Carbenes

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Non-Innocent Behavior of a Tridentate NHC Chelating Ligand Coordinated onto a Zirconium(IV) Center**

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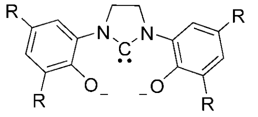
The use of N-heterocyclic carbenes (NHCs) as ancillary ligands for coordination to transition metal complexes has undoubtedly constituted a major breakthrough in the areas of organometallic chemistry and homogeneous catalysis over the past ten years.[1,2] When compared to their phosphine analogues, NHC-containing metal complexes usually exhibit an inert NHC–metal bond that affords these complexes an enhanced stability; this has opened the way for the development of various and numerous robust NHC-incorporating metal catalysts that often feature high catalytic activity. However, several reports have highlighted that the supporting carbene moiety in NHC–metal complexes is, in some instances, quite reactive and thus could be the source of the various observed deactivation processes. Until now, examples in this area, with fully characterized products, have been restricted to NHC-bearing late-transition-metal complexes. These pathways include: NHC-involving migratory insertion,[3] reductive elimination,[4] and heterocycle cleavage;[5] the formation of "abnormal" NHC–metal complexes;[6] and, very recently, C–C bond formation arising from the reaction of an NHC-containing Ni–H species with an alkene.[7] In view of the fast-growing development of NHC–transition metal complexes in synthesis and catalysis, well-identified reactions of NHC–transition metal complexes are of crucial importance to better understand and rationalize the catalytic performance of this class of compounds.

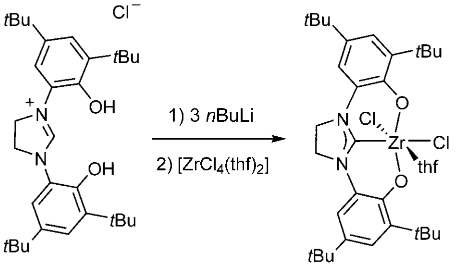
Despite their potential interest as catalysts, high-oxidation-state and oxophilic transition metal complexes that contain NHC ligands have received little attention, as these complexes are thought to be less stable because of easier M–C$_{\mathrm{carbene}}$ bond dissociation. However, the use of anionic NHC-containing chelating ligands for coordination to Group 4 and 5 metal centers has been shown to be beneficial to the stability of the derived complexes, although the suitability of these species as catalysts remains to be addressed.[8] We are interested in the synthesis of robust NHC-containing Group 4 metal complexes[9] and have developed a novel family of tridentate bis(aryloxide) NHC chelating ligands (**A**, Scheme 1) in which the NHC moiety is positioned as a central donor, a feature that is likely to disfavor deactivation processes.[10,11] Herein, however, we report that the coordination of tridentate ligand **A** to Zr$^{\mathrm{IV}}$ opens a way to an unprecedented rearrangement involving NHCs; this rearrangement constitutes the first instance in which an NHC that is coordinated to a high-oxidation-state and oxophilic transition metal exhibits such a behavior.



A

Scheme 1. Structure of NHC-containing anionic ligand **A**.

As an entry to Zr$^{\mathrm{IV}}$ complexes that are supported by tridentate ligand **A**, the well-established salt metathesis route was first considered as it is known to be a suitable route to closely related Zr$^{\mathrm{IV}}$ NHC complexes.[12] Therefore, the reaction of ligand **A**, generated in situ at −78 °C in THF by addition of three equivalents of *n*BuLi and $[\mathrm{ZrCl_4(thf)_2}]$, afforded the Zr–NHC dichloro complex $[\{^{t\mathrm{Bu}}(\mathrm{OCO})\}\mathrm{ZrCl_2(thf)}]$ where $\{^{t\mathrm{Bu}}(\mathrm{OCO})\}^{2-} = [\eta^3$-*O*,*C*,*O*-{(3,5-di-*tert*-butyl-$\mathrm{C_6H_2O})_2\mathrm{N_2C_3H_4}\}]^{2-}$ as an air-stable colorless solid in consistently modest yield (**2**-thf, Scheme 2). The NMR spectro-



1 **2**-thf

Scheme 2. Salt-metathesis route to access the zirconium NHC complex **2**-thf.

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scopic data for complex **2**-thf are as expected for this type of complex, and its solid-state structure, which was determined by X-ray crystallographic analysis, confirmed the chelation of a bis(aryloxide) moiety to the zirconium center. The zirconium atom in compound **2**-thf adopts a distorted octahedral geometry as a result of the *mer* coordination of the tridentate NHC ligand (O−Zr−O bite angle of 153.26(8)°; Figure 1). The Zr−C$_{carbene}$ bond distance (2.358(3) Å) is a bit below the previously observed range (2.43–2.46 Å) for other Zr−NHC complexes, which may reflect geometrical constraints in the tridentate ligand, thereby forcing the carbene moiety toward the metal center.

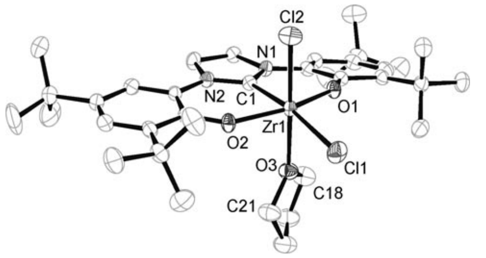
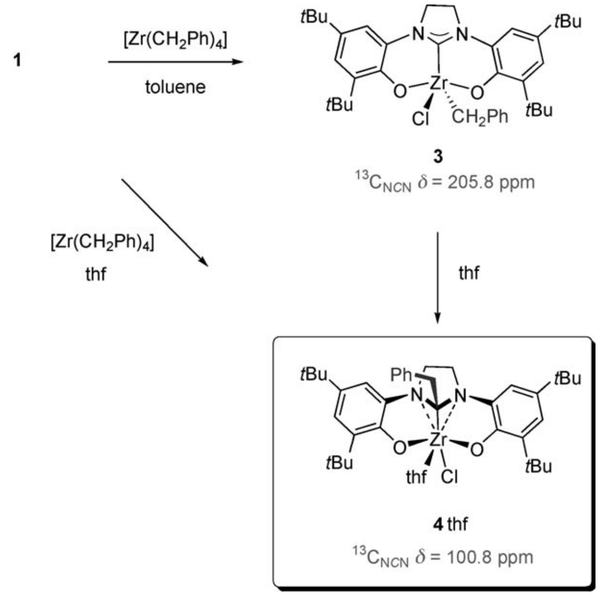


Figure 1. ORTEP of complex **2**-thf.[20] Ellipsoids set at the 50% probability level. Selected bond distances [Å] and angles [°]: Zr(1)–O(1) = 1.962(2), Zr(1)–O(2) = 1.965(2), Zr(1)–O(3) = 2.279(3), Zr(1)–C(1) = 2.358(3), Zr(1)–Cl(1) = 2.474(1), Zr(1)–Cl(2) = 2.441(1); O(1)-Zr(1)-C(1) = 76.4(1), O(2)-Zr(1)-C(1) = 77.3(1).

The modest yield of complex **2**-thf prompted us to investigate alternative syntheses, and toluene elimination involving the use of [Zr(CH$_2$Ph)$_4$] as a metal precursor was the most suitable. Therefore, the reaction of an equimolar amount of [Zr(CH$_2$Ph)$_4$] and proligand **1** (toluene, −78 °C to room temperature) yielded the Zr−NHC chlorobenzyl derivative [{^{tBu}(OCO)}Zr(Cl)(CH$_2$Ph)] as a colorless solid in quantitative yield (**3**, Scheme 3). The NMR data for compound **3** are consistent with a C_s-symmetric structure and include a characteristic ^{13}C resonance ($\delta = 205.8$ ppm) for a C$_{carbene}$ of NHCs. Whilst compound **3** is stable in noncoordinating solvents, such as dichloromethane and toluene, it was found to be quite reactive in the presence of THF (10 equivalents in a toluene solution of **3**) to readily and quantitatively form the heptacoordinate Zr–thf adduct [{^{tBu}(ONCNO)}Zr(Cl)(thf)], where [^{tBu}(ONCNO)]$^{2-}$ = [η^5-*O,N,C,N',ortho*-{(3,5-di-*tert*-butyl-C$_6$H$_2$O)$_2$N$_2$C$_3$H$_4$}]$^{2-}$) as a single isomer (**4**-thf, Scheme 3). This unexpected reaction may be described as a Lewis base assisted benzyl migration from the zirconium metal center to the C$_{carbene}$ of the NHC; this migration clearly illustrates the nucleophilic nature of the NHC moiety within the presumably planar {^{tBu}(OCO)}Zr chelate in complex **3**. Related benzyl migratory reactions have been observed for zirconium–alkyl complexes that are supported by tetraaza- and Schiff-base-type tetradentate ligands.[13]

In agreement with the reactivity of the latter complex, the reaction of imidazolium **1** with [Zr(CH$_2$Ph)$_4$] in THF (−78 °C to room temperature) cleanly and quantitatively afforded compound **4**-thf (Scheme 3). The NMR data supported the formation of **4**-thf with the presence of an extra ^{13}C resonance ($\delta = 100.8$ ppm) for the N*C*(CH$_2$Ph)N carbon atom compared with **3**, and no signal in the C$_{carbene}$ region. As determined by X-ray crystallography, the molecular structure of complex **4**-thf (Figure 2) features a heptacoordinate zirconium metal center[14] bearing an η^5-*O,N,C,N,O*-pentadentate trianionic supporting ligand, which consists of a central η^3-*N,C,N*-chelating 2-imidazolidinyl anionic unit that is flanked on each side by an aryloxide group; this binding, unlike that in **2**-thf, results in a {^{tBu}(ONCNO)}Zr chelate that is severely distorted from planarity (Figure 2). The bonding parameters within complex **4**-thf are as expected and closely relate to those observed for bis(amine)–bis(phenolate) zirconium derivatives.[15]



Scheme 3. Toluene-elimination route to complex **3** and THF-promoted formation of complex **4**.

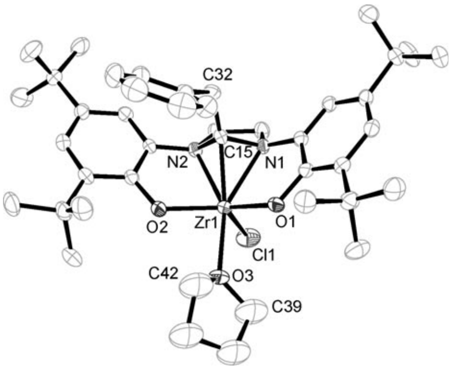


Figure 2. ORTEP of complex **4**-thf.[20] Ellipsoids set at the 50% probability level. Selected bond distances [Å] and angles [°]: Zr(1)–C(15) = 2.174(3), Zr(1)–N(1) = 2.308(3), Zr(1)–N(2) = 2.310(3), Zr(1)–O(1) = 2.036(2), Zr(1)–O(2) = 2.042(2), Zr(1)–O(3) = 2.279(3), Zr(1)–Cl(1) = 2.460(1); O(1)-Zr(1)-N(1) = 74.15(9), O(2)-Zr(1)-N(2) = 73.26(9), N(1)-Zr(1)-N(2) = 56.63(9).

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To shed more light on the THF-promoted rearrangement of NHC–zirconium complex **3** into **4**-thf, calculations were carried out on simplified models that did not include the *t*Bu groups on the aryl substituent (NHC–Zr complex **3***), the THF-free rearrangement product **4***, and their corresponding adducts **3***-thf and **4***-thf, respectively (Figure 3).[16] The structures of the complexes were calculated using density functional theory [B3LYP/SDD(Zr),-6-31G**(other atoms)][17] to gain an insight into the relative stabilities of the species. In the absence of THF, the model NHC–Zr complex **3*** was found to be about 12.1 kcal mol^{-1} more stable than the THF-free rearranged species **4*** (for details, see the Supporting Information), in agreement with the sole observation of the former species. In the presence of one molecule of THF, five isomers were found on the potential energy surface. The energy values of these THF adducts are summarized in Figure 3. These calculations are consistent with compound **4***-thf being energetically favored compared to all isomers of species **3***-thf.[18] Furthermore, the optimized structure of **3***-thf agrees with its solid-state structure (for the geometrical parameters, see the Supporting Information). To gain more insight into the pathway that affords **4***-thf, the energy profile of the rearrangement was calculated (Figure 4). Taking into account the weak coordination energy, species **3*** can readily form **3***-thf,[19] which then rearranges via the transition-state **TS** to form the thermodynamic product **4***-thf, which is experimentally observed. The energy barrier is about 25.2 kcal mol^{-1} (ΔG value or 23.6 kcal mol^{-1} for the value of ΔE). The geometrical features of the transition state correspond to a strongly synchronous process in which the Zr–C and Zr–C(1) bond lengths are between those of corresponding carbene complex **3***-thf and the final product **4***-thf.

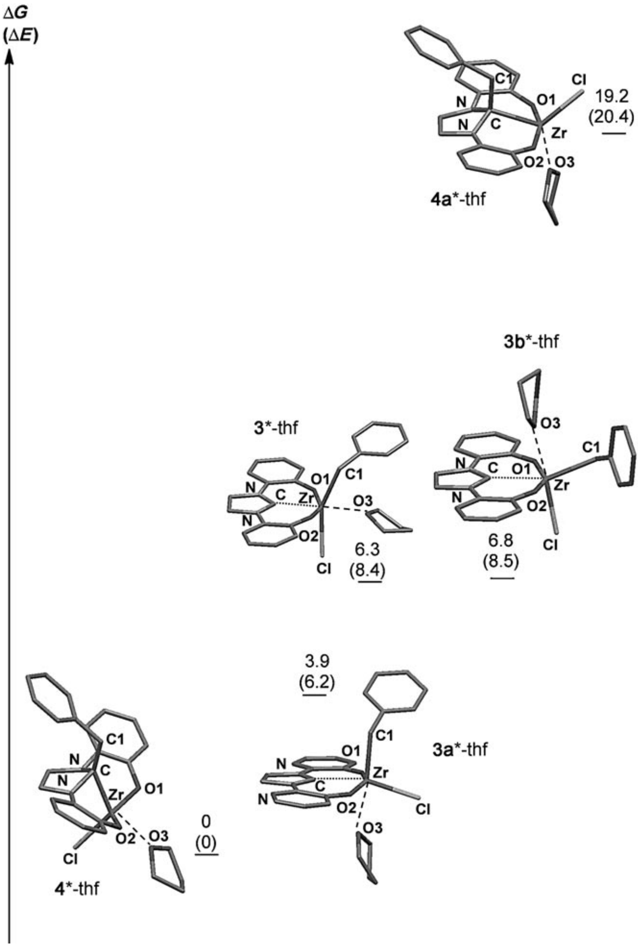

Figure 3. Gibbs free energies (ΔG), and total energies (ΔE; in brackets) of the calculated DFT structures **4***-thf (versus **3***-thf) and their respective isomers in kcal mol^{-1} (**4a***-thf, **3a***-thf, and **3b***-thf). Hydrogen atoms are omitted for clarity.

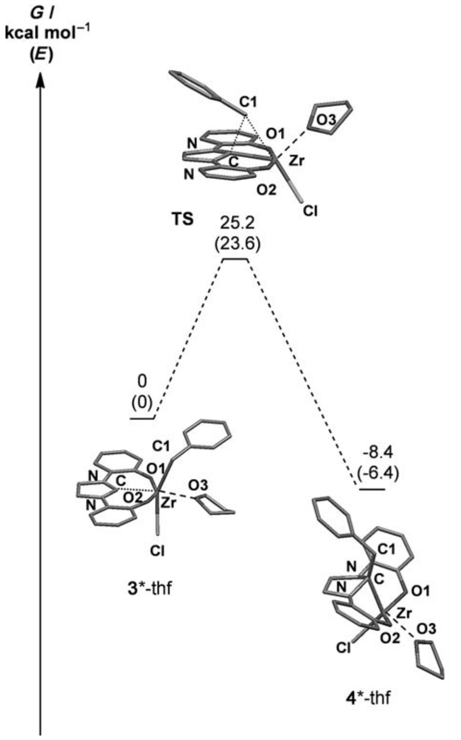

Figure 4. Energy profile of the rearrangement of the NHC–Zr THF adduct **3***-thf computed at the BP3LYP/SDD(Zr),6-31G**(other atoms) level of theory. Free energies (G), at 25 °C including ZPE correction are expressed in kcal mol^{-1}, total energies (E) are reported into brackets. Hydrogen atoms are omitted for clarity.

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[17] See the Supporting Information.

[18] Note that the other possible isomer of **4***-thf, model species **4a***-thf, which was not observed experimentally and in which THF sits in the axial position (Figure 3), was also optimized. This species was 19.2 kcal mol^{-1} higher in energy than the observed isomer, as expected.

[19] The energy difference between the model compound **3*** and the **3***-thf adduct was calculated to be -4.4 kcal mol^{-1} (ΔE).

[20] CCDC 755083 (**2**-thf), and CCDC 755084 (**4**-thf) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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