

# Reversible 1,2-Alkyl Migration to Carbene and Ammonia Activation in an N-Heterocyclic Carbene–Zirconium Complex

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**S** Supporting Information

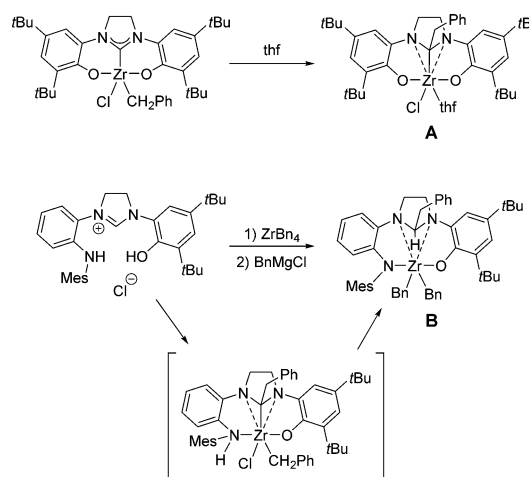
**ABSTRACT:** Addition of trimethylphosphine to a bis-(phenolate)benzylimidazolylidene(dibenzyl)zirconium complex induces migration of a benzyl ligand from the metal center to the C<sub>carbene</sub> atom. This process may be reversed, resulting in C<sub>sp<sup>3</sup></sub>–C<sub>sp<sup>3</sup></sub> activation, by abstraction of the phosphine, an example of regulated, reversible alkyl migration. Addition of ammonia to the dibenzyl complex results in migration of one benzyl group and protonolysis of the other to generate a bis(NH<sub>2</sub>)-bridged dimer via an NMR-observable intermediate NH<sub>3</sub> adduct.

N-Heterocyclic carbenes (NHCs) are useful ligands for various catalytic processes because of their strong  $\sigma$ -donor ability (compared with phosphines, for example) and their versatile steric protection.<sup>1</sup> Enhanced stability, activity, and selectivity have often been observed for these systems; one of the best-known examples is the second-generation Grubbs metathesis catalyst, an NHC–ruthenium complex.<sup>2</sup> In the past decade, polydentate NHC-based ligands have been shown to stabilize metal–ligand bonding to generate more robust catalysts.<sup>3</sup> Several tridentate ligands with outer O- or N-centered anionic groups have led to the development of early transition metal–NHC catalysts,<sup>4</sup> which previously were rare because of the poorer binding of the NHC carbene to these oxophilic metals. Group 4 NHC complexes have recently been shown to catalyze olefin polymerization,<sup>5</sup> ring-opening polymerization,<sup>6</sup> and hydroamination of unactivated alkenes.<sup>7</sup> Although the NHC normally serves as an ancillary ligand, a few unanticipated reactions, notably 1,2-alkyl migration, have been reported to occur at the carbene center.<sup>8</sup> For example, we and others have described an unusual migration of a benzyl group from the metal center to the NHC carbon for LX<sub>2</sub>-type [(OCO)Zr] or [(NCO)Zr] benzyl complexes that is effected by coordination of a ligand (Scheme 1), THF (A)<sup>8d</sup> or substituted aniline (B).<sup>8c</sup> The (presumed) irreversibility of this 1,2-alkyl migration process has been considered to play a key role in deactivation pathways during catalytic processes.

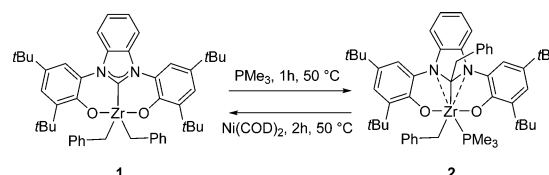
Here we report the first reversible 1,2-alkyl migration in transition metal–NHC complexes, which involves phosphine coordination/abstraction processes, the latter resulting in net C<sub>sp<sup>3</sup></sub>–C<sub>sp<sup>3</sup></sub> bond activation.<sup>9</sup> Furthermore, the use of ammonia as the L-type donor with NHC–zirconium complex 1 leads to N–H bond activation, a case of metal–ligand cooperativity.

The dibenzylzirconium complex (OCO)ZrBn<sub>2</sub> (1), prepared via treatment of the bis(phenolate)benzylimidazolylidene

**Scheme 1. Benzyl Migration Induced by L-Donor Ligands**



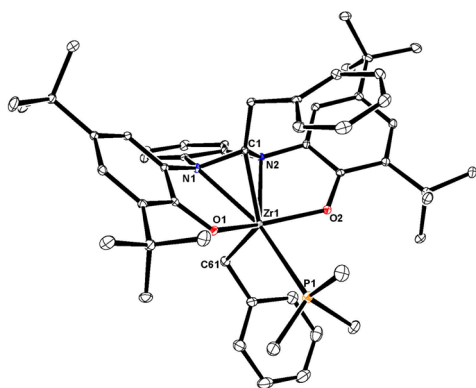
**Scheme 2. Reversible Benzyl Migration by Phosphine Addition/Abstraction**



ligand with tetrabenzylzirconium,<sup>8c</sup> reacts with trimethylphosphine to afford complex 2 quantitatively (Scheme 2). Migration of a benzyl group from the Zr center to the C<sub>carbene</sub> of the benzimidazolylidene moiety, analogous to the previous findings,<sup>8c,d</sup> was supported by NMR data, which showed two inequivalent benzyl methylene signals (<sup>1</sup>H and <sup>13</sup>C NMR: 2.26 and 57.2 ppm for Zr–CH<sub>2</sub>Ph; 3.38 and 34.2 ppm for NCH(CH<sub>2</sub>Ph)N), the absence of any carbene <sup>13</sup>C NMR resonance, and a <sup>31</sup>P NMR resonance at –34.5 ppm. Crystals of 2 suitable for X-ray diffraction were obtained by slow evaporation of a pentane solution, and the structure of 2 is shown in Figure 1. The (O,N,C,N,O) chelating ligand in 2 is effectively a pentadentate L<sub>2</sub>X<sub>3</sub>-type ligand (X<sub>3</sub> = two phenolates and the benzimidazolidinyl carbon; L<sub>2</sub> = the two benzimidazolidinyl nitrogens). The benzimidazolidinyl moiety is significantly distorted from planarity, with a very short Zr–

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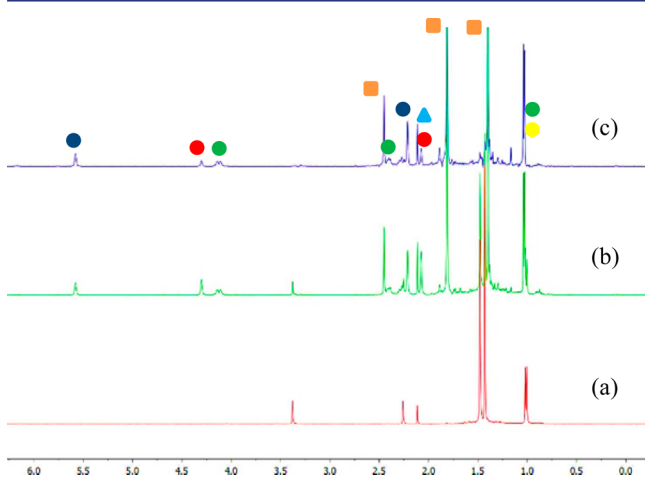
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**Figure 1.** Molecular structure of complex **2**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Zr(1)–O(1) = 2.0714(13), Zr(1)–O(2) = 2.0703(12), Zr(1)–C(1) = 2.1678(17), Zr(1)–N(1) = 2.4352(15), Zr(1)–N(2) = 2.4266(15), Zr(1)–C(61) = 2.2770(119), Zr(1)–P(1) = 2.8454(6).

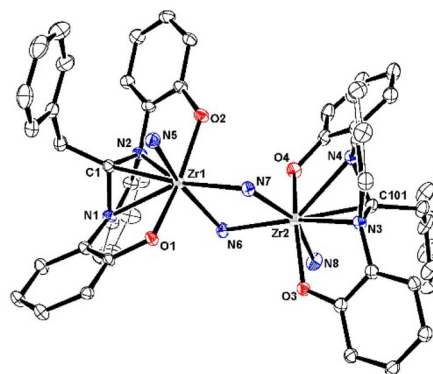
C(1) bond (2.17 Å; cf. the Zr–C<sub>benzyl</sub> distance of 2.28 Å). The Zr–N bonds are elongated in complex **2** relative to the THF adduct **A**<sup>8d</sup> (Zr(1)–N(1/2) = 2.43 Å for **2** vs 2.31 Å for **A**), probably as a consequence of the aromaticity of the NHC moiety in **2**, which attenuates the interaction of the nitrogen lone pairs with the empty d orbitals of the Zr center.

Because phosphines are expected to bind less strongly to early transition metal centers vis-à-vis late transition metals, we thought the alkyl migratory insertion might be reversed by abstraction of the trimethylphosphine ligand. Indeed, addition of 1 equiv of Ni(COD)<sub>2</sub> to **2** leads cleanly to complex **1** after 24 h at room temperature or 2 h at 50 °C (Scheme 2). Free COD, Ni(COD)(PMe<sub>3</sub>)<sub>2</sub>, and Ni(PMe<sub>3</sub>)<sub>4</sub> were observed when the reaction was monitored by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy (Figure 2), demonstrating abstraction of the phosphine ligand by the nickel complex. Triphenylborane can also be used as phosphine scavenger.<sup>10</sup> Presumably abstraction of trimethylphosphine first creates a vacant coordination site, after which a benzyl group migrates from C<sub>imidazolidiny</sub> to Zr, a formal C<sub>sp</sub><sup>3</sup>–C<sub>sp</sub><sup>3</sup> bond activation.



**Figure 2.** <sup>1</sup>H NMR spectra (C<sub>6</sub>D<sub>6</sub>, 25 °C) of (a) complex **2**, (b) **2** + 0.5 equiv of Ni(COD)<sub>2</sub> after 12h at room temperature, and (c) **2** + 0.5 equiv of Ni(COD)<sub>2</sub> after 1h at 50 °C. Legend: dark-blue ●, free COD; red ●, Ni(COD)<sub>2</sub>; green ●, Ni(COD)(PMe<sub>3</sub>)<sub>2</sub>; yellow ●, Ni(PMe<sub>3</sub>)<sub>4</sub>; orange ■, (OCO)ZrBn<sub>2</sub> (**1**); light-blue ▲, toluene.

Upon exposure of a solution of **1** to an atmosphere of the potential L-type donor ammonia, a new species is formed cleanly after 3 h at room temperature. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy showed only one benzyl signal, no carbene signal, and a methylene signal (at 3.46 and 33.6 ppm, respectively) characteristic of the [NC(CH<sub>2</sub>Ph)N] moiety resulting from benzyl migration from Zr to C<sub>carbene</sub>. One equivalent of toluene was liberated during the course of the reaction, and two additional <sup>1</sup>H signals were observed at 0.34 and 1.44 ppm, assigned to NH<sub>x</sub> species on the basis of two-dimensional <sup>1</sup>H–<sup>15</sup>N NMR spectra. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a pentane solution, allowing characterization of the product as the C<sub>2</sub>-symmetric dimer **3** (Figure 3). Each zirconium subunit features a

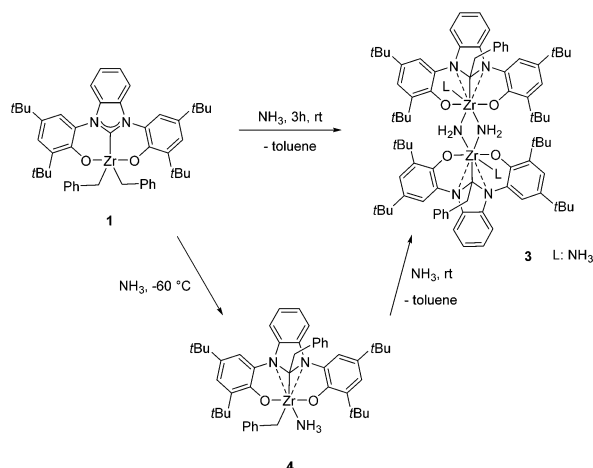


**Figure 3.** Molecular structure of complex **3**. *tert*-Butyl groups and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Zr(1)–C(1) = 2.214(4), Zr(2)–C(101) = 2.218(4), Zr(1)–N(1) = 2.474(3), Zr(1)–N(2) = 2.423(3), Zr(2)–N(3) = 2.461(3), Zr(2)–N(4) = 2.429(4), Zr(1)–N(6) = 2.260(4), Zr(2)–N(6) = 2.304(4), Zr(1)–N(7) = 2.298(4), Zr(2)–N(7) = 2.248(4), Zr(1)–N(5) = 2.402(4), Zr(2)–N(8) = 2.416(4), Zr(1)–O(1) = 2.075(3), Zr(1)–O(2) = 2.072(3), Zr(2)–O(3) = 2.098(3), Zr(2)–O(4) = 2.094(3).

pentadentate (O,N,C,N,O) trianionic imidazolidiny ligand as in **2**, with slightly elongated Zr–O (2.09 vs 2.07 Å) and Zr–C<sub>imidazolidine</sub> (2.21 vs 2.16 Å) bonds. The Zr–N<sub>imidazolidine</sub> bonds are unequal (Zr(1)–N(1) = 2.47; Zr(1)–N(2) = 2.42; Zr(2)–N(3) = 2.46; Zr(2)–N(4) = 2.43 Å) and also on average somewhat longer than those in complex **2** (2.43 Å). The Zr–μ<sub>2</sub>-NH<sub>2</sub> bond lengths are in the range of those reported in the literature for Zr–μ<sub>2</sub>-amido clusters.<sup>11</sup>

Monitoring the reaction of **1** with ammonia at room temperature by NMR spectroscopy revealed the formation of a transient intermediate. When the reaction was carried out at –60 °C in toluene, that species was sufficiently stable for characterization, and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy showed it to be the ammonia adduct analogous to **2**. Again, no carbene peak was observed, and inequivalent methylene signals corresponding to Zr- and NCH-bound benzyl groups appeared, supporting the assignment as complex **4** (Scheme 3). At –60 °C,<sup>12</sup> **4** exists as a mixture of two isomers in a ratio of 85:15; the <sup>1</sup>H/<sup>13</sup>C NMR signals for the Zr- and NHC-bound benzyl groups, respectively, are 2.32/52.2 and 3.73/33.4 ppm for the major isomer and 2.25/54.2 and 3.47/35.4 ppm for the minor isomer. Presumably these two isomers correspond to exchange of the positions of the Zr-bound benzyl and NH<sub>3</sub> groups; the larger steric bulk of PMe<sub>3</sub> may explain the observation of only a single isomer of **2**.

Scheme 3. N–H Bond Activation of Ammonia by Complex 1



When the above solution is allowed to warm from  $-60\text{ }^{\circ}\text{C}$  to room temperature, 4 disappears over the course of minutes as dimer 3 forms, establishing the reaction sequence shown in Scheme 3: migration of benzyl from Zr to the NHC induced by coordination of  $\text{NH}_3$ ; N–H abstraction by the remaining Zr-bound Bn group to eliminate toluene; and finally coordination of a second  $\text{NH}_3$  along with dimerization. Previous examples of N–H activation by  $d^0$  transition metal complexes (for which oxidative addition at the metal center is not possible)<sup>11,13</sup> are likewise believed to begin with coordination of  $\text{NH}_3$  before protonolysis events, but the M– $\text{NH}_3$  intermediate is seldom observable. Here the ability to track migration of the benzyl group to the carbene carbon provides a useful tool to monitor the stepwise mechanism of N–H activation.

Reversible C–C bond-making/breaking processes such as those documented here are relatively rare; most commonly they are observed in the form of equilibria between M– $\text{C}_{\text{alkyl}}$  and C– $\text{C}_{\text{alkyl}}$  species. Some examples include the equilibrium between an  $(\text{NC}_{\text{aryl}}\text{N})\text{Pt}-\text{Bn}$  complex and an arenium species featuring a  $\text{C}_{\text{aryl}}-\text{C}_{\text{Bn}}$  bond;<sup>14</sup> the migratory insertion of an alkyne into a niobium–alkyl bond and its reverse process, a  $\beta$ -alkyl elimination;<sup>15</sup> and a thermal equilibrium in a cobalt-to-carbon bond rearrangement in coenzyme  $\text{B}_{12}$ .<sup>16</sup> In contrast, here we are able to control the reversible benzyl migration by addition or abstraction of the phosphine to obtain stable complexes 1 and 2. Metal–ligand cooperativity in the form of reversible migrations—usually of hydrogen—between a metal and a “noninnocent” ligand<sup>17</sup> has been exploited for a number of catalytic applications,<sup>18</sup> and the ability to extend these—with control—to 1,2-migrations of C-centered groups offers the potential for further extending the scope of this approach.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06695.

Crystallographic data for 2 (CIF)

Crystallographic data for 3 (CIF)

Experimental details, NMR spectra, and crystallographic data (PDF)

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### Notes

The authors declare no competing financial interest.

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(10) For details, see Figures S11 and S12 in the [Supporting Information](#).

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