Syntheses and Structures of Five-Coordinate Zirconium Alkyl Complexes Supported by Diketiminate Ligands

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An alkane elimination reaction generates the diketiminate compound (TTP)Zr(CH_2Ph)$_3$ (**1**) from Zr(CH_2Ph)$_4$ and TTPH (TTPH = 2-*p*-tolylamino-4-*p*-tolylimino-2-pentene). The molecular structure of **1** was solved, and it shows a five-coordinate zirconium with three η^1-coordinated benzyl groups and an η^2-bound TTP ligand. When **1** is heated to 45 °C in hydrocarbon solvents, toluene is eliminated and the orthometalated product **2** is formed. The molecular structure of **2** indicates η^1 and η^2 benzyl groups. The variable-temperature ^{1}H NMR (−78 to 50 °C) spectra exhibit a single benzyl resonance. The magnitude of $^1J_{CH}$ for the benzyl methylene resonance is consistent with a rapid exchange between η^1 and η^2 bonding modes in solution. Isotopic labeling experiments employing (PPP-d_{10})Zr(CH_2Ph)$_3$-(**3**-d_{10}, PPP = 2-phenylamino-4-phenylimino-2-pentenato) support direct C−H activation through a four-centered transition state. Based on kinetic experiments, C−H activation is unimolecular, and the rate-limiting step exhibits a large kinetic isotope effect: $k_H/k_D = 5.2$-(5) at 65 °C. The thermal stability of alkyl complexes is improved by replacing the ortho protons with isopropyl groups. (DDP)ZrMe_3 (**5**) can be prepared from (DDP)ZrCl_3 via halide metathesis using MeLi (DDP = 2-(2,6-diisopropyl)phenylamino-4-(2,6-diisopropyl)phenylimino-2-pentenato). The thermal stability of **5** is greatly enhanced compared to those of **1** and **3**.

Introduction

The search for noncyclopentadienyl ligands in Ziegler−Natta catalysis has recently attracted considerable attention. In this respect, nitrogen-based ligands have been found to be particularly attractive in early and late transition metal systems.[1−5] Diketimines in their neutral and uninegative forms are potentially useful ligands for catalytic applications since they can be readily prepared by condensation reactions of amines with 2,4-pentanedione.[6−8] In addition to our own efforts in main-group and early transition metal systems, [9−11] other applications of β-diketimine and diketiminate ligands have recently appeared.[12−18] In this paper we describe synthesis, structure, and reactivity of five-coordinate Zr alkyl complexes supported by β-diketiminate ligands. In particular, ligand activation reactions are examined, and an approach for their prevention is described.

Results and Discussion

Alkyl migration to imine carbons of tetraazamacrocycles has been reported by Jordan and co-workers.[19] This is a potential point of vulnerability for closely related diketiminate compounds. Thus, our first goal in group 4 alkyl systems was to prepare diketiminate alkyl compounds and determine whether alkyl migrations would pose similar problems. The diketimine 2-*p*-tolylamino-4-*p*-tolylimino-2-pentene (TPPH) reacted

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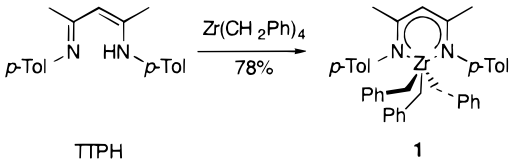
Table 1. NMR Data for the Benzyl Groups (CH_2Ph) in Compounds 1−4[a]

	1	3	2	4
^{1}H NMR	2.61	2.54[b]	2.14[c]	2.09[c]
			1.66[c]	1.57[c]
^{13}C NMR	75.62	75.4[b]	66.62	66.97
$^1J_{C-H}$ (Hz)	122.2	122.0	131.4	130.9

[a] NMR spectra were taken at room temperature in C_6D_6 and reported in ppm; ^{1}H NMR (500 MHz), ^{13}C NMR (75 MHz). [b] Ref 14. [c] Doublet, $|^2J_{HH}| = 9.6$ Hz.

smoothly with $Zr(CH_2Ph)_4$ to eliminate toluene, affording the diketiminate complex (TTP)$Zr(CH_2Ph)_3$ (**1**) in 78% yield (eq 1). The ^{1}H and ^{13}C{^{1}H} NMR spectra for



(1)

TTPH 1

compound **1** indicated one benzyl and symmetric ligand environments, proving that alkyl migration to the TTP imine carbon did not occur. The value of $^1J_{C-H}$ for the benzyl methylene resonance is sensitive to the hapticity of the benzyl group,[20−22] and the $^1J_{C-H}$ value of 122.0 Hz (Table 1) is consistent with η^1-coordination for the benzyl ligands in compound **1.** The spectroscopic data provided little information regarding the coordination geometry at Zr for compound **1** since the benzyl and TTP ligand resonances did not decoalesce at low temperature.

The molecular structure of **1** was determined, and its ORTEP diagram is shown in Figure 1 with selected bond lengths and angles. The geometry at zirconium is best described as square pyramidal with C(20) in apical and C(27), C(34), N(1), and N(2) in basal positions. Although the ligand set of compound **1** contains potential π-donors, theoretical treatments predict square pyramidal structures for five-coordinate d^0 hydride and alkyl derivatives, and a C_{4v} structure is observed for $TaMe_5$ in the gas phase.[23,24] The diketiminate ligand is η^2-bound to Zr, which contrasts structures of Zr{N($SiMe_3$)C(^{t}Bu)-CHC(Ph)N($SiMe_3$)}Cl_3 and (Cp)(PPP)$ZrCl_2$ (PPP = 2-phenylamino-4-phenylimino-2-pentenato), where the diketiminate ligands bind η^5 to the Zr centers.[14,25] Substitution of benzyl for chloride ligands should render the Zr center in compound **1** less electrophilic. Thus, the stabilization afforded by η^5-coordination may be reduced relative to the chloride complexes; however, the stabilization provided by η^5-coordination has not been quantified, and we have not determined whether steric factors could also be responsible for the change in hapticity. The benzyl ligands in compound **1** are η^1-coordinated, and the average Zr−C bond distance in **1** (2.290(5) Å) is very

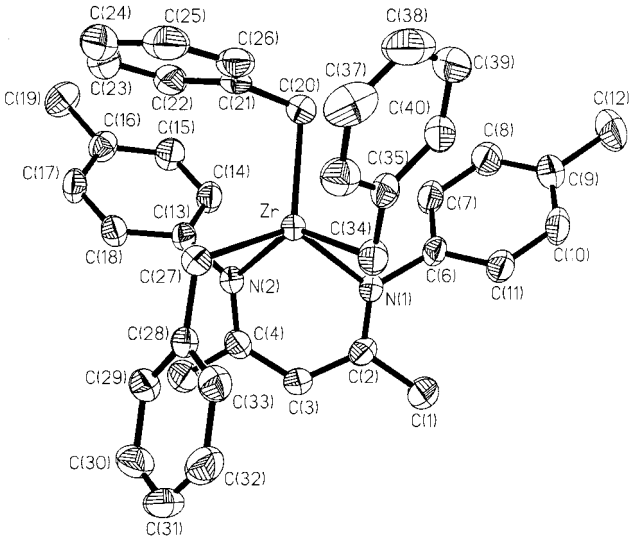
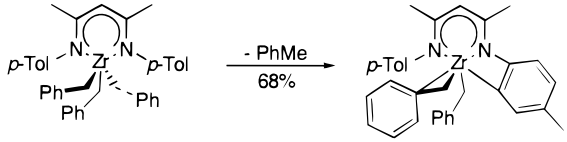


Figure 1. Molecular structure of (TTP)$Zr(CH_2Ph)_3$ (**1**) with atom-labeling scheme. Selected bond lengths (Å) and angles (deg): Zr−N(2), 2.189(2); Zr−N(1), 2.205(2); Zr−C(20), 2.253(3); Zr−C(27), 2.304(3); Zr−C(34), 2.313(3); N(2)−Zr−N(1), 76.51(8); N(2)−Zr−C(20), 111.35(11); N(1)−Zr−C(20), 112.51(10); N(2)−Zr−C(27), 84.79(9); N(1)−Zr−C(27), 133.30(9); C(20)−Zr−C(27), 114.13(11); N(2)−Zr−C(34), 139.09(10); N(1)−Zr−C(34), 81.81(10); C(20)−Zr−C(34), 108.90(12); C(27)−Zr−C(34), 85.48(11); C(21)−C(20)−Zr, 99.1(2); C(28)−C(27)−Zr, 117.6(2); C(35)−C(34)−Zr, 110.7-(2).

close to that in (η^5-C_5H_5)Zr(η^1-CH_2Ph)$_3$ (2.299(8) Å).[26] The Zr−C(20)−C(21) angle of 99.1(2)° is significantly more acute than the corresponding angles for the basal ligands (Zr−C(27)−C(28), 117.6(2)°; Zr−C(34)−C(35), 110.7(2)°). A similar ligation for benzyl groups in (η^5-C_5H_5)Zr(η^1-CH_2Ph)$_3$ was described as intermediate between η^1- and η^2-coordination.[26] In a related tribenzyl Zr complex supported by a hindered aryloxide ligand, one of the benzyl groups is η^2-bound (Zr−C−C_{ipso} = 88.0(3)°).[22] The increased benzyl hapticity for this compound parallels the decreased hapticity of the supporting ligand. The structure of compound **1** confirms the predominant η^1-coordination inferred from the spectroscopic data for the benzyl groups.

Attempted preparation of $(TTP)_2Zr(CH_2Ph)_2$ from compound **1** and TTPH resulted in toluene elimination; however, TTPH was not consumed. Independent thermolysis of **1** (45 °C, 48 h) confirmed that **1** eliminated toluene, and the orthometalated compound (η^3-MeC-(NC_7H_6)CHC(N-*p*-Tol)Me)Zr(η^2-CH_2Ph)(η^1-CH_2Ph) (**2**) was isolated in 68% yield (eq 2). Toluene loss was



(2)

1 2

confirmed by ^{1}H NMR and GC−MS data. This reaction is similar to an intramolecular alkane elimination reported by Schrock and co-workers.[27] Upon extended

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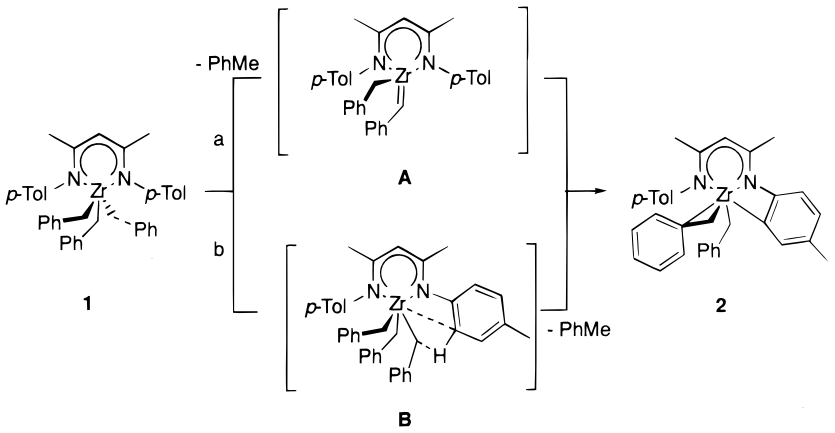
Scheme 1



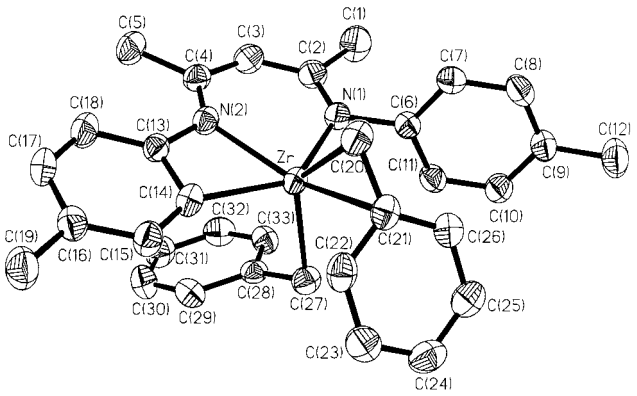


Figure 2. Molecular structure of (η^3-MeC(NC_7H_6)CHC(N-*p*-Tol)Me)Zr(η^2-CH_2Ph)(η^1-CH_2Ph) (**2**) with atom-labeling scheme. Selected bond lengths (Å) and angles (deg): Zr−N(1), 2.175(2); Zr−N(2), 2.253(2); Zr−C(13), 2.781(2); Zr−C(14), 2.260(2); Zr−C(27), 2.288(2); Zr−C(20), 2.302(2); Zr−C(21), 2.584(2); N(1)−Zr−N(2), 77.91(6); N(1)−Zr−C(14), 138.48(6); N(2)−Zr−C(14), 60.63(7); N(1)−Zr−C(27), 100.45(7); N(2)−Zr−C(27), 114.65(6); C(14)−Zr−C(27), 98.65(7); N(1)−Zr−C(20), 98.92(7); N(2)−Zr−C(20), 116.16(6); C(27)−Zr−C(20), 128.25(7); N(1)−Zr−C(21), 113.00(6); N(2)−Zr−C(21), 147.23(6); C(14)−Zr−C(21), 101.84(7); C(27)−Zr−C(21), 94.32(6); C(20)−Zr−C(21), 34.13(6); C(28)−C(27)−Zr, 99.64(11); C(21)−C(20)−Zr, 83.58(11); C(22)−C(21)−Zr, 91.32(11).

thermolysis at 90 °C, solutions of compound **2** darkened and intensities of ^{1}H NMR resonances for compound **2** diminished.

The ^{1}H and ^{13}C NMR data are consistent with orthometalation in compound **2**. The nonequivalence of tolyl and pentene methyl groups indicates that the symmetry of the TTP ligand has been broken, and diastereotopic benzylic proton resonances are observed at δ 2.14 and 1.58 ppm ($|^2J_{HH}| = 9.6$ Hz). The inferred orthometalation was crystallographically confirmed, and the molecular structure of compound **2** with selected bond distances and angles is shown in Figure 2. The X-ray study establishes that the diketiminate ligand is η^3-bonded to Zr. One of the benzyl groups is η^2-coordinated (Zr−C(20), 2.302(2) Å; Zr−C(21), 2.584(2) Å; Zr−C(20)−C(21), 83.58(11)°), while the other approaches η^1-coordination (Zr−C(27), 2.288(2) Å; Zr···C(28), 2.928(2) Å; Zr−C(27)−C(28), 99.64(11)°).

Even at −80 °C, one benzyl environment is observed in compound **2** by ^{1}H NMR. However, the value of 131 Hz for $^1J_{CH}$ in compound **2** is very near the weighted average of typical η^1 (119 Hz) and η^2 (145 Hz) values (Table 1).[21] This spectroscopic feature confirms that η^2-coordination is maintained in solution and supports rapid exchange between η^1- and η^2-coordinated benzyl groups in solution.

Two paths can be envisioned to account for the conversion of **1** to **2** (Scheme 1). Path a involves α-abstraction to form the zirconium benzylidene intermediate **A**, followed by arene C−H activation to give **2**. Path b involves a direct σ-bond metathesis via the four-centered transition state, **B**.

Paths a and b can be distinguished by isotopic labeling experiments. Specifically, deuterium labeling at the arene positions will give toluene-d_0 and toluene-d_1 for paths a and b, respectively. Collins and co-workers reported the synthesis of the related diketiminate compound, (PPP)Zr(CH_2Ph)$_3$ (**3**, PPP = 2-phenylamino-4-phenylimino-2-pentenato).[14] Since the desired isotopic label is more conveniently introduced by preparing PPPH-d_{10} from aniline-d_5 and 2,4-pentanedione, we have examined the thermolysis of **3**. Compound **3** reacts in analogous fashion to **1**, affording the orthometalated analogue of **2**, compound **4**. ^{1}H and ^{2}H NMR indicate that orthometalation of **3**-d_{10} gives toluene-d_1, predominantly (>95%).[28] This observation excludes path a in Scheme 1. Plots of ln{[**3**$_t$]/[**3**$_0$]} vs time are linear, and the slopes of these plots are concentration independent. The rate constants for arene activation in **3**-d_0 and **3**-d_{10} give $k_H/k_D = 5.2(5)$ at 65 °C. The kinetic data are consistent with unimolecular, rate-limiting C−H activation via transition state **B**. The magnitude of the primary kinetic isotope effect is slightly smaller than that reported by Wolczanski and co-workers for toluene loss from Zr(NHR)$_3$(CH_2Ph) and Zr(NDR)$_3$(CH_2Ph) (R = Si^{t}Bu$_3$, $k_H/k_D = 7.1(6)$).[29,30]

To prevent orthometalation, we attempted the synthesis of the ortho-substituted compound (DDP)Zr(CH_2Ph)$_3$ from DPPH (DPPH = 2-(2,6-diisopropyl)phenylamino-4-(2,6-diisopropyl)phenylimino-2-pentene) and

(28) The ^{1}H NMR spectrum of PhCH_2D (500 MHz, C_6D_6) contained a 1:1:1 triplet at δ 2.09 ($|^2J_{H-D}| = 2.0$ Hz). This chemical shift matches that of the compound independently prepared from PhCH_2MgCl and D_2O. Also, when the reaction was monitored by ^{2}H NMR (46 MHz) in C_6H_6, a peak corresponding to PhCH_2D at δ 2.06 was observed.

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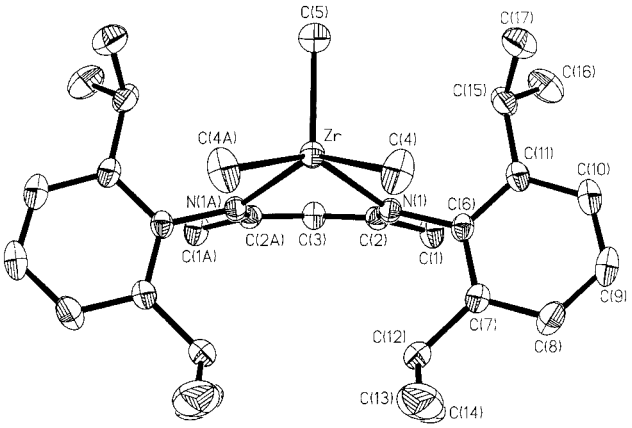

Figure 3. Molecular structure of (DDP)$ZrMe_3$ (**5**) with atom-labeling scheme. Selected bond lengths (Å) and angles (deg): Zr−N(1), 2.2712(14); Zr−N(1A), 2.2712(14); Zr−C(4), 2.274(2); Zr−C(4A), 2.274(2); Zr−C(5), 2.237(3); C(5)−Zr−N(1), 107.37(7); C(5)−Zr−N(1A), 107.37(7); N(1)−Zr−N(1A), 81.72(7); C(5)−Zr−C(4), 107.75(9); N(1)−Zr−C(4), 87.71(6); N(1A)-Zr−C(4), 144.88(8); C(5)−Zr−C(4A), 107.75-(9); N(1)−Zr−C(4A), 144.88(8); N(1A)-Zr−C(4A), 87.71(7); C(4)−Zr−C(4A), 81.95(12).

$Zr(CH_2Ph)_4$. $Zr(CH_2Ph)_4$ did not react with DDPH at room temperature, and at elevated temperatures $Zr(CH_2Ph)_4$ decomposed, leaving unreacted DDPH. Presumably, increased steric requirements of ^{i}Pr groups impose a substantial kinetic barrier on alkane elimination. Nonetheless, trialkyl compounds can be prepared by halide substitution routes, and we have synthesized (DDP)$ZrMe_3$ (**5**) from Zr(DDP)Cl_3 and MeLi (54% yield, eq 3). The identity of **5** was established by ^{1}H, ^{13}C NMR,

$$\underset{}{(\text{DDP})\text{ZrCl}_3} + 3\ \text{MeLi} \rightarrow \underset{\mathbf{5}}{(\text{DDP})\text{ZrMe}_3} + 3\ \text{LiCl} \qquad (3)$$

and X-ray diffraction methods. ^{1}H and ^{13}C NMR spectra indicate fluxional behavior, as a single Zr methyl resonance is observed from −70 to 25 °C.

The molecular structure of **5** is shown in Figure 3. The Zr center adopts a square pyramidal geometry with a crystallographic mirror plane passing through Zr, C(3), and C(5). As is commonly found in d^0 square pyramidal compounds, the apical Zr−C(5) distance in compound **5** (2.237(3) Å) is shorter than the basal Zr−C(4) distance (2.274(2) Å). The average Zr−C bond distance in compound **5** (2.262(4) Å) is significantly shorter than Zr−C distances in six- and eight-coordinate methyl compounds.[31−33] The Zr−N bonds in compound **5** (Zr−N(1), 2.2712(14) Å; Zr−N(1A), 2.2712(14) Å) are comparable with those of compound **1 (**Zr−N(1), 2.205-(2) Å; 1 (Zr−N(2), 2.189(2) Å). However, the bite angle for the diketiminate ligand in compound **5** is more obtuse than in compound **1**. This is reflected by comparing ∠N(1)−Zr−N(1A) = 81.72(7)° and ∠C(2)−C(3)−C(2A) = 129.5(2)° in compound **5** to ∠N(1)−Zr−N(2) = 76.51(8)° and ∠C(2)−C(3)−C(4) = 124.2(3)° in compound **1**. Furthermore, the diketiminate ligand backbones in compounds **1** and **5** have significantly different orientations. In Figure 4, the phenyl rings of the benzyl ligands in compound **1** have been removed, and the molecule has the same orientation as compound **5** in Figure 3. The least-squares plane defined by the TTP ligand atoms N(1), N(2), C(2), C(3), and C(4) in compound **1** forms an angle of 67.7(3)° with that of the least-squares plane defined by the basal atoms N(1), N(2), C(27), and C(34) (Figure 4). For compound **5**, the analogous least-squares plane defined by the DDP ligand atoms N(1), N(1A), C(2), C(2A), and C(3) is nearly parallel (7.0(3)°) to the least-squares plane defined by the basal atoms C(4), C(4A), N(1), and N(1A). A closer examination of the structure for compound **5** reveals several contacts between Zr methyl and ^{i}Pr methyl groups that approach the van der Waals limit. When the DDP backbone in compound **5** is constrained to the TTP geometry in compound **1**, severe steric interactions are apparent. These are relieved only by distortion of the DDP backbone. Thus, the differences in diketiminate ligand orientations almost certainly have steric origins.

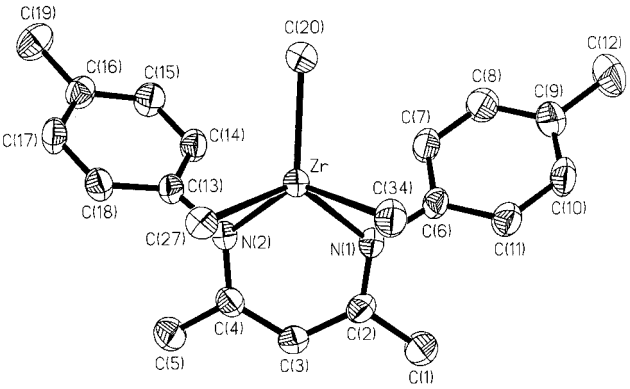

Figure 4. Another view of (TTP)$Zr(CH_2Ph)_3$ (**1**) with three phenyl groups removed from the benzyl groups for clarity. The angle between the N(1), C(2), C(3), C(4), N(2) plane and the square base C(27), C(34), N(1), N(2) is 67.7(3)°.

The thermal stability for **5** is greatly enhanced relative to compounds **1** and **3**. When solutions of compound **5** are heated (70 °C, 12 h, C_6D_6), decomposition is not evident by ^{1}H NMR. Significantly, we could not prepare the TTP derivative, (TTP)$ZrMe_3$, from (TTP)$ZrCl_3$ and MeLi.

Conclusions

Diketiminate ligands are compatible with zirconium alkyl functionality. In contrast to tetraazamacrocyclic systems, alkyl migration to imine carbons of diketiminate ligands does not occur. Orthometalation of (TTP)-$Zr(CH_2Ph)_3$ (**1**) proceeds through a four-centered transition state to give a bisbenzyl compound (**2**) and toluene. When the ortho hydrogens of the imine aryl groups are removed, stability of trialkyl derivatives is enhanced. We are actively investigating reactivity of the alkyl compounds reported in this paper.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk techniques. Solvents were freshly

(31) For the six-coordinate compound $[Li(tmed)]_2[ZrMe_6]$, Zr_{av} = 2.38(2) Å (tmed = *N,N,N′N′*-tetramethylethylenediamine).[32] In the eight-coordinate compound $(dmpe)_2ZrMe_4$, Zr_{av} = 2.440(11) Å (dmpe = 1,2-bis(dimethylphosphino)ethane).[33]

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Table 2. Crystal Data and Structure Refinement Parameters for Compounds 1, 2, and 5

	1	2	5
formula	$C_{40}H_{42}N_2Zr$	$C_{33}H_{34}N_2Zr$	$C_{32}H_{50}N_2Zr$
fw	641.98	549.84	553.96
temp/K	173(2)	173(2)	173(2)
wavelength/Å	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	triclinic	orthorhombic
space group	*C*2/*c*	$P\bar{1}$	*Pnma*
Unit cell			
a/Å	40.287(8)	10.167(2)	14.4931(1)
b/Å	9.191(2)	11.547(2)	21.8225(1)
c/Å	20.566(4)	13.192(3)	9.9150(1)
α/deg		87.81(3)	
β/deg	117.27(3)	72.59(3)	
γ/deg		69.06(3)	
V/Å^3	6769(2)	1376.0(5)	3135.87(3)
Z	8	2	4
d_{calc}/Mg/m^3	1.270	1.327	1.173
abs coeff/mm^{-1}	0.354	0.423	0.371
F(000)	2728	572	1184
cryst size	0.20 × 0.21 × 0.21	0.2 × 0.2 × 0.25	0.15× 0.15 × 0. 20
θ range/deg	1.98−28.40	1.62−28.32	1.87−28.14
index ranges	$-53 \le h \le 39$	$-13 \le h \le 13$	$-19 \le h \le 19$
	$-11 \le k \le 12$	$-15 \le k \le 14$	$-27 \le k \le 28$
	$-25 \le l \le 26$	$-17 \le l \le 17$	$-12 \le l \le 13$
no. of reflns collected	19 559	16 390	34 464
no. of ind reflections	7797 [*R*(int) = 0.0504]	6494 [*R*(int) = 0.0300]	3884 [*R*(int) = 0.0340]
no. of data/restraints/param	7796/0/556	6494/459/409	3884/0/163
GOF on F^2	1.000	1.009	1.025
final *R* [$I > 2\sigma(I)$]	*R*1 = 0.0446	*R*1 = 0.0305	*R*1 = 0.0332
	*wR*2 = 0.0822	*wR*2 = 0.0708	*wR*2 = 0.1221
R (all data)	*R*1 = 0.0811	*R*1 = 0.0416	*R*1 = 0.0455
	*wR*2 = 0.0939	*wR*2 = 0.0741	*wR*2 = 0.1315
largest diff peak and hole/e Å^{-3}	0.345 and −0.635	0.265 and −0.444	0.497 and −0.680

distilled over sodium/benzophenone ketyl and were saturated with nitrogen before use. Elemental analyses (C, H, N) were performed on a Perkin-Elmer CHN 2400 Series II CHNS/O analyzer at MSU. A Varian VXR-300 NMR spectrometer was used to record ^{1}H (299.96 MHz) and ^{13}C (75.43 MHz) NMR spectra unless noted otherwise, and chemical shifts were referenced to the residual solvent resonances. C_6D_6 was dried over activated 4-Å molecular sieves and vacuum-transferred to a sodium-mirrored air-free flask. Uncorrected melting points of crystalline samples in sealed capillaries (under an argon atmosphere) are reported as ranges. The synthesis and structural characterization of (DDP)$ZrCl_3$ have been submitted for publication.[11]

(TTP)Zr(CH_2Ph)$_3$ (1). A 20 mL toluene solution of TTPH (1.97 g, 7.08 mmol) was added dropwise to a stirred solution of Zr(CH_2Ph)$_4$ (3.21 g, 7.05 mmol) in 5 mL of toluene. The reaction mixture was stirred for 8 h at room temperature in the dark. The solvent volume was reduced under vacuum, and the solution was placed in a −80 °C freezer to precipitate (TTP)Zr(CH_2Ph)$_3$ as a yellow solid (3.55 g, 78%): mp 98−100 °C; ^{1}H NMR (C_6D_6) *δ* 7.09 (m, 6H), 6.90 (m, 7H), 6.73 (m, 10H), 5.06 (s, 1H), 2.61 (s, 6H), 2.08 (s, 6H), 1.62 (s, 6H); ^{13}C{^{1}H} NMR (C_6D_6) *δ* 160.58, 146.68, 143.52, 135.63, 130.02, 128.77, 127.65, 126.03, 121.84, 102.14, 75.62, 22.76, 20.84. Anal. Calcd for $C_{40}H_{42}N_2Zr$: C, 74.83; H, 6.59; N, 4.36. Found: C, 74.44; H, 6.56; N, 4.60.

(η^3-MeC(NC_7H_6)CHC(N-*p*-Tol)Me)Zr(η^2-CH_2Ph)(η^1-CH_2Ph) (2). A 5 mL toluene solution of compound **1** (1.1 g, 1.7 mmol) was heated at 45 °C for 48 h. All volatile materials were removed under vacuum. Orange-yellow crystals were obtained by cooling a toluene/pentane (1:1) solution to −30 °C (0.64 g, 68%): mp 140−142 °C (dec); ^{1}H NMR (300 MHz, C_6D_6) *δ* (7.80, m, 1H), 7.18−6.75 (m, 15H), 6.48 (m, 1H), 5.31 (s, 1H), 2.33 (s, 3H), 2.14 (d, *J* = 9.6 Hz, 2H), 2.13 (s, 3H), 2.07 (s, 3H), 1.66 (d, *J* = 9.6 Hz, 2H), 1.58 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, C_6H_6) *δ* 186.86, 159.11, 158.52, 141.80, 138.85, 137.45, 132.63, 130.44, 129.96, 129.84, 129.26, 128.17, 122.90, 118.71, 106.46, 66.62, 24.62, 24.23, 21.60, 20.90. Anal. Calcd for $C_{33}H_{34}N_2Zr$: C, 72.08; H, 6.23; N, 5.09. Found: C, 71.90; H, 6.46; N, 4.70.

(η^3-MeC(NC_6H_4)CHC(NPh)Me)Zr(η^2-CH_2Ph)(η^1-CH_2Ph) (4). In analogous fashion to the synthesis of compound **2**, compound **4** was prepared from (PPP)ZrBz_3 (**3**) in 51% yield as an orange yellow: mp 135−137 °C (dec); ^{1}H NMR (300 MHz, C_6D_6) *δ* 7.82 (m, 1H), 7.14−6.76 (m, 17H), 6.40 (m, 1H), 5.21 (s, 1H), 2.09 (d, *J* = 9.6 Hz, 2H), 2.08 (s, 3H), 1.57 (d, *J* = 9.6 Hz, 2H), 1.52 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, C_6H_6) *δ* 186.64, 160.59, 159.44, 157.88, 142.19, 141.44, 137.84, 130.42, 130.02, 129.61, 129.17, 128.96, 127.34, 123.08, 121.77, 118.83, 106.50, 66.97, 24.66, 24.37. Anal. Calcd for $C_{31}H_{30}N_2Zr$: C, 71.36; H, 5.80; N, 5.37. Found: C, 71.01; H, 5.53; N, 5.07.

(DDP)ZrMe_3 (5). At 0 °C, a 40 mL toluene solution of (DDP)$ZrCl_3$ (1.04 g, 1.7 mmol) was treated with ethereal LiMe (4.0 mL, 1.3 M, 5.2 mmol). The solution was warmed to room temperature and stirred for 5 h. The supernatant was separated by filtration, and the solvent was removed under vacuum to afford the crude compound. Pure compound **5** was isolated as a colorless solid by recrystallization from a toluene/hexane solution (0.51 g, 54%): mp 191−192 °C (dec); ^{1}H NMR (300 MHz, C_6D_6) *δ* 7.12 (m, 6H), 4.96 (s, 1H), 3.24 (sept, *J* = 6.9 Hz, 4H), 1.57 (s, 6H), 1.38 (d, *J* = 6.9 Hz, 12H), 1.15 (d, *J* = 6.9 Hz, 12H), 0.73 (s, 9H); ^{13}C{^{1}H} NMR (75 MHz, C_6H_6) *δ* 166.51, 147.70, 141.75, 126.54, 124.42, 98.68, 56.74, 28.98, 28.89, 25.60, 24.73. Anal. Calcd for $C_{32}H_{50}N_2Zr$: C, 69.38; H, 9.10; N, 5.05. Found: C, 69.25; H, 9.11; N, 5.25.

Kinetic Studies. A typical procedure is described as follows: In a glovebox, a 0.055 M solution of (PPP)$ZrBz_3$ was prepared by dissolving 20 mg of compound **3** in 0.60 mL of C_6D_6. The solution was transferred to a J-Young NMR tube, which was sealed. The tube was heated at 65 ± 0.5 °C in an oil bath, and the reaction was quenched by plunging the tube into an ice-bath at regular intervals. ^{1}H NMR spectra (500 MHz) were recorded at room temperature. Since the aromatic and alkyl resonances of **3** and **4** overlapped, the methine resonances at *δ* 5.01 and *δ* 5.21 for the ligand backbone in **3**

and **4**, respectively, were monitored by NMR spectroscopy. The reaction was monitored through three half-lives ($t_{1/2} = 52$ min). The plot of ln[$\mathbf{3}_t$] vs time was linear and gave $k_H = 1.82 \times 10^{-4}$ s^{-1}. When the concentration of **3** was halved ([$\mathbf{3}_0$] = 0.027 M), $k_H = 1.74 \times 10^{-4}$ s^{-1}. For (PPP-d_{10})ZrBz$_3$ ([**3**-d_{10}] = 0.027 M), $k_D = 3.43 \times 10^{-5}$ s^{-1}. Thus the kinetic isotopic effect (k_H/k_D) for loss of toluene in orthometalation was determined to be 5.2(5) at 65 ± 0.5 °C.

X-ray Structure Determination. All diffraction data were collected using a Siemens SMART CCD diffractometer using Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Crystals were cooled to 173 K, and data were collected at 30 s per frame. Initial cell parameters were calculated from three sets of 15 frames. All data sets were collected over a hemisphere of reciprocal space. Following integration using the SAINT program, final unit cell parameters were obtained by least-squares refinement of strong reflections. Absorption and decay corrections were applied to the data by SADABS.[34] The structures were solved by direct methods and refined using the SHELXTL programs.[35] Calculations were based on F^2 data. All non-hydrogen atoms were refined using anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined as riding models.

X-ray quality crystals of (TTP)Zr(CH_2Ph)$_3$ (**1**) were grown from a toluene solution at −30 °C. The choice of space group *C*2/*c* over *Cc* was based on intensity statistics and successful refinement of the structure in the *C*2/*c* space group. Cell parameters and refinement parameters are listed in Table 2.

X-ray quality crystals of (η^3-MeC(NC_7H_6)CHC(N-*p*-Tol)Me)-Zr(η^2-CH_2Ph)(η^1-CH_2Ph) (**2**) were grown from a toluene/hexane solution at −30 °C. *P*$\bar{1}$ was chosen as the space group based on intensity statistics and successful refinement of the structure. Cell parameters and refinement parameters are listed in Table 2.

X-ray quality crystals of (DDP)ZrMe_3 (**5**) were grown from a toluene/hexane solution at −30 °C. A procedure similar to **1** was followed in collecting the data set. The *Pnma* was chosen as the space group on the basis of systematic absences in reflection data and successful refinement of the structure. Cell parameters and refinement parameters are listed in Table 2.

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Supporting Information Available: Tables of X-ray diffraction data. This material is available free of charge via the Internet at http://pubs.acs.org.

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