a ¹H NMR Cp resonance at δ 6.31, which is identical with that for Cp₂Zr(Ph)(Cl) (generated independently via reaction of 6 and [(°Bu)₄N][Cl]. BPh₃ is also observed

^{(18) (}a) These resonances appear at δ 3.45 (br s), 1.62, (br s) in CD₃⁻ NO₂, identical with the literature values for poly(tetrahydrofuran) in this solvent (b, c). (b) Matyjaszewski, K.; Penczek, S. J. Polym. Sci., Polym. Chem. Educ. 1974, 12, 1905. (c) Hrkach, J. S.; Matyjaszewski, K. Macomolecules 1990, 23, 4042. (d) Neither BPh3 nor Na[BPh4] polymerize THF under these conditions.

^{(19) &}lt;sup>1</sup>H NMR of Cp₂Zr(Ph)(OCH₂CH₂CH₂CH₃) (THF-d₈): δ 6.09 (s, 10 H), 4.00 (t, J = 6.0 Hz, 2 H), 1.50–1.34 (m, 4 H), 0.95 (t, J = 7.0 Hz, 3 H).

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a manifestation of the electrophilicity of the metal center in $Cp_2Zr(R)(THF)^{+,2}$ The qualitative rates of reactions of Cp_2ZrR_2 complexes, and the selectivity observed in reactions of mixed $Cp_2Zr(R)(R')$ complexes, indicate that the general order of protonolysis is Zr-Ph > Zr-CH₃ > Zr-CH₂Ph. Thus, 1 and 5 react with HNMe₃⁺ rapidly at room temperature to yield ring-opened products 15 and 12, while 2 reacts only slowly at 50 °C to yield 13. The mixed complexes $Cp_2Zr(Ph)(CH_2Ph)$ (10) and $Cp_2Zr(Ph)(CH_3)$ (9) react with HNMe₃⁺ via selective Zr-Ph bond protonolysis to yield ring-opened products derived from $Cp_2Zr(CH_2Ph)(THF)^+$ (4) and $Cp_2Zr(CH_3)(THF)^+$ (3), respectively. While the mechanistic details of these reactions are not known, it is likely that direct protonolysis of Zr-R bonds occurs.²³ The observed selectivity for protonolysis of Zr-Ph bonds parallels that observed in acidolysis reactions of mixed aryl-alkyl organometallics of B,²⁴ Si, Ge, Sn, Pb,²⁵ Hg,²⁶ and Au.²⁷ The latter reactions proceed via an S_E2 mechanism involving direct attack of the carbon by H⁺, and the selectivity for M-aryl protonolysis is ascribed to resonance stabilization of the resulting Wheland intermediate.²⁸ Protonolysis of Zr-Ph bonds is probably favored for the same reason.

Steric effects are also very important in these protonolysis reactions. The relatively slow protonolysis of dibenzyl complex 2 by HNMe₃⁺ compared to the rapid reaction of dimethyl complex 1 is likely due to its crowded structure. In some cases steric effects can lead to a reversal in reactivity. For example, the very crowded ammonium reagent $HNBu_3^+$ reacts rapidly with 1 at room temperature but not with 2, 5, or 10.

Chemistry of Cp₂Zr(Ph)(THF)⁺ (6). Complex 6 reacts with excess PMe₃ to yield $Cp_2Zr(Ph)(PMe_3)_2^+$ (16). The mono-PMe₃ species $Cp_2Zr(Ph)(PMe_3)^+$, which might be stabilized by a β -agostic interaction involving a phenyl C-H bond similar to those observed in Hlatky and Turner's zwitterionic complex Cp*2Zr{2-Et,5-B(4-ethylphenyl)₃phenyl} and Cp₂Zr(CH₃)(picoline)⁺,^{2a,5b} is not stable in the presence of excess PMe₃. In fact, the reaction of 6 with 1 equiv of PMe₃ yields 1/2 equiv of 16 and 1/2equiv of unreacted 6. In contrast, Cp'2Zr(CH2CH2R)- $(THF)^+$ complexes (18) react with PMe_3 to yield the mono-PMe₃ complexes $Cp'_2Zr(CH_2CH_2R)(PMe_3)^+$, which have β -agostic structures. These complexes are stable in the presence of excess PMe₃.^{2j} This difference suggests that, in this system at least, agostic interactions involving alkyl C-H bonds are inherently stronger than those involving aryl C-H bonds.

The C-H activation reactivity of 6 is similar to that of methyl analogue 3. Both complexes react rapidly at room temperature with α -picoline in CD₂Cl₂ via ligand substitution and ortho C-H activation to yield $Cp_2Zr(\eta^2(N, -$

C)-picolyl)(THF)⁺ (17).^{5b} In view of the observation that Zr-Ph bonds undergo facile protonolysis by ammonium salts, it is not surprising the Zr-Ph group is an excellent H⁺ acceptor in this ligand C-H activation reaction.

The most striking difference between 6 and analogous alkyl complexes 3 and $Cp'_2Zr(CH_2CH_2R)(THF)^+$ (18)^{2h} is in the reactivity of these complexes with unsaturated hydrocarbons. While 3 and 18 catalyze ethylene polymerization and undergo rapid single insertion of 2-butyne, 6 is unreactive with both substrates. The observation that 6 initiates ring-opening polymerization of THF but 3 and 18 do not suggests that the THF ligand in 6 is more strongly bound than in the latter complexes. As substitution of THF by substrate likely precedes insertion,^{2c,e,i} this strong THF binding provides a rationale for lower insertion reactivity of 6. Consistent with this hypothesis, CH₃CN does displace the coordinated THF of 6 and undergoes rapid insertion.⁸

Experimental Section

All manipulations were performed under an inert atmosphere or under vacuum by using a Vacuum Atmospheres drybox or a high-vacuum line. Solvents were purified by initial distillation from an appropriate drying/deoxygenating agent, stored in evaculated bulbs, and vacuum-transferred into reaction vessels.²⁹ NMR spectra were obtained on a Bruker MSL-300, AC-300, or WP-360 instrument and are listed in Table I. Elemental analyses were performed by Analytische Laboratorien or Schwarzkopf Were performed by Analytische Laboratorien of Schwarzkopr Microanalytical Laboratory. The following compounds were prepared by literature methods: Ag[BPh],^{2f} [Cp₂Fe][BPh₄],^{2h} [Cp'₂Fe][BPh₄],^{2h} Cp₂Zr(Ph)₂,³⁰ Cp'₂Zr(Ph)₂,³¹ K[CH₂Ph],³² Cp₂Zr(CH₃),³⁰ [Cp₂Zr(CH₃)(THF)][BPh₄],^{2c} Cp₂Zr(CH₂Ph),²³ [Cp₂Zr(CH₂Ph)(THF)][BPh₄],⁸ [Cp₂Zr(CH₂Ph)(CH₃CN)][BPh₄],^{2e} Cp₂Zr(Ph)(CH₃),³⁴ [HN(ⁿBu)₃][BPh₄],³⁵ and [HN(CH₃)₂(Ph)]-[BPh] ³⁵ [HN(CH₃) | BPh₄],³⁵ and [HN(CH₃)₂(Ph)]-[BPh₄].³⁵ [HN(CH₃)₃][BPh₄] was purchased from Aldrich and used after drying on a high-vacuum line. Na[BPh]₄, (C₅H₄Me)₂Fe, and NMe₃ were purchased from Aldrich and used without further purification.

[Cp₂Zr(Me)(THF)][BPh₄] (3). A slurry of Cp₂Zr(CH₃)₂ (0.510 g, 2.03 mmol) and [HNBu₃][BPh₄] (1.13 g, 2.23 mmol) in THF (20 mL) was prepared at -78 °C and warmed to 23 °C. All the solids dissolved. The solution was stirred for 3 h, during which time an off-white crystalline precipitate formed. The solid was collected by filtration, washed with 2×5 mL of cold (-78 °C) THF, and dried under vacuum overnight. Yield: 1.10 g (86%). The ¹H NMR spectrum of this material is identical with that of samples prepared by oxidation of Cp₂Zr(CH₃)₂ by Ag⁺ or Cp'₂Fe⁺ reagents.^{2f}

Preparation of 3 via Oxidation of Cp₂Zr(CH₃)₂ with [Cp'₂Fe][BPh₄]. A slurry of Cp₂Zr(CH₃)₂ (5.00 g, 19.9 mmol) and [Cp'₂Fe][BPh₄] (11.2 g, 20.9 mmol) in THF (125 mL) was prepared at -78 °C and warmed to 23 °C. The slurry was stirred for 10 h, after which 75 mL of THF was removed under vacuum and replaced by 50 mL of toluene. The reaction mixture was filtered, and the precipitate was washed with 2×20 mL of THF

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and dried under vacuum. Recrystallization of the precipitate from THF afforded 6.74 g (53.9%) of 3. The ¹H NMR spectrum of 3 was identical with that of samples prepared via oxidation by

Ag⁺ or protonolysis by $HN(^{B}u)_{3}^{+}$ reagents. Preparation of $[Cp_2Zr(Ph)(THF)][BPh_4]$ (6) from $Cp_2Zr(Ph)(CH_2Ph)$. A slurry of $Cp_2Zr(CH_2Ph)(Ph)$ (0.489 g, 1.26 mmol) and $[Cp'_2Fe][BPh_4]$ (2.02 g, 3.78 mmol) in THF (15 mL) was prepared at -78 °C. The blue reaction mixture was warmed to 23 °C and stirred for 4 h, producing an orange slurry. The slurry was stirred overnight and then evaporated to dryness under vacuum. The resulting solid was washed with toluene to remove Cp'₂Fe and recrystallized from THF (-30 °C), yielding 0.32 g (36%) of bright yellow 6. A sample of 6 that analyzed acceptably was prepared via recrystallization from CH2Cl2/toluene at -78 °C. This sample contained 0.33 equiv of toluene (¹H NMR). Anal. Calc for C44H43BOZr-0.33C7H8: C, 77.22; H, 6.39; Zr, 12.66. Found: C, 76.80; H, 6.28; Zr, 12.79. Preparation of [Cp₂Zr(Ph)(THF)][BPh₄] (6) from

Cp₂Zr(Ph)₂. A slurry of Cp₂Zr(Ph)₂ (3.10 g, 8.26 mmol) and [HN(Me)₂(Ph)][BPh₄] (7.29 g, 16.52 mmol) in 60 mL of THF was prepared at -78 °C. The slurry was warmed to 23 °C and stirred for 1.5 h, after which 50 mL of THF was removed and 30 mL of toluene was added. The slurry was stirred for an additional 30 min and filtered, leaving a pale yellow precipitate. The precipitate was washed thoroughly with Et_2O and dried under vacuum overnight. Yield: 4.36 g (62.6%). This material contained excess THF (2 equiv by ¹H NMR).

 $Cp_2Zr(Ph)(CH_2Ph)$ (10). A slurry of $[Cp_2Zr(CH_2Ph)-(THF)][BPh_4]-0.43C_7H_8$ (2.02 g, 2.53 mmol) in THF (35 mL) was prepared at -78 °C. Under N₂ counterflow, 1.45 mL of PhLi solution (2.0 M in ether, 2.9 mmol) was added by syringe over a 2-min period. The mixture was stirred at -78 °C for 20 min. warmed to 0 °C, and stirred for an additional 40 min. The mixture was warmed to 23 °C and evaporated to dryness under vacuum. The resulting solid was extracted with hexane until the hexane extract was colorless. The hexane extracts were evaporated to dryness under vacuum yielding 0.83 g of crude 10, which consisted of 83% 10 and a total of 17% of $Cp_2Zr(Ph)_2$ and $Cp_2Zr(CH_2Ph)_2$. Fractional recrystallization from toluene/hexane improved the ratio to 90:10. An additional recrystallization gave 0.34 g (32%) of >99% pure 10. The reaction was reproducible at this scale; however, scale-up attempts resulted in increased amounts of $Cp_2Zr(Ph)_2$ and $Cp_2Zr(CH_2Ph)_2$. Anal. Calc for $C_{23}H_{22}Zr$: C, 70.99; H, 5.70; Zr, 23.41. Found: C, 70.63; H, 5.58; Zr, 23.15. $[Cp_2Zr(CH_2Ph)(OCH_2CH_2CH_2CH_2NMe_3)][BPh_4]$ (13). A slurry of Cp₂Zr(CH₂Ph)₂ (1.00 g, 2.48 mmol) and [HNMe₃][BPh₄] (0.47 g, 1.24 mmol) in THF (15 mL) was heated for 15 h at 50 °C. The THF was removed under vacuum, yielding a yellow foam. The foam was washed with hot toluene and filtered. The resulting white solid was washed with several small portions of toluene and dried under vacuum, yielding 0.61 g (64% based on $[HNMe_3]$ -[BPh₄]) of 13. Anal. Calc for C₄₈H₅₄BNOZr: C, 75.60; H, 7.15; N, 1.84. Found: C, 75.42; H, 6.95; N, 1.79.

 $[Cp_2Zr(CH_2Ph)(OCH_2CH_2CH_2CH_2PMe_2Ph)][BPh_4]$ (14). A solution of [Cp₂Zr(CH₂Ph)(CH₃CN)][BPh₄] (0.25 g, 0.36 mmol) and PMe₂Ph (55 μ L, 0.39 mmol) in 10 mL of THF was stirred for 4 days at 55 °C. The THF was removed under vacuum, leaving a foam. The foam was recrystallized twice from THF/Et₂O at -78 °C, yielding 0.14 g (46%) of pale yellow 14. Anal. Calc for C53H56BOPZr: Č, 75.60; H, 6.70. Found: C, 75.73; H, 6.91. 31P{1H} NMR (THF- d_8): δ 25.1.

[Cp₂Zr(CH₃)(OCH₂CH₂CH₂CH₂NMe₃)][BPh₄] (15). A slurry of Cp₂Zr(CH₃)₂ (0.18 g, 0.70 mmol) and [HNMe₃][BPh₄] (0.25 g, 0.66 mmol) in THF (20 mL) was stirred for 6 h at 23 °C. The THF was then removed under vacuum, leaving a white foam. The foam was washed with hot toluene and dried for 15 h under vacuum, yielding 0.34 g (76%) of 15.

 $[Cp_2Zr(Ph)(PMe_3)_2][BPh_4]$ (16). A solution of $[Cp_2Zr-$ (Ph)(THF)][BPh₄] (0.57 g, 0.81 mmol) and PMe₃ (0.16 mL, 1.6 mmol) in THF (25 mL) was prepared at -78 °C and warmed to 23 °C. After 10 min, a white solid precipitated. The slurry was stirred for an additional 30 min and filtered, leaving a white precipitate. The precipitate was recrystallized from THF and dried under vacuum overnight. Yield: 0.55 g (55%). This material contained excess THF (6 equiv by ¹H NMR) and <5% other unidentified Cp-containing impurities. ${}^{31}P{}^{1}H$ NMR (THF- d_8 , -43 °C): δ -12.4.

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Ligand Addition vs Substitution in the Reaction of ¹³CO with (OC)₃Fe⁻ in a Flowing Afterglow Apparatus

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The gas-phase reactions of $(OC)_3$ Fe⁻ with CO and ¹³CO were investigated. Only addition was observed with CO yielding $(OC)_4$ Fe⁻ $(k_{app} = (1.6 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$, but ¹³CO revealed both addition and ligand substitution with an appropriate increase in the rate constant. The average branching fractions for the addition and substitution channels were 0.71 and 0.29, respectively. From these results and the collision frequency for the excited intermediate $[(OC)_3(O^{13}C)Fe^-]^*$ (1) with the helium buffer gas, $k_g[He]$, lower limits on the lifetime of 1 and the rate constants for its unimolecular decomposition are calculated. The large k_{app} for the reaction of $(OC)_3 Fe^-$ with CO yielding the adduct $(OC)_4 Fe^-$ with a doublet electronic ground state suggests that (OC)₃Fe⁻ also has a doublet electronic ground state.

Introduction

Many condensed-phase ligand substitution reactions are stepwise, involving thermal dissociation of a ligand from the initial metal complex followed by association of the new ligand to the intermediate coordinatively unsaturated complex. For example, the 18-electron metal carbonyls $Ni(CO)_4$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ undergo ligand substitution with ${}^{13}CO, {}^1$ amines, 2 and phosphines³ by this

dissociative mechanism. This mechanism is expected since the associative mechanism would require formation of a 20-electron intermediate. However, a number of other 18-electron complexes, i.e. $V(CO)_6^{-4} Mn(CO)_5^{-5} Re(CO)_5^{-5}$

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