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# A zirconium dichloro complex supported by an ancillary stereorigid tetradentate bis(phenoxo-imino) Schiff-base-donor ligand: Evidence for a conformational equilibrium between two solution stereoisomers

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**Abstract**

Reaction of the dilithium salt of the Schiff-base *N*,*N*′-*o*-phenylene-bis(3,5-di-*tert*-butyl-salicylidene-imine) ($^t$Bu$_4$salophenH$_2$) with 1 equiv. of $ZrCl_4(THF)_2$ in toluene at −78 °C affords the dichloro complex $ZrCl_2[C_6H_4$-1,2-{N=CH-(3,5-$^t$Bu$_2C_6H_2$-2-O)}$_2$], isolated as a mixture of the $C_{2v}$-(**3a**) and $C_2$-(**3b**) symmetry isomers. Thermodynamic and kinetic parameters for the equilibrium between **3a** and **3b** have been determined and studied by $^1$H NMR spectroscopy. Reactions of $ZrCl_2[C_6H_4$-1,2-{N=CH-(3,5-$^t$Bu$_2C_6H_2$-2-O)}$_2$] with alkylating reagents gave an intractable, unidentified mixture of products from which the NMR spectra in $C_6D_6$ solution are unusable.


*Keywords:* Zirconium; Phenoxo-imino

## 1. Introduction

Over the two last decades organometallic chemists involved in polyolefin chemistry have mainly focused their attention and efforts on designing organometallic systems with a specific architecture which depends on the nature of the ligands. Organometallic complexes as olefin polymerization catalysts have appeared in various forms using different metals since Ziegler–Natta precursors [1]. Among those organometallic compounds based mainly on group 4 metals, metallocene, *ansa*-metallocenes and half-sandwich cyclopentadienyl complexes [2–11] comprise a large part of the research in polyolefin chemistry designed to obtain polymers with well-defined physical properties [12]. In recent years, a new class of group 4 post-metallocene complex containing heteroatom ligands has emerged promising to be excellent candidates [13–15] to compete in olefin polymerization processes with the cyclopentadienyl derivatives in terms of activities and selectivities [14,16,17]. Schiff-base ligands such as ancillary bidentate monoanionic ($^-$O,N) donors, non-ancillary tetradentate dianionic ($^-$O,N,N,O$^-$) donors, and ancillary stereorigid tetradentate dianionic ($^-$O,N,N,O$^-$) donors have been most widely employed. In the presence of the two first ligands, octahedral group 4 transition metal complexes [12,16–24] with appropriate steric factors, present several possible isomers (Fig. 1), offering possible isomerization processes during the polymerization reaction. In contrast, ancillary stereorigid tetradentate dianionic ($^-$O,N,N,O$^-$) Schiff-base-donor-group 4 complexes [25–35], with steric hindrance on phenoxo moieties and exhibiting at least two heteroatoms set in a *cis*-position, avoid these isomerization processes, consequently reducing the presence of stereoisomers (Fig. 2). We have been involved in part in ancillary stereorigid tetradentate dianionic ($^-$O,N,N,O$^-$) Schiff-base-donor monocyclopentadienyl zirconium complex synthesis [36], exploiting these features in olefin polymerization. We are now placing great emphasis on the preparation and reactivity of octahedral

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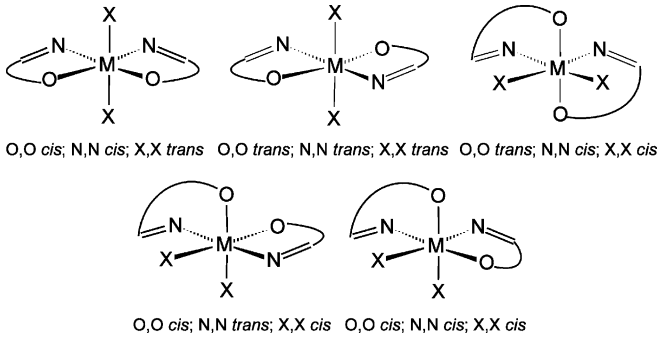



Fig. 1. Possible stereoisomers for $MX_2(^-O,N)_2$ compounds.

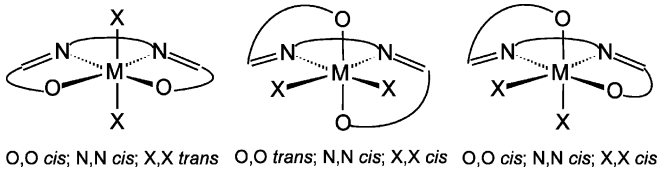



Fig. 2. Possible stereoisomers for $MX_2(^-O,N,N,O^-)$ compounds.

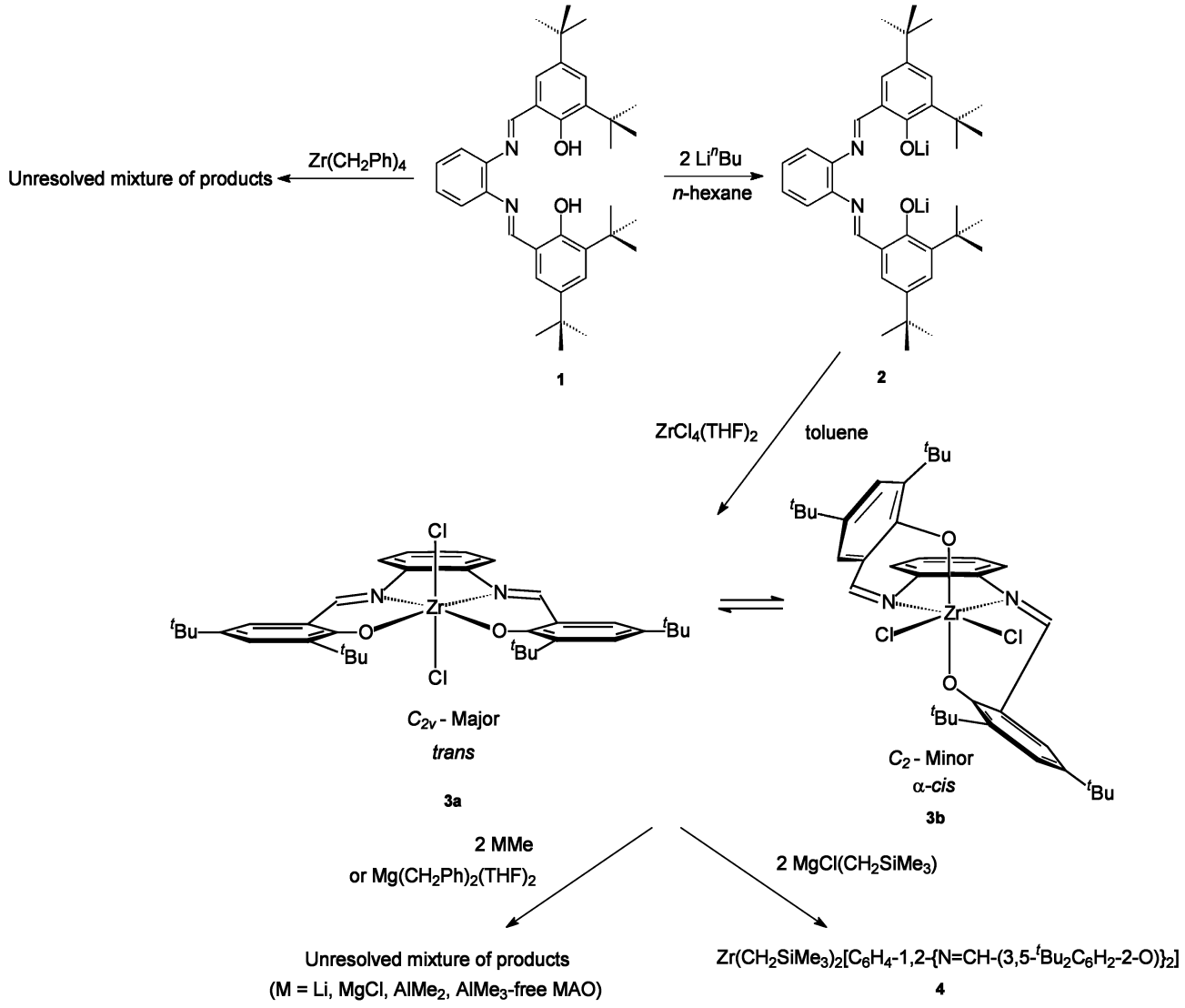
dichloro and dialkyl group 4 metal complexes of the type $ZrX_2(^-O,N,N,O^-)$ (X = Cl, alkyl) with a view to having an appropriate symmetry and bulky factors around the metal center to produce the desired site-controlled 1-olefin polymerization [37]. In this paper we report the synthesis and characterization of the dichloro zirconium complex $ZrCl_2[C_6H_4\text{-}1,2\text{-}\{N{=}CH\text{-}(3,5\text{-}^tBu_2C_6H_2\text{-}2\text{-}O)\}_2]$ obtained as a mixture of two $C_{2v}$- and $C_2$-symmetry isomers. A conformational equilibrium between these two stereoisomers in solution has been studied. In addition, we have investigated the reactivity of $ZrCl_2[C_6H_4\text{-}1,2\text{-}\{N{=}CH\text{-}(3,5\text{-}^tBu_2C_6H_2\text{-}2\text{-}O)\}_2]$ toward various alkylating reagents under different reaction conditions.

## 2. Results and discussion

### 2.1. Dichloro derivatives supported by an ancillary stereorigid tetradentate dianionic bis(phenoxo-imino) donor ligand: synthesis, spectroscopic characterization and reactivity studies

The dilithiated **2**, isolated in high yield from a *n*-hexane solution after deprotonation of the tetradentate Schiff base *N*,*N*′-*o*-phenylene-bis(3,5-di-*tert*-butyl-salicylidene-imine) ($^t$Bu$_4$salophen$H_2$) (**1**) [36] with 2 equiv. of a 1.6 M solution of Li$^n$Bu at −78 °C, reacts with 1 equiv. of $ZrCl_4(THF)_2$ in toluene at low temperature to produce the dichloro complex $ZrCl_2[C_6H_4\text{-}1,2\text{-}\{N{=}CH\text{-}(3,5\text{-}^tBu_2C_6H_2\text{-}2\text{-}O)\}_2]$ (**3**) after elimination of LiCl and the solvent (Scheme 1). Compound **3** is obtained as an analytically pure orange solid as supported by elemental analysis.

NMR spectroscopic analysis reveals that **3**, obtained according to this procedure, is indeed a mixture of two stereoisomers **3a** and **3b**. The $^1$H NMR spectrum ($CDCl_3$, 20 °C) exhibits two different sets of sharp signals. The major, less tensioned, and more stable $C_{2v}$-symmetry isomer **3a** (O,O *cis*; N,N *cis;* X,X *trans*) shows a signal of the methine proton C*H*=N at 8.99 ppm, noticeably downfield shifted compared with the imino C*H*=N at 8.65 ppm of **1** in the same NMR spectroscopic conditions, eventually increasing its acidic character after binding to the zirconium metal. In addition, the chemical shifts of the AB spin system of the phenoxo protons in **3a** at 7.74 and 7.44 ppm with coupling constants $^4J$ of 2.5 Hz and 2.3 Hz, respectively, differ from that of **1** (7.42 and 7.20 ppm with coupling constants $^4J$ of 2.1 Hz and 2.4 Hz, respectively). Similar features are observed for the resonances of the AA′BB′ spin system of the phenylene protons of compound **3a**, appearing at 7.73 and 7.47 ppm, downfield shifted compared to **1** (7.30 and 7.23 ppm) with coupling constants of 3.4 Hz, 6.0 Hz and 3.3 Hz, 6.0 Hz, respectively. The chemical shifts of the two *tert*-butyl protons of **3a** (1.58 and 1.35 ppm) vary slightly compared to **1** (1.42 and 1.31 ppm). The $^{13}$C resonances ($CDCl_3$, 20 °C) of the *C*H=N imino and *C*–O for **3a** (164.3 and 158.7 ppm) and **1** (164.4 and 158.3 ppm) are almost identical. The other $^{13}$C NMR data for both compounds demonstrate no significant variation. The minor $C_2$-symmetry isomer **3b** (O,O *trans*; N,N *cis*; X,X *cis*), due to the more constrained geometry at the stereorigid $C_6H_4$-1,2-$\{N{=}CH\}_2$ moiety, exhibits some $^1$H-NMR slight differences from complex **3a**, namely in the resonances of the C*H*=N imino and the AB spin system protons of the phenoxo fragment for **3b** [8.76 (C*H*=N), 7.66 and 7.36 ppm (phenoxo)]. Analogously, they also differ slightly downfield from those of compound **1**. The phenylene proton resonances of **3b** appear at 7.59 and 7.39 ppm with coupling constants of 3.3 Hz, 6.2 Hz, and 3.1 Hz, 6.0 Hz, respectively, shifted considerably upfield from the corresponding resonances of isomer **3a**, although they remain downfield compared to those of precursor **1**. These spectroscopic features are probably again due to the torsion at the $C_2$-symmetry of **3b**. The chemical shifts of the two *tert*-butyl protons of **3b** at 1.48 and 1.32 ppm, compared with those of **3a** at 1.58 and 1.35 ppm, fluctuate slightly. Although some proton resonances for each signal from compounds **3a** and **3b** are analogous, while others are essentially disparate, the carbon resonances for both **3a** and **3b** show no relevant, overall inconsistency. The molecular structure of the $C_{2v}$-isomer **3a** has been determined by X-ray diffraction methods and the results are completely coincident with that previously reported [34]. The synthesis and characterization of **3a**, resulting from the reaction of $ZrCl_4$ with the sodium salt analogous to dilithiated compound **2**, has been described recently [32]. Preparation, characterization, reactivity and α-olefin polymerization studies of $^t$Bu$_4$salophen zirconium dichloro derivatives have also been reported [32,34]. However to the best of our knowledge, studies on the solution equilibrium between a stereoenriched isomer mixture of the hexacoordinated octahedral $^t$Bu$_4$salophen zirconium dichloro complex have not yet been reported elsewhere.




Scheme 1.

A strong solvent effect affecting the **3a**/**3b** ratio at room temperature has been found. The molar ratio of the two stereoisomers is equal to 1.56 in toluene solution but is soon shifted towards **3a** (2.71:1) when dissolved in halogenated solvents: the latter is the more thermodynamically stable stereoisomer in the temperature range of 25–120 °C (see *infra* for details). At room temperature, complex **3b** interconverted slowly but appreciably in toluene solution into complex **3a** when dissolved in a Teflon valved NMR tube. Addition of $N^nBu_4Cl$ [38] as a chloride ion source, has no significant influence on the **3a**:**3b** molar ratio, suggesting that chloro dissociation is not involved in the ligand isomerization, which more probably occurs *via* an intramolecular reaction. Recently, Mountford and coworkers studied [38] the interconversion of $C_s$- and $C_1$-symmetry dichloro zirconium complexes bearing an pyridino-amino-diphenoxo-Kol-type ligand and demonstrated that the reaction proceeds through an intramolecular exchange.

The kinetics of the exchange process between **3a** and **3b** has been studied by EXSY $^1$H NMR at room temperature in $CDCl_3$ and 1,1,2,2-tetrachloroethane-$d_2$ solution. The intensity of the correlation peaks found for the "C*H*═N─" imino signals of the two stereoisomers permitted the rate constant (***k***) to be assessed using the Eq. (1) [39]:

$$k = 1/t_m \ln(r+1)/(r-1) \quad (1)$$

where $r = 4X_AX_B\ (I_{AA} + I_{BB})/(I_{AB} + I_{BA}) - (X_A - X_B)^2$, $X_A$ and $X_B$ are the mole fractions of **3a** and **3b**, respectively, $I_{nm}$ is the area volume of the diagonal ($I_{nn}$; n = A or B) and cross peaks ($I_{nm}$; n = A, m = B; m = A, n = B) of the 2D EXSY plot, and $t_m$ is the mixing time of the pulse sequence (see Section 4).

The value of 7.2 $s^{-1}$ actually found for $k$ suggests a fast isomerization of the ligand at room temperature in halogenated solvents. In contrast, the kinetic constant for the same process in toluene is too low to be measured by this method (thus less than $10^{-2}$ $s^{-1}$) and no cross peaks were detected in the EXSY experiments carried out with a $t_m$ value of 0.7 s or shorter. The rate constant for the ligand isomerization in **3** producing interconversion between the

O,O *cis*; N,N *cis*; X,X *trans* and O,O *trans*; N,N *cis*; X,X *cis* forms is higher than that found ($k = 0.4\ s^{-1}$) for the $^{t}Bu_4$salen zirconium complex detected in equilibrium between the O,O *trans*; N,N *cis*; X,X *cis* and O,O *cis*; N,N *cis*; X,X *cis* forms [37].

We also evaluated the thermodynamic parameters for the equilibrium between **3a** and **3b** in 1,1,2,2-tetrachloroethane-$d_2$ solution by $^1$H NMR methods. The equilibrium constant values $K_{eq}$ were calculated at different temperatures according to Eq. 2,

$$\mathbf{3a} \leftrightarrows \mathbf{3b} \qquad K_{eq} = \mathbf{3b}/\mathbf{3a} \tag{2}$$

where the relative concentrations of **3a** and **3b** were evaluated from the intensities of the "C*H*═N─" imino resonances of the two forms, respectively. The $K_{eq}$ values at different temperatures are given in Table 1. The standard enthalpy ($\Delta H^0 = 1.5 \pm 0.0$ Kcal mol$^{-1}$ ($6.2 \pm 0.1$ KJ mol$^{-1}$)) and the standard entropy ($\Delta S^0 = 1.4 \pm 0.0$ cal mol$^{-1}$ K$^{-1}$ ($8.0 \pm 0.0$ J mol$^{-1}$ K$^{-1}$)) were extrapolated from the inverse temperature plot of $\ln(K_{eq})$ (see Eq. 3 and Fig. 3).

$$\ln(K_{eq}) = -\Delta H^0/RT + \Delta S^0/R \tag{3}$$

Estimated standard deviations ($\sigma$) in the slope and intercept of the Vant'Hoff plot were determined to evaluate the error affecting the $\Delta H^0$ and $\Delta S^0$ values, respectively.

Table 1
Equilibrium constants $K_{eq}$ between the $C_{2v}$-symmetry (O,O *cis*; N,N *cis*; X,X *trans*) and $C_2$-symmetry (O,O *trans*; N,N *cis*; X,X *cis*) isomers **3a/3b** at different temperatures (by VT NMR experiments in 1,1,2,2-tetrachloroethane-$d_2$ solution)

| $T$ (K) | $1/T$ (K$^{-1}$ 10$^{-3}$) | $K_{eq}$ = **3b/3a** | $\ln(K_{eq})$ |
|---|---|---|---|
| 303 | 3.3 | 0.17 | −1.77 |
| 323 | 3.1 | 0.20 | −1.63 |
| 343 | 2.9 | 0.23 | −1.48 |
| 363 | 2.7 | 0.27 | −1.32 |

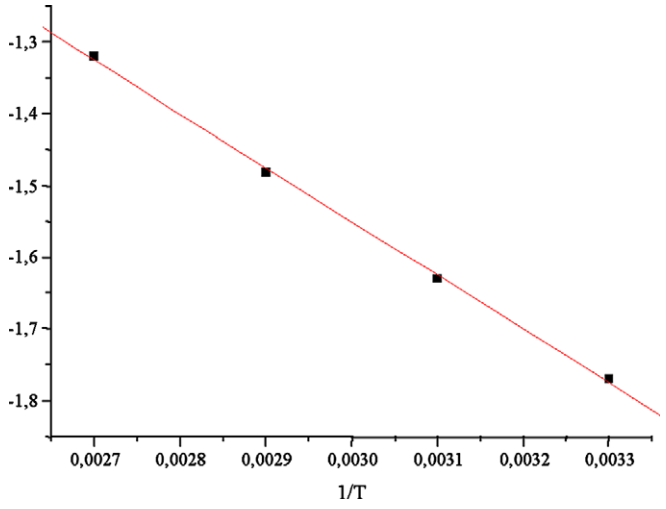



Fig. 3. Inverse temperature plot of $\ln(K_{eq})$ for the equilibrium between the $C_{2v}$-symmetry and $C_2$-symmetry isomers **3a/3b**.

Attempts to synthesize alkyl derivatives of **3** in which bulky alkyl groups replace the chloro ligands were carried out to highlight the influence of bulky ancillary ligands on the isomerization reaction. The **3a,b** mixture was subject to alkylation by treatment with various alkylating reagents under different reaction conditions. Several attempts to methylate this mixture proved unfruitful. The **3a,b** mixture was treated with 2 equiv. of MMe (M = Li, MgCl, $AlMe_2$, $AlMe_3$-free MAO) in different solvents such as *n*-hexane, toluene, diethyl ether, and THF at −78 °C followed by warming slowly at −10 °C, and then at room temperature. Unfortunately, the $^1$H NMR analysis of the final product reveals that the expected methylation compound $ZrMe_2[C_6H_4$-1,2-{N═CH-(3,5-$^{t}Bu_2C_6H_2$-2-O)}$_2$] was not obtained whatever the alkylating agents and solvents employed. The resulting NMR spectra show relatively uninformative broad signals. Due to the unexpected poor behavior of the methyl ligand to create a stable coordination environment at the zirconium center, the use of more voluminous ligands was explored with a view to blocking some thermodynamically unfavorable isomers and rendering the NMR spectra clear. Thus, the trimethylsilylmethyl ligand seemed to be one of the best candidates, as the methyl protons of the trimethylsilyl moiety could serve as a probe in the appropriate upfield region in NMR spectroscopy to define the presence or absence of a number of isomers. When the **3a,b** mixture reacts with 2 equiv. of $MgCl(CH_2SiMe_3)$ at −78 °C in *n*-hexane, the formation of the bis(trimethylsilylmethyl) complex $Zr(CH_2SiMe_3)_2[C_6H_4$-1,2-{N═CH-(3,5-$^{t}Bu_2C_6H_2$-2-O)}$_2$] (**4**), as a mixture of $C_{2v}$- and $C_2$-symmetry isomers **4a** and **4b** in a *ca.* 1:1 molar ratio, was spectroscopically observed. Repeated efforts to purify the mixture at low temperature were not rewarded. The mixture remained intractable, preventing any possible full characterization. Warming the mixture of **4** slowly to room temperature resulted in a decomposition process giving a complex $C_6D_6$-solution $^1$H NMR spectrum. When the **3a,b** mixture reacts with 1 equiv. of $Mg(CH_2Ph)_2(THF)_2$ [40] in polar or non-polar solvents at −78 °C, the $C_6D_6$-solution $^1$H NMR spectrum of the resulting reaction product shows a complex and unresolved mixture of compounds. Side-reactions [29,31,36], occurring when the nucleophile acts on the electrophilic carbon of the double bond imino function, which may be favored by coordination of the $N_{sp2}$ atom of the imino bond to the zirconium Lewis acid, can be proposed. An alternative route to access the desired dibenzyl complex has been the reaction of $Zr(CH_2Ph)_4$ with **1** at low temperature. Thus, when $Zr(CH_2Ph)_4$ reacted at −78 °C with 1 equiv. of **1**, the $^1$H NMR analysis ($C_6D_6$, 20 °C) of the resulting reaction product, after appropriate workup, shows the disappearance of **1** and the tetrabenzyl zirconium complex. However, the spectrum remained unusable, only revealing the presence of an intractable mixture of substances difficult to identify.

## 3. Concluding remarks

In this contribution we describe the synthesis and characterization of the bis(phenoxo-imino) dichloro zirconium derivative $ZrCl_2[C_6H_4$-1,2-{N=CH-(3,5-$^tBu_2C_6H_2$-2-O)}$_2$] (**3**) supported by an ancillary, stereorigid tetradentate dianionic Schiff-base-donor ligand. We have established that compound **3** exists in solution as a mixture of the $C_{2v}$- and $C_2$-symmetry isomers **3a** and **3b**. Thermodynamic and kinetic parameters for the equilibrium between these two solution stereoisomers have been determined and studied. We suggest that the interconversion of the $C_{2v}$-symmetry isomer **3a** into the $C_2$-symmetry one **3b** proceeds through an intramolecular exchange mechanism. The alkylation of **3** by some alkylating reagents does not give the observable as well as isolable dialkyl derivatives due to either no reaction or the formation of an intractable mixture.

## 4. Experimental

### 4.1. General considerations

All manipulations and reactions of air- and/or moisture sensitive compounds were carried out under argon (Air Liquide N45, $O_2$: 1 ppm; $H_2O$: 3 ppm) using Schlenk and high-vacuum line techniques or in a dry argon atmosphere MBraun glovebox model MB150B-G. All glassware was dried under vacuum with a heat gun and purged three times using vacuum-argon filling cycles. All Luer–Lock syringes and cannulas were oven-dried overnight and rapidly transferred to the reaction flask to be flushed under argon pressure upon cooling at room temperature. The solvents (Baker and SDS) used for air- and/or moisture sensitive compounds were of reagent grade and were purified by distillation under argon before use by employing the appropriate drying agent, and collected under argon in a Schlenk-type vessel followed by several freeze-thaw cycles when necessary. Deuterated solvents were firstly degassed by several freeze-thaw cycles, held at room temperature over fresh activated 4 Å molecular sieves (10% w/v) for several days, and then stored at room temperature over freshly activated 4 Å molecular sieves (10% w/v). Compound **1** [36], $Mg(CH_2Ph)_2(THF)_2$ [40], $ZrCl_4(THF)_2$ [41] and $Zr(CH_2Ph)_4$ [42], were prepared by a known procedure. Methyllithium, methylmagnesium chloride, trimethylaluminium, $MgCl(CH_2SiMe_3)$ (Aldrich) were used as received. $N^nBu_4Cl$ with a water content less than 1% from Fluka Chemika was treated at room temperature over fresh $P_2O_5$ under vacuum for several days, further dried at 110 °C over fresh $P_2O_5$ under vacuum for several more days, and then stored in a dry argon atmosphere glovebox. Solid $AlMe_3$-free methylaluminoxane (MAO) was obtained from methylaluminoxane (MAO) (CROMPTON, 10 wt% solution in toluene) by drying under reduced pressure at 50 °C to remove the uncoordinated $AlMe_3$ and used after washing with *n*-hexane and complete dryness. C, H, and N microanalyses were performed on a Perkin–Elmer 240B and/or Heraeus CHN-O-Rapid microanalyzer. The NMR samples of air- and/or moisture sensitive compounds were prepared under argon at room temperature in a 5 mm Wilmad 507-PP tubes fitted with a J. Young Teflon valve. The NMR spectra were recorded on Varian Mercury VX-300 PFG at 20 °C. The chemical shifts $\delta$ and coupling constant $J$ are quoted in ppm and in hertz (Hz), respectively, and are referenced with respect to residual proton and carbon resonances of the solvent ($CDCl_3$: $^1$H: 7.25 ppm, $^{13}$C: 77.1 ppm; $C_6D_6$: $^1$H: 7.15 ppm, $^{13}$C: 128.0 ppm). The assignment of the signals in NMR spectra was made by using standard and $^1$H-homodecoupling Varian pulse sequences.

### 4.2. EXSY NMR experiments

EXSY NMR experiments in $CDCl_3$ solution were recorded on Bruker Avance 400 at 20 °C using a NOESY pulse sequence ($\pi/2$–$t_1$-$\pi/2$–$t_m$–$\pi/2$–$t_2$), in TPPI mode [43] with phase-sensitive detection. The 2D EXSY spectra were collected with 256 $t_1$ points, 1024 data points in $t_2$ and 24 scans for each $t_1$ point using a repetition time of 2 s and mixing time $t_m$ of 0.7 s. The exchange rate $k$ was calculated as described in the text.

### 4.3. Synthesis of $ZrCl_2[C_6H_4$-1,2-{N=CH-(3,5-$^tBu_2C_6H_2$-2-O)}$_2$] (3)

A 1.6 M solution of Li$^n$Bu in hexanes (21.5 mL, 34.40 mmol) was added by syringe to a stirred solution of **1** (9.00 g, 16.64 mmol) in *n*-hexane (250 mL) at −78 °C. The mixture was stirred for 1 h and slowly warmed to room temperature. The yellow solid was isolated by filtration, successively washed three times with 100 mL of *n*-hexane and filtered, and then further dried under reduced pressure giving 8.82 g of a yellow powder of the dilithiated salt **2**. A stirred suspension of **2** (8.82 g, 15.96 mmol) in toluene (230 mL) was added by cannula transfer to a stirred suspension of $ZrCl_4(THF)_2$ (6.02 g, 15.96 mmol) in toluene (180 mL) at −78 °C. The mixture was slowly warmed to room temperature overnight while stirring. The volatiles were removed under reduced pressure and the solid was extracted into $CH_2Cl_2$ (350 mL). The solution was filtered over celite and the solvent removed under reduced pressure. The solid was triturated with toluene (100 mL) while stirring and the impurities were allowed to settle for 2 days at −10 °C. The solution was filtered through a short pad of celite and the volatiles were subsequently removed under reduced pressure yielding 8.41 g of an orange powder (75% yield based on dilithiated salt) identified as **3**. Orange single crystals of **3a** · $1/2CH_2Cl_2$ suitable for X-ray diffraction studies were grown by slow evaporation of a $CH_2Cl_2$-toluene solution. Anal. Calc. for $C_{36}H_{46}Cl_2N_2O_2Zr$: C, 61.69; H, 6.62; N, 4.00. Found: C, 62.23; H, 6.17; N, 4.33%.

Compound **3a**: $C_{2v}$-symmetry (O,O *cis*; N,N *cis*; X,X *trans*); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.99 (2H, s, C*H*=N), 7.74 (2H, AB spin system, $^4J = 2.5$ Hz, C*H*-phenoxo), 7.73

(2H, AA′BB′ spin system, $J = 3.4$; 6.0 Hz, C*H*-phenylene), 7.47 (2H, AA′BB′ spin system, $J = 3.3$; 6.0 Hz, C*H*-phenylene), 7.44 (2H, AB spin system, $^4J = 2.3$ Hz, C*H* − phenoxo), 1.58 (18H, s, C(C$H_3$)$_3$), 1.35 (18H, s, C(C$H_3$)$_3$). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) $\delta$ 164.3 (*C*H=N), 158.7 (*C*-O), 145.1 (*C-ipso* phenylene), 143.4 (*C-ipso* phenoxo), 139.5 (*C-ipso* phenoxo), 133.1 (*C*H phenylene), 129.2 (*C*H phenoxo), 129.1 (*C*H phenoxo), 122.4 (*C-ipso* phenoxo), 117.8 (*C*H phenylene), 35.6 (*C-ipso*, *tert*-butyl), 34.5 (*C-ipso*, *tert*-butyl), 31.4 (*Me*, *tert*-butyl), 30.2 (*Me*, *tert*-butyl).

Compound **3b**: $C_2$-symmetry (O,O *trans*; N,N *cis*; X,X *cis*); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.76 (2H, s, C*H*=N), 7.66 (2H, AB spin system, $^4J = 2.3$ Hz, C*H* phenoxo), 7.59 (2H, AA′BB′ spin system, $J = 3.3$; 6.2 Hz, C*H* phenylene), 7.39 (2H, AA′BB′ spin system, $J = 3.1$; 6.0 Hz, C*H* phenylene), 7.36 (2H, AB spin system, $^4J = 2.3$ Hz, C*H* phenoxo), 1.48 (18H, s, C(C$H_3$)$_3$), 1.32 (18H, s, C(C$H_3$)$_3$). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) $\delta$ 163.7 (*C*H=N), 160.2 (*C*-O), 142.7 (*C-ipso* phenylene), 142.0 (*C-ipso* phenoxo), 138.8 (*C-ipso* phenoxo), 134.1, 131.6, 129.7, 117.2 (*C*H phenylene + phenoxo), 124.1 (*C-ipso* phenoxo), 35.4 (*C-ipso*, *tert*-butyl), 34.4 (*C-ipso*, *tert*-butyl), 31.4 (*Me*, *tert*-butyl), 29.7 (*Me*, *tert*-butyl).

### 4.4. General procedure for the alkylation of *3a,3b*

A solution of the alkylating reagent (2 equiv., except for $Mg(CH_2Ph)_2(THF)_2$ as 1 equiv.) was added dropwise under argon to a solution of the **3a,b** mixture (1 equiv.) in the defined solvent (10 mL per equiv. of **3**) at −78 °C with vigorous stirring. The resulting mixture was stirred at −78 °C for 1 h, and then warmed slowly to −10 °C. The volatiles were completely removed under reduced pressure at −10 °C, and the residue was repeatedly extracted with cold *n*-hexane and filtered. The combined organic layers were evaporated at −10 °C until completely dry. As quickly as possible, a sample under argon was placed into an NMR tube, dissolved in $C_6D_6$ and thereafter frozen. The sample was analyzed as rapidly as practical by $^1$H NMR spectroscopy in due course.

Compounds **4a,b** in a 1:1 molar ratio, respectively; reaction done in *n*-hexane. $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ 8.44 (2H, s, C*H*=N), 8.25 (2H, s, C*H*=N), 7.82 (2H, AB spin system, $^4J = 3.3$ Hz, C*H* phenoxo), 7.70 (2H, AB spin system, $^4J = 3.6$ Hz, C*H* phenoxo), 7.59 (2H, AB spin system, $^4J = 3.6$ Hz, C*H*-phenoxo), 7.26 (2H, AB spin system, $^4J = 3.6$ Hz, C*H* phenoxo), 6.88 (4H, m, C*H* phenylene), 6.57 (4H, m, C*H* phenylene), 1.81 (18H, s, C(C$H_3$)$_3$), 1.68 (18H, s, C(C$H_3$)$_3$), 1.42 (18H, s, C(C$H_3$)$_3$), 1.30 (18H, s, C(C$H_3$)$_3$), 0.54 (4H, AB spin system, $J = 12$; 20 Hz, ZrC$H_2$), 0.12 (4H, s, ZrC$H_2$), −0.15 (18H, s, SiC(C$H_3$)$_3$), -0.18 (18H, s, SiC(C$H_3$)$_3$).

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