Formation of Zirconium Chloride Guanidinate Complexes from the Reaction of Their Amide Analog with CCl_4

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Abstract

Reaction of CCl_4 with zirconium amide guanidinate $Zr(NMe_2)_2[^iPrNC(NMe_2)N^iPr]_2$ (**1**) has been found to give $ZrCl(NMe_2)[^iPrNC(NMe_2)N^iPr]_2$ (**2**) as an intermediate and later $ZrCl_2[^iPrNC(NMe_2)N^iPr]_2$ (**3**). The reaction is likely radical in nature. Complex **2** has been independently prepared from the reaction of $ZrCl(NMe_2)_3$ with 2 equiv of diisopropylcarbodiimide, $^iPr\text{-}N{=}C{=}N\text{-}^iPr$, and characterized by NMR and elemental analysis.

Keywords: Zirconium; Chlorine; Amide complex

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Introduction

Earlier transition metal complexes with alkyl, amide, and hydride ligands[1-5] often contain polar bonds between metal atoms and anionic ligands. These ligands usually behave as nucleophiles similar to their main group counter parts such as LiR, RMgX (X = halide), $LiNR_2$ and $NaBH_4$. Early transition metal amidinate and guanidinate complexes have attracted much research interest recently[6-18]. In certain reactions, amidinate and guanidinate ligands act as spectators. We reported earlier the reaction of guanidinate amide $Zr(NMe_2)_2[^iPrNC(NMe_2)N^iPr]_2$ (**1**) with O_2 (Scheme 1)[19], as part of the studies of O_2 reactions with d^0 transition metal complexes[20-37]. The d^0 metal centers in the complexes formally have no d electrons. Their reactions with the oxidant O_2 thus typically involve the ligand oxidation. This is in contrast to the reactions of d^n complexes, in which the metal centers are often oxidized. From the chemistry shown Scheme 1[19], it appears to be a good candidate to test the radical trapping[38-40]. Because of $CH_2(NMe_2)_2$ formed as a side product in this reaction in Scheme 1[19], the reaction is believed to follow a radical mechanism. In addition, the rate of the reaction was enhanced several folds with the addition of the radical initiator 2,2′-azobis(2-methylpropionitrile) (AIBN)[19].

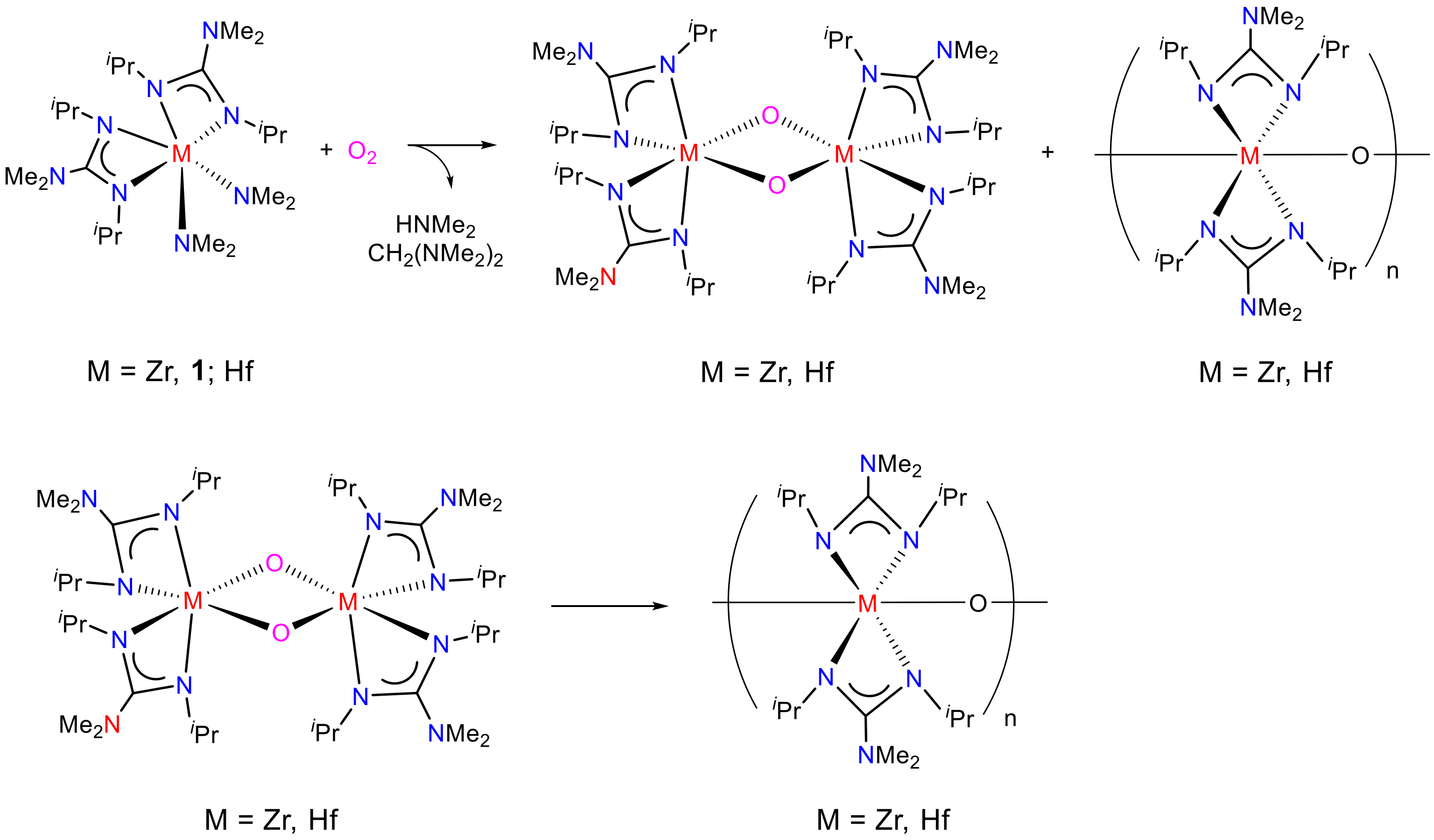
$CBrCl_3$ and CCl_4 have been used extensively for radical trapping[38-40]. For example, cyclopropyl radical is known to behave as a rapidly inverting σ radical of high reactivity. Experiments have been performed using radical trapping to determine the extent to which a variety of substituted cyclopropyl radicals are capable of maintaining their original configuration[38]. $BrCCl_3$ was chosen as a trap for the cyclopropyl radical (Eq. 1).

$$c\text{-}C_3H_5\bullet + BrCCl_3 \rightarrow c\text{-}C_3H_5Br + \bullet CCl_3 \qquad \text{(Eq. 1)}$$

Radical trapping has also been used to probe organometallic reactions[39].For example, irradiation of metal-metal bonded complexes leads to the formation of radicals that may be captured by chlorine atom abstraction from CCl_4 (Eq. 2)[39].

$$Cp_2Mo_2(CO)_6 + 2\ CCl_4 \rightarrow 2\ CpMo(CO)_3Cl + 2\ \bullet CCl_3 \qquad \text{(Eq. 2)}$$

Prior to the use of CCl_4 as a radical trap to probe the reaction of $Zr(NMe_2)_2[^iPrNC(NMe_2)N^iPr]_2$ (**1**) with O_2, it is, however, necessary to investigate whether **1** would react with CCl_4 itself in the absence of O_2. Indeed we have found that $Zr(NMe_2)_2[^iPrNC(NMe_2)N^iPr]_2$ (**1**) does react with CCl_4, yielding sequentially $ZrCl(NMe_2)[^iPrNC(NMe_2)N^iPr]_2$ (**2**) and $ZrCl_2[^iPrNC(NMe_2)N^iPr]_2$ (**3**). Complex **2** is a new compound. In addition to observing **2** from the reaction between CCl_4 and **1**, **2** has been prepared by a different route – direct insertion of $^iPr\text{-}N{=}C{=}N\text{-}^iPr$ into Zr-NMe_2 bonds in $ZrCl(NMe_2)_3$. Our studies of the reaction between CCl_4 and **1**, preparation of **2**, and its characterization are reported.



Scheme 1. Reaction of **1** and its Hf analog with O_2[19].

Experimental Section

All manipulations were performed under a dry nitrogen atmosphere with the use of either a drybox or standard Schlenk techniques. All solvents such as pentane, THF, hexanes were dried over potassium/benzophenone, distilled, and stored under nitrogen. Benzene-d_6 was dried over activated molecular sieves and stored under nitrogen. CCl_4 was also dried over activated molecular sieves and stored under nitrogen. NMR spectra were recorded on a Varian 500 MHz Fourier transform spectrometer unless otherwise noted, and were referenced to solvents. Elemental analyses were conducted via Complete Analysis Laboratories, Inc., Parsippany, NJ.

*Reaction of **1** with CCl_4*

In a Young's NMR tube, **1** (15 mg, 0.029 mmol) was dissolved in benzene-d_6. Excess CCl_4 was then added to this Young's tube. Immediately after the addition of CCl_4, the intensities of the peaks corresponding to **1** started decreasing. The progress of the reaction was followed with ^1H NMR spectroscopy. The ^1H NMR peaks of **2** first started to appear after ~2 h. This process eventually led to the formation of **3**.

*Synthesis of $ZrCl(NMe_2)[^iPrNC(NMe_2)N^iPr]_2$ (**2**) from the Reaction of $ZrCl(NMe_2)_3$ with $^iPr\text{-}N{=}C{=}N\text{-}^iPr$*

$ZrCl_4$ (1.620 g, 6.952 mmol) in THF was added 3 equiv of $LiNMe_2$ (1.062 g, 20.84 mmol) in THF. After stirring overnight, the solution was filtrated to remove LiCl, and volatiles were removed in vacuo to give crude $ZrCl(NMe_2)_3$ (0.963 g, 3.72 mmol, 59.4% yield). This crude product was then re-dissolved in hexanes and cooled to give pure $ZrCl(NMe_2)_3$ as crystals. These crystals were then separated from mother liquor solution and washed with cooled hexanes.

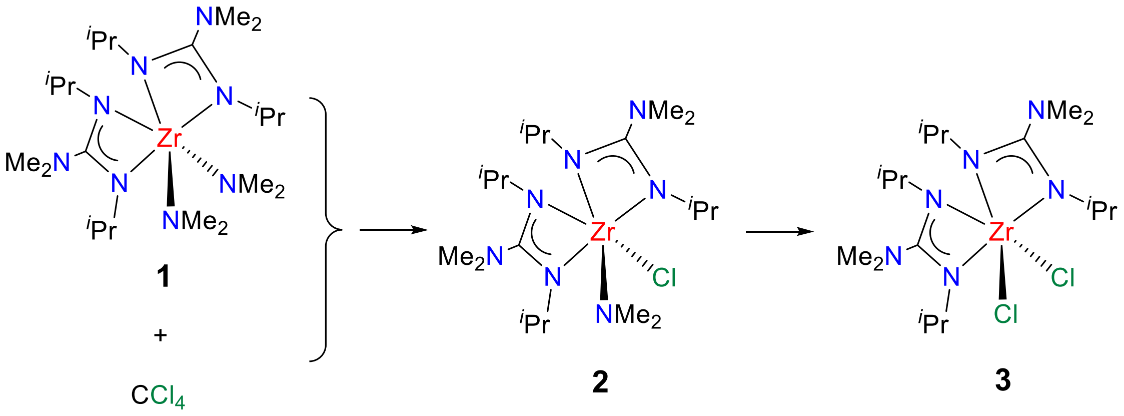
$ZrCl(NMe_2)_3$ (282.6 mg, 1.092 mmol) was then reacted with 2 equiv of ^{i}Pr-N=C=N-^{i}Pr (275.7 mg, 2.185 mmol) in pentane overnight. The volatiles were then removed in vacuo to give the crude product of **2** as an off-white solid (isolated solid: 198 mg, 0.388 mmol, 70.1% yield). Repeated attempts to grow the crystals of **2** in different solvents did not yield crystals suitable for X-ray single-crystal diffraction. ^{1}H NMR (benzene–*d*$_6$, 499.7 MHz, 25 °C) δ 3.59 (m, 4H, C*H*Me$_2$), 3.39 (s, 6H, Zr-N*Me*$_2$), 2.43 (s, 12H, C-N*Me*$_2$), 1.37 (d, 12H, ${}^{3}J_{H\text{-}H}$ = 6.43 Hz, CH*Me*$_2$), 1.32 (d, 12H, ${}^{3}J_{H\text{-}H}$ = 6.42 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (benzene–*d*$_6$, 125 MHz, 25 °C) δ 172.01 (*C*-NMe$_2$), 47.58 (*C*HMe$_2$), 47.12 (Zr-N*Me*$_2$), 39.75 (C-N*Me*$_2$), 25.18 (CH*Me*$_2$), 24.99 (CH*Me*$_2$). Anal. Calcd for $C_{20}H_{46}ClN_7Zr$: C, 46.98; H, 9.07; N, 19.18. Found: C, 46.91; H, 9.13; N, 19.11.

Results and Discussion

*Reaction of $Zr(NMe_2)_2[{}^{i}PrNC(NMe_2)N{}^{i}Pr]_2$ (**1**) with CCl_4*

The reaction between **1** and CCl_4 is given in Scheme 2. ^{1}H NMR spectrum of **1** itself is given in Figure S1 (Supporting Information) for comparison. In a Young's tube, **1** in benzene-*d*$_6$ was added CCl_4, and the progress of the reaction was followed by ^{1}H NMR spectroscopy. Right after the addition of CCl_4, new NMR peaks were observed, which were assigned to

$ZrCl(NMe_2)[^iPrNC(NMe_2)N^iPr]_2$ (**2**), a mono-chloride derivative of **1** (Scheme 2, Figure S2). With the passage of time, ^1H NMR peaks of **1** decreased in intensity. After 2-3 days at room temperature, ^1H NMR peaks corresponding to $ZrCl_2[^iPrNC(NMe_2)N^iPr]_2$ (**3**), a di-chloride derivative of **1**, started to appear as well (Scheme 2). After ca. 1 week, ^1H NMR spectrum of the solution showed only **3** (Figure S3). Complex **3** has been reported by Arnold, Bergman and coworkers[41], and it was prepared by direct insertion of $^iPr\text{-}N{=}C{=}N\text{-}^iPr$ into the Zr-NMe₂ bonds in $(Me_2N)_2ZrCl_2(THF)_2$. Comparison of its ^1H (Figure S3) and $^{13}C\{^1H\}$ NMR spectra with those reported confirmed the formation of **3** in the reaction in Scheme 2.

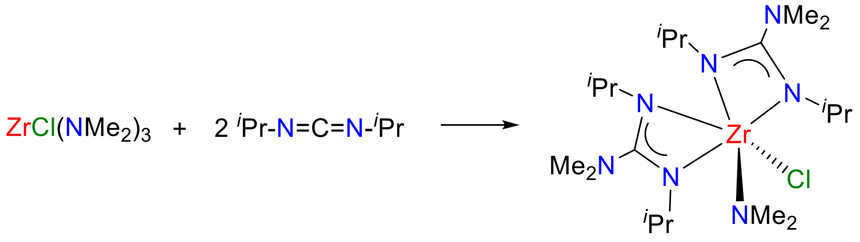


Scheme 2. Reaction of **1** with CCl_4, yielding amide chlorides **2** and **3**.

*Synthesis of **2** via the Reaction of $ZrCl(NMe_2)_3$ with $^iPr\text{-}N{=}C{=}N\text{-}^iPr$ and Characterization of **2***

The mono-chloride $ZrCl(NMe_2)[^iPrNC(NMe_2)N^iPr]_2$ (**2**) is a new compound. In the reaction between $Zr(NMe_2)_2[^iPrNC(NMe_2)N^iPr]_2$ (**1**) with CCl_4, it is an intermediate in the formation of the di-chloride **3** (Scheme 2) and it was difficult to control the reaction to just form **2**. Thus, **2** from this reaction was not isolated. Instead, **2** was directly prepared through the insertion of ^{i}Pr-N=C=N-^{i}Pr into two Zr-NMe$_2$ bonds in ZrCl(NMe$_2$)$_3$. ZrCl(NMe$_2$)$_3$, as solvent-free [Cl(Me$_2$N)$_2$Zr(μ-NMe$_2$)]$_2$, has been prepared by the reaction of ZrCl$_4$ with LiNMe$_2$ in ether[42]. Its X-ray structure showed a dimer with two NMe$_2$ bridges. Our group has earlier prepared ZrCl(NMe$_2$)$_3$ as a THF adduct, (Me$_2$N)$_3$Zr(μ-Cl)$_2$(μ-NMe$_2$)Zr(NMe$_2$)$_2$(THF), from either the reaction between 1 equiv of ZrCl$_4$ and 3 equiv of LiNMe$_2$ in THF or 1 equiv of Zr(NMe$_2$)$_4$ and 1 equiv of (Me$_2$N)$_2$ZrCl$_2$(THF)$_2$ in THF[43]. The THF adduct is a dimer bridged by one chloride and one amide ligand.

In the current work, ZrCl(NMe$_2$)$_3$ was synthesized by the direct reaction of 3 equiv of LiNMe$_2$ with ZrCl$_4$ in THF. After filtration to remove LiCl and volatiles were removed in vacuo, the crude product was recrystallized in hexanes to give THF-free ZrCl(NMe$_2$)$_3$, as its ^{1}H NMR spectrum in Figure 4 shows. ZrCl(NMe$_2$)$_3$ was then reacted with 2 equiv of ^{i}Pr-N=C-N-^{i}Pr, resulting in the formation of ZrCl(NMe$_2$)[^{i}PrNC(NMe$_2$)N^{i}Pr]$_2$ (**2**, Scheme 3). This compound was then characterized by ^{1}H, ^{13}C{^{1}H} and HSQC NMR spectroscopies (Figures S5-S7). In ^{1}H NMR spectrum (Figure S5), two doublets at 1.32 and 1.37 ppm are assigned to the two different CH*Me*$_2$ groups. One peak at 2.43 ppm is observed for the C-N*Me*$_2$ groups on the guanidinate ligands. These may be understood by the Bailar twist mechanism in Scheme 4[44]. The exchange leads to an intermediate **B** in which there is a mirror plane through the molecule. As a result, the two ^{i}Pr groups in the bottom face of **B** from two different guanidinate ligands are chemically equivalent. Similarly the two ^{i}Pr groups on the top face, also from two different guanidinate ligands, are chemically equivalent. The two C-N*Me*$_2$ groups on the two guanidinate ligands are equivalent. The multiplet at 3.59 ppm is assigned to C*H*Me$_2$, and the resonances from two different ^{i}Pr groups may overlap here. The peak at 3.39 ppm is assigned to the Zr-N*Me*$_2$ group.



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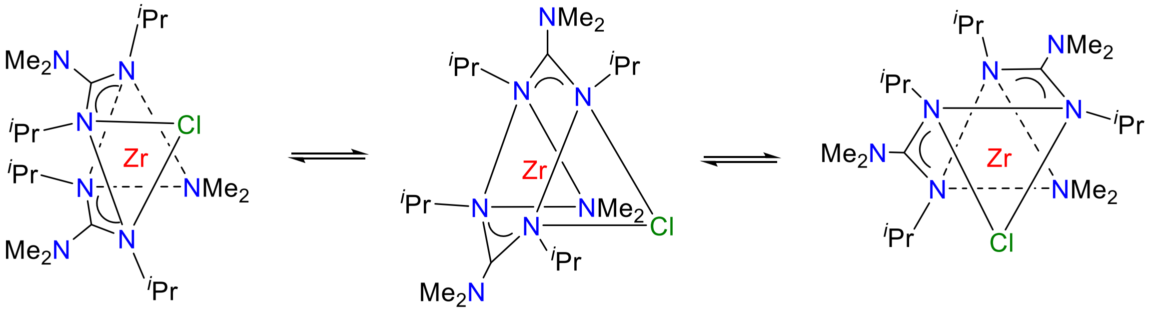
Scheme 3. Synthesis of **2.**



A **B** **C**

Scheme 4. Bailar twist mechanism for the exchange in **2**. There is a mirror plane in **B**.

In the $^{13}C\{^{1}H\}$ NMR spectrum (Figure 6) of ZrCl(NMe$_2$)[^{i}PrNC(NMe$_2$)N^{i}Pr]$_2$

(**2**), the two peaks at 24.99 and 25.18 ppm are assigned to the CH*Me*$_2$ groups. The C-N*Me*$_2$ group is observed at 39.75 ppm. The Zr-N*Me*$_2$ group appears at 47.12 ppm. The peak at 47.58 ppm is assigned to the *C*HMe$_2$ group. Finally the peak at 172.01 ppm was assigned to the quaternary carbon atom of the *C*-NMe$_2$ group. These assignments were confirmed with an HSQC experiment (Figure S7), and it is consistent with the Bailar twist mechanism in Scheme 4.

The solid product of **2** from the reaction in Scheme 3, without further purification, passed elemental analysis.

*Mechanistic Considerations for the Reaction between **1** and CCl$_4$*

The mechanistic pathway in the reaction between **1** and CCl$_4$ was not investigated in the current work. The following are considerations are based in part on observations in the current studies and in part on the reported properties of CCl$_4$ and Zr(NMe$_2$)$_2$[^{i}PrNC(NMe$_2$)N^{i}Pr]$_2$ (**1**). It should be pointed out that these considerations are essentially speculations.

CCl$_4$ is a radical trap, forming •CCl$_3$ through its reaction with another radical, as discussed earlier (Eq. 2)[39]. The C-Cl bond in CCl$_4$ may also undergo homolytic splitting to give two radicals, •CCl$_3$ and •Cl, especially under photo-irradiation (Eq. 3)[45-46]. Our earlier studies of the reactions of **1** with O$_2$ (Scheme 1) showed **1** may undergo reactions with radicals such as O$_2$[19].

$$CCl_4 \xrightarrow{h\nu} \bullet Cl + \bullet CCl_3 \qquad \text{(Eq. 3)}$$

One possible pathway in the reaction of **1** with CCl_4 in Scheme 2 is that CCl_4 undergoes the homolytic splitting in Eq. 3 in its solution with $Zr(NMe_2)_2[^iPrNC(NMe_2)N^iPr]_2$ (**1**) in benzene-d_6, perhaps during the initial brief exposure of CCl_4 to room light during the sample preparation. The newly formed •Cl radical attacks a $Zr-NMe_2$ bond in **1**, forming $ZrCl(NMe_2)[^iPrNC(NMe_2)N^iPr]_2$ (**2**) and radical $•NMe_2$. **2** may react with another •Cl radical, giving the dichloride complex $ZrCl_2[^iPrNC(NMe_2)N^iPr]_2$ (**3**). The radicals $•CCl_3$, $•NMe_2$ and •Cl may react with each other or attack other bonds of the molecules, including those of CCl_4, in the solution, giving new radicals such as •Cl. The newly formed •Cl may repeat the process described above, giving more products **2** and **3**. It is not clear why **2** and **3** are the major products, but not other possible complexes such as $(Cl_3C)(Me_2N)Zr[^iPrNC(NMe_2)N^iPr]_2$ from the hypothetical attack of $•CCl_3$ on **1**. Giving the nature of radical reactions, it is perhaps not surprising that no major organic products appeared in ^1H NMR spectrum of the reaction mixture at the end of the reaction (Figure S3).

Metathesis or substitution reactions, also known as double displacement reactions, are those involving the exchanges between two reacting chemical species[47-50]. If metathesis occurs in the reaction of $Zr(NMe_2)_2[^iPrNC(NMe_2)N^iPr]_2$ (**1**) with CCl_4, formation of Me_2N-CCl_3 and/or $(Me_2N)_2CCl_2$ as major products is expected. Since no major organic product appeared to be obvious in the reaction mixture (Figure S3), metathesis is probably unlikely the pathway.

Concluding Remarks

CCl_4 has been used in various reactions as a radical trap. It is essential to first make sure that CCl_4 does not directly react with reactants. It is not surprising to discover that CCl_4 in fact reacts with **1**, first giving monochloride **2** and then dichloride **3**. Complex **2** is a new compound, and it has been prepared from direct insertion reaction between $ZrCl(NMe_2)_3$ and 2 equiv of diisopropyl carbodiimide.

Supporting Information

NMR spectra in Figures S1-S7.

Acknowledgment

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胍基锆酰胺配合物与四氯化碳的反应生成氯化锆胍基衍生物

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摘要

四氯化碳与 $Zr(NMe_2)_2[{}^iPrNC(NMe_2)N^iPr]_2$ (1)的反应先生成中间体 $ZrCl(NMe_2)_2[{}^iPrNC(NMe_2)N^iPr]_2$ (2) 然后 $ZrCl_2[{}^iPrNC(NMe_2)N^iPr]_2$ (3)。该反应可能是自由基反应。配合物 2 另可由 $ZrCl(NMe_2)_3$ 与二异丙基碳二亚胺 ${}^iPr\text{-}N{=}C{=}N\text{-}{}^iPr$ 的反应制备. 对配合物 2 **做了核磁共振**和元素分析。

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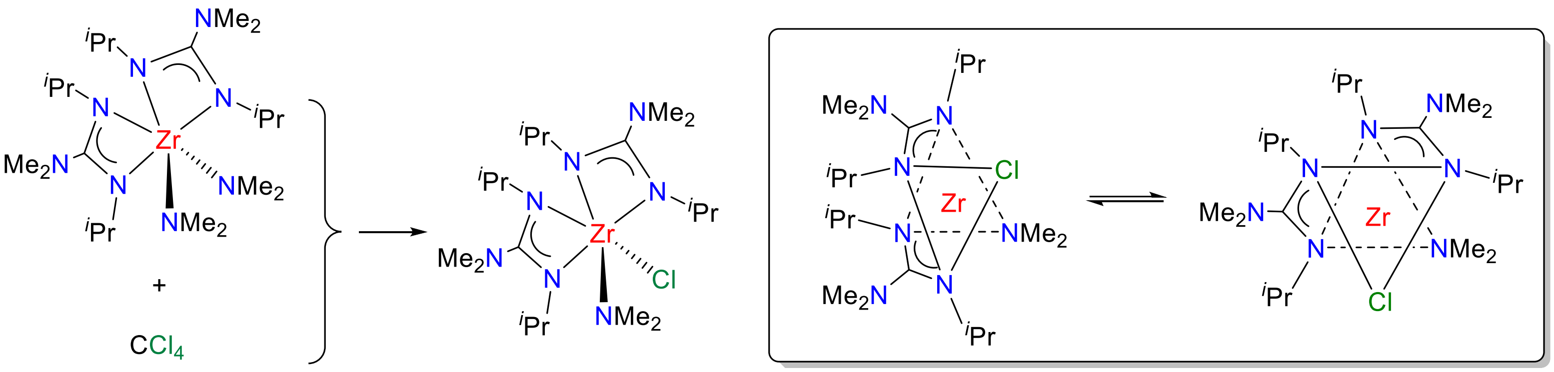
Graphical Abstract



Reaction of CCl_4 with Zr amide guanidinate $Zr(NMe_2)_2[^iPrNC(NMe_2)N^iPr]_2$ gives monochloride $ZrCl(NMe_2)[^iPrNC(NMe_2)N^iPr]_2$ as an intermediate and later dichloride $ZrCl_2[^iPrNC(NMe_2)N^iPr]_2$.