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Note

Piano stool complexes containing the bulky pentaphenylcyclopentadienyl(C_5Ph_5) ligand: Preparation, characterization and X-ray structure of $C_5Ph_5Zr(N(CH_3)_2)_3$ (**I**)

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Abstract

Tris(dimethylamido) pentaphenylcyclopentadienyl zirconium (**I**) has been prepared and characterized by NMR spectroscopy and X-ray crystallography. The structure reflects the strong p–d amido donation with short Zr–N distances and Zr–C distances that are longer than those in the 16 electron $C_5Ph_5(C_5H_5)ZrCl_2$. The reaction of **I** with (*R*)-(+)-sec-phenethyl alcohol to form the alkoxide complexes proceeds rapidly to the spectroscopically characterized tris((*R*)-(+)-sec-phenethyl alkoxide) complex, suggesting an activating effect upon alkoxide substitution.

Keywords: Pentaphenylcyclopentadienyl; Zirconium; Piano stool; Dimethylamido; Chiral complex

1. Introduction

Developing catalysts capable of producing one stereoisomer from achiral reactants has great practical and academic importance. Higher yields of a desired biologically active substance can be achieved as well as eliciting the factors that can contribute to such selectivity. As a result, considerable effort has been directed towards development of catalysts. Our previous work with Zr complexes containing the pentaphenylcyclopentadienyl (C_5Ph_5) and the *m*-tolyltetraphenylcyclopentadienyl (*mt*-Cp) ligands, has shown that $C_5Ph_5ZrCl_3$ and *mt*-$CpZrCl_3$ promote [4 + 2] cyclization of cyclopentadiene with acrolein and methylacrylate with diastereospecificity [1,2]. Our aims are to develop chiral derivatives of these complexes, but traditional salt metathesis routes to alkoxide complexes have been, to date, unproductive.

Amido complexes have the ability to stabilize low electron counts and also can serve as convenient leaving groups when reacted with alcohols or other moderately acidic ligand precursors [3–12]. The utility and limitations of homoleptic amido reagents as precursors and reagents have been previously discussed [13]. Recently the typical three-legged piano stool complexes (C_5Me_5)$Zr(NMe_2)_3$, (C_5Me_5)$Ti(NMe_2)_3$ have been synthesized [14] and DFT calculations on the model complex (5-C_5H_5)$Ti(NMe_2)_3$ and its X-ray structure have been reported [10,15].

Herein, we describe the synthesis characterization and X-ray structure of pentaphenylcyclopentadienyltris(dimethylamido)zirconium (**I**) and the results of the reaction of **I** with -α-methylbenzyl alcohol. Complex **I**

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is of interest as it is one of few structurally characterized group 4 complexes with the pentaphenylcyclopentadienyl ligand [16,1] whereas later transition metal complexes of this ligand have been more extensively studied [17–34]. In addition, the structural data suggest an agostic interaction with one of the amido methyl groups.

2. Results and discussion

Compound **I** was prepared by the reaction of pentaphenylcyclopentadiene with tetrakis(dimethylamido)zirconium in toluene in 88% yield.

$$Zr(NMe_2)_4 + HC_5Ph_5 \rightarrow HNMe_2 + C_5Ph_5Zr(NMe_2)_3 \quad (1)$$

The compound is quite moisture sensitive and elemental analysis results are most consistent with the oxo-bridged dimer that would result by hydrolysis. The X-ray structure of **I** is shown in Fig. 1 and the crystal data are in Table 1. The structural features are generally consistent with a 12 electron piano stool structure.

The bond distances and angles in Fig. 1 suggest that π donation by the amido ligands is more important in **I** than in analogous complexes. The Zr–N distances in **I** range from 2.036(3) to 2.055(3) Å, shorter than the Zr–N distances of 2.072(10) Å in $(C_5Me_5)Zr(NMe_2)_3$ [10] and those in the sterically encumbered 2,6-diphenyl-benzene-cyclopentadienyl-tris(diethylamido)zirconium which range from 2.0689(13) to 2.0888(13) Å [35]. A concomitantly weaker Zr–cyclopentadienyl bond is shown by the bond distances to that fragment, with longer zirconium centroid and average Zr–C(Cp) distances (2.340 and 2.634 Å, respectively) than the 2.276 and 2.576 Å observed in the 2,6-diphenyl-benzene-cyclopentadienyl-tris(diethylamido)zirconium complex which itself has relatively long Zr–Cp distances [35]. These longer distances have been noted in earlier reports, where the distance to a C_5Ph_5 ligand is 0.8 Å longer than that of a Cp ligand in $CpC_5Ph_5ZrCl_2$ [2].

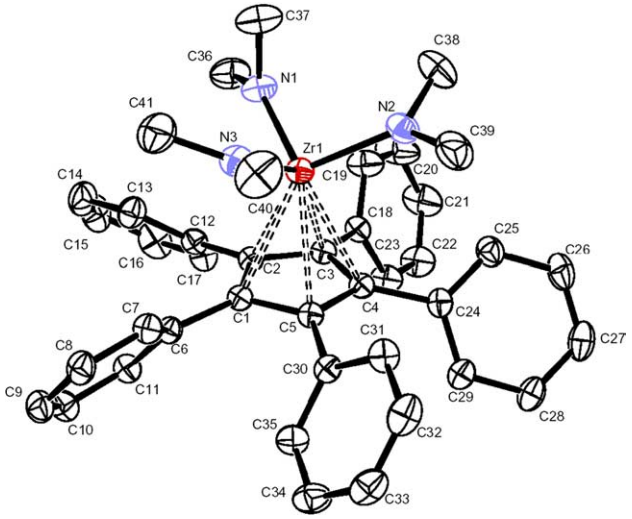

Fig. 1. ORTEP diagram and atom labeling scheme for I. Selected bond distances (Å) and angles (°): Zr–CNT 2.340 Å, Zr(1)–C(1) 2.648(3), Zr(1)–C(2) 2.657(3), Zr(1)–C(3) 2.627(3), Zr(1)–C(4) 2.619(3), Zr(1)–C(5) 2.619(3), Zr(1)–N(1) 2.036(3), Zr(1)–N(2) 2.052(3), Zr(1)–N(3) 2.055(3), N(1)–C(36) 1.454(6), N(1)–C(37) 1.481(6), N(2)–C(39) 1.441(6), N(2)–C(38) 1.456(6), N(3)–C(40) 1.417(6), N(3)–C(41) 1.451(7), N(1)–Zr(1)–N(2) 101.39(15), N(1)–Zr(1)–N(3) 101.50(15), N(2)–Zr(1)–N(3) 102.83(14), C(36)–N(1)–Zr(1) 143.7(3), C(37)–N(1)–Zr(1) 107.4(3), C(38)–N(2)–Zr(1) 123.3(3), C(39)–N(2)–Zr(1) 127.8(3), C(40)–N(3)–Zr(1) 129.1(3), C(41)–N(3)–Zr(1) 122.0(3), C–N–C angles, 108.9(4)°.

Table 1
Crystal data and structure refinement for $C_5Ph_5Zr(N(CH_3)_2)_3$ (**I**)

Empirical formula	$C_{44}H_{43}N_3Zr$
Formula weight	705.03
T (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	11.9928(12)
b (Å)	12.4371(13)
c (Å)	14.8101(15)
α (°)	85.546(2)
β (°)	73.502(2)
γ (°)	64.945(2)
V (Å3)	1916.4(3)
Z	2
D (calcd) (g/cm3)	1.222
Absorption coefficient (mm^{-1})	0.320
$F(000)$	736
Crystal size (mm)	$0.71 \times 0.37 \times 0.04$
θ Range (°)	1.44–27.53
Index ranges	$-14 \leqslant h \leqslant 13$, $-14 \leqslant k \leqslant 15$, $-16 \leqslant l \leqslant 18$
Reflections collected	11860
Independent reflections	8285 ($R_{int} = 2.39\%$)
Transmission factors	min/max ratio: 0.831
Goodness-of-fit (F_2)	1.052
Final R indices ($I > 2\sigma(I)$) (%)	$R = 0.0592$, $R_w = 0.1699$
R indices (all data) (%)	$R = 0.0728$, $R_w = 0.1805$
Difference peak and hole (e $Å^{-3}$)	1.284, −0.534

Also, one of the dimethyl-amido ligands, that containing N(1), is not equivalent to the other two in the solid state. The N–C distances in **I** range from 1.417(6) to 1.481(6) Å, where longer distances are to N(1). This is the amido ligand in which the plane containing N(1), C(36) and C(37) is roughly parallel to the Zr–Cp centroid line, where the other amido ligands' planes are roughly orthogonal to that line. This arrangement has been observed in other tris-amidocyclopentadienyl complexes of group 4 metals [13], as has the converse, where only one ligand is nearly orthogonal to the Zr-centroid line [35].

This difference is marked by a slightly shorter Zr–N distance, slightly longer N–C distances and Zr–N–C angles significantly different from the other two ligands. These parameters suggest a marginally higher Zr–N bond order than in the other two ligands. The unique amido group in Zr complexes typically has a

shorter bond distance. This is consistent with the suggestion of Curnow et al. [35], that the geometrically different amido undergoes more effective pπ donation to a d orbital than the other two amido ligands which must both share a single, other d-orbital. However, this distinction apparently does not persist in solution as the proton NMR in solution shows a single resonance for methyl groups, suggesting either a different conformation in solution or fluxional behavior, a result which is not surprising considering the more sterically encumbered 2,6-diphenyl-benzene-cyclopentadienyl-tris(diethylamido)zirconium shows equivalent ethyl groups at ambient temperature [35].

Another structural anomaly of the N(1) amido group is observed in the Zr–N–C angles, 143.7(3)° and 107.4(3)°, compared to the 125.5(3)° average for the four other Zr–N–C angles. The Zr–C(amido) distances for the ligand containing N(1) are asymmetric, Zr–C(37) 2.854 Å and Zr–C(36) 3.321 Å, compared to an average Zr–C (amido) of 3.12(3) Å for the other amido ligands. In addition, the N(1)–C(37) distance at 1.481 Å is the longest of the N–C distances. One explanation for these observations is an agostic interaction between the C(37) methyl and the Zr center causing this amido ligand to tilt toward the metal. An appropriate HFIX command was used to locate the methyl hydrogens and an H atom was found with a Zr–H distance of 2.624 Å, within the range of an agostic interaction [36]. Therefore, the large difference in the Zr–N(1)–C bond angles may be due to an agostic interaction with a C(37) methyl hydrogen.

Our current efforts are directed at using complex **I** as a synthon for derivatives by reaction with alcohols as in Eq. (2) to give alkoxide complexes:

$$C_5Ph_5Zr(NMe_2)_3 + n\mathrm{ROH} \rightarrow C_5Ph_5Zr(NMe_2)_{3-n}(OR)_n + n\mathrm{HNMe_2} \quad (2)$$

Formation of the trisubstituted complex ($n = 3$) proceeds cleanly as monitored by ^{1}H NMR, with either racemic or resolved *R*-α-methylbenzyl alcohol (**II**). Complex **II** did not analyze cleanly and attempts to obtain high resolution mass spectroscopy were unsuccessful, probably owing to its high propensity to hydrolysis with loss of pentaphenylcyclopentadienene.

Attempts to form complexes with $n = 1$ or 2 by addition of stoichiometric amounts of the alcohol gave mixtures whose ^{1}H NMR shows the presence of **I** as well as the $n = 3$ complex and other signals, presumably $n = 2$ are present, regardless of the temperature and addition rate. This result suggests that substitution of one amido ligand activates the complex, making it more reactive to further amido ligand replacement by alkoxide thus making controlled substitution difficult. We are currently pursuing other avenues to attain controlled, sequential substitution of the amido ligands to produce chiral complexes.

3. Summary

The reaction of tetrakis-dimethylamidozirconium(IV) with pentaphenylcyclopentadiene cleanly gives the piano stool complex (**I**) which has been characterized by X-ray diffraction. In the solid state, one of the dimethylamido ligands displays bonding metrics that imply that particular Zr–N bond is slightly stronger than the other two. The three amido ligands react readily with sec-phenethyl alcohol to give the tris-alkoxide complex, however sequential substitution is not achieved by simple slow addition at ambient or temperatures as low as −77 °C.

4. Experimental

4.1. General procedures

All operations were carried out under nitrogen using Schlenk and glovebox (VAC HE-43 with HE-493 Dritrain or VAC Omnilab) techniques. Solvents were anhydrous grade from Aldrich and purified using a Braun SPS-1 and stored over activated molecular sieves in Strauss flasks. NMR solvents were either dried by standard methods [37] or dried twice over activated sieves and freeze–thaw degassed three cycles. Commercial $ZrCl_4$ and 95% $LiN(CH_3)_2$, racemic and (*R*)-(+)-sec-phenethyl alcohol from Aldrich were used, the latter two reagents being dried over 4 Å molecular sieves. $Zr(N(CH_3)_2)_4$ was synthesized according to the literature with minor modifications [38,39]. Pentaphenylcyclopentadiene was prepared as in our previous work [1]. The ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker Aspect 3000 spectrometers at 300 MHz. The samples were prepared in Young valve rotationally symmetric tubes using the residual proton resonance as internal standards.

4.1.1. Preparation of $C_5Ph_5Zr(N(CH_3)_2)_3$ (**I**)

A slurry of $Zr(N(CH_3)_2)_4$ (0.7 g, 2.7 mmol) and pentaphenylcyclopentadiene (1.2 g, 2.7 mmol) in dry toluene (20 ml) was refluxed under nitrogen in a Schlenk flask for about 20 h. The yellow solution was cooled and concentrated under vacuum. A yellow precipitate formed which dissolved when heated and the solution was slowly cooled to room temperature to give yellow crystals after 1 day. The crystals were filtered and washed with pentane. A second crop of yellow crystals was obtained from the supernatant after cooling 48 h at −20 °C. The combined solids were dried under vacuum (1.6 g, 88%) ^{1}H NMR (C_6D_6): δ 7.33 (d, 9H, part C_6H_5), δ 7.02–6.88 (m, 16H, part C_6H_5), 2.96 (s, 18H, $N(CH_3)_2$). ^{13}C NMR (C_6D_6): δ 135.99 (s), 132.89(s), 128.00(s), 126.56(s), Ph and sp^2 cyclopentadiene carbons, δ 45.26-(s, $N(CH_3)_2$). Anal. Calc. for the dimer, $C_5Ph_5Zr(N(CH_3)_2)_2$–O–$C_5Ph_5Zr(N(CH_3)_2)_2$ ($C_{78}H_{74}N_4OZr_2$):

C, 74.01; H, 5.89; N, 4.45. Found: C, 71.81; H, 6.21; N, 4.43%.

4.1.2. Preparation of $C_5Ph_5Zr((R)$-(+)-$OCH(CH_3)$-$(C_6H_5))_3$ (II)

A solution of (*R*)-(+)-sec-phenethyl alcohol (36.6 mg, 0.3 mmol) in toluene (15 ml) was added to a solution of **I** (66.9 mg, 0.1 mmol) in toluene (5 ml) at room temperature during 3 h. The light yellow mixture was obtained after stirring over night at room temperature. Then dried under vacuum, recrystallization with toluene/pentane, light yellow solid **II** (78 mg, 86%) were obtained. ^{1}H NMR (C_6D_6): δ 7.27–6.92 (m, 40H, C_6H_5), 5.16 (*q*, 3H, $OCH(CH_3)(C_6H_5)$), 1.37 (*d*, 9H, $OCH(H_3)(C_6H_5)$) [13]. C NMR (C_6D_6): δ 134.44 (s), 122.06(s), 119.86(s), 114.46(s), 113.91(s), 113.57(s), Ph and sp^2 cyclopentadiene carbons, 66.14(s, $OCH(CH_3)(C_6H_5)$), 14.68(s, $OCH(C_3)(C_6H_5)$). High resolution MALDI mass spectra of **II** were not obtained on successive attempts, probably owing to its high propensity to hydrolysis with loss of pentaphenylcyclopentadienene.

4.1.3. X-ray diffraction studies of the toluene solvate of I

Crystals of **I** were grown by dissolving the sample in a heated solution of toluene. The solution was then allowed to cool to room temperature and crystals grew after 1 day. These crystals proved to be extremely air sensitive and were subsequently mounted in 0.7 mm quartz capillaries inside an argon-filled glove box. Relevant crystallographic details are given in Table 1. Diffraction data for **I** were collected at room temperature ($T = 23$ °C) using a SMART/APEX CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$). The unit cell dimensions for **I** were obtained from the least-squares refinement of the spots from 60 frames using the SMART program. A full hemisphere of data was collected up to a resolution of 0.75 Å according to the unit cell information. The intensities were processed using the SAINT PLUS program. All calculations for structure determination were carried out using the SHELXTL package (version 5.1) [40]. Initial atomic positions were located by direct methods, and the complete structure was refined by least-squares methods with 8285 independent reflections and within the range of theta 1.44–27.53 (completeness = 94%). Absorption corrections were applied using SADABS [41]. Calculated hydrogen positions for the phenyl rings were input and refined in a riding manner along with attached carbons. Hydrogen positions for the amido ligands were located and refined using the appropriate HFIX card. Disorder was apparent in the solvent molecule and those atom positions were restrained and refined using the appropriate DFIX command. All non-hydrogen atoms were refined anisotropically except for the solvent molecule that was refined isotropically. X-ray crystallography data (the. cif files) for **I** (CCDC 271207) have been deposited with the Cambridge Crystallographic Data Center as supplementary material.

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