75-05-8; $Ru_3(CO)_{10}(MeCN)_2$, 103257-53-0; $[HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\sigma\text{:}\eta^2\text{-}C_6H_7)]$, 128363-70-2; $[HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)][BF_4]$, 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 $Cp_2Zr(Ph)(THF)^+$. Selectivity of Protolytic and Oxidative Zr–R Bond-Cleavage Reactions

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The neutral complexes $Cp_2Zr(R)_2$ (R = CH_3 (1), CH_2Ph (2)) react with $[Cp'_2Fe][BPh_4]$ in THF via oxidative Zr–R bond cleavage to yield $[Cp_2Zr(R)(THF)][BPh_4]$ (R = CH_3 (3), R = CH_2Ph (4)). No reaction is observed with $Cp_2Zr(Ph)_2$ (5). The mixed phenyl–alkyl complexes $Cp_2Zr(Ph)(R)$ (R = CH_3 (9), CH_2Ph (10)) react with Cp'_2Fe^+ in THF to yield 3 and $Cp_2Zr(Ph)(THF)^+$ (6), respectively. The susceptibility of Zr–CH_2Ph 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 $[Cp_2Zr(R)(OCH_2CH_2CH_2CH_2N(CH_3)_3][BPh_4]$ (R = CH_3 (15), CH_2Ph (13), and Ph (12)) via Zr–R bond protonolysis and subsequent nucleophilic THF ring opening. Reactions of 10 and 9 with $[HN(CH_3)_3][BPh_4]$ yield 13 and 15 via initial selective Zr–Ph protonolysis. Complex 1 reacts with $[HN(^nBu)_3][BPh_4]$ 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–CH_3 > Zr–CH_2Ph and that steric effects also strongly influence reactivity. Complex 6 reacts rapidly with 2 equiv of PMe_3 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) complexes[1-3] is motivated by the proposed role of closely related 14-electron $Cp_2M(R)^+$ ions in Cp_2MX_2-based Ziegler–Natta olefin polymerization catalyst systems[4] and by the potential utility of these complexes in catalytic C–H activation/C–C coupling chemistry.[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 Cp_2ZrR_2 complexes.[2,3] Related Ti cations have also been prepared by halide displacement reactions of $Cp_2Ti(CH_3)X$ in coordinating solvents, protonolysis of $Cp^*_2TiR_2$ and by one-electron oxidation of $Cp^*_2Ti(R)$.[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 $Cp_2Zr(R)(L)^+$ 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 $Cp_2Zr(R)(THF)^+$ 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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(6) Anions such as PF_6^-, BF_4^-, $CF_3SO_3^-$, etc. react with or coordinate strongly to $Cp_2Zr(R)^+$ ions. See: (a) Jordan, R. F. *J. Organomet. Chem.* **1985**, *294*, 321. (b) Roddick, D. M.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1989**, *8*, 324. (c) Martin, B. D.; Matchett, S. A.; Norton, J. R.; Anderson, O. P. *J. Am. Chem. Soc.* **1985**, *107*, 7952. (d) Siedle, A. R.; Newmaark, R. A.; Gleason, W. B.; Lammanna, W. M. *Organometallics* **1990**, *9*, 1290.

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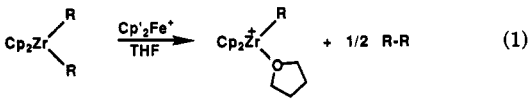
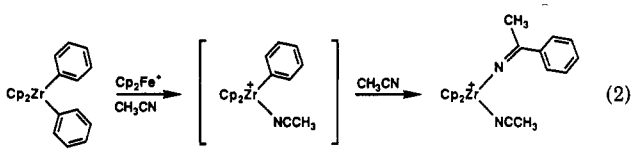
$Cp_2Zr(Ph)(CH_2Ph)$. The neutral complexes $Cp_2Zr(CH_3)_2$ (1) and $Cp_2Zr(CH_2Ph)_2$ (2) react with $[Cp'_2Fe][BPh_4]$ at room temperature in THF to yield $Cp_2Zr(CH_3)(THF)^+$ (3) and $Cp_2Zr(CH_2Ph)(THF)^+$ (4), respectively (eq 1).[2e,k] The



(1)

R = CH_3 1 3
R = CH_2Ph 2 4

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 $Cp_2Zr(R)(CH_3CN)_n^+$ 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 $[Cp_2Fe][BPh_4]$ nor $Ag[BPh_4]$ induces Zr–Ph bond cleavage of 5, and the former salt decomposes. Also, no reaction is observed in THF between these reagents and Cp'_2ZrPh_2, which should be more easily oxidized due to increased electron donation from the Cp′ rings.[7] In contrast, both $Ag[BPh_4]$ and $[Cp_2Fe][BPh_4]$ react rapidly with 5 in CH_3CN to yield $Cp_2Zr(Ph)(CH_3CN)_n^+$ (7), but this species rapidly rearranges to the CH_3CN insertion product 8 (eq 2).[8] It is not clear why 5 reacts with these reagents in

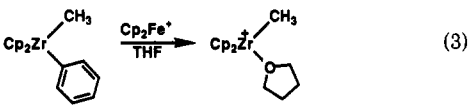


(2)

5 7 8

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.

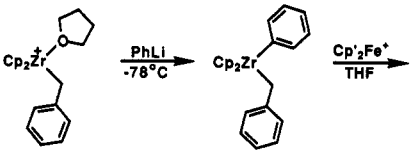
The reactions of a series of mixed alkyls $Cp_2Zr(Ph)(R)$ with Cp_2Fe^+ oxidants in THF were explored with the expectation that the more weakly bonded R ligand would undergo oxidative cleavage yielding $Cp_2Zr(Ph)(THF)^+$. On the basis of the Zr–R bond strength trend[9] Zr–Ph > Zr–CH_3 > Zr–CH_2Ph, we 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



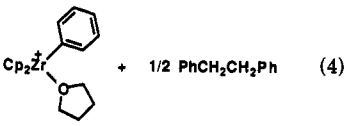
(3)

9 3

minor product (13% NMR yield, δ(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).



4 10

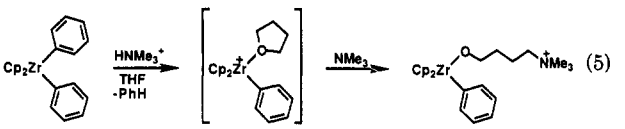


(4)

6

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 $[Cp'_2Fe][BPh_4]$ 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 Cp_2ZrPh_2. The reaction of 5 with $[HNBu_3][BPh_4]$[1e,2a,l,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 $[HNMe_3][BPh_4]$ at 23 °C (THF, 3 h) to yield $[Cp_2Zr(Ph)(OCH_2CH_2CH_2CH_2NMe_3)][BPh_4]$ (12) via Zr–Ph bond protonolysis followed by nucleophilic THF ring-opening (eq 5). This product is formed in 50% NMR yield along



(5)

5 6 12

with several unidentified Cp_2Zr compounds, from which it could not be obtained analytically pure, and has been characterized by ^1H and ^{13}C 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 $[Cp_2Zr(Ph)(OCD_2CD_2CD_2CD_2NMe_3)][BPh_4]$ (12-d_8, 75% complete after 30 min) without detectable intermediates was observed. The THF ring-opening reaction is avoided by using the more acidic ammonium reagent $HNMe_2Ph^+$, the conjugate base of which is less nucleophilic than NMe_3. The reaction of 5 with 2 equiv of $[HNMe_2Ph][BPh_4]$ 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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(10) Reaction of $Cp_2Zr(CH_2Ph)Cl$ (prepared by reaction of $Cp_2Zr(CH_2Ph)_2$ with 1 equiv of HCl in THF at −78 °C; ^1H NMR (benzene-d_6) δ 5.63 Cp, 2.24 CH_2) with LiPh (Et_2O, −40 °C to room temperature) gave a 60:20:20 mixture of $Cp_2Zr(CH_2Ph)(Ph)$, $Cp_2Zr(Ph)_2$, and $Cp_2Zr(CH_2Ph)_2$.

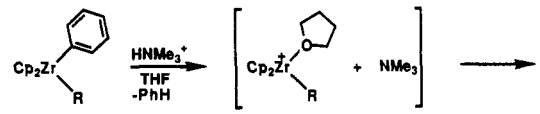
(11) An NMR scale reaction of $Cp_2Zr(Ph)(CH_2Ph)$ with 3 equiv of $[Cp'_2Fe][BPh_4]$ (THF-d_8, 23 °C, 1 h) yielded only $Cp_2Zr(Ph)(THF)^+$ (48%) along with 52% unreacted $Cp_2Zr(CH_2Ph)(Ph)$.

(6)

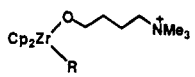
5 6

convenient synthesis of **6**. The excess $[HNMe_2Ph][BPh_4]$ 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 HNR_3^+ reagents were investigated to compare selectivity trends with those observed in the Cp_2Fe^+ reactions described above. The reaction of phenyl benzyl complex **10** with $[HN^nBu_3][BPh_4]$ 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 $[Cp_2Zr(CH_2Ph)(OCH_2CH_2CH_2CH_2NMe_3)][BPh_4]$ (**13**, 90% NMR yield) and 1 equiv of benzene in 24 h (eq 7). Complex **13** is



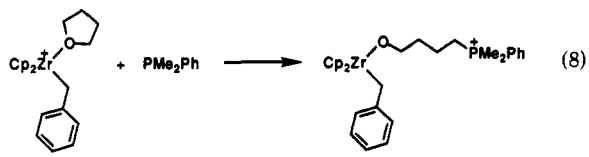
R = CH_3 9 3
R = CH_2Ph 10 4



(7)

15
13

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 $[Cp_2Zr(CH_2Ph)(OCH_2CH_2CH_2CH_2PMe_2Ph)][BPh_4]$ (**14**, eq 8) as noted in

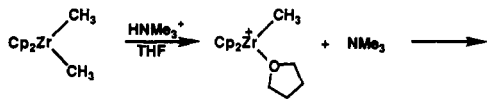


(8)

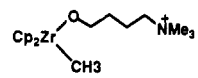
4 14

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 $HNMe_3^+$ 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 $Cp_2Zr(CH_3)(OCH_2CH_2CH_2CH_2NMe_3)^+$ (**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 $Cp_2Zr(CH_3)(THF\text{-}d_8)^+$ (**3**-d_8, 70%), benzene, and free NMe_3 is observed, followed by slower conversion to $Cp_2Zr(CH_3)(OCD_2CD_2CD_2CD_2NMe_3)^+$ (**15**-d_8). Small amounts of **12**-d_8 (10%) derived from Zr–CH_3 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).



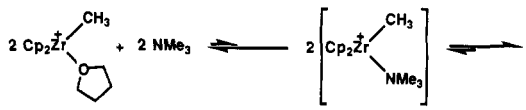
1 3



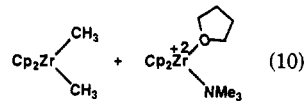
(9)

15

Several mechanisms are possible for these THF ring-opening reactions. When the reaction of **3** and NMe_3 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 NMe_3 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 Cp_2Zr species is the dication $Cp_2Zr(NMe_3)(THF)_n^{2+}$ (n = 1 or 2) formed by disproportionation of $Cp_2Zr(CH_3)(NMe_3)^+$, which is in equilibrium with **3** and free NMe_3 (eq 10). Similar disproportionation reactions



3 + 2 THF



(10)

+ THF + NMe_3

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 NMe_3 as in eq 9 or by intramolecular ring opening of $Cp_2Zr(NMe_3)(THF)^{2+}$ followed by ligand redistribution.

The importance of steric effects in these protonolysis and ring-opening reactions is illustrated by the reactions of $HNBu_3^+$. 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 $N(^nBu)_3$ analogue of **15** is observed. This is the most convenient synthesis of **3**.

Characterization and Chemistry of $Cp_2Zr(Ph)(THF)^+$ (6). Cationic Zr–Ph complex **6** is characterized by NMR spectroscopy (Table I) and analysis. The low-temperature ^1H NMR spectrum in CD_2Cl_2 (−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% $Cp_2Zr(Ph)(CH_2Ph)$ is converted to a mixture of products with Cp_2Zr 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 $HNMe_3^+$ is monitored by ^1H NMR spectroscopy.

(14) R. F. Jordan and G. D. Hinch, unpublished results.

(15) ^1H NMR of free THF (−90 °C, CD_2Cl_2): δ 3.62, 1.74.

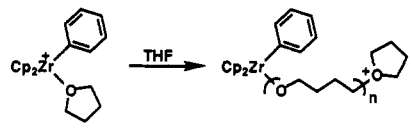
Table I. ^1H NMR and ^{13}C NMR Data (ppm) for New Compounds[a]

^1H NMR	assgnt	^{13}C NMR	assgnt
	$[Cp_2Zr(Ph)(THF)][BPh_4]$ (6)		
7.19 (t, J = 6.8, 2 H)[b,e]	*m*-phenyl	184.9[f]	i-phenyl
7.11 (t, J = 6.6, 1 H)	*p*-phenyl	133.7	*o*-phenyl
7.09 (d, J = 7.1, 2 H)	*o*-phenyl	128.2	*m*-phenyl
6.29 (s, 10 H)	C_5H_5	127.8	*p*-phenyl
3.27 (br m, 4 H)	THF	116.6	C_5H_5
1.71 (br m, 4 H)	THF		
	$[Cp_2Zr(Ph)(THF)][BPh_4]$ (6)		
7.30–1.18 (br m, 5 H)[c,f]	aryl		
6.46 (s, 10 H)	C_5H_5		
	$Cp_2Zr(CH_2Ph)(Ph)$ (10)		
7.11 (d, of d, J = 7.8, 1.3, 2 H)[c,f]	*o*-phenyl	183.3[g]	i-phenyl
7.03 (t, J = 7.3, 2 H)	*m*-benzyl	152.5	i-benzyl
7.01 (t, J = 7.3, 2 H)	*m*-phenyl	136.0	aryl
6.90 (t of t, J = 7.3, 1.4, 1 H)	*p*-phenyl	128.3	aryl
6.86 (d of d, J = 7.7, 1.16, 2 H)	*o*-benzyl	127.0	aryl
6.71 (t of t, J = 7.3, 1.2, 1 H)	*p*-benzyl	125.7	aryl
6.10 (s, 10 H)	C_5H_5	125.3	*p*-phenyl
2.11 (s, 2 H)	CH_2Ph	121.0	*p*-benzyl
		112.7	C_5H_5
		62.6	$ZrCH_2$
	$[Cp_2Zr(Ph)(OCH_2CH_2CH_2CH_2NMe_3)][BPh_4]$ (12)		
7.4–6.8 (m, obscured by BPh_4^-)	aryl	179.4[h]	i-phenyl
6.13 (s, 10 H)[c,h]	C_5H_5	139.7	*o*-phenyl
4.02 (t, J = 6.1, 2 H)	$ZrOCH_2$	127.4	*m*-phenyl
3.18–3.07 (m, 2 H)	NCH_2	125.0	*p*-phenyl
2.89 (s, 9 H)	$N(CH_3)_3$	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_{CN} = 4)	$N(CH_3)_3$
		30.9	OCH_2CH_2
	$[Cp_2Zr(CH_2Ph)(OCH_2CH_2CH_2CH_2NMe_3)][BPh_4]$ (13)		
7.12 (t, J = 7.6, 2 H)[b,h]	*m*-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)	*p*-benzyl	127.4	aryl
5.96 (s, 10 H)	C_5H_5	120.8	*p*-benzyl
3.90 (t, J = 6.1, 2 H)	OCH_2	73.1	OCH_2
3.14–3.09 (m, 2 H)	NCH_2	67.4 (t, J_{CN} = 5)	NCH_2
2.92 (s, 9 H)	$N(CH_3)_3$	53.8 (t, J_{CN} = 4)	NCH_3
2.25 (s, 2 H)	CH_2Ph	46.5	CH_2Ph
1.68–1.59 (m, 2 H)	OCH_2CH_2	30.9	OCH_2CH_2
1.44–1.36 (m, 2 H)	NCH_2CH_2	20.4	NCH_2CH_2
	$[Cp_2Zr(CH_2Ph)(OCH_2CH_2CH_2CH_2PMe_2Ph][BPh_4]$ (14)		
7.8–6.7 (m, 30 H)[d,g]	aryl, BPh_4^-	154.5[f,i]	i-benzyl
5.83 (s, 10 H)	C_5H_5	135.3 (d, J_{PC} = 4)	*p*-PMe_2Ph
3.79 (t, J = 6.0, 2 H)	$ZrOCH_2$	131.8 (d, J_{PC} = 10)	*o*-PMe_2Ph
2.16 (s, 2 H)	$ZrCH_2Ph$	130.9 (d, J_{PC} = 13)	*m*-PMe_2Ph
1.6–1.0 (m, 6 H)	$PCH_2CH_2CH_2$	128.2	*o*- or *m*-benzyl
1.26 (d, J_{PH} = 13, 6 H)	$P(CH_3)_2$	127.2	*o*- or *m*-benzyl
		120.7	*p*-benzyl
		111.9	C_5H_5
		73.0	$ZrOCH_2$
		46.8	$ZrCH_2Ph$
		24.3 (d, J_{PC} = 51)	$ZrOCH_2CH_2CH_2CH_2$
		23.3 (d, J_{PC} = 16)	$ZrOCH_2CH_2CH_2$
		19.1 (d, J_{PC} = 4)	$ZrOCH_2CH_2$
		6.8 (d, J_{PC} = 55)	$P(CH_3)_2Ph$
	$[Cp_2Zr(CH_3)(OCH_2CH_2CH_2CH_2NMe_3][BPh_4]$ (15)		
6.06 (s, 10 H)[c,h]	C_5H_5	111.5[h]	C_5H_5
3.86 (t, J = 5.9, 2 H)	OCH_2	72.6	OCH_2
3.08–3.03 (m, 2 H)	NCH_2	67.4 (br s)	NCH_2
2.88 (s, 9 H)	$N(CH_3)_3$	53.7 (br s)	$N(CH_3)_3$
1.66–1.53 (m, 2 H)	OCH_2CH_2	31.1	$Zr(CH_3)$
1.41–1.28 (m, 2 H)	NCH_2CH_2	20.3	OCH_2CH_2
−0.06 (s, 3 H)	$Zr(CH_3)$	18.2	NCH_2CH_2
	$[Cp_2Zr(Ph)(PMe_3)_2][BPh_4]$ (16)		
7.46–7.38 (m, 2 H)[c,j]	*m*-phenyl	140.9[j,k]	*o*-phenyl
7.02–6.95 (m, 3 H)	*o*- and *p*-phenyl	127.3	*m*- or *p*-phenyl
6.07 (t, J_{PH} = 1.9, 10 H)	C_5H_5	126.5	*m*- or *p*-phenyl
1.03 (d, J_{PH} = 7.4, 18 H)	$P(CH_3)_3$	108.6	C_5H_5
		15.5 (d, J_{PC} = 20)	$P(CH_3)_3$

[a] Spectra of cationic complexes also contain normal BPh_4^- resonances; see ref 2. J values in Hz. [b] 360 MHz. [c] 300 MHz. [d] 200 MHz. [e] CD_2Cl_2, −90 °C. [f] THF-d_8, ambient T. [g] CD_2Cl_2, ambient T. [h] CD_3CN, ambient T. [i] ipso-C of P–Ph ring not observed. [j] THF-d_8, −43 °C. [k] ipso-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 ^{1}H 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

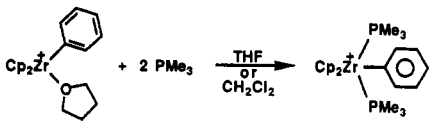


(11)

6 11

that for $Cp_2Zr(Ph)(OCH_2CH_2CH_2CH_3)$, generated in THF-$d_8$ by reaction of **2** with 1 equiv of ^{n}BuOH,[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–CH_3 bond cleavage occurs in this reaction.

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

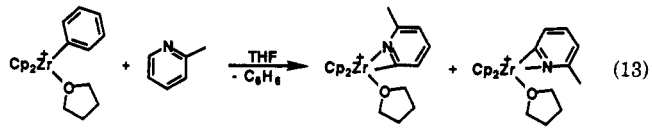


(12)

6 16

The ^{1}H 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 Hz) at −43 °C. However, the Cp resonance of **16** shifts only slightly upon addition of excess (6 equiv total) PMe_3 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 PMe_3 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 ^{1}H NMR spectrum of a THF-d_8 solution of **6** containing 1 equiv of PMe_3 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



(13)

6 17a 17b

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

Complex **6** reacts rapidly in CH_3CN via ligand substitution and CH_3CN 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 $Cp_2Zr(Ph)(Cl)$ (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 $Cp_2Zr(CMe{=}CMe_2)(THF)^+$.[20] Similarly, only traces of polyethylene are formed when a CD_2Cl_2 solution of **6** is charged with 1 atm of ethylene.

Discussion

Oxidation Chemistry. Neutral Cp_2ZrR_2 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–CH_2Ph > Zr–Ph, Zr–CH_3. Thus, $Cp_2Zr(CH_2Ph)_2$ (**2**) reacts with Cp'_2Fe^+ rapidly at room temperature and below, $Cp_2Zr(CH_3)_2$ (**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 orbital[21] followed by R$^\bullet$ extrusion and trapping of the resulting Zr cation by solvent.[2e,22] The facile cleavages of weak Zr–CH_2Ph bonds,[9] and the lack of reaction of Cp_2ZrPh_2, which contains strong Zr–Ph bonds and exhibits a relatively high (irreversible) $E_{1/2}$(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 Cp_2ZrR_2 complexes react with HNR_3^+ 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,l,m] and by Marks[3] for the synthesis of $Cp^*_2ZrCH_3^+$ and $Cp^*_2ThCH_3^+$ complexes. In the case of the $HNMe_3^+$, the unhindered amine NMe_3 released in the protonolysis step undergoes nucleophilic THF ring-opening reactions with $Cp_2Zr(R)(THF)^+$ yielding $Cp_2Zr(R)(OCH_2CH_2CH_2CH_2NMe_3)^+$ 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 Cp_2Zr decomposition product exhibits a ^{1}H NMR Cp resonance at δ 6.31, which is identical with that for $Cp_2Zr(Ph)(Cl)$ (generated independently via reaction of **6** and $[(^nBu)_4N][Cl]$). BPh_3 is also observed.

(18) (a) These resonances appear at δ 3.45 (br s), 1.62, (br s) in CD_3NO_2, 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. *Macromolecules* **1990**, *23*, 4042. (d) Neither BPh_3 nor $Na[BPh_4]$ polymerize THF under these conditions.

(19) ^{1}H NMR of $Cp_2Zr(Ph)(OCH_2CH_2CH_2CH_3)$ (THF-d_8): 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–CH_3 > Zr–CH_2Ph. Thus, **1** and **5** react with $HNMe_3^+$ 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 $HNMe_3^+$ 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 $HNMe_3^+$ 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 $Cp_2Zr(Ph)(THF)^+$ (6). Complex **6** reacts with excess PMe_3 to yield $Cp_2Zr(Ph)(PMe_3)_2^+$ (**16**). The mono-PMe_3 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 $Cp^*_2Zr\{2\text{-Et},5\text{-B}(4\text{-ethylphenyl})_3\text{phenyl}\}$ and $Cp_2Zr(CH_3)(\text{picoline})^+$,[2a,5b] is not stable in the presence of excess PMe_3. In fact, the reaction of **6** with 1 equiv of PMe_3 yields $^1/_2$ equiv of **16** and $^1/_2$ equiv of unreacted **6**. In contrast, $Cp'_2Zr(CH_2CH_2R)(THF)^+$ complexes (**18**) react with PMe_3 to yield the mono-PMe_3 complexes $Cp'_2Zr(CH_2CH_2R)(PMe_3)^+$, which have β-agostic structures. These complexes are stable in the presence of excess PMe_3.[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 CD_2Cl_2 via ligand substitution and ortho C–H activation to yield $Cp_2Zr(\eta^2(N,C)\text{-picolyl})(THF)^+$ (**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, CH_3CN 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 Microanalytical Laboratory. The following compounds were prepared by literature methods: $Ag[BPh]_4$,[2f] $[Cp_2Fe][BPh_4]$,[2h] $[Cp'_2Fe][BPh_4]$,[2h] $Cp_2Zr(Ph)_2$,[30] $Cp'_2Zr(Ph)_2$,[31] $K[CH_2Ph]$,[32] $Cp_2Zr(CH_3)_2$,[30] $[Cp_2Zr(CH_3)(THF)][BPh_4]$,[2f] $Cp_2Zr(CH_2Ph)_2$,[33] $[Cp_2Zr(CH_2Ph)(THF)][BPh_4]$,[8] $[Cp_2Zr(CH_2Ph)(CH_3CN)][BPh_4]$,[2e] $Cp_2Zr(Ph)(CH_3)$,[34] $[HN(^nBu)_3][BPh_4]$,[35] and $[HN(CH_3)_2(Ph)][BPh_4]$.[35] $[HN(CH_3)_3][BPh_4]$ was purchased from Aldrich and used after drying on a high-vacuum line. $Na[BPh]_4$, $(C_5H_4Me)_2Fe$, and NMe_3 were purchased from Aldrich and used without further purification.

$[Cp_2Zr(Me)(THF)][BPh_4]$ (3). A slurry of $Cp_2Zr(CH_3)_2$ (0.510 g, 2.03 mmol) and $[HNBu_3][BPh_4]$ (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 $Cp_2Zr(CH_3)_2$ by Ag^+ or Cp'_2Fe^+ reagents.[2f]

Preparation of 3 via Oxidation of $Cp_2Zr(CH_3)_2$ with $[Cp'_2Fe][BPh_4]$. A slurry of $Cp_2Zr(CH_3)_2$ (5.00 g, 19.9 mmol) and $[Cp'_2Fe][BPh_4]$ (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 $HN(^nBu)_3^+$ 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 CH_2Cl_2/toluene at -78 °C. This sample contained 0.33 equiv of toluene (^1H NMR). Anal. Calc for $C_{44}H_{43}BOZr \cdot 0.33C_7H_8$: C, 77.22; H, 6.39; Zr, 12.66. Found: C, 76.80; H, 6.28; Zr, 12.79.

Preparation of $[Cp_2Zr(Ph)(THF)][BPh_4]$ (6) from $Cp_2Zr(Ph)_2$. A slurry of $Cp_2Zr(Ph)_2$ (3.10 g, 8.26 mmol) and $[HN(Me)_2(Ph)][BPh_4]$ (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 $[Cp_2Zr(CH_2Ph)(THF)][BPh_4] \cdot 0.43C_7H_8$ (2.02 g, 2.53 mmol) in THF (35 mL) was prepared at -78 °C. Under N_2 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 $Cp_2Zr(CH_2Ph)_2$ (1.00 g, 2.48 mmol) and $[HNMe_3][BPh_4]$ (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 $[HNMe_3][BPh_4]$) of **13**. Anal. Calc for $C_{48}H_{54}BNOZr$: 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 $[Cp_2Zr(CH_2Ph)(CH_3CN)][BPh_4]$ (0.25 g, 0.36 mmol) and PMe_2Ph (55 μL, 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/Et_2O at -78 °C, yielding 0.14 g (46%) of pale yellow **14**. Anal. Calc for $C_{53}H_{56}BOPZr$: C, 75.60; H, 6.70. Found: C, 75.73; H, 6.91. $^{31}P\{^1H\}$ NMR (THF-d_8): δ 25.1.

$[Cp_2Zr(CH_3)(OCH_2CH_2CH_2CH_2NMe_3)][BPh_4]$ (15). A slurry of $Cp_2Zr(CH_3)_2$ (0.18 g, 0.70 mmol) and $[HNMe_3][BPh_4]$ (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 $[Cp_2Zr(Ph)(THF)][BPh_4]$ (0.57 g, 0.81 mmol) and PMe_3 (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. $^{31}P\{^1H\}$ NMR (THF-d_8, -43 °C): δ -12.4.

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Ligand Addition vs Substitution in the Reaction of ^{13}CO with $(OC)_3Fe^-$ in a Flowing Afterglow Apparatus

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The gas-phase reactions of $(OC)_3Fe^-$ with CO and ^{13}CO were investigated. Only addition was observed with CO yielding $(OC)_4Fe^-$ ($k_{app} = (1.6 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}), but ^{13}CO 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_s[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 $(OC)_3Fe^-$ with CO yielding the adduct $(OC)_4Fe^-$ 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 phosphines[3] 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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