



**HAL**  
open science

## Group IV Complexes with Sterically Congested N -Aryl-adamantylcarbamidate Ligands

Bahareh Rezaei Kheirkhah, Wimonsiri Huadsai, Phil Liebing, Sébastien  
Bontemps, Matthias Westerhausen

► **To cite this version:**

Bahareh Rezaei Kheirkhah, Wimonsiri Huadsai, Phil Liebing, Sébastien Bontemps, Matthias Westerhausen. Group IV Complexes with Sterically Congested N -Aryl-adamantylcarbamidate Ligands. *Organometallics*, 2023, 42 (16), pp.2304-2311. 10.1021/acs.organomet.3c00291 . hal-04196519

**HAL Id: hal-04196519**

**<https://hal.science/hal-04196519v1>**

Submitted on 5 Sep 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Group IV Complexes with Sterically Congested *N*-Aryl-adamantylcarbamidate Ligands

Bahareh Rezaei Kheirkhah,<sup>a</sup> Wimonsiri Huadsai,<sup>a,b</sup> Phil Liebing,<sup>a</sup> Sébastien Bontemps,<sup>\*,b</sup> Matthias Westerhausen<sup>\*,a</sup>

<sup>a</sup>) Institute of Inorganic and Analytical Chemistry, Friedrich Schiller University Jena (FSU), Humboldtstraße 8, D-07743 Jena, Germany

<sup>b</sup>) CNRS Laboratoire de Chimie de Coordination, UPR 8241, 205 Route de Narbonne, 31077 Toulouse Cedex 4, France

---

**ABSTRACT:** Metalation of *N*-(2,6-dibenzhydryl-4-tolyl)adamantane-1-carboxamide (**1**, Ar\*N(H)-C(O)-Ad) with M(NMe<sub>2</sub>)<sub>4</sub> (M = Ti, Zr, Hf) yields the amidate complexes Ar\*N=C(Ad)-O-Ti(NMe<sub>2</sub>)<sub>3</sub> (**2**) as well as the bis(amidate) compounds (Ar\*N=C(Ad)-O)<sub>2</sub>M(NMe<sub>2</sub>)<sub>2</sub> (M = Zr (**3**), Hf (**4**)). In **2** the amidate ligand acts as a monodentate base via the oxygen atom with the Ti center in a slightly distorted tetrahedral environment. The steric requirement of the amidate ligand stabilizes the unique coordination number of four of the Ti atom. In the congeners **3** and **4**, two bidentate amidate ligands exist in the coordination spheres leading to hexacoordinate group IV metal atoms. The small bite angles of the Zr- and Hf-bound amidate ligands lead to severe distortion of the octahedral environments of the Zr and Hf centers. The titanium compound **2** is an unsuitable choice to catalyze hydrofunctionalization of alkynes with amines and phosphane oxides despite the significantly smaller pK<sub>a</sub> value of the carboxylic amide and formation of carboxamide **1** is the dominant reaction upon addition of amines or phosphane oxides to release intramolecular steric strain introduced by the very bulky adamantylamidato ligand.

---

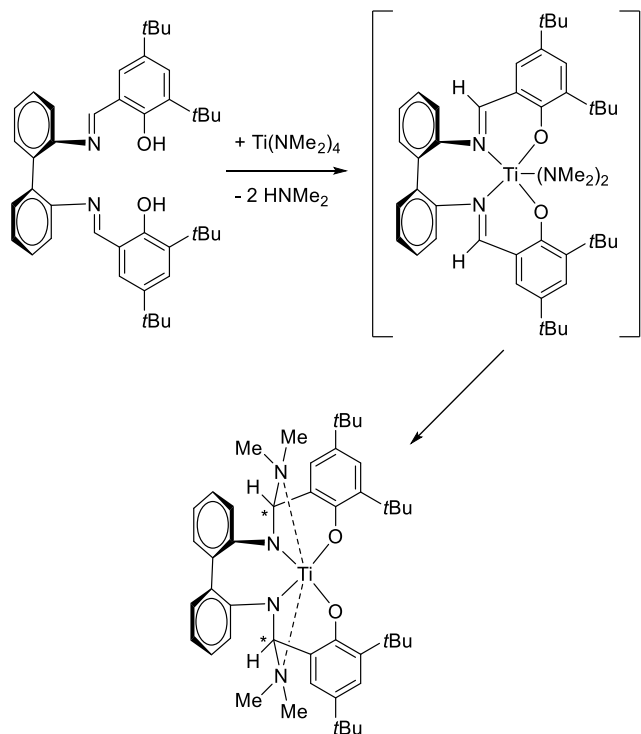
## INTRODUCTION

The complexes of the group IV elements are of tremendous relevance in catalysis with polymerization of alkenes probably being the standard example in many textbooks.<sup>1</sup> Beyond that the coordination compounds of these metals play an important role in hydrofunctionalization processes such as e.g. hydroamination reactions of unsaturated compounds.<sup>2</sup> The radii of the group IV metals gradually differ in size (tetra-/hexacoordinate Ti<sup>4+</sup> 56/74.5 pm, tetra-/hexacoordinate Zr<sup>4+</sup> 73/86 pm, and tetra-/hexacoordinate Hf<sup>4+</sup> 72/85 pm)<sup>3a</sup> and Allred-Rochow electronegativity (Ti 1.32, Zr 1.22, Hf 1.23)<sup>3b</sup> with very similar values for Zr and Hf. These highly charged electropositive metal ions are very hard Lewis acids, attracting electron-rich ligands such as alkenes, alkynes and their heteroatom-substituted congeners. This behavior enables manifold applications in catalysis such as e.g. polymerization of alkenes as well as hydrofunctionalization of alkenes and alkynes,<sup>1,2,4</sup> leading to an extensive research on coordination compounds of group IV elements.

Advantageous starting materials for metalation reactions and syntheses of precatalysts are the easily accessible tetrakis(dialkylamido) compounds M(NR<sub>2</sub>)<sub>4</sub>. Thus, the reaction of these group IV amides with tetradentate Jacobsen-type Schiff base ligands with a biphenyl backbone leads to the formation of 2,2'-bis[(2-oxido-3,5-di(*tert*-butyl)phenyl)-dimethylaminomethylamino]-1,1'-biphenyl tita-

nium(IV) with a distorted octahedrally coordinated titanium center as depicted in Scheme 1.<sup>5</sup> The Ti(IV) atom is effectively shielded by this hexadentate ligand and hence catalytically inactive in hydroamination processes.

**Scheme 1. Twofold Metalation of the Schiff Base 2,2'-Bis[2-hydroxy-3,5-di(*tert*-butyl)benzylideneamino]-1,1'-biphenyl with Ti(NMe<sub>2</sub>)<sub>4</sub> Followed by an Intramolecular Addition of the Dimethylamido ligands onto the Imine Functionalities (Stereocenters are Marked with Asterisks).**



Therefore, another ligand class with the opportunity to easily vary bulkiness to tune the reactivity attracted our attention. Generally, deprotonation of carboxylic acid amides with  $\text{Ti}(\text{NR}_2)_4$  yields complexes of the type  $(\text{R}_2\text{N})_2\text{Ti}[\text{OC}(\text{NR}')-\text{R}'']_2$  with bidentate *N,O*-donating iminocarboxy ligands. In these complexes, the titanium atoms have the coordination number six, too, but two dimethylamido groups enable intermolecular hydroamination of unsaturated compounds.<sup>6</sup> The substituents  $\text{R}'$  and  $\text{R}''$  allow to influence steric as well as electronic properties of the amidates. Very often,  $\text{R}''$  is an aryl group such as phenyl,<sup>7</sup> pentafluorophenyl,<sup>8</sup> and *ortho*-substituted aryl groups<sup>9,10</sup> but also alkyl substituents have been used in this ligand.<sup>10,11</sup> The addition of the metal-bound dialkylamido group onto the  $\text{C}=\text{N}$  double bond has not been observed but occasionally, the dimethylamido ligands show a peculiar reactivity, leading to metallaaziridines via liberation of an amine.<sup>12</sup> The amidate ligands commonly act as bidentate Lewis bases with very few exceptions leading to pentacoordinate group IV transition metal centers,<sup>7e,9,13</sup> coordination numbers smaller than five have not been observed for this compound class up to now.

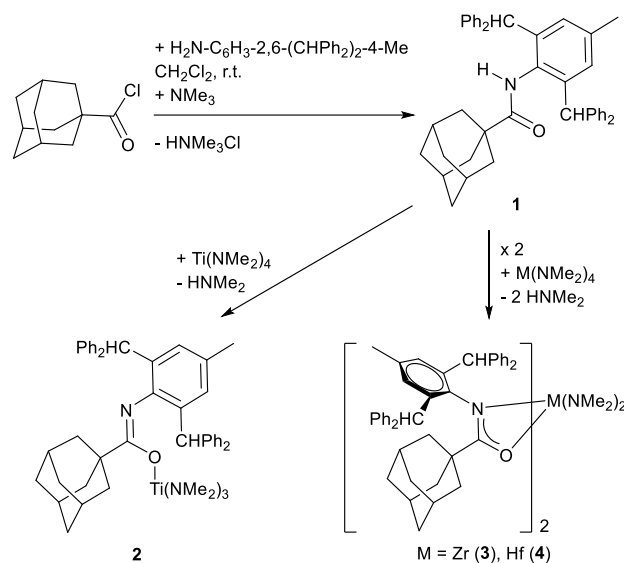
We became interested in complexes of the group IV metals containing heavily congested amidate ligands with bulky substituents  $\text{R}'$  and  $\text{R}''$  to elucidate the influence of overcrowding on the molecular structures of group IV complexes also containing dimethylamido anions.

## RESULTS AND DISCUSSION

The sterically crowded 2,6-dibenzhydrylphenylamine and adamantoyl chloride were combined in dichloromethane at room temperature and then, trimethylamine was added dropwise as depicted in Scheme 2. During stirring overnight, a white solid precipitated which was redis-

solved in dichloromethane. After addition of aqueous  $\text{NaHCO}_3$ , colorless **1** was isolated from the organic phase and could be recrystallized from toluene.

### Scheme 2. Synthesis of the Group IV Complexes Containing the Bulky Adamantylamidate Ligand via Metalation of *N*-(2,6-Dibenzhydryl-4-tolyl)adamantane-1-carboxamide (**1**) with $\text{M}(\text{NMe}_2)_4$ ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ) Yielding the Amidate Complexes **2**, **3** and **4**.



A solution of  $\text{M}(\text{NMe}_2)_4$  in *n*-hexane was added to a suspension of equimolar amounts of **1** in the same solvent. The Ti compound reacts according to the stoichiometric ratio of the substrates yielding yellow complex **2**, whereas the heavier homologous metalation reagents formed the colorless bis(amidate) complexes **3** and **4** regardless of the applied stoichiometry, and despite the molar 1:1 ratio, the metalation reagents of the heavier metals Zr and Hf reacted with two equivalents of **1**. Compound **2** was highly soluble in toluene, **3** and **4** were sparingly soluble in toluene but all complexes were insoluble in aliphatic hydrocarbons.

All new compounds were authenticated by X-ray structure determinations, allowing structural comparison depending on the binding partner of the amidate. For comparison reasons, the molecular structure of **1** has also been determined. Molecular structure and atom labeling scheme of **1** are depicted in Figure 1. Intramolecular steric strain is minimized by an *E* arrangement of the bulky adamantyl and dibenzhydryl-4-tolyl substituents. Despite the valence of three for N1, the 1-aza-3-oxaallylic system shows a significantly shorter N1-C1 bond of 136.8(3) pm than the N1-C12 distance of 143.3(3) pm to the ipso-carbon atom of the aryl group (Table 1). The angle of 67.7° between the planes of the O1-C1-N1 unit and the crowded aryl group shows a twisting of these substructures precluding an effective interaction between their  $\pi$ -systems. Due to an efficient shielding of the CO-NH moiety by the bulky aryl group, no intermolecular hydrogen bonds exist in the crystal structure of **1**.

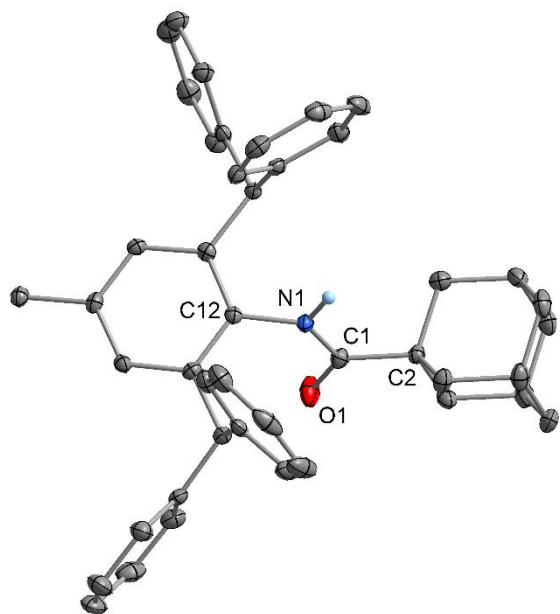


Figure 1. Molecular structure and atom labeling scheme of *N*-(2,6-dibenzhydryl-4-tolyl)adamantane-1-carboxamide (**1**). Displacement ellipsoids represent a probability of 50 %, C-bound H atoms are omitted for clarity reasons. Selected structural parameters are given in Table 1.

As depicted in Scheme 2, the titanium complex **2** contains three dimethylamido ligands and one monodentate amidate- $\kappa O$  group. The molecular structure and atom labeling scheme are depicted in Figure 2. The Ti1 atom shows an unusually low coordination number of four with a slightly distorted tetrahedral environment of the Ti1 atom. The O1-Ti1-N bond angles (av. value  $112.6(4)^\circ$ ) are larger than the N-Ti1-N values with an average of  $106.1(5)^\circ$  due to the much larger steric demand of the *O*-bound amidate ligand.

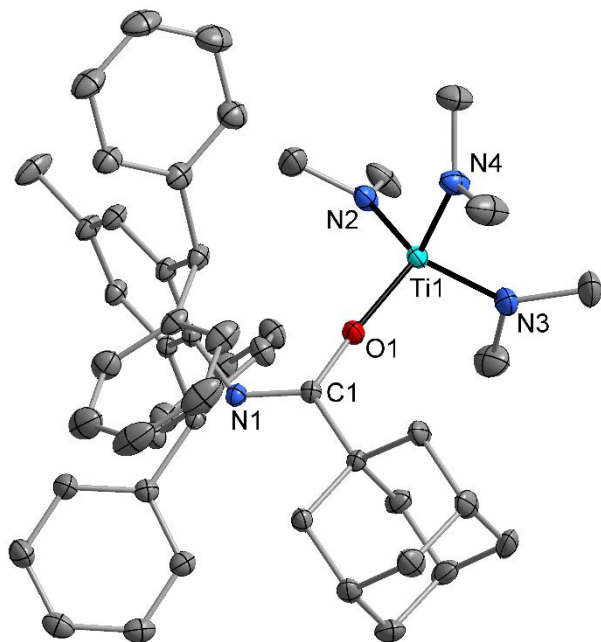


Figure 2. Molecular structure and atom labeling scheme of titanium complex **2**. Displacement ellipsoids represent a probability of 50 %, H atoms are omitted for clarity reasons. Selected structural parameters are given in Table 1. Environment of Ti1: O1-Ti1-N2  $113.81(4)$ , O1-Ti1-N3  $112.56(4)$ , O1-Ti1-N4  $111.54(5)$ , N2-Ti1-N3  $105.93(5)$ , N2-Ti1-N4  $105.33(5)$ , N3-Ti1-N4  $107.14(5)$ .

As in the starting material **1**, the organic adamantyl and aryl groups of **2** are *trans*-arranged to each other and the O1-C1-N1 plane and the aryl group are nearly perpendicular to each other ( $84.8^\circ$ ) excluding an interaction between these two  $\pi$ -systems. The  $\text{Ti}(\text{NMe}_2)_3$  fragment binds to the O1 atom and intramolecular restraints lead to a nearly linear Ti1-O1-C1 moiety of  $173.67(8)^\circ$  and a slightly widened O1-C1-N1 bond angle of  $124.5(1)^\circ$ .

**Table 1. Selected Structural Parameters (Bond Lengths [pm] and Angles [deg.]) of *N*-(2,6-Dibenzhydryl-4-tolyl)adamantane-1-carboxamide (**1**) and Its Amidate Complexes **2**, **3** and **4** of the Group IV Metals.**

|            | <b>1</b> | <b>2</b>  | <b>3</b> | <b>4</b> |
|------------|----------|-----------|----------|----------|
| M1-O1      | -        | 187.31(9) | 214.0(3) | 219.9(2) |
| M1-O2      | -        | -         | 221.1(3) | 222.0(1) |
| M1-N1      | -        | -         | 234.6(3) | 225.7(2) |
| M1-N2      | -        | 188.0(1)  | 237.3(3) | 225.8(2) |
| M1-N3      | -        | 188.6(1)  | 203.1(3) | 203.7(2) |
| M1-N4      | -        | 188.9(1)  | 208.4(3) | 204.7(2) |
| C1-O1      | 122.7(3) | 133.0(1)  | 132.0(4) | 129.7(2) |
| C1-N1      | 136.8(3) | 127.4(1)  | 131.0(5) | 132.2(3) |
| C1-C2      | 152.6(3) | 151.8(1)  | 152.0(5) | 152.0(3) |
| N1-C12     | 143.3(3) | 141.1(1)  | 144.0(5) | 143.3(2) |
| C45-O2     | -        | -         | 129.0(5) | 129.4(2) |
| C45-N2     | -        | -         | 132.7(5) | 132.9(2) |
| C45-C46    | -        | -         | 152.9(5) | 152.3(3) |
| N2-C56     | -        | -         | 143.5(5) | 143.7(2) |
| O1-C1-N1   | 121.3(2) | 124.5(1)  | 113.3(3) | 113.2(2) |
| O2-C45-N2  | -        | -         | 114.0(3) | 113.1(2) |
| C1-N1-C12  | 121.7(2) | 121.31(9) | 128.6(3) | 129.9(2) |
| C45-N2-C56 | -        | -         | 127.0(3) | 129.8(2) |
| M1-O1-C1   | -        | 173.67(8) | 98.6(2)  | 95.3(1)  |
| M1-O2-C45  | -        | -         | 98.4(2)  | 95.3(1)  |

The molecular structure of **2** is quite unique and the only example of an amidate complex with a tetracoordinate titanium atom although a monodentate *O*-bound amidate has been observed earlier when bulky *N*-bound 2,6-diisopropylphenyl groups are present.<sup>7e,10</sup> In these complexes with penta-coordinate Ti atoms,  $\kappa^1 O$ - and  $\kappa^2 O, N$ -bound amidate ligands coexist allowing the comparison of Ti-O bond lengths depending on the binding mode. Thus, monodentate

$\kappa^1O$ -coordination leads to a shortening of the Ti-O bond by approx. 20 pm and values of 190.2(1) (O-C(Ph)=N-Dipp ligand)<sup>7c</sup> and 185.8 pm (O-C(*t*Bu)=N-Dipp ligand)<sup>10</sup> are observed. In **2**, the Ti-O bond length lies in the same range despite the smaller coordination number of the Ti center due to the enormous bulkiness of the amidate ligand.

The molecular structures of the Zr and Hf compounds **3** and **4** are very similar. The Hf congener **4** is depicted in Figure 3 and the Zr derivative is shown in the Supporting Information (Figure S17). The Hf complex **4** has been recrystallized from toluene to isolate single crystals in which five toluene molecules are intercalated between the complex molecules. Therefore, the crystal structures are not isotypic despite rather similar binding parameters and very similar radii of the metal ions. The bidentate binding mode of the amidate ligands leads to  $\Delta$ - and  $\Lambda$ -isomers. The bulky organic groups stabilize again a nearly perpendicular arrangement of the 1-aza-3-oxaallyl plane versus the phenyl ring (**3**: 84.6° and 89.3°, **4**: 87.8° and 87.3°).

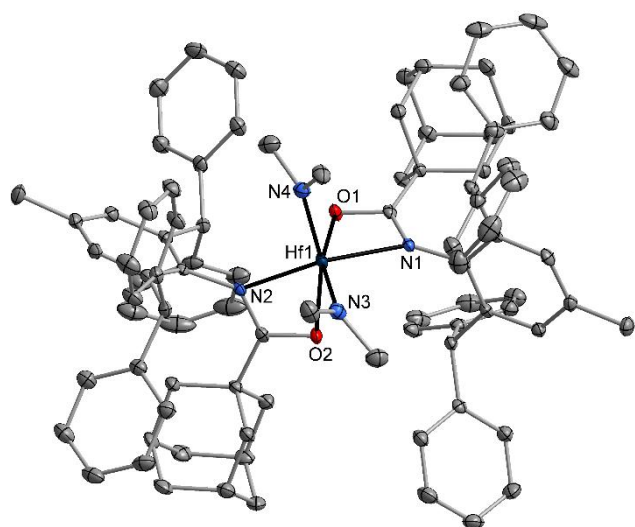


Figure 3. Molecular structure and atom labeling scheme of hafnium complex **4** · 5MePh. Displacement ellipsoids represent a probability of 50 %, H atoms and intercalated toluene molecules are omitted for clarity reasons. Selected structural parameters are given in Table 1. Environment of Hf1 (values for Zr1 in **3** are given in square brackets): O1-Hf1-O2 86.59(5) [94.4(1)], O1-Hf1-N1 58.77(5) [58.4(1)], O1-Hf1-N2 88.03(6) [88.6(1)], O1-Hf1-N3 160.04(6) [147.8(1)], O1-Hf1-N4 90.95(6) [92.3(1)], O2-Hf1-N1 89.51(5) [90.4(1)], O2-Hf1-N2 58.49(5) [57.1(1)], O2-Hf1-N3 90.10(6) [91.0(1)], O2-Hf1-N4 162.26(6) [158.2(1)], N1-Hf1-N2 136.27(6) [132.9(1)], N1-Hf1-N3 101.57(7) [89.9(1)], N1-Hf1-N4 104.21(6) [110.7(1)], N2-Hf1-N3 106.94(7) [120.5(1)], N2-Hf1-N4 103.89(6) [102.5(1)], N3-Hf1-N4 97.93(7) [94.2(1)].

The small bite angles O1-M1-N1 (Zr: 58.4(1)°, Hf: 58.77(5)°) and O2-M1-N2 (Zr: 57.1(1)°, Hf 58.49(5)°) enforce distortion of the octahedral environment of the metal centers. The dimethylamido ligands are *cis*-arranged with N3-M1-N4 bond angles of 94.2(1)° and 97.93(7)° for **3** and **4**, respectively. Despite the bulky adamantyl and dibenzhydrylphenyl substituents, both amidato- $\kappa^2O,N$  ligands act as bidentate Lewis bases. Monodentate coordination behavior of an amidate group via the oxygen atom has been observed

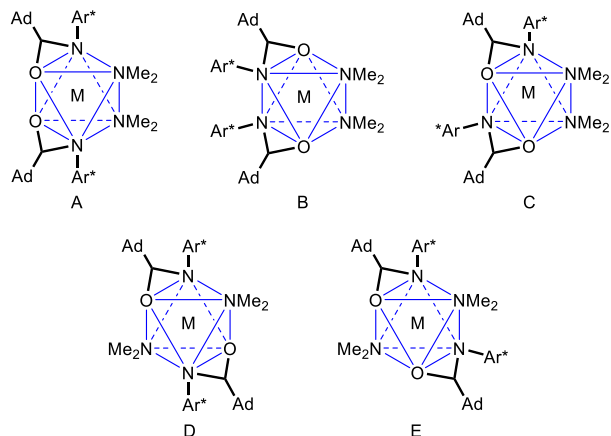
earlier for a Zr complex leading to a pentacoordinate zirconium atom only when the two amidate functionalities are interconnected by a rather stiff biphenyl backbone.<sup>13</sup> In addition, in [Zr(NMe<sub>2</sub>)( $\kappa^1O$ -OC(*t*Bu)=N*t*Bu)( $\kappa^2O,N$ -OC(*t*Bu)=N*t*Bu)<sub>2</sub>] mono- and bidentate amidate ligands are present side by side stabilizing a distorted octahedral environment of the Zr center<sup>14</sup> whereas [Zr(NMe<sub>2</sub>)( $\kappa^2O,N$ -OC(Naph)=N-Dipp)<sub>3</sub>] contains a hepta-coordinate metal atom.<sup>7c</sup>

In compound **3**, one amidate ligand is slightly pushed out of the coordination sphere leading to elongated Zr1-O2 and Zr1-N2 bonds compared to the other ligand with the O1 and N1 donor atoms. This asymmetry can also be observed for the dimethylamido groups with a difference of more than 5 pm between Zr1-N3 and Zr1-N4. On the contrary, in the hafnium congener similar Hf1-O1/O2, Hf1-N1/N2 as well as Hf1-N4/N4 values are observed. It is noteworthy, that the bond length difference of 18.4 pm between av. Zr1-O1/O2 (217.6 pm) and av. Zr1-N1/N2 (236.0 pm) is much more expressed than the corresponding difference of 4.8 pm between av. Hf1-O1/O2 (221.0 pm) and av. Hf1-N1/N2 (225.8 pm) values. This finding hints toward an increasing oxophilicity for the lighter metals of this titanium group favoring the bond to the oxygen rather than to the nitrogen base. Steric reasons play a minor role due to the very same radii of Zr and Hf ions.<sup>3</sup> In Table 2 selected bond lengths in compounds of the type [M(NR<sub>2</sub>)<sub>2</sub>( $\kappa^2O,N$ -O-C(R')=NR'')<sub>2</sub>] with hexa-coordinate group IV metal atoms are compared. Complexes with additional ring strain by bridging benzo<sup>15</sup> and biaryl<sup>9a,16</sup> fragments are omitted in this table. Hafnium congeners attract much less attention and only very few derivatives have been authenticated by solid-state structures.<sup>17</sup> Contrary to the adamantylamidate in **2**, **3** and **4**, even rather bulky amidate ligands form isostructural compounds for titanium and zirconium (entries 1/10, 6/11, 7/12, 8/13, and 9/14). In complexes with hexa-coordinate group IV metals the M-O bond lengths are smaller than the M-N distances due to the oxophilic character of the metal ions. Exceptions have been observed if outer Lewis bases such as methoxy or dimethylamino substituents are able to bind to the metals which enhances their coordination number and pushes the oxygen-base out of the vicinity of the metal centers (entries 6-8 as well as 12 and 13).

<< Insert Table 2 >>

In principle, five diastereomers exist for octahedral complexes of the type [M(NR<sub>2</sub>)<sub>2</sub>( $\kappa^2O,N$ -O-C(R')=NR'')<sub>2</sub>] as depicted in Scheme 3 which are distorted due to the small bites of the amidate ligands. In the solid state the dimethylamido substituents show a *cisoid* arrangement and the nitrogen atoms of the amidate ions (carrying the bulky aryl groups) are *trans*-arranged due to steric reasons. The asymmetric binding mode of the amidate ligands could hint toward dissociation and intermediate formation of a penta-coordinate metal center easing isomerization processes in solution. Alternatively, the isomers can be interconverted into each other via rotation of two opposite triangular faces of the octahedral coordination polyhedron. In isomers A and D the bulky N-Ar\* fragments are in favored *trans* positions.

**Scheme 3. Possible Diastereomeric Isomerism in Complexes of the Type  $[M(NR_2)_2(\kappa^2O,N-O-C(R')=NR'')]_2$  ( $M = Zr, Hf$ ) with Hexa-Coordinate Group IV Metal Atoms. In Diastereomers A, B and C, the  $NMe_2$  ligands are *cis*-arranged, in D and E, these ligands are in *trans* positions.**



Due to the enormous steric demand of the adamantylamidato ligands in the group IV complexes **3** and **4**, hindered rotation of substituents can abrogate the chemical and magnetic equivalence of the *ortho*-CHPh<sub>2</sub> substituents which leads to broad and overlapping signals in the NMR spectra. Both phenomena enhance the complexity of the NMR spectra which showed temperature-dependent appearance, however, concrete rotational barriers could not be determined due to overlapping signals. In addition, the complexes **3** and **4** are only sparingly soluble exacerbating the interpretation of <sup>13</sup>C{<sup>1</sup>H} NMR experiments at diluted solutions.

The crowding adamantylamidato ligands ensure a small coordination number of the titanium cation in compound **2** and we expected that this fact should ease hydrofunctionalization processes. Therefore, we studied the hydroamination of alkynes following a published procedure.<sup>19</sup> In a typical protocol, 1 mmol of alkyne, 1 mmol of primary amine and 5 mol-% of compound **2** were stirred in 2 mL of toluene at 80 °C for 4 hours. The progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy. Contrary to our expectation, which was based on the highly different pK<sub>a</sub> values of amines (approx. 35) and carboxylic amides (approx. 18), significant amounts of *N*-(2,6-dibenzhydryl-4-tolyl)adamantane-1-carboxamide (**1**) formed during this reaction (see Figures S13-S16). We interpret this finding that preferably steric pressure was released by competing reactions of the amines with the amido substituents on the one hand and preferentially with the adamantylamidato ligands on the other. Furthermore, hydrophosphorylation, i.e. the addition of diarylphosphane oxides across alkynes, failed as well because compound **1** formed again predominantly; the nature of the titanium-containing compounds remained unknown but the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum verified the formation of phosphinites with Ti-O-PAr<sub>2</sub> moieties. Again, the release of intramolecular strain and hence the preferred formation of the carboxylic amide **1** seemed to be the driving force in these reactions. In summary, the accessibility of the two-coordinate O- and N-bases of the amidato ligand by weak Brønsted acids such as amines and phosphane oxides is

much more important than the higher basicity of the amido groups with three-coordinate N-donor atoms.

## CONCLUSION

In this investigation we elucidate the influence of extremely bulky amidato ligands on the structures of group IV metal complexes. Therefore has been deprotonated with M(NMe<sub>2</sub>)<sub>4</sub> ( $M = Ti, Zr, Hf$ ) in hydrocarbons. *N*-(2,6-Dibenzhydryl-4-tolyl)adamantane-1-carboxamide (**1**) crystallizes with a sterically favored *trans*-arrangement of the adamantyl and 2,6-dibenzhydryl-4-tolyl substituents at the 1-aza-3-oxaallyl system. Metalation with Ti(NMe<sub>2</sub>)<sub>4</sub> yields yellow tris(dimethylamido)titanium *N*-(2,6-dibenzhydryl-4-tolyl)adamantane-1-carbamidate (**2**) with maintenance of the *trans*-arrangement of the bulky adamantyl and tolyl groups. The amidate ion acts as a monodentate ligand and binds via the oxygen atom to the tetracoordinate titanium atom, an unusually small coordination number for derivatives of this compound class.

Deprotonation of **1** with M(NMe<sub>2</sub>)<sub>4</sub> ( $M = Zr$  and  $Hf$ ) yields colorless bis(dimethylamido)zirconium bis[*N*-(2,6-dibenzhydryl-4-tolyl)adamantane-1-carbamidate] (**3**) and the isostructural hafnium congener **4** regardless of the applied stoichiometry. In these compounds, the amidato ligands act as bidentate bases with *cis*-arranged adamantyl and tolyl substituents leading to complexes with common hexacoordinate metal centers. Steric strain induced by the bulky dibenzhydryl groups and ring strain due to the small bite of the ligands leads to severe distortion of the octahedral environment of the metal atoms.

Most commonly, Ti and Zr derivatives show very similar solid-state structures and here, a rare example is observed where the bulky amidate ligand enforces a low coordination number four at titanium whereas the distorted octahedral coordination sphere of zirconium follows the expectation. Very few hafnium derivatives have been structurally authenticated and it is not surprising that the Zr and Hf congeners are isostructural based on very similar radii of these metal ions.

In all these group IV metal complexes with *N*-(2,6-dibenzhydryl-4-tolyl)adamantane-1-carbamidate ligands the intramolecular transfer of a dimethylamido ligand onto the 1-aza-3-oxaallyl moiety has not been observed. This finding makes these compounds possible candidates for metal-mediated intermolecular hydrofunctionalization reactions. However, compound **2**, having a weakly shielded titanium center with the coordination number of four due to the monodentate binding mode of the amidato ligand, decomposes during intermolecular hydroamination and hydrophosphorylation of alkynes via preferred protonation of the adamantylamidato ligand and hence formation of *N*-(2,6-dibenzhydryl-4-tolyl)adamantane-1-carboxamide (**1**), the obvious reason being the release of intramolecular steric strain introduced by this bulky adamantylamidato ligand. The titanium complexes, which are summarized in Table 2, contain bidentate amidato ligands and catalytically enable hydroamination reactions, supposing that the monodentate binding mode and excessive bulkiness of the amidato ligand in compound **2** is disadvantageous for the use of this Ti compound as catalyst in hydrofunctionalization processes.

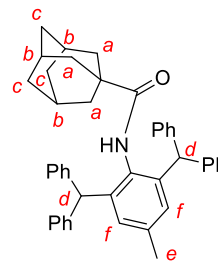
## EXPERIMENTAL SECTION

**General.** All manipulations were carried out under anaerobic conditions in an argon atmosphere using standard *Schlenk* techniques. The solvents were dried according to common procedures and distilled in an argon atmosphere; deuterated solvents were dried over sodium, degassed, and saturated with argon. The yields given are not optimized.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AC 400, AC 500 and AC 600 spectrometers. Chemical shifts are reported in parts per million (ppm,  $\delta$  scale) relative to the residual signal of the solvent.<sup>91</sup> Samples for MS were measured on a Finnigan MAT SSQ710 mass spectrometer operating with an EI ionization source operating at 70 eV. Samples were measured using a direct ionization probe (DIP) by placing a minute amount on the rhenium wire of the probe and heating the wire up during measurement. Mass spectra were averaged from the maximum of the thermogram. The 2,6-dibenzhydryl-4-tolylamine was prepared according to a literature procedure.<sup>20</sup> The complexes **3** and **4** are only sparingly soluble and we were unable to elucidate reliable  $^{13}\text{C}\{^1\text{H}\}$  NMR parameters. Due to sensitivity of the metal complexes toward moisture and air and due to loss of intercalated solvent molecules, no reliable C,H,N analyses could be performed for **3** and **4**.

**Synthesis of 1.** The 2,6-dibenzhydryl-4-tolylamine (11.26 g, 25.61 mmol) and Ad-C(O)Cl (5.95 g, 29.97 mmol) were added in 125 ml of dichloromethane. Then distilled trimethylamine (4.64 ml, 33.30 mmol) was added dropwise to this solution at room temperature. The reaction mixture was stirred overnight, giving a white solid. This precipitate was dissolved in dichloromethane, quenched with 1M aqueous solution of  $\text{NaHCO}_3$  and washed twice with 50 ml of distilled water. The organic layer was separated and dried over anhydrous  $\text{MgSO}_4$ . Volatiles were removed from the filtrate in vacuo yielding the product **1** as a white powder (yield: 14.6 g, 24.26 mmol, 95 %). Recrystallization from toluene gave single crystals suitable for X-ray diffraction studies.

Physical data of **1**.  $^1\text{H}$  NMR ( $[\text{D}_8]$ toluene):  $\delta$  = 1.51 (m, 6H, Ad-H<sup>c</sup>), 1.64 (m, 6H, Ad-H<sup>a</sup>), 1.77 (m, 3H, Ad-H<sup>b</sup>), 1.84 (s, 3H, CH<sub>3</sub><sup>e</sup>), 5.82 (s, 2H, CH<sup>d</sup>-Ph<sub>2</sub>), 5.97 (s, 1H, NH), 6.75 (s, 2H, Ar-H<sup>f</sup>), 6.97-7.16 (m, overlapping phenyl protons with  $[\text{D}_7]$ toluene).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $[\text{D}_8]$ toluene):  $\delta$  = 21.3 (CH<sub>3</sub><sup>e</sup>) 28.6 (Ad-CH<sup>b</sup>), 36.7 (Ad-CH<sup>c</sup>), 39.1 (Ad-CH<sup>a</sup>), 41.2, 52.9 (CH<sup>d</sup>-Ph<sub>2</sub>), 126.6, 129.1, 130 (Ar-CH<sup>f</sup>), 132.6, 136.9, 142.7, 144.1, 175.4 (C=O). The assignment of the signals is marked with superscripts and depicted in Scheme 4. Elemental analysis (C<sub>44</sub>H<sub>43</sub>NO, 601.83): calcd.: C 87.81, H 7.20, N 2.33; found: C 87.86, H 7.16, N 2.31. MS (APCI<sup>+</sup>, m/z): 601 (36) [ $\text{M}^+$ ], 167 (100). MS (APCI<sup>+</sup>, m/z): 602 (76) [ $\text{M}+1$ ]<sup>+</sup>, 601 (31) [ $\text{M}^+$ ], 434 (14) [ $\text{M}^+$ -CHPh<sub>2</sub>], 167 (100) [CHPh<sub>2</sub>]<sup>+</sup>. IR (ATR, cm<sup>-1</sup>): 3425 (w,  $\nu$ (N-H)), 3058 (w), 3023 (w), 2920 (w), 2851 (w), 1957 (vw), 1889 (vw), 1815 (vw), 1764 (vw), 1659 (m,  $\nu$ (C=O)), 1597 (w), 1580 (w), 1494 (m), 1471 (m), 1445 (m), 1368 (vw), 1346 (vw), 1319 (vw), 1252 (w), 1247 (w), 1228 (w), 1183 (w), 1156 (vw), 1132 (vw), 1102 (vw), 1076 (m), 1032 (m), 979 (vw), 942 (vw), 921 (vw), 882 (w), 858 (w), 828 (w), 766 (m), 746 (s), 703 (vs), 688 (vw), 666 (vw), 650 (w), 641 (w), 629 (w), 621 (w), 605 (w).

### Scheme 4. Assignment of the Signals in the NMR Spectra with the Red Letters a to f as Superscripts.



**Synthesis of the Ti complex 2.** Compound **1** (0.255 g, 0.423 mmol) was suspended in 20 ml of *n*-hexane. Then  $\text{Ti}(\text{NMe}_2)_4$  (0.1 ml, 0.947g/ml, 0.423 mmol) was added to this suspension. The cloudy reaction mixture was stirred overnight at room temperature. Afterwards, the solution was stirred at 70 °C for 3 hours and 10 ml of *n*-hexane and 2 ml of toluene were added to obtain a clear reaction solution. Yellow crystals began to form when the mixture slowly cooled to ambient temperature (yield: 250 mg, 0.32 mmol, 76 %).

Physical data of **2**.  $^1\text{H}$  NMR ( $[\text{D}_8]$ toluene):  $\delta$  = 1.66 (m, 6H, Ad-H<sup>c</sup>), 1.83 (m, 6H, Ad-H<sup>a</sup>), 1.94 (overlapping, 6H, H<sup>b</sup> and H<sup>e</sup>), 2.95 (s, 18H, NMe<sub>2</sub>), 5.81 (s, 2H, CH<sup>d</sup>-Ph<sub>2</sub>), 6.77 (s, 2H, Ar-H<sup>f</sup>), 6.98-7.27 (m, overlapping phenyl protons with  $[\text{D}_7]$ toluene).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $[\text{D}_8]$ toluene):  $\delta$  = 21.2 (CH<sub>3</sub><sup>e</sup>) 29.1 (Ad-CH<sup>b</sup>), 37.4 (Ad-CH<sup>c</sup>), 40.4 (Ad-CH<sup>a</sup>), 44.5 (NMe<sub>2</sub>), 52.6 (CH<sup>d</sup>-Ph<sub>2</sub>), 126.03, 126.07, 128.4, 129.2, 129.4 (Ar-CH<sup>f</sup>), 129.9, 130.5, 133.9, 144.9, 145.7, 166.7 (C=N). Elemental analysis (C<sub>50</sub>H<sub>60</sub>N<sub>4</sub>O<sub>2</sub>Ti, 780.92): calcd.: C 76.90, H 7.74, N 7.17; found: C 76.96, H 7.68, N 7.26. MS (ESI<sup>+</sup>, m/z): 648 (45) [ $\text{M}^+$ -3(NMe<sub>2</sub>)], 647 (100) [ $\text{M}^+$ -3(NMe<sub>2</sub>)-H]. IR (ATR, cm<sup>-1</sup>): 2846 (m); 2771 (m); 1633 (m); 1599 (m); 1493 (m); 1465 (m); 1446 (m); 1418 (m); 1323 (m); 1273 (m); 1245 (s); 1183 (w); 1148 (m); 1118 (w); 1103 (m); 1075 (m); 1053 (m); 1031 (m); 986 (w); 939 (s); 854 (m); 839 (w); 829 (m); 814 (w); 800 (w); 764 (m); 745 (s); 721 (m); 699 (s); 665 (m).

**Synthesis of the Zr complex 3.** The carboxamide **1** (0.862 g, 1.43 mmol) was suspended in 15 ml of *n*-hexane. A solution of  $\text{Zr}(\text{NMe}_2)_4$  (0.383 g, 1.43 mmol) dissolved in 10 ml of *n*-hexane was added. After 45 min of stirring at room temperature, the reaction solution became clear. Overnight stirring at room temperature led to formation of a white solid. This precipitate was collected by filtration and washed with cold *n*-pentane (yield: 661 mg, 0.48 mmol, 67 %). Crystallization succeeded via diffusion of *n*-pentane into a saturated toluene solution yielding colorless crystals of **3**.

Physical data of **3**.  $^1\text{H}$  NMR ( $[\text{D}_6]$ benzene):  $\delta$  = 1.23, 1.35, 1.38, 1.40, 1.46, 1.59, 1.69, 1.90, 1.92, 2.18, 2.19, 2.85, 2.96 (s, NMe<sub>2</sub>), 3.25, 6.01 (s, CH<sup>d</sup>-Ph<sub>2</sub>), 7.06, 7.19, 7.21, 7.27, 7.34, 7.44, 7.59, 7.71.  $^{13}\text{C}\{^1\text{H}\}$  NMR (benzene-*d*<sub>6</sub>):  $\delta$  = 14.4, 21.3, 23.1, 27.2, 28.1, 32.0, 36.3, 38.3, 42.4 (NMe<sub>2</sub>), 44.0, 52.4 (CH<sup>d</sup>-Ph<sub>2</sub>), 126.2, 126.6, 126.8, 128.7, 128.8, 130.0, 130.1, 130.5, 133.0, 136.9, 141.6, 143.3, 145.2, 188.3 (OCN). MS (APCI<sup>+</sup>, m/z): decomposition, 601 (36) [ $\text{1}^+$ ], 167 (100) [CHPh<sub>2</sub>]<sup>+</sup>. IR (ATR, cm<sup>-1</sup>): 3416 (w), 3057 (w), 3023 (m), 2902 (m), 2847 (m), 1672 (w), 1642 (m), 1631 (m), 1621 (m), 1613 (m), 1597 (m), 1493 (m), 1470 (m), 1448 (m), 1328 (m), 1279 (m), 1256 (m), 1183 (w), 1077 (m), 1030 (m), 764 (m), 744 (s), 699 (vs), 665 (m), 642 (m), 622 (m), 605 (s), 532 (s), 522 (s), 477 (s), 438 (s), 412 (s), 405 (s).

**Synthesis of the Hf complex 4.** The carboxamide **1** (0.602 g, 1.00 mmol) was suspended in 15 ml of toluene. A 1M solution of  $\text{Hf}(\text{NMe}_2)_4$  in toluene (1.1 ml, 0.328 g/ml, 1.01 mmol) was added to this suspension. Immediately, the reaction mixture became clear. The reaction solution was stirred overnight at room temperature. Reduction of the volume of the solution under reduced pressure and cooling of the solution to +5°C led to precipitation of colorless crystals of **4** · 5 toluene (yield: 770 mg, 0.40 mmol, 80 %). Recrystallization from toluene gave single crystals with the same composition.

Physical data of **4**.  $^1\text{H}$  NMR ( $[\text{D}_8]$ toluene):  $\delta$  = 0.95, 1.13, 1.16, 1.30, 1.33, 1.39, 1.53, 1.58, 1.71, 1.92, 2.11, 2.22, 2.99 (s, NMe<sub>2</sub>), 3.05, 3.29, 5.97 (s, CH<sup>d</sup>-Ph<sub>2</sub>), 6.17, 6.56, 7.04, 7.07, 7.12, 7.14, 7.16, 7.18, 7.27, 7.29, 7.37, 7.39, 7.49, 7.73.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $[\text{D}_8]$ toluene):  $\delta$  = 21.4, 28.0, 36.0, 36.2, 37.9, 38.1, 42.2 (NMe<sub>2</sub>), 43.7, 44.6, 52.3 (CH<sup>d</sup>-Ph<sub>2</sub>), 125.6, 125.6, 126.1, 126.6, 126.7, 127.4, 128.1, 128.3, 128.5, 128.8, 129.3, 130.1, 130.2, 130.5, 131.0, 137.2, 137.2, 137.7, 140.9, 143.2, 145.1, 188.6 (OCN). MS (EI, m/z): decomposition, 601 (46) [1<sup>+</sup>], 167 (100) [CHPh<sub>2</sub><sup>+</sup>]. IR (ATR, cm<sup>-1</sup>): 3418 (w), 3082 (w), 3057 (w), 3025 (w), 2902 (m), 2847 (m), 2776 (w), 1666 (w), 1640 (w), 1629 (w), 1619 (w), 1597 (m), 1564 (w), 1548 (w), 1527 (w), 1511 (w), 1493 (m), 1448 (m), 1407 (w), 1381 (m), 1364 (m), 1342 (w), 1330 (w), 1313 (w), 1279 (w), 1258 (m), 1215 (w), 1185 (m), 1154 (w), 1103 (m), 1077 (m), 1030 (m), 985 (m), 958 (w), 932 (m), 883 (w), 864 (m), 844 (w), 797 (m), 764 (m), 744 (s), 732 (m), 699 (vs), 665 (m), 644 (m), 622 (m), 605 (s), 560 (m), 530 (m), 503 (s), 475 (s), 465 (s), 450 (s), 436 (s), 403 (s).

**X-Ray structure determinations.** The single-crystal X-ray intensity data for the reported compounds were collected on a Bruker-Nonius Kappa-CCD diffractometer, equipped with a Mo-K $\alpha$   $\mu\text{S}$  microfocus source and an Apex2 CCD detector, at  $T = 120(2)$  K. The crystal structures were solved with SHELXT-2018/3<sup>21</sup> and refined by full matrix least-squares methods on F2 with SHELXL-2018/3,<sup>22</sup> using the OLEX 1.2 environment.<sup>23</sup> Multi-scan absorption correction was applied to the intensity data.<sup>24</sup> CCDC 2220636–2220639 contain the supplementary crystallographic data for this paper (cf. Table S1). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC; <http://www.ccdc.cam.ac.uk>).

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

NMR spectra of all new compounds, table with crystallographic and refinement details, representation of the molecular structure of zirconium complex **3** (PDF format)

Supplementary crystallographic data has also been deposited at The Cambridge Crystallographic Data Centre (CCDC) with the numbers CCDC-2220636 for **1**, 2220637 for **2**, 2220638 for **3**, and 2220639 for **4** · 5MePh (<http://www.ccdc.cam.ac.uk>)

## AUTHOR INFORMATION

### Corresponding Authors

\* S. Bontemps – CNRS Laboratoire de Chimie de Coordination (LCC), UPR 8241, 205 Route de Narbonne, BP44099, 31077 Toulouse, Cedex 4, France, [orcid.org/0000-0002-4950-9452](http://orcid.org/0000-0002-4950-9452); E-mail: [sebastien.bontemps@lcc-toulouse.fr](mailto:sebastien.bontemps@lcc-toulouse.fr).

\* M. Westerhausen – Institute of Inorganic and Analytical Chemistry, Friedrich Schiller University Jena (FSU), Humboldtstraße 8, D-07743 Jena, Germany, [orcid.org/0000-0002-1520-2401](http://orcid.org/0000-0002-1520-2401); E-mail: [m.we@uni-jena.de](mailto:m.we@uni-jena.de); fax: +49 (0) 3641 948132.

### Authors

B. Rezaei Kheirkhah – Institute of Inorganic and Analytical Chemistry, Friedrich Schiller University Jena, Germany

W. Huadsai – CNRS Laboratoire de Chimie de Coordination, Toulouse, France

P. Liebing – Institute of Inorganic and Analytical Chemistry, Friedrich Schiller University Jena, Germany, [orcid.org/0000-0002-4660-1691](http://orcid.org/0000-0002-4660-1691)

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENT

This research has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 860322.

B.R.K. is grateful to the German Academic Exchange Service (DAAD, Bonn, Germany; grant no. 57440921) for a generous Ph.D. stipend. We acknowledge the valuable support of the NMR service platform ([www.nmr.uni-jena.de](http://www.nmr.uni-jena.de)) and of the mass spectrometry platform ([www.ms.uni-jena.de](http://www.ms.uni-jena.de)) of the Faculty of Chemistry and Earth Sciences of the Friedrich Schiller University Jena, Germany.

## REFERENCES

- (1) Selected textbooks: a) Omai, I.: *Applications of Organometallic Compounds*, Wiley, Chichester, 1998. b) Cornils, B.; Herrmann, W. A.: *Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook*, Wiley-VCH, Weinheim, Germany, **2000**. c) Hartwig, J.: *Organotransition Metal Chemistry: From Bonding to Catalysis*, University Science Books, Sausalito, **2010**. d) Behr, A.; Neubert, P.: *Applied Homogeneous Catalysis*, Wiley-VCH, Weinheim, Germany, **2012**. e) Beller, M.; Renken, A.; van Santen, R. A.: *Catalysis: From Principles to Applications*, Wiley-VCH, Weinheim, Germany, **2012**. f) Steinborn, D.: *Fundamentals of Organometallic Catalysis*, Wiley-VCH, Weinheim, Germany, **2012**. g) Bochmann, M.: *Organometallics and Catalysis: An Introduction*, Oxford University Press, New York, **2015**.
- (2) Selected reviews: a) Nobis, M.; Drießen-Hölscher, B. Recent Developments in Transition Metal Catalyzed Intermolecular Hydroamination Reactions – A Breakthrough? *Angew. Chem. Int. Ed.* **2001**, *40*, 3983–3985. b) Pohlki, F.; Doye, S. The Catalytic Hydroamination of Alkynes. *Chem. Soc. Rev.* **2003**, *32*, 104–114. c) Hutzsch, K. C. Catalytic Asymmetric Hydroamination of Non-Activated Olefins. *Org. Biomol. Chem.* **2005**, *3*, 1819–1824. d) Severin, R.; Doye, S. The Catalytic Hydroamination of Alkynes. *Chem. Soc. Rev.* **2007**, *36*, 1407–1420. e) Aillaud, I.; Collin, J.; Hannedouche, J.; Schulz, E. Asymmetric Hydroamination of Non-Activated Carbon-Carbon Multiple Bonds. *Dalton Trans.* **2007**, 5105–5118. f) Müller, T. E.; Hutzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. Hydroamination: Direct Addition of Amines to Alkenes and Alkynes. *Chem. Rev.* **2008**, *108*, 3795–3892. g) Chemler, S. R. The Enantioselective Intramolecular Aminative Functionalization of Unactivated Alkenes, Dienes, Allenes and Alkynes for the Synthesis of Chiral Nitrogen Heterocycles. *Org. Biomol. Chem.* **2009**, *7*, 3009–3019. h) Roesky, P. W. Catalytic Hydroaminoalkylation. *Angew. Chem. Int. Ed.* **2009**, *48*, 4892–4894. i) Yadav, J. S.; Antony, A.; Rao, T. S.; Reddy, B. V. S. Recent Progress in Transition Metal Catalyzed Hydrofunctionalisation of Less Activated Olefins. *J. Organomet. Chem.* **2011**, *696*, 16–36. j) Zi, G. Asymmetric Hydroamination/Cyclization Catalyzed by Group IV Metal Complexes with Chiral Biaryl-Based Ligands. *J. Organomet. Chem.* **2011**, *696*, 68–75. k) Patil, N. T.; Singh, V. Alkyne Hydroamination Triggered Cyclizations: A Powerful Tool for the Construction of Biologically Important Structural Motifs. *J. Organomet. Chem.* **2011**, *696*, 419–432. l) Reznichenko, A. L.; Hutzsch, K. C. Early Transition Metal (Group 3–5, Lanthanides and Actinides) and Main Group Metal (Group 1, 2, and 13) Catalyzed Hydroamination. *Top. Organomet. Chem.* **2013**, *43*, 51–114. m) Coman, S. M.; Parvulescu, V. I. Nonprecious Metals Catalyzing Hydroamination and C–N Coupling Reactions. *Org. Process Res. Dev.* **2015**, *19*, 1327–1355. n) Ryken, S. A.; Schafer, L. L. *N,O*-Chelating Four-Membered Metallacyclic Titanium(IV) Complexes for Atom-Economic Catalytic Reactions. *Acc. Chem. Res.* **2015**, *48*, 2576–2586. o) Hannedouche, J.;



- Schulz, E. Hydroamination and Hydroaminoalkylation of Alkenes by Group 3 – 5 Elements: Recent Developments and Comparison with Late Transition Metals. *Organometallics* **2018**, *37*, 4313-4326. p) Manßen, M.; Schafer, L. L. Titanium Catalysis for the Synthesis of Fine Chemicals – Development and Trends. *Chem. Soc. Rev.* **2020**, *49*, 6947-6994.
- (3) a) Holleman, A. F.; Wiberg, E.; Wiberg, N.: *Inorganic Chemistry, (Holleman-Wiberg)*, W. de Gruyter, Berlin, New York, **2001**, pp. 1756-1759. b) Holleman, A. F.; Wiberg, E.; Wiberg, N.: *Inorganic Chemistry, (Holleman-Wiberg)*, W. de Gruyter, Berlin, New York, **2001**, p. XXXVIII.
- (4) Smolensky, E.; Eisen, M. S. Design of Organometallic Group IV Heteroallylic Complexes and Their Catalytic Properties for Polymerizations and Olefin Centered Transformations. *Dalton Trans.* **2007**, 5623-5650.
- (5) Rezaei Kheirkhah, B.; Al-Shboul, T. M. A.; Pröhl, F. E.; Kriek, S.; Görls, H.; Westerhausen, M. Isomerism in Hexacoordinate Ti(IV) and Zr(IV) Complexes with a Tetradentate ONNO-Schiff Base Ligand. *Eur. J. Inorg. Chem.* **2022**, e202200528.
- (6) a) Lee, A. V.; Schafer, L. L. Modular *N,O*-Chelating Ligands: Group-4 Amidate Complexes for Catalytic Hydroamination. *Eur. J. Inorg. Chem.* **2007**, 2243-2255. b) Yim, J. C.-H.; Schafer, L. L. Efficient Anti-Markovnikov-Selective Catalysts for Intermolecular Alkyne Hydroamination: Recent Advances and Synthetic Applications. *Eur. J. Org. Chem.* **2014**, 6825-6840.
- (7) a) Zhang, Z.; Schafer, L. L. Anti-Markovnikov Intermolecular Hydroamination: A Bis(amidate) Titanium Precatalyst for the preparation of Reactive Aldimines. *Org. Lett.* **2003**, *5*, 4733-4736. b) Thomson, R. K.; Zahariev, F. E.; Zhang, Z.; Patrick, B. O.; Wang, Y. A.; Schafer, L. L. Structure, Bonding, and Reactivity of Ti and Zr Amidate Complexes: DFT and X-Ray Crystallographic Studies. *Inorg. Chem.* **2005**, *44*, 8680-8689. c) Payne, P. R.; Thomson, R. K.; Medeiros, D. M.; Wan, G.; Schafer, L. L. Synthesis, Structure, and Reactivity of Tris(amidate) Mono(amido) and Tetrakis(amidate) Complexes of Group 4 Transition Metals. *Dalton Trans.* **2013**, *42*, 15670-15677. d) Lui, E. K. J.; Hergesell, D.; Schafer, L. L. *N*-Silylenamines as Reactive Intermediates: Hydroamination for the Modular Synthesis of Selectively Substituted Pyridines. *Org. Lett.* **2016**, *20*, 6663-6667. e) Lui, E. K. J.; Brandt, J. W.; Schafer, L. L. Regio- and Stereoselective Hydroamination of Alkynes Using an Ammonia Surrogate: Synthesis of *N*-Silylenamines as Reactive Synthons. *J. Am. Chem. Soc.* **2018**, *140*, 4973-4976. f) Hao, H.; Schafer, L. L. Metal-Ligand Cooperativity in Titanium-Catalyzed Anti-Markovnikov Hydroamination. *ACS Catal.* **2020**, *10*, 7100-7111. g) Hao, H.; Schafer, L. L. Titanium-Catalyzed Hydroamination of an Organometallic Acetylide to Access Copper Enamides. *Organometallics* **2021**, *40*, 3255-3239. h) Hao, H.; Bagnol, T.; Pucheault, M.; Schafer, L. L. Using Catalysts to Make Catalysts: Titanium-Catalyzed Hydroamination to Access P,N-Ligands for Assembling Catalysts in One Pot. *Org. Lett.* **2021**, *23*, 1974-1979.
- (8) Li, C.; Thomson, R. K.; Gillon, B.; Patrick, B. O.; Schafer, L. L. Amidate Complexes of Titanium and Zirconium: A New Class of tunable Precatalysts for the Hydroamination of Alkynes. *Chem. Commun.* **2003**, 2462-2463.
- (9) a) Zi, G.; Liu, X.; Xiang, L.; Song, H. Synthesis of Group 4 Metal Amides with New Chiral Biaryldiimine-Based Ligands and Their Use as Catalysts for Asymmetric Hydroamination/Cyclization. *Organometallics* **2009**, *28*, 1127-1137. b) Wang, Q.; Song, H.; Zi, G. Synthesis, Structure, and Catalytic Activity of Group 4 Complexes with New Chiral Biaryl-Based NO<sub>2</sub> Ligands. *J. Organomet. Chem.* **2010**, *695*, 1583-1591.
- (10) Horillo-Martinez, P.; Leitch, D. C.; Ryken, S. A.; Thomson, R. K.; Beard, J. D.; Patrick, B. O.; Schafer, L. L.; Giesbrecht, G. R. Titanium Amidate Complexes as Active Catalysts for the Synthesis of High Molecular Weight Polyethylene. *Can. J. Chem.* **2015**, *93*, 775-783.
- (11) Coles, N. T.; Gasperini, D.; Provis-Evans, C. B.; Mahon, M. F.; Webster, R. L. Heterobimetallic Complexes of 1,1-Diphosphineamide Ligands. *Organometallics* **2021**, *40*, 148-155.
- (12) a) Bexrud, J. A.; Eisenberger, P.; Leotch, D. C.; Payne, P. R.; Schafer, L. L. Selective C-H Activation  $\alpha$  to Primary Amines. Bridging Metallaaziridines for Catalytic, Intramolecular  $\alpha$ -Alkylation. *J. Am. Chem. Soc.* **2009**, *131*, 2116-2118. b) Beweries, T.; Hansen, S.; Kessler, M.; Klahn, M.; Rosenthal, U. Catalytic Dehydrogenation of Dimethylamine Borane by Group 4 Metallocene Alkyne Complexes and Homoleptic Amido Compounds. *Dalton Trans.* **2011**, *40*, 7689-7692. c) Bielefeld, J.; Doye, S. Dimethylamine as a Substrate in Hydroaminoalkylation Reactions. *Angew. Chem. Int. Ed.* **2017**, *56*, 15155-15158. See also the comparable aziridine formation from a Ta(V)-bound NMe<sub>2</sub> group: Eisenberger, P.; Ayinla, R. O.; Lauzon, J. M. P.; Schafer, L. L. Tantalum-Amidate Complexes for the Hydroaminoalkylation of Secondary Amines: Enhanced Substrate Scope and Enantioselective Chiral Amine Synthesis. *Angew. Chem. Int. Ed.* **2009**, *48*, 8361-8365.
- (13) Yonson, N.; Yim, J. C.-H.; Schafer, L. L. Alkene Hydroamination with a Chiral Zirconium Catalyst. Connecting Ligand Design, Precatalyst Structure and Reactivity Trends. *Inorg. Chim. Acta* **2014**, *422*, 14-20.
- (14) Catherall, A. L.; Hill, M. S.; Johnson, A. L.; Kociok-Köhn, G.; Mahon, M. F. Homoleptic Zirconium Amidates: Single Source Precursors for the Aerosol-Assisted Chemical Vapour Deposition of ZrO<sub>2</sub>. *J. Mater. Chem. C* **2016**, *4*, 10731-10739.
- (15) Giesbrecht, G. R.; Shafir, A.; Arnold, J. Synthesis and Structure of a Linked-Bis(amidate) Ligand and Some Complexes with Titanium. *Inorg. Chem.* **2001**, *40*, 6069-6072.
- (16) a) Gott, A. L.; Clarke, A. J.; Clarkson, G. J.; Scott, P. Structure-Activity Relationship for Group 4 Biaryl Amidate Complexes in Catalytic Hydroamination/Cyclization of Aminoalkenes. *Organometallics* **2007**, *26*, 1729-1737. b) Wood, M. C.; Leitch, D. C.; Yeung, C. S.; Kozak, J. A.; Schafer, L. L. Chiral Neutral Zirconium Amidate Complexes for the Asymmetric Hydroamination of Alkenes. *Angew. Chem. Int. Ed.* **2007**, *46*, 354-358; corrigendum: *ibid.* **2007**, *46*, 6937. c) Zi, G.; Zhang, F.; Xiang, L.; Chen, Y.; Fang, W.; Song, H. Synthesis and Characterization of Group 4 Metal Amides with new *C*<sub>2</sub>-Symmetric Binaphthylidine-Based Ligands and Their Use as Catalysts for Asymmetric Hydroamination/Cyclization. *Dalton Trans.* **2010**, *39*, 4048-4061. d) Reznichenko, A. L.; Hultzsch, K. C. *C*<sub>2</sub>-Symmetric Zirconium Bis(Amidate) Complexes with Enhanced Reactivity in Aminoalkene Hydroamination. *Organometallics* **2020**, *29*, 24-27. e) Ayinla, R. O.; Gibson, T.; Schafer, L. L. Amidate Ligand Design Effects in Zirconium-Catalyzed Enantioselective Hydroamination of aminoalkenes. *J. Organomet. Chem.* **2011**, *696*, 50-60.
- (17) Palomero, O. E.; Jones, R. A. Accessing Pentagonal Bipyramidal Geometry with Pentadentate Pincer Amido-bis(amidate) Ligands in Group IV and V Early Transition Metal Complexes. *Organometallics* **2020**, *39*, 3689-3694.
- (18) Bexrud, J. A.; Li, C.; Schafer, L. L. Enhanced Reactivity Results in Reduced Catalytic Performance: Unexpected Ligand Reactivity of a Bis(*N*-2,6-diisopropylphenylperfluorophenyl-amidate)titanium-bis(diethylamido) Hydroamination Precatalyst. *Organometallics* **2007**, *26*, 6366-6372.
- (19) Heutling, A.; Pohlki, F.; Doye, S. [Ind<sub>2</sub>TiMe<sub>2</sub>]: A General Catalyst for the Intermolecular Hydroamination of Alkynes. *Chem. Eur. J.* **2004**, *10*, 3059-3071.
- (20) Bresien, J.; Goicoechea, J. M.; Hinz, A.; Scharnholz, M. T.; Schulz, A.; Suhrbier, T.; Villinger, A. Increasing Steric Demand Through Flexible Bulk – Primary Phosphanes with 2,6-Bis(benzhydryl)phenyl Backbones. *Dalton Trans.* **2019**, *48*, 3786-3794.
- (21) Sheldrick, G. M. *SHELXT* – Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr.* **2015**, *A71*, 3–8.

- (22) Sheldrick, G. M. Crystal Structure Refinement with *SHELXL*. *Acta Crystallogr.* **2015**, *C71*, 3–8.
- (23) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- (24) Bruker AXS **2001**, *Apex4 and SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA.

**Table 2. Comparison of M-O and M-N Bond Lengths (pm, average values for M-N<sub>NR2</sub>) of Complexes of the Type [M(NR<sub>2</sub>)<sub>2</sub>(κ<sup>2</sup>O,N-O-C(R')=NR'')<sub>2</sub>] with Hexa-Coordinate Group IV Metal Atoms.<sup>a</sup>**

| Entry | M  | R  | R'                            | R''   | M-O <sub>amidate</sub> | M-N <sub>amidate</sub> | M-N <sub>NR2</sub> | Ref.   |
|-------|----|----|-------------------------------|---|------------------------|------------------------|--------------------|--------|
| 1     | Ti | Et | Ph                            | <i>t</i> Bu   | 203.5(4)               | 223.4(5)               | 190.7(6)           | 7b     |
| 2     | Ti | Et | Ph                            | C <sub>6</sub> H <sub>3</sub> -2,6-Me <sub>2</sub>                        | 207.6(1), 200.4(1)     | 221.1(1), 237.5(1)     | 189.8(1)           | 7b     |
| 3     | Ti | Et | Ph                            | Dipp  | 214.6(1)               | 215.6(1)               | 189.9(2)           | 7a, 7b |
| 4     | Ti | Et | C <sub>6</sub> F <sub>5</sub> | <i>t</i> Bu   | 204.4(6)               | 235.6(7)               | 188.7(7)           | 8      |
| 5     | Ti | Et | C <sub>6</sub> F <sub>5</sub> | Dipp  | 217.0(1)               | 220.1(1)               | 190.3(1)           | 18     |
| 6     | Ti | Me | Mes                           | C <sub>6</sub> H <sub>3</sub> -3-Me-2-Aryl-OMe                            | 213.1(1)               | 212.5(1), 214.3(1)     | 190.8(1)           | 9b     |
| 7     | Ti | Me | Mes                           | C <sub>6</sub> H <sub>3</sub> -3-Me-2-Aryl-NMe <sub>2</sub>               | 211.9(1)               | 202.9(2)               | 190.5(2)           | 9a     |
| 8     | Ti | Me | Mes                           | Naph-Naph'-NMe <sub>2</sub>   | 214.7(3)               | 202.9(4)               | 190.7(4)           | 9a     |
| 9     | Ti | Me | <i>t</i> Bu                   | C <sub>6</sub> H <sub>3</sub> -2,6-Me <sub>2</sub>                        | 211.8(2), 214.2(2)     | 211.2(3), 210.9(3)     | 190.6(3)           | 10     |
| 10    | Zr | Et | Ph                            | <i>t</i> Bu   | 218.7(3)               | 231.8(3)               | 204.3(3)           | 7b     |
| 11    | Zr | Me | Mes                           | C <sub>6</sub> H <sub>3</sub> -3-Me-2-Aryl-OMe                            | 222.4(2)               | 227.8(2), 228.3(2)     | 204.8(2)           | 9b     |
| 12    | Zr | Me | Mes                           | C <sub>6</sub> H <sub>3</sub> -3-Me-2-Aryl-NMe <sub>2</sub>               | 222.2(3)               | 217.1(3)               | 203.4(3)           | 9a     |
| 13    | Zr | Me | Mes                           | Naph-Naph'-NMe <sub>2</sub>   | 224.3(3)               | 218.1(4)               | 204.1(4)           | 9a     |
| 14    | Zr | Me | <i>t</i> Bu                   | C <sub>6</sub> H <sub>3</sub> -2,6-Me <sub>2</sub>                        | 215.0, 220.3           | 240.1, 230.5           | 204.5              | 10     |
| 15    | Zr | Me | Ad                            | C <sub>6</sub> H <sub>2</sub> -4-Me-2,6-(CHPh <sub>2</sub> ) <sub>2</sub> | 214.0(3), 221.1(3)     | 234.6(3), 237.3(3)     | 205.8(3)           | Here   |
| 16    | Hf | Me | Ad                            | C <sub>6</sub> H <sub>2</sub> -4-Me-2,6-(CHPh <sub>2</sub> ) <sub>2</sub> | 219.9(2), 222.0(1)     | 225.7(2), 225.8(2)     | 204.2(2)           | Here   |

<sup>a</sup>) Ad 1-adamantyl, Bu butyl, Dipp 2,6-diisopropylphenyl, Et ethyl, Me methyl, Mes 2,4,6-trimethylphenyl (mesityl), Naph naphthyl, Ph phenyl.

Table of Contents artwork:

