Cationic Zirconium Dialkyl and Alkyl Complexes Supported by DAC (Deprotonated 4,13-Diaza-18-crown-6) Ligation

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The synthesis, characterization, and reactivity of a series of neutral and cationic Zr alkyls supported by DAC (deprotonated 4,13-diaza-18-crown-6) ligation are reported. Reaction of H_2DAC with $Zr(CH_2Ph)_4$ affords a 1:4 mixture of *cis*- and *trans*-Zr(DAC)$(CH_2Ph)_2$ (***cis-/trans*-1a**). The pure isomers undergo slow *cis*−*trans* isomerization in solution to regenerate the 1:4 *cis:trans* equilibrium mixture. X-ray crystallographic results are reported for both ***cis***- and ***trans*-1a**. Reaction of $Zr(CH_2Ph)_2Cl_2$ with H_2DAC, followed by treatment with LiR (2 equiv), gives *cis*-Zr(DAC)R_2 (R = CH_2SiMe_3, ***cis*-1b**; R = CH_2CMe_3, ***cis*-1c**) exclusively. Alkyl abstraction from ***cis***- or ***trans*-1a** using $B(C_6F_5)_3$ (1 equiv) produces the stable cation $[Zr(DAC)(CH_2Ph)]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (**2a**) as a yellow oil. NMR studies on **2a** in CD_2Cl_2 show no evidence for η^2-benzyl formation or anion coordination. Protonation of ***cis***- or ***trans*-1a** with $[n\text{-}Bu_3NH]^+[BPh_4]^-$ similarly yields $[Zr(DAC)(CH_2Ph)]^+[BPh_4]^-$ (**2b**). Cation **2a** reacts with *t*-BuNC to form the vinyl amide complex $[Zr(DAC)\{N(t\text{-}Bu)CH{=}CHPh\}]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (**3**). *p*-Tolylacetylene undergoes catalytic dimerization to (*Z*)-1,4-di-*p*-tolyl-1-buten-3-yne in the presence of **2a**.

Recently we have been investigating the use of deprotonated 4,13-diaza-18-crown-6 (DAC) as an ancillary ligand in group 3 and f-element chemistry.[1] From our previous studies, it is apparent that DAC is the approximate steric equivalent of two Cp* ($C_5Me_5^-$) ligands; however, greater flexibility and variable donor capacity distinguish the DAC ligand system from Cp*. The successful synthesis of Y(DAC)R (R = CH_2SiMe_3, $CH(SiMe_3)_2$)[1b] suggested that preparation of the isoelectronic (DAC)$Zr(R)^+$ cations should be possible.

Cationic d^0 $Cp_2M(R)^+$ (M = Ti, Zr, Hf) complexes exhibit impressive stoichiometric and catalytic reactivity due to the increased Lewis acidity at the metal center and the presence of a vacant site *cis* to a highly polarized $M^{\delta+}-R^{\delta-}$ bond.[2] Specifically, Jordan has demonstrated rich insertion chemistry[2] while several groups have explored the high Ziegler-Natta olefin polymerization activity of these systems.[2,3] By comparison, the reactivity of group 4 alkyl cations with ancillary ligands other than Cp has not been as well-studied. Recently, tetraaza macrocycles,[4] porphyrins,[5] and acyclic Schiff base ligands ($[R_6\text{-acen}]Zr(R')^+$; R = H, F)[6] have seen increasing use. The DAC ligand system differs from these ligands in three important ways: (i) greater flexibility, (ii) complete saturation, and (iii) increased electron-donating ability. While the last point may be expected to decrease the reactivity of the DAC-derived alkyl complexes, the saturated framework avoids problems associated with alkyl migration to an unsaturated center on the ancillary ligand.[4a,6f] In any event, a comparison of the reactivity of DAC, Schiff base macrocycles, and Cp ligand systems should provide valuable insights into ancillary ligand effects for this important class of organometallic molecules.

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In this contribution, we report the synthesis and characterization of dialkyl and cationic alkyl complexes of zirconium which contain the DAC ligand: Zr(DAC)-R_2 (R = CH_2Ph, **1a**; R = CH_2SiMe_3, **1b**; R = CH_2CMe_3, **1c**) and $[Zr(DAC)(CH_2Ph)]^+[BR_4]^-$ (**2**: (BR_4 = $B(CH_2Ph)(C_6F_5)_3$, **2a**; BR_4 = BPh_4, **2b**). Preliminary reactivity studies are also reported for **2a**.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere, with the rigorous exclusion of oxygen and water, using standard glovebox (Braun MB150-GII) or Schlenk techniques, except as noted in the text. Tetrahydrofuran (THF), diethyl ether, hexane, and toluene were dried by distillation from sodium benzophenone ketyl under argon immediately prior to use. 4,13-Diaza-18-crown-6 (H_2DAC) was prepared according to a literature procedure[7] from 1,2-bis(2-iodoethoxy)ethane[8] and 1,8-diamino-3,6-dioxaoctane[7] in 30% yield after recrystallization from hexane. Anhydrous $ZrCl_4$ was purchased from Aldrich and used without further purification. $Zr(CH_2Ph)_4$[9] and $Zr(CH_2Ph)_2Cl_2$[10] were prepared according to literature procedures. Tris(pentafluorophenyl)boron was a gift from Boulder Scientific Co.

^{1}H and ^{13}C spectra were recorded on a Bruker WM 250 MHz or a Bruker AMX 360 MHz spectrometer. Spectra were recorded in C_6D_6, C_7D_8, or C_4D_8O solvent, previously distilled from sodium under argon or in CD_2Cl_2 dried over 4 Å molecular sieves, using 5 mm tubes fitted with a Teflon valve (Brunfeldt). All solvents were thoroughly degassed prior to use. ^{1}H and ^{13}C NMR data for all compounds are collected in Tables 1 and 2, respectively. Melting points were recorded using a Reichert hot stage and are not corrected. Elemental analyses were performed by Canadian Microanalytical, Delta, BC, Canada, or Atlantic Microanalytical, Atlanta, GA. Gas chromatography was performed using a Varian 3700 gas chromatograph.

***cis*- and *trans*-Zr(DAC)(CH_2Ph)$_2$ (*cis*-/*trans*-1a).** A solution of H_2DAC (0.215 g, 0.953 mmol) in 20 mL of toluene was added rapidly to a stirred solution of $Zr(CH_2Ph)_4$ (0.434 g, 0.953 mmol) in 20 mL of toluene. After the mixture was stirred for 1 h, the stirbar was removed and the reaction solution was cooled at −30 °C overnight. Pale yellow ***cis*-1a** and orange ***trans*-1a** slowly deposited and were collected by decanting the mother liquor. Combined yield: 0.41 g (80%). Manual separation afforded the pure *cis* and *trans* isomers in a 1:4 ratio. ***cis*-1a**: mp 85−86 °C. Anal. Calcd for $C_{26}H_{38}N_2O_4Zr$: C, 58.50; H, 7.18; N, 5.24. Found: C, 58.05; H, 7.11; N, 4.95. ***trans*-1a**: mp 108−110 °C. Anal. Calcd for $C_{26}H_{38}N_2O_4Zr$: C, 58.50; H, 7.18; N, 5.24. Found: C, 57.92; H, 7.15; N, 5.00. Pure samples of ***cis*-** or ***trans*-1a** slowly isomerized back to a 1:4 equilibrium mixture over a period of days in d_6-benzene or weeks in d_8-THF.

***cis*-Zr(DAC)R_2 (R = CH_2SiMe_3, *cis*-1b; R = CH_2CMe_3, *cis*-1c).** H_2DAC (0.053 g, 0.20 mmol) and $Zr(CH_2Ph)_2Cl_2$ (0.10 g, 0.20 mmol) were separately dissolved in 10 mL of toluene, followed by dropwise addition of the H_2DAC solution to that of the zirconium complex. Immediate precipitation of a white solid, presumed to be polymeric $[Zr(DAC)Cl_2]_x$, was observed. After the mixture was stirred for 1 h, a solution of the appropriate alkyllithium reagent (2 equiv) was added and the resulting suspension was stirred for a further 30 min. This suspension was then filtered through Celite, and the clear, pale yellow filtrate was concentrated to ca. 2 mL and cooled to −30 °C. Crystals of pure ***cis*-1b** (colorless) and ***cis*-1c** (pale yellow) were collected by decanting the mother liquors. ***cis*-1b**: yield 0.097 g (92%); mp 165 °C dec. ^{29}Si NMR (d_6-benzene, 49.69 MHz): δ 0.24. ***cis*-1c**: yield: 0.080 g (81%); mp 190 °C dec. Anal. Calcd for $C_{22}H_{46}N_2O_4Zr$: C, 53.51; H, 9.39; N, 5.67. Found: C, 52.49; H, 9.01; N, 5.19.

Table 1. ^{1}H NMR Spectroscopic Data[a]

compd	δ, ppm (int)	mult	J, Hz	assignt
***cis*-1a**[b]	7.22−7.31 (8)	m		*o,m*-aryl
	6.84 (2)	tt	7.0, 1.5	*p*-aryl
	3.57 (4), 3.15[c] (4)	m		$NCH_2CH_2OCH_2$
	3.40 (4), 2.84[c] (4)	m		$NCH_2CH_2OCH_2$
	3.05[d] (8)	m		$NCH_2CH_2OCH_2$
	2.46 (4)	s		CH_2Ph
***trans*-1a**[b,e]	7.11 (4)	t	7.3	*m*-aryl
	6.81 (4)	br d	7.8	*o*-aryl
	6.72 (2)	t	7.3	*p*-aryl
	3.52 (8)	t	5.2	$NCH_2CH_2OCH_2$
	3.37 (8)	br s		$NCH_2CH_2OCH_2$
	3.11 (8)	t	5.2	$NCH_2CH_2OCH_2$
	1.71 (4)	s		CH_2Ph
***cis*-1b**[b]	3.47 (4), 3.12[c] (4)	m		$NCH_2CH_2OCH_2$
	3.05 (4), 2.68[c] (4)	m		$NCH_2CH_2OCH_2$
	2.93 (4), 2.51[c] (4)	m		$NCH_2CH_2OCH_2$
	0.43 (18)	s		$SiMe_3$
	−1.39 (4)	s		CH_2SiMe_3
***cis*-1c**[b]	3.50 (4), 3.13[c,d] (4)	m		$NCH_2CH_2OCH_2$
	3.13[d] (4), 2.74[c] (4)	m		$NCH_2CH_2OCH_2$
	2.99 (4), 2.54[c] (4)	m		$NCH_2CH_2OCH_2$
	1.49 (18)	s		CMe_3
	0.09 (4)	s		CH_2CMe_3
2a[f]	6.78−6.98 (10)	m		aryl
	4.29 (4), 4.02[c] (4)	m		$NCH_2CH_2OCH_2$
	3.88 (8)	m		$NCH_2CH_2OCH_2$
	3.58 (4), 3.13[c] (4)	m		$NCH_2CH_2OCH_2$
	2.86 (2)	br s		BCH_2Ph
	2.20 (2)	s		$ZrCH_2Ph$
2b[g]	7.31 (8)	br m		*m*-aryl B
	6.98 (2)	t	7.5	*m*-aryl (benzyl)
	6.90 (8)	t	7.4	*o*-aryl B
	6.76 (4)	tt	7.3, 1.0	*p*-aryl B
	6.74 (2)	d	7.0	*o*-aryl (benzyl)
	6.63 (1)	tt	7.3, 1.0	*p*-aryl (benzyl)
	3.90 (4), 3.77[c,d] (4)	m		$NCH_2CH_2OCH_2$
	3.77[d] (4), 3.05[c] (4)	m		$NCH_2CH_2OCH_2$
	3.64 (4), 3.38[c] (4)	m		$NCH_2CH_2OCH_2$
	1.87 (2)	s		$ZrCH_2Ph$
3[f]	7.35 (2)	m		*m*-aryl B[h]
	7.22 (3)	m		*o,p*-aryl B[h]
	7.14 (1)	d	14.0	NCH=CH
	6.92 (2)	m		*m*-aryl (benzyl)[h]
	6.74 (3)	m		*o,p*-aryl (benzyl)[h]
	6.42 (1)	d	14.0	NCH=CH
	4.42 (2), 4.32 (2), 4.25 (2), 4.19 (2), 4.00 (2), 3.95 (2), 3.89 (2), 3.84 (2), 3.73 (2), 3.53 (2), 3.32 (4)	m		DAC CH_2
	2.86 (2)	br s		BCH_2Ph
	1.26 (9)	s		CMe_3

[a] Spectra were recorded at 360 MHz and 293 K unless otherwise specified. [b] d_6-Benzene. [c] *exo* and *endo* protons have not been assigned. [d] Partially overlapping resonances. [e] Recorded at 343 K. [f] CD_2Cl_2. [g] d_8-THF. [h] Assignments tentative.

[Zr(DAC)(CH_2Ph)]$^+$[B(CH_2Ph)(C_6F_5)$_3$]$^-$ (2a). Reaction of a mixture of ***cis*-** and ***trans*-1a** (1.00 g, 1.88 mmol) with 1 equiv of $B(C_6F_5)_3$ (0.960 g, 1.88 mmol) in benzene resulted in quantitative formation of **2a** as a sparingly soluble, bright yellow oil. This oil was freely soluble in d_8-THF and CD_2Cl_2, but we were unsuccessful in crystallizing **2a** from these solvents, either as a neat compound or as mixtures with toluene or hexane. Satisfactory elemental data could not be obtained, probably due to difficulties in removing trace solvent. ^{19}F NMR (CD_2Cl_2, 338.86 MHz): δ −129.6 (*o*-aryl*F*, d, J_{FF} = 22 Hz), −162.9 (*m*-aryl*F*, t, J_{FF} = 22 Hz), −165.8 (*p*-aryl*F*, t, J_{FF} = 21 Hz).

[Zr(DAC)(CH_2Ph)]$^+$[BPh_4]$^-$ (2b). Reaction of a mixture of ***cis*-** and ***trans*-1a** (0.060 g, 0.11 mmol) with 1 equiv of $[n\text{-}Bu_3NH]^+[BPh_4]^-$ (0.057 g, 0.11 mmol) in benzene resulted

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Table 2. $^{13}C\{^1H\}$ NMR Spectroscopic Data[a]

compound	δ, ppm (assignt)
***cis*-1a**[b]	154.7 (*ipso*-aryl), 127.6 (*o*-aryl), 126.8 (*m*-aryl), 118.7 (*p*-aryl), 73.9 (OCH_2), 72.0 (OCH_2), 56.3 (NCH_2), 60.0 (CH_2Ph, $^1J_{CH} = 119$ Hz)
***trans*-1a**[b,c]	155.3 (*ipso*-aryl), 127.5 (*o*-aryl), 125.9 (*m*-aryl), 117.7 (*p*-aryl), 74.5 (OCH_2), 71.6 (br s, OCH_2), 56.1 (NCH_2), 54.2(CH_2Ph, $^1J_{CH} = 120$ Hz)
***cis*-1b**[b]	71.5 (OCH_2), 67.6(OCH_2), 52.7 (NCH_2), 4.9 ($SiMe_3$), −9.9 (CH_2Si, $^1J_{CH} = 103$ Hz)
***cis*-1c**[b]	71.4 (OCH_2), 67.5 (OCH_2), 53.0 (NCH_2), 37.6 (CMe_3), 33.0 (CMe_3), 29.2 (CH_2CMe_3, $^1J_{CH} = 100$ Hz)
2a[d]	148.9 (*ipso*-aryl), 148.0 (*o*-aryl *C*F, $^1J_{CF} = 228$ Hz), 144.4 (*ipso*-aryl), 137.9 (*p*-aryl *C*F, $^1J_{CF} = 243$ Hz), 136.9 (*m*-aryl*C*F, $^1J_{CF} = 258$ Hz), 129.2 (aryl), 129.1 (aryl), 128.7 (aryl), 127.20 (aryl), 123.2 (aryl), 122.9 (aryl), 75.8 (OCH_2), 72.3 (OCH_2), 53.8 (NCH_2), 59.8 ($ZrCH_2Ph$, $^1J_{CH} = 127$ Hz), 32.4 (BCH_2Ph)
2b[e]	152.5 (benzyl *ipso*-aryl), 137.2 (*o*-BPh_4), 128.1 (benzyl *o*-aryl), 127.4 (benzyl *m*-aryl), 125.9 (*m*-BPh_4), 122.1 (*p*-BPh_4), 120.4 (benzyl *p*-aryl), 76.1 (OCH_2), 73.5 (OCH_2), 59.1 ($ZrCH_2Ph$), 56.8 (NCH_2)
3[d,f]	148.9 (*ipso*-aryl), 148.6 (aryl *C*F, $^1J_{CF} = 241$ Hz), 139.1 (*ipso*-aryl), 137.9 (aryl*C*F, $^1J_{CF} = 244$ Hz), 135.4 (aryl*C*F, $^1J_{CF} = 246$ Hz), 135.0 (N*C*H=CH), 129.0 (aryl), 129.0 (aryl), 127.2 (aryl), 125.8 (aryl), 125.4 (aryl), 122.8 (aryl), 111.2 (CH=*C*HPh), 77.1 (OCH_2), 73.6 (OCH_2), 73.2 (OCH_2), 69.2 (OCH_2), 58.5 ($NCMe_3$), 55.1 (NCH_2), 54.8 (NCH_2), 32.3 (BCH_2Ph), 30.2 ($NCMe_3$)

[a] Spectra were recorded at 90.55 MHz and 293 K unless otherwise specified. [b] d_6-Benzene. [c] Recorded at 343 K. [d] CD_2Cl_2. [e] d_8-THF. [f] *ipso*-C_6F_5B resonance not observed.

Table 3. Summary of Crystallographic Data for *cis*-1a

formula	$C_{26}H_{38}N_2O_4Zr$	Z	4
fw	533.81	ρ(calcd) (g cm^{-3})	1.391
cryst syst	monoclinic	μ (cm^{-1})	38.34
space group	$P2_1/c$ (No. 14)	radiation, λ (Å)	Cu Kα, 1.542
a (Å)	20.178(3)	T	ambient
b (Å)	7.805(2)	$2\theta_{max}$ (deg)	100
c (Å)	16.711(2)	no. of obsd rflns	2663
α (deg)	90	no. of unique rflns	2447
β (deg)	104.350(9)	R^a	0.0634
γ (deg)	90	$R_w{}^b$	0.0754
V (Å^3)	2549.5		

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|^2)/\Sigma w(|F_o|)^2]^{1/2}$.

in precipitation of **2b** as a pale yellow solid: yield 0.080 g (95%); mp 180 °C dec. Anal. Calcd for $C_{43}H_{51}BN_2O_4Zr$: C, 67.79; H, 6.75; N, 3.67. Found: C, 66.80; H, 6.44; N, 3.44.

[Zr(DAC)(N(t-Bu)CH=CHPh)]$^+$[B(CH$_2$Ph)(C$_6$F$_5$)$_3$]$^-$ (3). A toluene solution of *tert*-butyl isocyanide (0.413 mL of a 0.136 M solution; 0.056 mmol) was added to a stirred solution of **2a** (generated *in situ* from 0.030 g of ***cis*-/*trans*-1a** and 0.029 g of $B(C_6F_5)_3$ in 10 mL of toluene). After the mixture was stirred for 1 h, the volatiles were removed under reduced pressure to yield **3** as a yellow oil. ^{19}F NMR (CD_2Cl_2, 338.86 MHz): δ −129.6 (*o*-aryl*F*, d, $J_{FF} = 24$ Hz), −162.8 (*m*-aryl*F*, m), −165.8 (*p*-aryl*F*, t, $J_{FF} = 21$ Hz).

Reaction of 2a with Excess *p*-Tolylacetylene. An excess of *p*-tolylacetylene (20-fold excess, 2.0 mmol) was added to a Schlenk tube containing a solution of **2a** in toluene (0.10 mmol in 20 mL). The solution was stirred vigorously, and samples were withdrawn periodically and examined by GC to determine the extent of conversion. Catalytic dimerization of *p*-tolylacetylene to an isomeric mixture of 1,4-di-*p*-tolyl-1-buten-3-ynes (*Z*:*E* ratio = 85:15) was observed. An initial turnover rate of 2 mol of enyne/(mol of **2a** h) was observed. The product was identified by comparison of the ^1H and ^{13}C NMR spectra with literature values for the phenyl analog[11] and by comparison of the GC−MS traces of the hydrolyzed product with an authentic sample.

X-ray Structural Studies of 1a. Both ***cis*-** and ***trans*-1a** were characterized by X-ray crystallography; however, disorder in the DAC backbone of ***trans*-1a** prevented satisfactory refinement of this structure. Further crystallographic details for ***trans*-1a** are included in the supporting material. Crystallographic data for ***cis*-1a** is given in Table 3. A crystal of ***cis*-1a** (0.9 × 0.4 × 0.4 mm) was loaded into a glass capillary in the glovebox and subsequently examined by photographic methods using Weissenberg and precession cameras. The space group was determined by the systematic absences. The crystal was transferred to a Nonius CAD4F diffractometer equipped with Ni-filtered Cu Kα radiation. The unit cell was refined using 25 reflections in the 2θ range 48−76°. Experimental density was not determined because of the air and moisture sensitivity of the compound. Three standard reflections, measured periodically during data collection (10,0,0, 040, and 802), showed no significant decline in combined intensity. Intensity measurements were collected for one-fourth of the sphere. After the usual data reduction procedures, the structure was solved using SHELX76 and the Patterson function. The refinements minimized $\Sigma w((|F_o| - |F_c|)^2)$ and proceeded normally using SHELX76.[12] The criterion for inclusion of reflections was $I > 2.5\sigma(I)$. The weighting scheme was determined by counting statistics using $w = 1/\sigma^2(F) + 0.001(F^2)$. Convergence was satisfactory: max shift/esd = 0.004. A total of 298 parameters (33 × 9 parameters per atom + scale) were refined. No intermolecular contacts shorter than 3.4 Å were observed. The structural plots were drawn with ORTEP[13] or the ZORTEP[14] modification.

Results and Discussion

Synthesis of *cis*- and *trans*-Zr(DAC)R$_2$ (R = CH$_2$Ph, 1a; R = CH$_2$SiMe$_3$, 1b; R = CH$_2$CMe$_3$, 1c). Direct protonation of $Zr(CH_2Ph)_4$ with H_2DAC proceeds smoothly in toluene to produce a 1:4 mixture of ***cis*-** and ***trans*-1a** (Scheme 1). The isomers are difficult to separate by fractional crystallization, but small quantities of the pure isomers can be separated manually (***cis*-1a**, pale yellow; ***trans*-1a**, orange). The *cis* isomer is identifiable by the presence of six DAC multiplets in the ^1H NMR spectrum due to inequivalent *exo* and *endo* protons on each of the three unique DAC carbons (Tables 1 and 2). The *trans* isomer is expected to show only three CH_2 multiplets, since the protons on each unique DAC carbon are equivalent in this geometry. At room temperature, however, ***trans*-1a** shows six proton and six carbon resonances for the DAC ligand. When the temperature is raised, the resonances in both the ^{13}C and ^1H NMR spectra coalesce between ca. 30 and 50 °C and re-emerge as three new resonances at 70 °C. The variable-temperature behavior of ***trans*-1a** is most clearly illustrated by ^{13}C NMR (Figure 1). The lower molecular symmetry apparent in the room-temperature

(11) Bianchini, C.; Frediani, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Organometallics* **1994**, *13*, 4616.

(12) Sheldrick, G. M. SHELX76, Programs for Crystal Structure Determination; University of Cambridge, Cambridge, U.K., 1976.

(13) Johnson, C. K. ORTEPII; Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

(14) Zsolnai, L. ZORTEP; University of Heidelberg, Heidelberg, Germany, 1995.

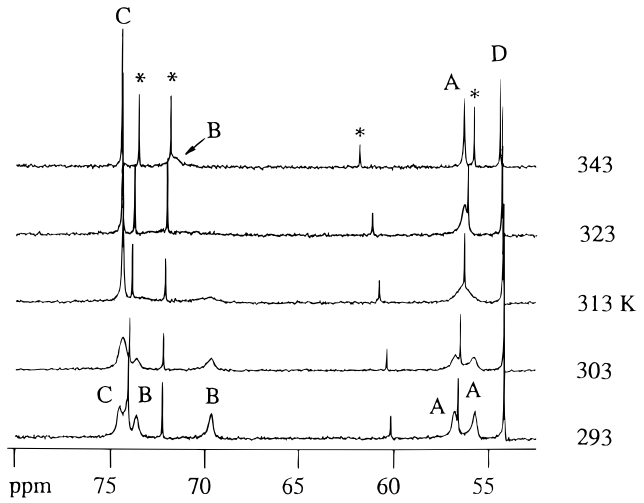
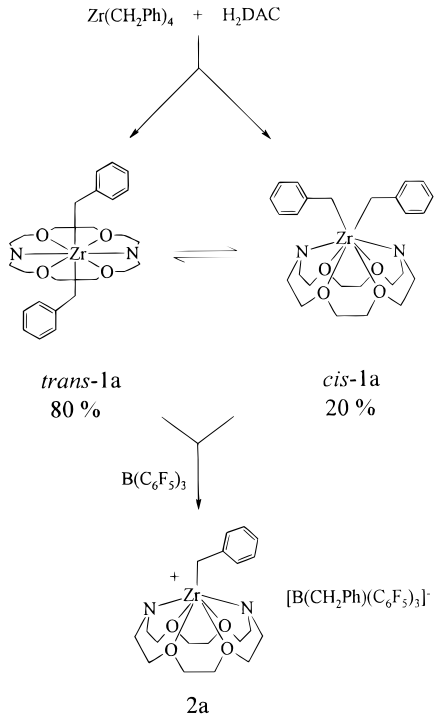


Figure 1. Variable-temperature $^{13}C\{^1H\}$ NMR spectra of the DAC region of ***trans*-1a** in d_6-benzene: (A) NCH_2; (B) OCH_2; (C) OCH_2; (D) CH_2Ph (***cis*-1a** impurity resonances are denoted by an asterisk).

Scheme 1



NMR spectrum of ***trans*-1a** is most easily explained by asymmetric coordination of the DAC ligand. The solid-state structure of ***trans*-1a** (*vide infra*) shows a seven-coordinate, distorted-pentagonal-bipyramidal structure with one dangling oxygen donor (Figure 2). While this structure cannot represent the room-temperature solution structure since it would have 12 inequivalent carbons, a similar structure with two dangling oxygens is reasonable. The dynamic process therefore likely involves rapid dissociation and reassociation of the DAC oxygens ($\Delta G^* = 62 \pm 2$ kJ/mol).[15]

Pure ***cis*-** and ***trans*-1a** slowly undergo isomerization to a 1:4 *cis*:*trans* equilibrium mixture when redissolved. Isomerization proceeds more rapidly in d_6-benzene (days) than in d_8-THF (weeks). *cis*−*trans* isomerization requires one benzyl group to pass through the DAC ring.[16] This appears to be possible, given the NMR and

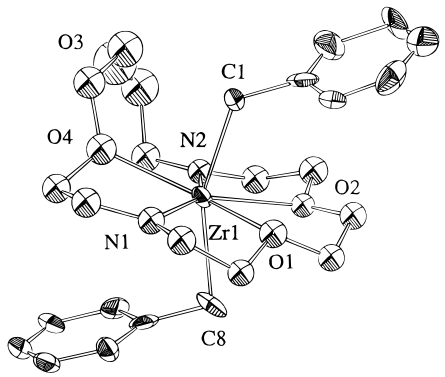
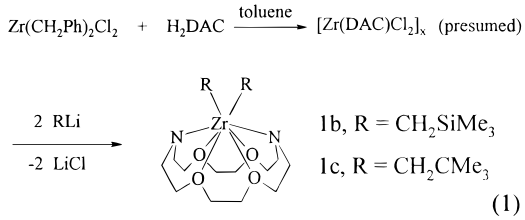


Figure 2. ZORTEP[14] drawing illustrating the general coordination geometry in one molecule of ***trans*-1a**.

structural evidence for oxygen dissociation noted above for ***trans*-1a** and the large DAC ring size. The slower rate of isomerization in THF could be due to strong solvent coordination which enforces a high coordination number at Zr and prevents rearrangement on steric grounds.

In order to establish a more general route to compounds of this type, we also explored the preparation of $Zr(DAC)Cl_2$. Attempts to prepare the dichloride from $ZrCl_4$ and M_2DAC (M = Li, Na, K) failed to yield clean products. However, reaction of $Zr(CH_2Ph)_2Cl_2$ with H_2-DAC produced an insoluble powder, presumed to be polymeric $[Zr(DAC)Cl_2]_x$. Alkylation of this dichloride, prepared *in situ* in toluene, with LiR (2 equiv) produced *cis*-$Zr(DAC)R_2$ (R = CH_2SiMe_3, **1b**; CH_2CMe_3, **1c**) exclusively (eq 1). Isomerization was not observed for



either ***cis*-1b** or ***cis*-1c** over a period of weeks in d_6-benzene. The increased size of CH_2CMe_3 and CH_2-$SiMe_3$ relative to CH_2Ph may make isomerization impossible for steric reasons, or the *cis* isomers may simply represent the thermodynamically more stable forms.

X-ray Structures of $Zr(DAC)(CH_2Ph)_2$. ***cis*-** and ***trans*-1a** were investigated by X-ray crystallography. Refinement was not satisfactory for the *trans* isomer due to unreasonable thermal parameters for the macrocyclic ring atoms, especially the dangling oxygen (O3). As a result, the bond distances and angles are of low precision and do not warrant further discussion. A plot of the structure (Figure 2) reveals a distorted pentagonal

(15) The free energy of activation for this process was calculated from the coalescence temperature (T_c) using the equal-population, two-site exchange equation: $\Delta G^* = (1.912 \times 10^{-2})T_c[9.972 + \log(T_c/\delta\nu)]$ in kJ/mol, where $\delta\nu$ is the separation of the resonances in Hz and T_c is in K (Sandstrom, J. *Dynamic NMR Spectroscopy*; Pergamon: London, 1982; pp 77−91). The value of ΔG^* was estimated for the δ 73.6 and 69.6 ($\delta\nu$ = 366 Hz, T_c = 323 K) and for the δ 56.5 and 55.35 ppm ($\delta\nu$ = 100 Hz, T_c = 308 K) sets of resonances. The error in ΔG^* of ±2 kJ/mol was estimated by assuming liberal errors of ±5 K in T_c and ±5 Hz in $\delta\nu$.

(16) This is based on the assumption that the process is unimolecular in nature. A bimolecular process involving alkyl transfer between two Zr centers cannot be ruled out.

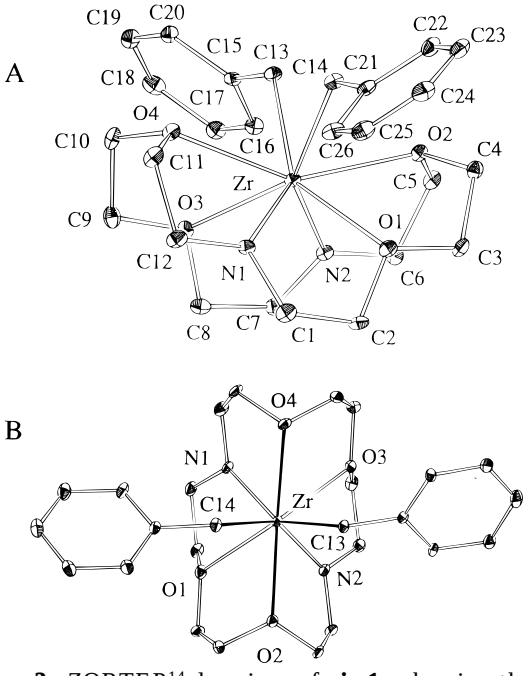


Figure 3. ZORTEP[14] drawings of ***cis*-1a** showing the side (A) and top (B) views.

Table 4. Selected Bond Distances (Å) and Angles (deg) for *cis*-1a[a]

Distances			
Zr(1)−O(1)	2.471(5)	Zr(1)−O(2)	2.466(6)
Zr(1)−O(3)	2.477(5)	Zr(1)−O(4)	2.470(5)
Zr(1)−N(1)	2.119(7)	Zr(1)−N(2)	2.2124(6)
Zr(1)−C(13)	2.417(7)	Zr(1)−C(14)	2.389(8)
Angles			
O(1)−Zr(1)−O(2)	65.3(2)	O(1)−Zr(1)−O(3)	128.4(2)
O(1)−Zr(1)−O(4)	131.4(2)	O(1)−Zr(1)−N(1)	68.4(2)
O(1)−Zr(1)−N(2)	81.8(2)	O(1)−Zr(1)−C(13)	143.2(2)
O(1)−Zr(1)−C(14)	81.4(2)	O(2)−Zr(1)−O(3)	130.8(2)
O(2)−Zr(1)−O(4)	148.8(2)	O(2)−Zr(1)−N(1)	133.7(2)
O(2)−Zr(1)−N(2)	68.9(2)	O(2)−Zr(1)−C(13)	79.1(2)
O(2)−Zr(1)−C(14)	75.5(2)	O(3)−Zr(1)−O(4)	64.6(2)
O(3)−Zr(1)−N(1)	81.1(2)	O(3)−Zr(1)−N(2)	67.9(2)
O(3)−Zr(1)−C(13)	82.0(2)	O(3)−Zr(1)−C(14)	144.5(2)
O(4)−Zr(1)−N(1)	68.8(2)	O(4)−Zr(1)−N(2)	132.4(2)
O(4)−Zr(1)−C(13)	76.8(2)	O(4)−Zr(1)−C(14)	81.3(2)
N(1)−Zr(1)−N(2)	106.5(2)	N(1)−Zr(1)−C(13)	145.5(3)
N(1)−Zr(1)−C(14)	96.3(3)	N(2)−Zr(1)−C(13)	94.4(2)
N(2)−Zr(1)−C(14)	144.2(3)	C(13)−Zr(1)−C(14)	80.8(3)
Zr(1)−C(13)−C(15)	123.7(5)	Zr(1)−C(14)−C(21)	128.3(6)

[a] Estimated standard deviation in parentheses.

bipyramid with one dangling oxygen donor. It appears that Zr is too small to coordinate all six donors in a planar array without introducing strain into the macrocyclic ring.

The structure of ***cis*-1a** is shown in Figure 3. Fractional atomic coordinates are given in the Supporting Information, and selected bond distances and angles are collected in Table 4. The zirconium center is eight-coordinate, with all four ether oxygens of the DAC ligand being coordinated. The coordination geometry may be described as a highly distorted square antiprism (Figure 3B). The most significant features of the structure are the open $Zr-CH_2-C_{ipso}$ angles (123.7(5) and 128.3(6)° for Zr−C13−C15 and Zr−C14−C20, respectively), indicating strictly η^1-benzyl coordination.[17] The Zr−N distances (2.124(6) and 2.119(7) Å) are very similar to those found in seven-coordinate Y(DAC)(CH_2SiMe_3) (2.27(2) and 2.26(2) Å) after correcting for the 0.12 Å larger ionic radius of the Y^{3+} ion.[18] However, the Zr−C bond lengths are long by the same comparison (***cis*-1a**, 2.417(7) and 2.389(6) Å; Y(DAC)(CH_2SiMe_3), 2.45(2) Å). Unlike the Y−O distances in Y(DAC)(CH_2SiMe_3), which were found to span a wide range (2.431(13)−2.622(11) Å), the four Zr−O distances (2.466(6)−2.477(5) Å) in ***cis*-1a** are very nearly identical with one another. Despite the fact that the basket geometry found in ***cis*-1a** appears to provide a better fit to Zr than the distorted-belt arrangement in ***trans*-1a**, NMR evidence (*vide supra*) points to the latter complex as the most stable in benzene solution.

Synthesis of Cationic Zirconium Complexes. Treatment of either ***cis*-** or ***trans*-1a** with $B(C_6F_5)_3$ in toluene yielded $[Zr(DAC)(CH_2Ph)]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (**2a**) as a bright yellow oil which dissolved readily in THF or CH_2Cl_2 (Scheme 1). The ^1H NMR spectrum, recorded in CD_2Cl_2 (Table 1), shows the presence of inequivalent *exo* and *endo* protons on each of the three unique DAC carbons. In comparison to ***cis*-1a**, the DAC protons are shifted downfield by 0.3−0.6 ppm, in keeping with coordination of the DAC ring to a positively charged center. However, little difference in ^{13}C chemical shift is observed for the ring carbons. The $ZrCH_2$ proton resonance shifts *upfield* by 0.26 ppm in cationic **2a**; a similar upfield shift has been observed previously for Schiff base supported zirconium alkyl cations.[6f] The presence of a benzyl group bound to boron is clearly evident from the broad singlet at δ 2.86 and the presence of two sets of aryl proton and carbon resonances. A number of NMR parameters which have been cited as evidence for an η^2-CH_2Ph interaction are notably absent. Specifically, upfield shifts of the benzyl *ipso* carbon and *ortho* proton resonances to ca. 137.5 and less than 6.40 ppm,[19] respectively, and an unusually large $^1J_{CH}$ value of greater than 140 Hz for the benzyl CH_2 group[20] are not observed here (for **2a**: benzyl *ipso* carbon, δ 148.93 ppm; *ortho* benzyl proton, δ 6.78−6.85 ppm; benzyl CH_2, $^1J_{CH}$ = 127 Hz). The small $\Delta\delta(m,p\text{-F})$ value of 2.9 ppm and the upfield *ipso* carbon resonance (δ 144.4 ppm; free anion, δ 148.6 ppm) for the $B(CH_2Ph)(C_6F_5)_3^-$ anion in the ^{19}F and ^{13}C NMR spectra indicate that no significant anion−cation interactions are present.[20]

Reaction of **1a** with $[n\text{-}Bu_3NH]^+[BPh_4]^-$ afforded a pale yellow precipitate of $[Zr(DAC)(CH_2Ph)]^+[BPh_4]^-$ (**2b**) in high yield. Complex **2b**, unlike **2a**, does not dissolve in CD_2Cl_2, presumably reflecting stronger anion−cation interactions in **2b**. However, **2b** dissolves readily in d_8-THF and shows no evidence for strong anion−cation pairing in this solvent.

Reaction Chemistry of $[Zr(DAC)(CH_2Ph)]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (2a). Reaction of **2a** with *p*-

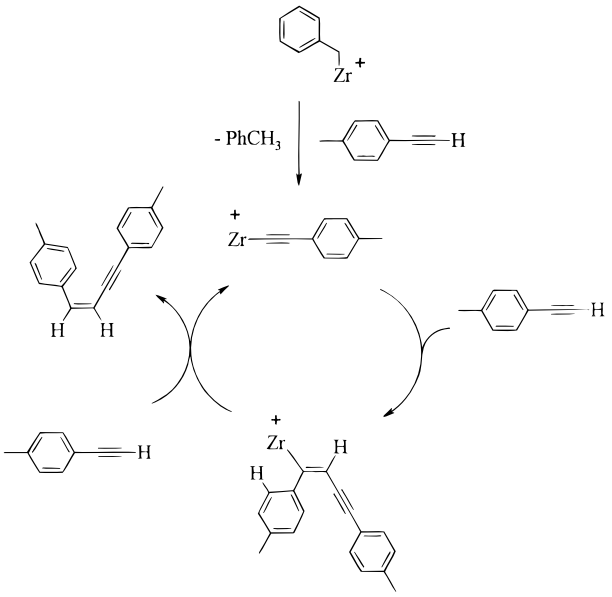
(17) Many examples of η^2-benzyl ligands are known in early-transition-metal and lanthanide chemistry, typically with $M-C-C_{ipso}$ angles of less than 100°. See for example: (a) Mintz, E. A.; Moloy, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 4692. (b) Girolami, G. S.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 2789. (c) Edwards, P. G.; Andersen, R. A.; Zalkin, A. *Organometallics* **1984**, *3*, 293. (d) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902. (e) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (f) Jordan, R. F.; LaPointe, R. E.; Baenziger, N.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539.

(18) Shannon, R. D. *Acta Crystallogr. Sect. A* **1976**, *A32*, 751.

(19) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473.

(20) Horton, A. D.; de With, J.; van der Linden, A.; van de Weg, H. *Organometallics* **1996**, *15*, 2672.

Scheme 2[a]

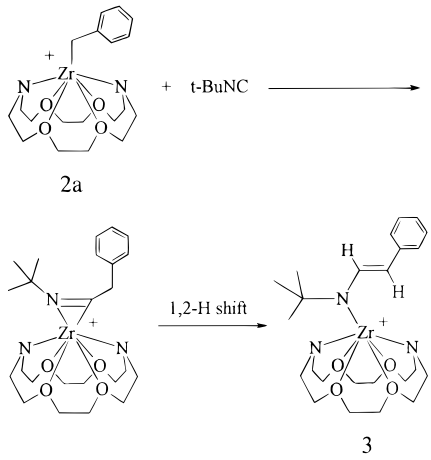


[a] DAC ligands omitted.

tolylacetylene leads to slow catalytic production of 1,4-di-*p*-tolyl-1-buten-3-yne (*Z*:*E* ratio = 85:15) at an initial rate of 2 turnovers/h. Catalytic dimerization of *p*-tolylacetylene by $Cp_2ZrCH_2Ph^+$ has previously been reported to yield 2,4-di-*p*-tolyl-1-buten-3-yne by a simple insertion/protonolysis cycle.[21] It is likely that an equivalent cycle (Scheme 2) is operative here, although it is not obvious why a 1,4-substituted enyne is obtained in this case while a 2,4-substituted product ("head-to-tail" insertion) was obtained in the Cp system. This result appears quite surprising, because **2a** is more sterically congested than $[Cp_2Zr(CH_2Ph)]^+$ and would therefore be expected to favor formation of the 2,4-substituted enyne since the insertion leading to this isomer is clearly less sterically crowded.[22] It is possible that the DAC backbone is flexible enough to allow electronic factors to dictate "tail-to-tail" insertion.[23]

Cation **2a** reacts rapidly with 1 equiv of *t*-BuNC to produce the vinylamide complex **3**. The ^{1}H NMR of **3** shows two alkenyl proton resonances at 7.14 and 6.42 ($^3J_{HH}$ = 14 Hz) ppm with corresponding ^{13}C NMR resonances at 135.04 and 111.16 ppm (^{1}H−^{1}H and ^{1}H−^{13}C COSY). The $^3J_{HH}$ coupling constant suggests a *trans* stereochemistry about the double bond. ^{19}F NMR data again indicate that the anion is not coordinated in CD_2Cl_2 ($\Delta\delta(m,p\text{-F}) = 3.0$ ppm).[20]

Formation of a vinylamide is likely to arise by a 1,2-proton rearrangement of the iminoacyl group formed by initial insertion of the isonitrile into the zirconium−carbon bond (eq 2). A similar rearrangement has



(2)

previously been reported in the reaction of $Cp_2Zr[CH_2$-(2-Me-py)$]_2$ with xylyl isocyanide.[24] Surprisingly, however, a very stable iminoacyl derivative was obtained upon xylyl isocyanide insertion into the corresponding Zr−benzyl bond of $Cp_2Zr(CH_2Ph)_2$.[24] In fact, to the best of our knowledge this is the first example of isonitrile insertion into the Zr−alkyl bond of a *cationic* complex which does not yield a stable iminoacyl.[25,26] It is possible that steric crowding drives the η^2-iminoacyl to η^1-vinylamido rearrangement in the present case.

Concluding Remarks

The results presented here extend the use of the deprotonated aza crown ether, DAC, to organozirconium chemistry. It is evident from the successful preparation of $Zr(DAC)R_2$ and $Zr(DAC)R^+$ derivatives that DAC behaves similarly to the bis(cyclopentadienyl) ancillary ligand set. The greater flexibility of the DAC framework can, however, lead to geometries such as that found in *trans*-$Zr(DAC)(CH_2Ph)_2$ (***trans*-1a**), which are not possible in the bis-Cp system. Although some variation in reactivity, such as the regiochemistry of alkyne insertion (Scheme 2), has been noted here, further studies are necessary to determine whether differences in geometry and ligand flexibility will translate into major differences in reactivity.

Acknowledgment. We thank Mrs. C. Greenwood for assistance with the NMR experiments and Ms. Becky Chak for help with the X-ray structural studies. A gift of tris(pentafluorophenyl)boron from the Boulder Scientific Co. is gratefully acknowledged. This research was supported by the NSERC (Canada) and a University of Victoria Internal Research Grant (to D.J.B.).

Supporting Information Available: Text giving X-ray experimental details for ***trans*-1a** and tables giving complete bond distances and angles, anisotropic thermal parameters, and positional parameters for ***cis*-1a** (7 pages). Ordering information is given on any current masthead page.

OM961027N

(21) Horton, A. D. *J. Chem. Soc., Chem. Commun.* **1992**, 185.

(22) This conclusion is based on a comparison of the neutral dibenzyl complexes. The substituted Cp derivatives $Zr(EBTHI)_2(CH_2Ph)_2$ (EBTHI = *rac*-(ethylenebis(tetrahydroindenyl))[17f] (2.314(4) Å) and $Zr(Me_3SiC_5H_4)_2(CH_2Ph)_2$ (see reference below, 2.291(5)−2.323(5) Å), which may be expected to be *more* crowded than the simple Cp complex $Cp_2Zr(CH_2Ph)_2$, show Zr−C bond lengths which are much shorter than those found in ***cis*-1a** (2.417(7) and 2.389(6) Å): (a) Thiele, K. H.; Böhme, U.; Sieler, A. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1951.

(23) One possible explanation for the observed insertion regiochemistry might involve an interaction between the alkenyl phenyl ring and the Zr center, either through the arene π-system or, more likely, through an *ortho*-aryl C−H agostic interaction (see Scheme 2). In our opinion, this remains a possibility even though **2a** is more crowded than $Cp_2Zr(CH_2Ph)^+$ because of the flexibility of the DAC ligand.

(24) (a) Beshouri, S. M.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1987**, *6*, 891. (b) Beshouri, S. M.; Chebi, D. E.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1990**, *9*, 2375. For a closely related rearrangement see: (c) Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 2665.

(25) Most neutral Zr dialkyls insert isonitriles to form stable η^2-iminoacyls. For a brief review see: Jubb, J.; Song, J.; Richeson, D.; Gambarotta, S. In *Comprehensive Organometallic Chemistry*, 2nd ed.; Lappert, M. F., Ed.; Pergamon Press: Oxford, U.K., 1995; Vol. 4, pp 582−585.

(26) Guram, A. S.; Jordan, R. F. *J. Org. Chem.* **1993**, *58*, 5595.