# Inorganic Chemistry

## Communication

# Intramolecular σ-Bond Metathesis/Protonolysis on Zirconium(IV) and Hafnium(IV) Pyridylamido Olefin Polymerization Catalyst Precursors: Exploring Unexpected Reactivity Paths

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A temperature-controlled metathesis/protonolysis takes place on group 4 amidopyridinate polymerization catalyst precursors. Unraveling this unprecedented reactivity path allowed us to highlight the importance of the metal precursor choice while preparing improved catalytic structures or studying new catalytic processes.

In conjunction with a variety of nitrogen ligands, hafnium(IV) and zirconium(IV) tetrakis(dimethylamidates), $M(NMe_2)_4$, are largely used as precursors to organometallic species and, in particular, to generate olefin polymerization catalysts via transamination reactions. Within the latter field, cyclometalated hafnium(IV) complexes, stabilized by dianionic amidopyridinate ligands, have recently attracted much interest in view of their outstanding catalytic performance,[1–3] as well as the wealth of their activation chemistry centered on the unusual $Hf-C^{Ar}$ bond.[4] In addition to classical transamination reactions, early amido group 4 metal complexes can undergo intramolecular σ-bond metathesis, providing unconventional cyclometalated frameworks.[1,2,4] In particular, one or more $NHMe_2$ groups are generated that can remain in the metal coordination sphere[5] or be definitively removed.

Herein we describe the first examples of zirconium(IV) and hafnium(IV) amidopyridinate tautomers that reversibly interconvert via a temperature-controlled $C^{Ar}-H/Zr-NMe_2$ σ-bond metathesis/$Me_2N-H/Zr-C^{Ar}$ protonolysis. We feel that the results presented in this Communication are of broad interest because they contribute to a better understanding of the organometallic chemistry of $M^{IV}(NMe_2)_4$-based complexes, especially toward a rational design of metal catalysts for polymerization reactions.

As part of our continuing interest in developing early-transition-metal-based systems for efficient and selective olefin upgrade,[6] we have studied the reactivity of $Zr^{IV}(NMe_2)_4$ and $Hf^{IV}(NMe_2)_4$ with a series of aminopyridinate ligands bearing different aryl or heteroaryl substituents on the pyridine 6 position. We have observed that the reaction of **1** with $Zr(NMe_2)_4$ proceeds smoothly in benzene at room temperature with complete substrate conversion within 3 h and the loss of 1 equiv of dimethylamine. Solvent evaporation provides a pale-yellow solid highly soluble in aromatic and aliphatic hydrocarbons, whose 1D and 2D NMR spectroscopy (toluene-$d_8$, 298 K) reveals the coexistence of two distinct isomeric forms (tautomers **2** and **3**) in an about 70:30 ratio, with the minority being unambiguously attributed to the hexacoordinated cyclometalated $N_2^{Th}Zr-(NMe_2)_2(\eta^1\text{-}HNMe_2)$ species (**3**; Scheme 1) with a dimethylamine ligand as part of the metal coordination sphere.

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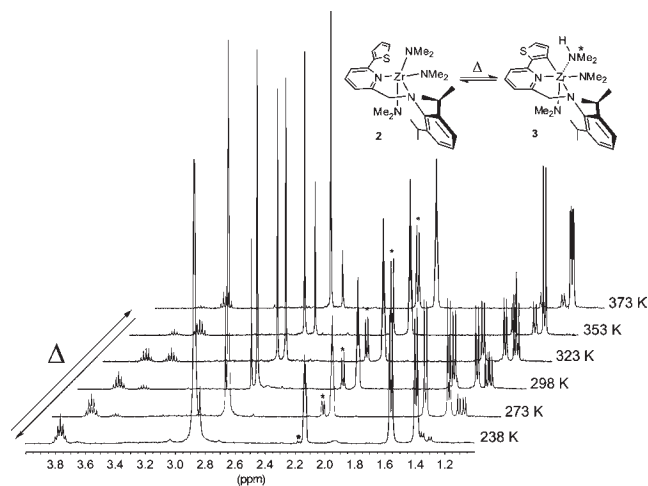
**Figure 1.** Selected variable-temperature $^1H$ NMR spectra [400 MHz, $C_7D_8$, $4 \geq \delta$ (ppm) $\geq 1$] of **2** and **3**. Full spectroscopic data are provided in the Supporting Information.
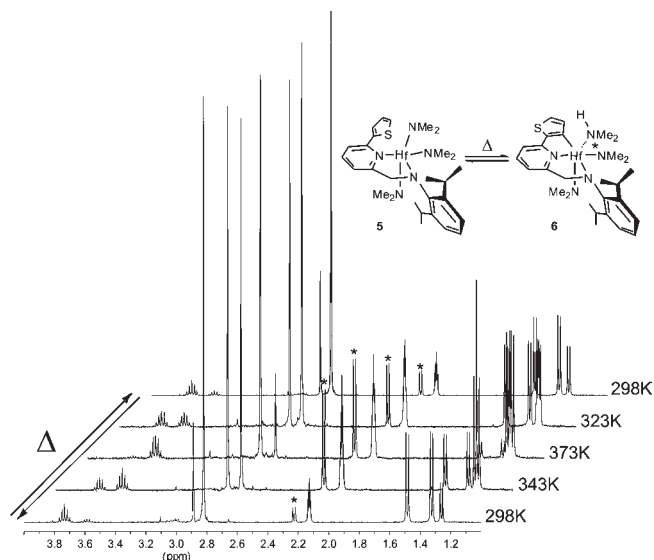
**Scheme 1.** Synthesis of $Zr^{IV}$ (**2-3** and **4**) and $Hf^{IV}$ (**5-6** and **7**) complexes
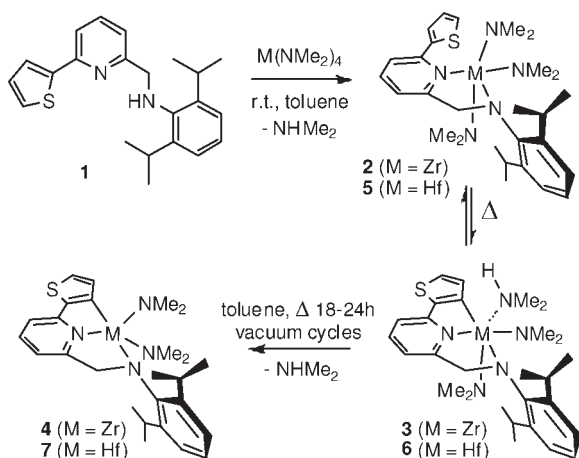


This result suggests that the initial N,N-chelation facilitates cyclometalation at the $\beta$ position of the thienyl moiety, by locking the heteroaryl group close to the orientation for $\sigma$-bond metathesis of [Zr-NMe$_2$].

Varying the temperature from 238 to 373 K results in interconversion of the isomeric mixture of **2** and **3** from 94:6 to 25:75 ratios, respectively (from $^1H$ NMR signal integration, Figure 1). It is worth noting that a complete reversibility of the process was maintained throughout several thermal cycles with no apparent mixture decomposition. From a careful process analysis, it appears that $Me_2N-H/C_\beta^{Th}-Zr$ protonolysis competes with $C_\beta^{Th}-H/Zr-NMe_2$ $\sigma$-bond metathesis, with the latter being predominant at high temperature. The dimethylamine generated upon cyclometalation reaction (**2 → 3**) strongly coordinates the metal center[5] as a noninnocent ligand, ultimately acting as a temperature-controlled proton shuttle for the $M-C^{Ar}$ bond protonolysis.[7]

To the best of our knowledge, no example of temperature-controlled metathesis/protonolysis has been reported in the literature so far. Moreover, it is generally accepted that C−H bond activations on early-transition-metal species are irreversibly inhibited in the presence of protic groups like

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**Figure 2.** Selected variable-temperature $^1H$ NMR spectra [400 MHz, $C_7D_8$, $4 \geq \delta$ (ppm) $\geq 1$] of **5** and **6**. Full spectroscopic data are provided in the Supporting Information.

alcohols or amines.[7] Therefore, the present case constitutes a useful reference to gain further insight into C−H bond functionalization reactions of early-transition-metal complexes.

Finally, a prolonged heating (24 h) of the **2−3** mixture in refluxing toluene, combined with static vacuum cycles, yields the amine-free species $N_2^{Th}Zr(NMe_2)_2$ (**4**; Scheme 1) as an analytically pure yellow-brown solid.[5d]

The very fast (**2−3**) tautomer equilibration at different temperatures does not allow the assignment of a precise kinetic order to the process, while a standard reaction enthalpy ($\Delta H°$) of $5.17 \pm 0.2$ kcal mol$^{-1}$ has been calculated from the van't Hoff plot. Finally, NMR studies conducted on the hafnium(IV) congeners **5** and **6** (Scheme 1) have shown analogous temperature-induced tautomeric interconversion. Indeed, temperature variation between 298 and 373 K led to isomeric mixtures of **5** and **6** from 83:17 to 11:89 ratios, respectively, with complete retention of reversibility after several thermal cycles (Figure 2).

Similarly to **4**, complex **7** was isolated as a dark-brown microcrystalline solid after prolonged heating in refluxing toluene (18 h) and degassing cycles to remove volatiles.[5d]

A theoretical analysis of the energy profile for the **2−3** equilibrium has contributed to a better process understanding (Figure 3). An independent optimization of **2** starting with an initial S-coordination to zirconium led to a final geometry where the thiophene ring is *not* coordinated [optimized $d(Zr-S) = 3.76$ Å], with the heterocycle tilted away from the metal center [optimized $\theta(N^{Py}-C^{Py}-C^{Th}-S) = 47°$; Figure S16 in the Supporting Information]. This suggests that the presence of three amido groups on zirconium is enough to satisfy the electronic requirements of the electron-poor early-transition-metal ion.

Thus, the overall process starts from a rotational isomer of **2** (**2'**), in which the $C_\beta^{Th}-H$ bond is pointing toward one NMe$_2$ group [C−H$\cdots$N = 2.24 Å, optimized $\theta(N^{Py}-C^{Py}-C^{Th}-S) = 149°$; Figure S17 in the Supporting Information]. **2'** lies 1.2 kcal mol$^{-1}$ below **2**, providing evidence for a facile thiophene rotation around the $C^{Py}-C^{Th}$ bond [an additional experimental proof is provided by the ($^1H-^1H$) NOESY
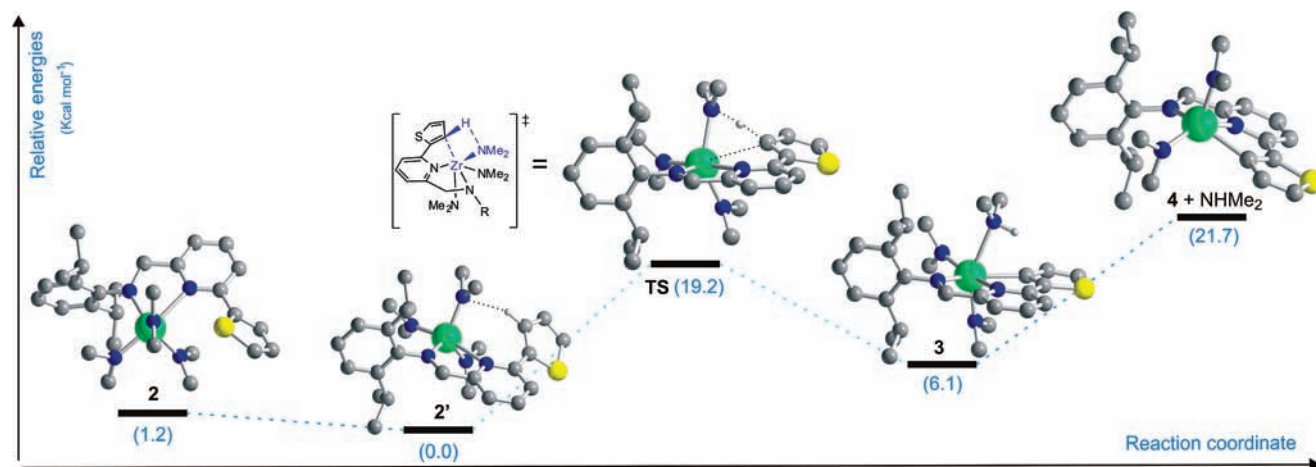
**Figure 3.** Energy profile in toluene for the C−H bond activation of the thiophene ring of **2** and optimized structures for **2**, **2′**, **TS**, **3**, and **4**.

spectrum; see Figure S7 in the Supporting Information]. Density functional theory calculations carried out on the real system at the M06/6-31G* level (toluene, PCM) reveal that the σ-bond metathesis reaction has a rather low barrier (19.2 kcal mol$^{-1}$; Figure 3), and it is slightly endothermic (6.1 kcal mol$^{-1}$, in excellent agreement with the experimental $\Delta H^0$ value reported above). An extra energy of 15.6 kcal mol$^{-1}$ is finally required in order to obtain the amine-free complex **4**, in line with the experimental results.

This result is of major importance in the field of polymerization catalysis by zirconium(IV) and hafnium(IV) pyridyl-amido catalysts, in light of their well-established efficiency (in high-temperature solution processes in particular) for the production of specialty polyolefins.[1−4] Indeed, the dramatic change at the metal coordination sphere of the zirconium(IV) and hafnium(IV) pyridylamido systems [from five-coordinated species (**2** and **5**) stabilized by bidentate monoanionic (N$^-$) ligands to six-coordinated complexes (**3** and **6**) with tridentate dianionic (N$^-$, C$^-$) ones] as a consequence of a simple temperature variation, makes the true catalyst identity in solution elusive. In spite of this, it is intriguing to note that related zirconium(IV) complexes containing either a phenyl or a 2-furanyl group instead of the 2-thienyl fragment do not show any detectable aryl metalation at room temperature, with the cyclometalated isomers appearing on the NMR spectra only above 310 K (Figures S11 and S12 in the Supporting Information).

These findings ultimately highlight the importance of the metal precursor choice[8] for the obtainment of tailored catalysts of unambiguous identity. A reliable identification of the catalyst precursor, along with knowledge of the true active species involved in the process,[4] is indeed of mandatory importance while designing improved catalytic structures and studying catalytic processes.

Ethylene polymerization tests have been carried out with precatalysts (**2** and **3**) and **4** using methylaluminoxane as the activator (Al/Zr > 1000) in the 40−80 °C temperature range. Turnover frequencies (TOFs) and gel permeation chromatography (GPC) profiles for the high-density polyethylenes (HDPEs) produced suggest that only the ortho-metalated species are responsible for generation of the catalytically active forms.[1−3] The TOFs observed with **2**−**3** are, in fact, comparable to those obtained with **4** when only the molar percentage of **3**, at the corresponding temperature, is taken into account (see the Supporting Information). Finally, perfectly matching GPC traces for the HDPEs produced by the two catalyst precursors imply identical active species at work (Figures S21 and S22 in the Supporting Information).

In conclusion, we have reported an original example of temperature-controlled σ-bond metathesis/protonolysis occurring at N,N group 4 amido complexes, a discovery that highlights how the chemistry of well-known metal precursors such as M$^{IV}$(NMe$_2$)$_4$ (M = Zr, Hf) may deserve new and unexpected reactivity paths. We also feel that the results presented here may lead to a better understanding of the structure−activity relationships of group 4 amido-based olefin polymerization catalysts.

**Supporting Information Available:** Text giving full experimental data and details on VT NMR experiments, 1D and 2D NMR spectra of **2**−**4**, van't Hoff plots, computational details, optimized Cartesian coordinates, internal energies, and pictures of **2**, **2′**, **TS**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

(8) The reaction of **1** with Zr(CH$_2$Ph)$_4$ results in the formation of the unique cyclometallated N$_2$$^{Th}$Zr(CH$_2$Ph)($\eta^2$-CH$_2$Ph) complex. These results will be reported elsewhere.