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1,4-Diaza-1,3-diene (DAD) complexes of early transition metals. Synthesis and structural characterization of (t-Bu-DAD)ZrCl(μ-Cl)$_3$Zr(t-Bu-DAD)(THF) and its reaction with benzophenone

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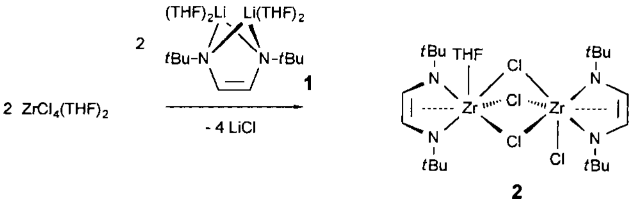
Abstract

The reaction of $ZrCl_4(THF)_2$ with one equivalent of $[\{Li(THF)_2\}_2(t\text{-Bu-DAD})]$ (**1**), t-Bu-DAD≡(t-Bu)N=CHCH=N(t-Bu), in THF produces the pale-yellow zirconium complex [(t-Bu-DAD)$ZrCl_2$(THF)] which dimerizes in the solid state to [(t-Bu-DAD)ZrCl(μ-Cl)$_3$Zr(t-Bu-DAD)(THF)] (**2**) using three chlorine atoms as bridging ligands. Treatment of **2** with two equivalents of benzophenone in ether affords the novel zirconium complex [Zr{$OCPh_2$CH(CH=Nt-Bu)N(t-Bu)}Cl_2(THF)] (**3**) which is formed by a cycloaddition reaction of the Zr − N=C unit to the C=O carbonyl group of benzophenone. In complex **3** the zirconium is octahedrally coordinated by the new tripodal α-aminoalkoxy ligand {$OCPh_2$CH(CH=Nt-Bu)N(t-Bu)}, two Cl^- ligands and one molecule of THF. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Zirconium complexes; Heterodiene; 1,4-Diaza-1,3-diene; Cycloaddition reaction

1. Introduction

During the last few years, Group 4 complexes that contain chelating diamido ligand systems [1] have received increased attention as alkene polymerization catalysts [2]. The potential advantage of the bis(amido)metal system relative to the metallocene or the half-sandwich amidometal complexes is their lower formal electron count which results in a more electrophilic and therefore potentially more active catalyst fragment [3]. An important recent result in this context is the finding that propylene-bridged aryl-substituted diamido titanium complexes promote the living polymerization of neat α-olefins [2c]. Moreover, the use of variable functionalized diamido ligand systems opens the chance to create a more different steric environment at the reactive complex site. Already, a dramatic effect of the chelate ring size of zirconium complexes on the ethylene polymerization activity has been found [3].



Scheme 1. Synthesis of the dimeric zirconium DAD complex [(t-Bu-DAD)ZrCl(μ-Cl)$_3$Zr(t-Bu-DAD)(THF)] (**2**).

As a part of our program to investigate the utility of 1,4-diaza-1,3-diene (DAD) [4] ligands in early transition and lanthanide metal chemistry [5], we were attracted to the DAD Group 4 metal halogenide complexes of the type (DAD)MCl_2 (M = Ti, Zr) for a variety of reasons, among them preparing new olefin polymerization catalysts. In the majority of the early transition metal DAD complexes the heterodienes are coordinated in their dianionic form as chelating enediamides and therefore are reminiscent of diamido ligands. In this contribution, we present the synthesis and X-ray crystal

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structure of the first DAD dichlorozirconium complex and describe initial investigations on the cycloaddition reactivity of this complex with ketones.

2. Results and discussion

2.1. Synthesis of the 1,4-diaza-1,3-diene dichlorozirconium complex

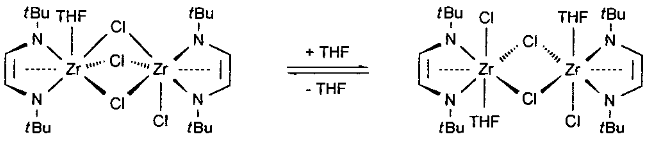
The dilithium DAD compound $[\{Li(THF)_2\}_2(t\text{-Bu-DAD})]$ (**1**) which was synthesized by reaction of *t*-Bu-DAD with two equivalents of lithium in THF [5f,6] is most suitable for transferring the DAD dianion to the transition metal. Reaction of the dilithium salt **1** with an equimolar amount of $ZrCl_4(THF)_2$ in THF, followed by extraction of the crude residue with diethyl ether, afforded a yellow microcrystalline complex $[(t\text{-Bu-DAD})ZrCl(\mu\text{-Cl})_3Zr(t\text{-Bu-DAD})(THF)]$ (**2**) in 63% yield containing 0.5 equivalents THF per zirconium (Scheme 1).

Complex **2** has been characterized by ^1H- and $^{13}C\{^1H\}$-NMR spectroscopy in THF-d_8. The observation of only single resonances for the *t*-Bu groups (δ 1.22) and the imine protons CH=CH (δ 5.61) in the ^1H-NMR spectrum is consistent with a C_{2h} symmetry in solution or, perhaps, a lower symmetry species undergoing rapid THF exchange (Scheme 2).

However, crystallization of the dizirconium species in diethyl ether resulted in partial loss of THF and the formation of **2**. The molecular structure of **2** together with selected bond lengths is illustrated in Fig. 1.

Both zirconium atoms are hexacoordinated: one by three bridging chloride ligands, two nitrogen atoms of the chelating enediamido ligand and one molecule of THF; the other by one terminal and three bridging chloride ligands as well as by two nitrogen atoms of the second enediamido ligand, respectively. Thus, the geometry about each zirconium atom can be described as a distorted octahedron, and the nitrogen atoms of the chelating enediamido ligands at each zirconium are nearly staggered with respect to the three bridging chloride ligands.

Binuclear Zr(IV) halogenide complexes with chelating diamido ligands usually tend to form double bridged planar structures, as observed in $[1,2\text{-}C_6H_4(NSiMe_2R)_2ZrCl]_2(\mu\text{-Cl})_2$ [1o] and $[1,8\text{-}C_{10}H_6(NSiR_3)_2ZrCl]_2(\mu\text{-Cl})_2$ (R = Me [1m], *i*-Pr [1k]). Triply bridged zirconium complexes are rare, and only few other structures containing trichloro-bridged zirconium have been reported [7]. In contrast, due to the smaller size of Ti(IV) relative to Zr(IV) the dimeric titanium analogue of **2**, $[\{(t\text{-Bu-DAD})TiCl\}_2(\mu\text{-Cl})_2]$, contains only two bridging chloride ligands and no molecule of THF [8].



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Scheme 2. Apparent symmetry equivalence of the two Zr centers achieved by a rapid THF exchange process.

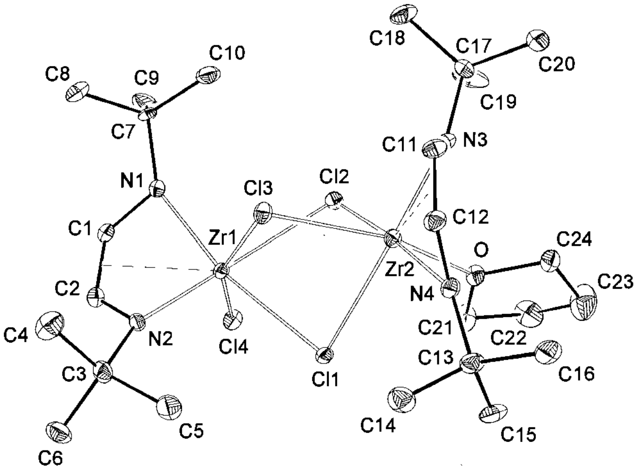
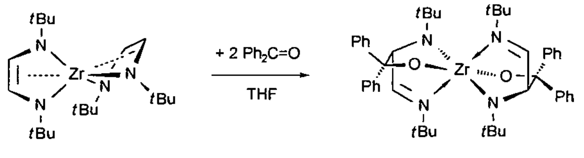


Fig. 1. Structural representation of **2**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 40% probability. Selected bond distances (Å) and angles (°): Zr1–N1 2.035(5), Zr1–N2 2.037(5), Zr2–N3 2.023(5), Zr2–N4 2.041(5), Zr1–Cl4 2.441(2), Zr1–Cl1 2.674(2), Zr1–Cl2 2.681(2), Zr1–Cl3 2.705(2), Zr2–Cl1 2.665(2), Zr2–Cl2 2.626(2), Zr2–Cl3 2.536(2), Zr2–O 2.227(4), Zr1–C1 2.457(6), Zr1–C2 2.446(6), Zr2–C11 2.431(6), Zr2–C12 2.421(7), N1–C1 1.379(8), N2–C2 1.386(9), N3–C11 1.375(9), N4–C12 1.388(9), C1–C2 1.368(10), C11–C12 1.373(10), N1–Zr1–N2 87.2(2), N3–Zr2–N2 88.8(2), Zr1–Cl1–Zr2 86.71(6), Zr1–Cl2–Zr2 87.38(5), Zr1–Cl3–Zr2 88.71(5), sum of angles at N1 358.5(4), sum of angles at N2 360.0(4), sum of angles at N3 354.9(4), sum of angles at N4 353.7(4), (Zr1, N1, N2) (N1, C1, C2, N2) 55.2(2), (Zr2, N3, N4) (N3, C11, C12, N4) − 55.3(2), N1–C1–C2–N2 0.5(5), N3–C11–C12–N4 2.9(5).

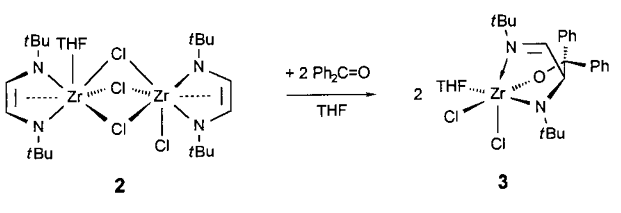
The five-membered 1,3-diaza-2-zironacyclopent-4-ene rings in **2** are not planar. They are folded along the N–N axis by 55.2(2) and − 55.3(2)°, respectively. Despite this folding which moves the olefinic bonds of the enediamide ligands close to the zirconium atoms (Zr1–C1 2.457(6), Zr1–C2 2.446(6), Zr2–C11 2.431(6), Zr2–C12 2.421(7) Å) and enhances the possibility of electron donation, the nitrogen atoms maintain a nearly planar sp^2 environment, as seen by the summation of angles at the N atoms (average 356.8(4)°). Moreover, the average Zr–N distances of 2.034(5) Å are comparatively short in agreement with the assumption that a significant p_π–d_π interaction can be largely contributed by the two nitrogen σ lone pairs [9,10]. As expected, the bond distances from the zirconium atom to the bridging chloride ligands (average Zr1–Cl 2.687(2), Zr2–Cl 2.609(2) Å) are elongated from the terminal distance Zr1–Cl4 2.441(2) Å.

2.2. Reaction of the 1,4-diaza-1,3-diene dichlorozirconium complex **2** with benzophenone

Recently, we reported on the novel reaction of DAD complexes with ketones. We had found that DAD ligands that are bound to early transition metals or lanthanide metals can be selectively functionalized forming a new C–C bond between one of the imine carbon atoms and the carbonyl carbon atom of the electrophilic substrate [11,12]. Thus, the reaction of ketones with (t-Bu-DAD)$_2$M (M = Zr, Hf) leads to complexes in which the metal atom is octahedrally coordinated by two novel tridentate ligands (Scheme 3).



Scheme 3. Reaction of (t-Bu-DAD)$_2$Zr with benzophenone [11].



Scheme 4. Reaction of [(t-Bu-DAD)ZrCl(μ-Cl)$_3$Zr(t-Bu-DAD)(THF)] (**2**) with benzophenone.

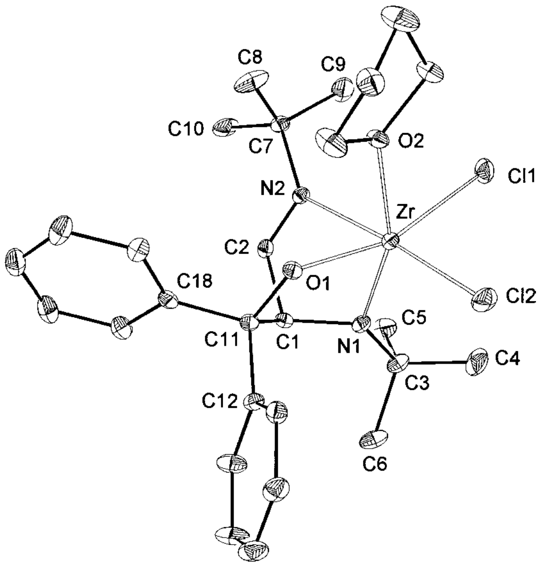


Fig. 2. Structural representation of **3**. Hydrogen atoms are omitted for clarity. The thermal ellipsoides correspond to 40% probability. Selected bond distances (Å) and angles (°): Zr–N1 2.041(3), Zr–N2 2.495(3), Zr–O1 1.995(3), Zr–O2 2.295(3), Zr–Cl1 2.488(1), Zr–Cl2 2.452(1), N1–C1 1.476(5), N2–C2 1.270(5), O1–C11 1.419(4), C1–C2 1.530(5), C1–C11 1.579(5), N1–Zr–N2 73.12(11), N1–Zr–O1 80.07(11), N1–Zr–O2 159.15(11), N2–Zr–O1 76.42(10), Cl1–Zr–Cl2 93.77(4), N2–Zr–Cl2 176.03(7), O1–Zr–Cl1 161.39(8), Zr–N1–C1 105.2(2), Zr–N2–C2 104.5(2), Zr–O1–C11 118.6(2), N1–C1–C2–N2 −35.4(3), sum of angles at N1 356.7(3), sum of angles at N2 359.1(2).

Unfortunately, the mechanism of this multistep reaction is not fully understood. However, with respect to similar reactions of late transition metal DAD complexes with electrophiles reported by Frühauf et al., this reaction may be described as a 1,3-dipolar cycloaddition [13]. Furthermore, from the practical point of view this reaction opens a new strategy to transfer a dianionic N,N'-bonded DAD into a tridentate O,N,N'-bonded oxoamidoimine ligand.

We have since turned our attention to prepare a zirconiumdichloride complex with this oxoamidoimine ligand starting from complex **2** (Scheme 4).

The addition of one equivalent of benzophenone to a stirred solution of **2** in THF at −20 °C results in a transient color change of the reaction mixture from pale yellow to dark green which fades to colorless on warming up to room temperature. Finally, complex **3** was isolated as an analytically pure colorless solid by crystallization from diethyl ether in 87% yield. It is very soluble in THF, soluble in diethyl ether, but only sparingly so in aliphatic solvents.

The ^{1}H- and ^{13}C{^{1}H}-NMR spectra of complex **3** are consistent with the formation of the expected oxoamidoimine ligand within the coordination sphere of the metal atom. The most noteworthy NMR spectral features are the following: (i) The imine protons give rise to two doublets at δ 8.66 and 4.98 which dramatically reflects the change in the bonding feature of the t-Bu-DAD ligand. The $^{3}J_{\mathrm{H,H}}$ coupling constant for these vicinal imine protons (2.8 Hz) shows that the C–H bonds are twisted against each other [14]. (ii) In the ^{13}C{^{1}H} NMR-spectrum the chemical shift values of the neighboring imine carbon atoms of the heterodiene backbone are quite different too. As expected, the carbon resonance of the coordinated imine function is observed at δ 180.04. In contrast, the resonance for the second imine carbon atom appears at δ 71.89. The large upfield-shift of this signal corresponds with the change in hybridization from sp^2 to sp^3 of this carbon atom which is coupled to the carbonyl carbon atom of benzophenone. (iii) Two independent sets of phenyl resonances of the OCPh$_2$ building block indicate that these groups are diastereotopic which is caused by the adjacent chiral carbon atom and which verifies the expected structure of **3**.

An X-ray diffraction study was performed to determine the metal geometry and the structure of the new oxoamidoimine ligand. Single crystals were readily grown by slow cooling of a saturated solution of **3** in diethyl ether. The molecular structure along with selected bond lengths and angles is shown in Fig. 2. Complex **3** is monomeric and has a metal center with a hexacoordinate geometry which as a consequence of the rigid [2.2.1] bicyclic structure of the newly formed tripodal ligand can be described as being distorted octahedral. If the plane occupied by the oxygen atom O1 and the imine nitrogen atom N2 of the oxoamidoimine ligand as well as the two chlorine atoms Cl1 and Cl2 is designated as the equatorial plane, the oxygen atom O2 of the THF and the amido nitrogen atom N1 occupy the axial positions with a N1–Zr–O2 angle of 159.15(11)°. The Zr–N1 and the Zr–O1 distances (2.041(3) and 1.995(3) Å) compare well with those for alkylamido and alkoxide ligands bound to Zr(IV) [10,15]. As expected, the Zr–N2 bond is much longer (2.495(3) Å) and is representative of a weak dative N(imino)–Zr bond [16]. Accordingly, the sum of angles about N2 (359.1(2)°) indicate that the imine nitrogen atom is sp^2 hybridized. Nevertheless, the sum of the angles about N1 (356.7(3)°) suggests that the amido nitrogen atom is also in an sp^2 hybridized environment donating π-electrons to the electrophilic zirconium center. Interestingly, the Zr–Cl bonds (2.488(1) and 2.452(1) Å) are nearly of the same length and do not indicate a strong difference in the *trans*-influence between the Zr–O1 and the Zr–N2 bond. The Cl1–Zr–Cl2 angle (93.77(4)°) is close to the expected right angle.

The bond distances and interbond angles within the newly formed tridentate ligand are nearly identical to those found for the cycloaddition products of $(t\text{-Bu-DAD})_2M$ (M = Zr, Hf) with acetophenone or benzophenone [11]. Due to the C–C coupling, the former C=O double bond of benzophenone is reduced to a C–O single bond [C11–O1 1.419(4) Å]. Furthermore, as expected from the NMR spectra, the nitrogen and carbon atoms of the starting enediamide skeleton, N–C=C–N, are not in the same plane (N1–C1–C2–N2 − 35.4(3)°), and the observed imine N–C distance (N2–C2 1.270(5) Å) is shorter than that in the amido group (N1–C1 1.476(5) Å). The special structural feature of this new ligand is the combination of the chelating dianionic oxoamido function with an additional neutral imino donor function. It is expected that the imine donor function is less strongly bound to the metal center which enhances the flexibility in the coordination geometry and influences the reactivity.

Numerous early transition metal complexes containing new types of diamido ligands with additional amino, ether, organosulfido or organophosphino donor functions have been prepared in the last few years [17]. In catalytic applications of these complexes, the availability of additional weakly coordinated donor functions may crucially determine the lifetimes of certain intermediates in the catalytic cycle and thus the nature of the reaction product [18]. Thus, the results presented in this study confirm that the cycloaddition reaction of DAD zirconium complexes with ketones is a facile route for the preparation of complexes with such a particular type of a tripodal ligand. Future efforts will be aimed at a further exploration of this remarkable preparation method. Olefin polymerization studies on the title compounds and related molecules with a variety of co-catalysts are also currently underway.

3. Experimental

All manipulations were performed under an inert atmosphere (Ar) using Schlenk type glassware. Solvents were dried and freshly distilled from sodium–benzophenone and saturated with Ar prior to use. Deuterated THF-d_8 was treated with sodium–potassium alloy, then distilled, and stored under Ar. The ^{1}H- and the $^{13}C\{^1H\}$-NMR spectra were recorded on a Varian Gemini 300 spectrometer at 300.075 MHz (^{1}H) and 75.462 MHz (^{13}C) with TMS as reference. Elemental analyses were carried out at the Department of Chemistry of the Martin-Luther-University Halle-Wittenberg. $ZrCl_4(THF)_2$ [19a] and *t*-Bu-DAD [19b] were prepared according to literature procedures.

3.1. [(t-Bu-DAD)ZrCl(μ-Cl)$_3$Zr(t-Bu-DAD)(THF)] (**2**)

A solution of 49.3 mmol Li_2(*t*-Bu-DAD) (**1**), prepared from *t*-Bu-DAD (8.30 g, 49.3 mmol) and lithium (0.684 g, 98.6 mmol) in THF (150 ml), was added dropwise to a stirred suspension of $ZrCl_4(THF)_2$ (18.60 g, 49.3 mmol) in THF (200 ml) at − 78 °C. The mixture was warmed to room temperature (r.t.) and subsequently stirred for 24 h. After evaporation of the THF, the resultant yellow solid was extracted with 100 ml of Et_2O. The solution was concentrated and stored at − 20 °C. Complex **2** precipitated as yellow crystals which were isolated by filtration and subsequently dried in vacuo. Crystals of **2** suitable for X-ray diffraction were prepared by slow crystallization at 0 °C from a saturated Et_2O solution prepared at r.t. Yield: 12.6 g (63%). m.p. 112 °C. Anal. Found: C, 39.72; H, 6.62; N, 7.77. Calc. for $C_{24}H_{48}Cl_4N_4OZr_2$: C, 39.56; H, 6.64; N, 7.69%. ^{1}H-NMR (20 °C, THF-d_8): $\delta = 5.61$ (s, 2H; *H*C=C*H*), 3.61 (m, 4H; OC*H*$_2$, THF), 1.76 (m, 4H; OCH$_2$C*H*$_2$, THF), 1.22 (s, 18H; C*Me*$_3$); $^{13}C\{^1H\}$-NMR (25 °C, THF-d_8): $\delta = 105.37$ (dd, $^1J_{C,H} = 167.8$ Hz, $^2J_{C,H} = 10.9$ Hz; H*C*=*C*H), 71.12 (t; $^1J_{C,H} = 139.2$ Hz, THF), 57.68 (s; *C*Me$_3$), 30.39 (q, $^1J_{C,H} = 125.2$ Hz; C*Me*$_3$), 27.42 (t; $^1J_{C,H} = 126.1$ Hz, THF).

3.2. Zr[OC(Ph)$_2$CH{CH=N(t-Bu)}N(t-Bu)]Cl$_2$(THF) (**3**)

A solution of benzophenone (1.13 g, 6.20 mmol) in 20 ml THF was slowly added to a stirred solution of the DAD complex **2** (2.27 g, 3.10 mmol) in 50 ml THF, which was cooled to − 20 °C. The reaction mixture was warmed to r.t. and subsequently stirred for 24 h. After evaporation of the solvent the residue was extracted with 50 ml of Et_2O. The solution was concentrated and stored at −20 °C. Complex **3** precipitated as colorless crystals which were isolated by filtration and subsequently dried in vacuo. Crystals for the X-ray diffraction study were grown from a solution of 3 in THF over an extended period of time. Yield: 3.15 g (87%). m.p. 128–130 °C. Anal. Found: C, 55.38; H, 6.51; N, 4.86. Calc. for $C_{27}H_{38}Cl_2N_2O_2Zr$: C, 55.46; H, 6.55; N, 4.79%. ^{1}H-NMR (20 °C, THF-d_8): $\delta = 8.66$ (d, $^3J_{H,H} = 2.8$ Hz, 1H; N=CH), 7.81 (d, $^3J_{H,H} = 7.7$ Hz, 2H; o-Ph), 7.61 (d, $^3J_{H,H} = 7.9$ Hz, 2H; o-Ph), 7.25–7.01 (m, 6H; m,p-Ph), 4.98 (d, $^3J_{H,H} = 2.8$ Hz, 1H; NCH), 3.58 (m, 4H; OCH_2, THF), 1.73 (m, 4H; OCH$_2$CH_2, THF), 1.06 (s, 9H; CMe_3), 0.90 (s, 9H; CMe_3); ^{13}C{^{1}H}-NMR (25 °C, THF-d_8): $\delta = 182.63$ (d, $^1J_{C,H} = 167.0$ Hz; N=CH), 148.65 (s; i-Ph), 147.24 (s; i-Ph), 128.61 (d, $^1J_{C,H} = 159.0$ Hz; o,m-Ph), 127.96 (d, $^1J_{C,H} = 158.8$ Hz; o,m-Ph), 127.94 (d, $^1J_{C,H} = 158.8$ Hz; o,m-Ph), 127.71 (d, $^1J_{C,H} = 157.2$ Hz; o,m-Ph), 127.12 (d, $^1J_{C,H} = 160.7$ Hz; p-Ph), 126.77 (d, $^1J_{C,H} = 159.4$ Hz; p-Ph), 96.74 (s; ZrOC), 71.89 (d, $^1J_{C,H} = 142.3$ Hz, $^2J_{C,H} = 12.2$ Hz; ZrNCH), 68.21 (t, $^1J_{C,H} = 139.0$ Hz, THF), 60.19 (s; CMe$_3$), 58.08 (s; CMe$_3$), 29.90 (q, $^1J_{C,H} = 126.7$ Hz; CMe_3), 26.29 (t, $^1J_{C,H} = 126.2$ Hz, THF).

4. X-ray crystal structure determination of 2 and 3

Crystals of **2** and **3** suitable for X-ray structure determination were grown from Et_2O solutions at −20 °C. The intensity data for **2** were collected on a Nonius CAD4 diffractometer and those for complex **3** on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo–K_α radiation ($\lambda = 0.7107$ Å). Data were corrected for Lorentz and polarization effects, but not for absorption [20,21]. The structures were solved by direct methods (SHELXS [22]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97 [23]). The hydrogen atoms of the methine groups of **3** were located by difference Fourier synthesis and refined isotropically. The other hydrogen atoms were included at calculated positions with fixed thermal parameters. All nonhydrogen atoms were refined anisotropically [23]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

4.1. Crystal data for 2

$C_{24}H_{48}Cl_4N_4OZr_2$, $M_r = 732.90$ g mol^{-1}, yellow prism, size $0.40 \times 0.38 \times 0.36$ mm^3, monoclinic, space group $P2_1/n$, $a = 13.563(3)$, $b = 13.523(3)$, $c = 18.846(4)$ Å, $\beta = 100.29(3)°$, $V = 3401(1)$ Å^3, $T = -90$ °C, $Z = 4$, $\rho_{calc} = 1.431$ g cm^{-3}, μ(Mo–K_α) = 9.49 cm^{-1}, $F(000) = 1504$, 4999 reflections in $h(-15/10)$, $k(-6/15)$, $l(-20/20)$, measured in the range $6.40 \le \Theta \le 23.26°$, completeness $\Theta_{max} = 97.8\%$, 4768 independent reflections, $R_{int} = 0.0368$, 3942 reflections with $F_o > 4\sigma(F_o)$, 317 parameters, 0 restraints, $R1_{obs} = 0.049$, $wR^2_{obs} = 0.154$, $R1_{all} = 0.067$, $wR^2_{all} = 0.168$, goodness-of-fit = 1.087, largest difference peak and hole: 2.092/−1.596 e Å^{-3}.

4.2. Crystal data for 3

$C_{27}H_{38}Cl_2N_2O_2Zr \cdot 0.5C_4H_{10}O$, $M_r = 621.77$ g mol^{-1}, bright yellow prism, size $0.32 \times 0.28 \times 0.22$ mm^3, monoclinic, space group $P2_1/n$, $a = 9.7660(5)$, $b = 21.288(1)$, $c = 15.5659(7)$ Å, $\beta = 104.286(3)°$, $V = 3136.1(3)$ Å^3, $T = -90$ °C, $Z = 4$, $\rho_{calc} = 1.317$ g cm^{-3}, μ(Mo–Kα) = 5.49 cm^{-1}, $F(000) = 1300$, 12 598 reflections in $h(-12/12)$, $k(-27/27)$, $l(-20/20)$, measured in the range $3.16 \le \Theta \le 27.49°$, completeness $\Theta_{max} = 98.8\%$, 7115 independent reflections, $R_{int} = 0.054$, 4657 reflections with $F_o > 4\sigma(F_o)$, 324 parameters, 0 restraints, $R1_{obs} = 0.058$, $wR^2_{obs} = 0.127$, $R1_{all} = 0.105$, $wR^2_{all} = 0.144$, goodness-of-fit = 1.011, largest difference peak and hole: 0.952/−0.792 e Å^{-3}.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 165219 (**2**), and 165220 (**3**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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