BCSJ Bulletin of the Chemical Society of Japan

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Advance Publication on the web August 24, 2018
doi:10.1246/bcsj.20180181

# Synthesis and Structure of a Bis(indolyl)–Coordinated Titanium Diamido Complex, and Its Catalytic Applications in the Intermolecular Hydroamination of Alkynes

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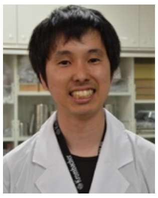


Shun Ohta
Shun Ohta received Ph.D. degree from Nagoya University under the supervision of Prof. Kazuyuki Tatsumi in 2012. He joined in Prof. Gerhard Erker's group at Münster University as a researcher of a JSPS program (the program for advancing strategic international networks to accelerate the circulation of talented researchers) in 2012, and then in the group of Prof. Zhaomin Hou at the Riken institute as a special postdoctoral researcher in 2014. In 2015, he was appointed to his current position as assistant professor at Hirosaki University, where he has been working with Prof. Masaaki Okazaki. His current research interests include coordination chemistry and organometallic chemistry of benzo-fused N-heterocycles.

**Abstract**

Titanium bis(diethylamido) complex **1**, which contains a carbon–bridged bis(indolyl) ligand, was obtained in 69% yield from the reaction of Ti(NEt$_2$)$_4$ with the corresponding bis(indole) ligand. Its molecular structure in the crystal was unequivocally determined by a single-crystal X-ray diffraction analysis, Furthermore, we examined applications of **1** as a catalyst for the intermolecular hydroamination of alkynes. When using phenylacetylene or 1–hexyne as alkynes, the Markovnikov products were obtained selectively, while the reaction with 1–phenyl–1–propyne afforded an imine of phenylacetone.

**Keywords:** titanium complex, bis(indolyl) ligand, hydroamination

## 1. Introduction

The deprotonation of the N–H group in indole derivatives generates anionic indolyls. When indolyls coordinate to a metal center, they exhibit a variety of coordination modes (Figure 1(a))[1–5]. The most common is the $\eta^1$-coordination mode, where the nitrogen atom of the indolyl is bound to a metal center as an amido ligand.[1,2] The $\eta^5$-coordination is also known,[3] which is comparable to the $\eta^5$-coordination of the cyclopentadienido ligand, albeit that one carbon atom is replaced by nitrogen. Moreover, a $\eta^6$-mode has been reported, wherein $\pi$-coordination occurs via the six-membered ring of indolyl.[4] In addition, a $\eta^3$-mode is known, albeit that this mode has only been reported for indolyl complexes of yttrium and samarium.[5] The haptotropic rearrangement of an indolyl-ligated molybdenum complex has been reported by Parkin,[6] and a mechanism for this rearrangement has recently been discussed by Saillard and Oprunenko *et al.* based on DFT calculations.[7] It is highly intriguing that indolyls are able to change their coordination mode in response to the steric and electronic environment of the metal center. Yet, the coordination chemistry of indolyl moieties incorporated in multidentate ligands, which are often supporting ligands in chemical transformations catalyzed by metal complexes, is not well explored.

In this study, our interest was focused on 2,2'-bis(indolyl)methanes (henceforth: bis(indolyl)s). Metal complexes bearing a deprotonated bis(indolyl) have been reported mainly by the group of Mason.[8–11] They have synthesized and characterized monomeric titanium and zirconium complexes,[8–10] some of which show catalytic activity for the polymerization of ethylene.[9] Moreover, the coordination of these ligands toward main group elements has been investigated.[11] Meyer *et al.* have used a bis(indolyl) ligand to obtain a synthetic analogue of Rieske-type [2Fe-2S] clusters.[12] Herein, we report the synthesis and structural characterization of a titanium(IV) complex that contains a carbon-bridged bis(indolyl) ligand. Although this type of titanium complex (**A**; Figure 1(b)) has previously been reported by Mason *et al*,[8,9] characteristic structural features around the bis(indolyl) ancillary ligands have not yet been described. The catalytic activity of complexes **1** and **A** toward the intermolecular hydroamination of alkynes with aniline is also discussed in this article.

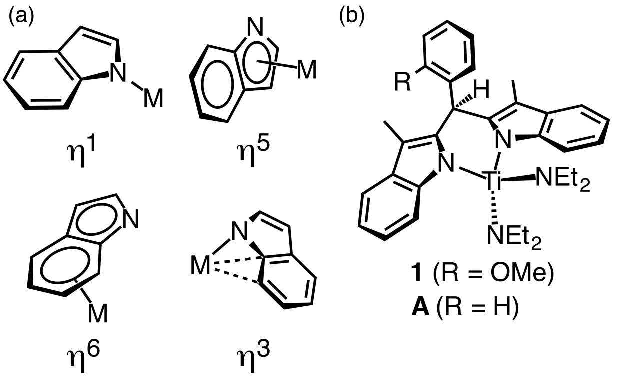


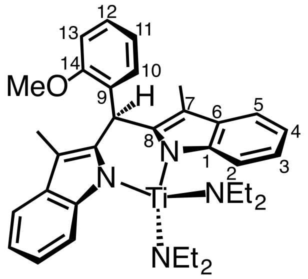
**Figure 1.** (a) Known coordination modes of indolyl ligands towards metals. (b) Bis(indolyl)–coordinated titanium complexes studied in this work.

## 2. Experimental

### General Procedures

All manipulations of air- and moisture-sensitive compounds were performed under an atmosphere of nitrogen using standard Schlenk-line or glovebox techniques. Anhydrous solvents (toluene, pentane, and THF) were purchased from common commercial suppliers and used without further purification. NMR solvents were distilled from sodium–benzophenone ketyl (C$_6$D$_6$ and toluene-$d_8$) or CaH$_2$ (CDCl$_3$). Alkynes (phenylacetylene, 1–hexyne, and 1–phenyl–1–propyne) and amines (aniline, cyclohexylamine, and tert-butylamine) were purified by distillation from CaH$_2$. HCPh$_3$ was dried at reduced pressure. $Ti(NEt_2)_4$,[13] 2–methoxyphenyldi(3–methylindol–2–yl)methane,[14] and **A**[9] were prepared according to literature methods. NMR spectra were recorded on a JEOL JNM-ECZ500R spectrometer; chemical shifts are reported in δ and referenced to the $^1H$ signals of residual protons or the $^{13}C\{^1H\}$ signals of deuterated solvents as internal standards. Elemental analyses were performed on a vario MICRO tube.

### Synthesis of 1.



A mixture of $Ti(NEt_2)_4$ (520 mg, 1.55 mmol) and 2–methoxyphenyldi(3–methylindol–2–yl)methane (500 mg, 1.31 mmol) in toluene (7.5 mL) was heated to reflux for 11 h. Removal of all volatiles *in vacuo*, followed by washing with cold pentane (15 mL, 10 mL, and then 2 x 5 mL) afforded a yellow to brown powder of **1** in 69% yield (520 mg, 0.91 mmol). Anal. Calcd for $C_{34}H_{42}N_4OTi$: C, 71.57; H, 7.42; N, 9.82, Found: C 71.10; H, 7.31; N. 9.32. $^1H$ NMR (500 MHz, 25 ºC, $C_6D_6$) $\delta =$ 7.66 (m, 2H, H2), 7.44 (m, 2H, H5), 7.30–7.25 (m, 4H, H3 + H4), 7.10 (m, 1H, H10), 7.00 (m, 1H, H12), 6.67 (s, 1H, CH), 6.61 (m, 1H, H11), 6.49 (m, 1H, H13), 3.49 (q, $^3J_{H–H} = 7$ Hz, 4H, $\mathrm{NC}H_2\mathrm{CH_3}$), 3.42 (q, $^3J_{H–H} = 7$ Hz, 4H, $\mathrm{NC}H_2\mathrm{CH_3}$), 3.16 (s, 3H, $OCH_3$), 2.50 (s, 6H, $CH_3$), 0.90 (t, $^3J_{H–H} = 7$Hz, 6H, $\mathrm{NCH_2C}H_3$), 0.67 (t, $^3J_{H–H} = 7$Hz, 6H, $\mathrm{NCH_2C}H_3$). $^{13}C\{^1H\}$ NMR (126 MHz, 25 ºC, $C_6D_6$) $\delta =$ 157.8 (C14), 145.9 (C8), 143.4 (C1), 132.9 (C9), 131.0 (C6), 129.4 (C10), 127.3 (C12, overlapping with the solvent peak) 121.5 (C3), 120.6 (C4), 120.1 (C11), 118.5 (C2), 115.5 (C5), 110.9 (C13), 109.3 (C7), 55.0 ($OCH_3$), 48.0 ($\mathrm{N}C\mathrm{H_2CH_3}$), 46.5 ($\mathrm{N}C\mathrm{H_2CH_3}$), 37.4 (CH), 15.2 ($\mathrm{NCH_2}C\mathrm{H_3}$), 14.9 ($\mathrm{NCH_2}C\mathrm{H_3}$), 9.5 ($CH_3$). $^1H$-$^1H$ COSY (500 MHz, 25 ºC, $C_6D_6$) $\delta\,^1H / \delta\,^1H$ = 7.66 / 7.30–7.25 (H2 / H3), 7.44 / 7.30–7.25 (H5 / H4), 7.10 / 6.61 (H10 / H11), 7.00 / 6.61, 6.49 (H12 / H11, H13), 3.49 / 0.90 ($\mathrm{NC}H_2\mathrm{CH_3}$ / $\mathrm{NCH_2C}H_3$), 3.42 / 0.67 ($\mathrm{NC}H_2\mathrm{CH_3}$ / $\mathrm{NCH_2C}H_3$). $^1H$-$^{13}C$ HMQC (500 / 126 MHz, 25 ºC, $C_6D_6$) $\delta\,^1H / \delta\,^{13}C$ = 7.66 / 118.5 (H2 / C2), 7.44 / 115.5 (H5 / C5), 7.30–7.25 / 121.5, 120.6 (H3 + H4 / C3, C4), 7.10 / 129.4 (H10 / C10), 7.00 /127.3 (H12 / C12), 6.67 / 37.4 (CH), 6.61 / 120.1 (H11 / C11), 6.49 / 110.9 (H13 / C13), 3.49 / 46.5 ($\mathrm{NC}H_2\mathrm{CH_3}$), 3.42 / 48.0 ($\mathrm{NC}H_2\mathrm{CH_3}$), 3.16 / 55.0 ($OCH_3$), 2.50 / 9.5 ($CH_3$), 0.90 / 14.9 ($\mathrm{NCH_2C}H_3$), 0.67 / 15.2 ($\mathrm{NCH_2C}H_3$). $^1H$-$^{13}C$ HMBC (500 / 126 MHz, 25 ºC, $C_6D_6$) $\delta\,^1H / \delta\,^{13}C$ = 7.66 / 143.4, 121.5 (H2 / C1, C3), 7.44 / 131.0, 120.6 (H5 / C6, C4), 7.30–7.25 / 143.4, 131.0, 118.5, 115.5 (H3 + H4 / C1, C6, C2, C5), 7.10 / 157.8, 127.3 37.4 (H10 / C14, C12, CH), 7.00 / 157.8, 129.4 (H12 / C14, C10), 6.67 / 157.8, 145.9, 132.9, 129.4, 109.3 (CH / C14, C8, C9, C10, C7), 6.61 / 132.9, 110.9 (H11, C9, C13), 6.49 / 157.8, 132.9, 120.1 (H13 / C14, C9, C11), 3.49 / 46.5, 14.9 ($\mathrm{NC}H_2\mathrm{CH_3}$ / $\mathrm{N}C\mathrm{H_2CH_3}$, $\mathrm{NCH_2}C\mathrm{H_3}$), 3.42 / 48.0, 15.2 ($\mathrm{NC}H_2\mathrm{CH_3}$ / $\mathrm{N}C\mathrm{H_2CH_3}$, $\mathrm{NCH_2}C\mathrm{H_3}$), 3.16 / 157.8 ($OCH_3$ / C14), 2.50 / 145.9, 131.0, 109.3 ($CH_3$ / C8, C6, C7), 0.90 / 46.5 ($\mathrm{NCH_2C}H_3$ / $\mathrm{N}C\mathrm{H_2CH_3}$), 0.67 / 48.0 ($\mathrm{NCH_2C}H_3$ / $\mathrm{N}C\mathrm{H_2CH_3}$).

### Intermolecular hydroamination of alkynes

A stock catalyst solution of **1** (0.12 M) was prepared by dissolving **1** (1.00 g, 1.75 mmol) in toluene (15 mL), while that of **A** (0.13 M) was prepared from **A** (360 mg, 0.65 mmol) and toluene (5 mL). Even though the preparation of 0.13 M catalyst solution for **1** was not possible due to the low solubility of **1** in toluene, the difference should not affect the principal outcome of the study. A toluene solution (0.44 M, 30 mL) of $HCPh_3$ was prepared as an internal standard to determine the product yield. A Schlenk flask with a Teflon valve was charged with alkyne (1.3 mmol), amine (4.0 mmol), the catalyst solution (1.0 mL), and the $HCPh_3$ solution (3.0 mL, 1.33 mmol), and then toluene was added to make the total volume of 6 mL. The resulting brown solution was stirred for 8 h at 75 ºC. All volatiles were removed under reduced pressure, before the $^1H$ NMR spectrum of the residue was measured in $CDCl_3$. Resonances from the generated imines were identified by comparison with reported data.[15]

### Monitoring of the stepwise reaction between A with aniline and 1–phenyl–1–propyne.

A mixture of **A** (30 mg, 0.06 mmol) and aniline (5 mg, 0.06 mmol) in toluene-$d_8$ (0.6 mL) was prepared. After measurement of the $^1H$ NMR spectrum, the mixture was heated for 6 h. at 75 ºC. 1–phenyl–1–propyne (6 mg, 0.06 mmol) was added to the mixture, and then the $^1H$ NMR was measured. After heating at 75 ºC for 1 h, the $^1H$ NMR was measured to indicate the formation of an imine of phenylacetone.

### X–ray diffraction study of 1.

Single crystals, suitable for an X–ray diffraction analysis of **1**, were obtained from THF at –30 ºC. Data were collected at 123 K on a Rigaku RAXIS RAPID imaging plate diffractometer using graphite monochromated MoKα radiation ($\lambda = 0.71069$ Å), and corrected for Lorentz, polarization, and absorption effects. Calculations were carried out using the CrystalStructure program package, and the structure was solved by direct methods and refined on $F^2$ by full matrix least-squares (non-H atoms: anisotropic; H atoms: riding mode). Crystallographic Data: Empirical Formula, $C_{34}H_{42}N_4OTi$; Formula weight, 570.63; Crystal System, monoclinic; Space group, $P21/n$; $a$ = 12.3675(17) Å; $b$ = 15.9091(19) Å; $c$ = 15.1944(19) Å; $\alpha$ = 92.174(4)º; $V$ = 2987.4(7) Å$^3$; $Z$ = 4; Density, 1.269 mg/m$^3$; Absorption coefficient, 1.709 mm$^{-1}$; Crystal size, 0.29 x 0.19 x 0.15 mm$^3$; Reflections collected, 42349; Independent reflections, 6725; Data / restraints / parameters, 6725 / 0 / 361; Goodness–of–fit on $F^2$, 1.039; $R1$ ($I > 2\sigma(I)$) = 0.0755; $wR2$ (all data) = 0.1840. The CIF file has been deposited at the Cambridge Crystallographic Data Centre (CCDC) under reference number CCDC-1846843. The data can be obtained free of charge from the CCDC.

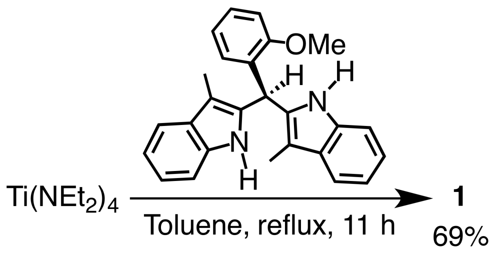
## 3. Results and Discussion

### Synthesis of complex 1.

A mixture of $Ti(NEt_2)_4$[13] and 2–methoxyphenyldi(3–methylindol–2–yl)methane[14] in a 1.2:1 molar ratio was heated to reflux in toluene and stirred for 11 h. Even though the solubility of the bis(indolyl)methane ligand in toluene is relatively low, it gradually dissolved as the reaction progressed, and finally, a homogeneous dark brown solution was obtained. Evaporation of all volatiles *in vacuo* afforded a brown residue that was subsequently washed with cold pentane to remove a small amount of unreacted $Ti(NEt_2)_4$, resulting in pure **1** as a yellow to brown powder in 69% yield (Scheme 1).

### Solid-state structure of 1.

An X–ray diffraction analysis of **1** was carried out on a single crystal obtained from THF at –30 ºC, and the thus determined structure and the crystallographic data are given in Figure 2 and the experimental section, respectively. The titanium center, with a distorted tetrahedral geometry, is bound to four nitrogen atoms,



**Scheme 1.** Synthesis of **1**.

two of which are from the bis(indolyl) ligand, while the other two belong to two NEt$_2$ ligands. The Ti–N1 (1.878(3) Å) and Ti–N2 (1.869(3) Å) bonds are shorter than the Ti–N3 (1.986(3) Å) and Ti–N4 (1.960(4) Å) bonds, indicating that the $p_{\mathrm{N}}\rightarrow d_{\mathrm{Ti}}$ π-bonding interaction between Ti and N(NEt$_2$) is higher than that between Ti and N(indolyl). This feature is consistent with the metric parameters observed for the relevant titanium complex **A** by Mason *et al.* (Figure 1(b)).[9] Similar to **A**, agostic interactions occur between the titanium center and the CH$_2$ groups of the NEt$_2$ ligands. Among the four Ti–C(CH$_2$) bonds, the Ti–C18 (2.766(4) Å) and Ti–C20 (2.801(5) Å) bonds are significantly shorter than the Ti–C19 (3.122(4) Å) and Ti–C21 bonds (3.054(5) Å).

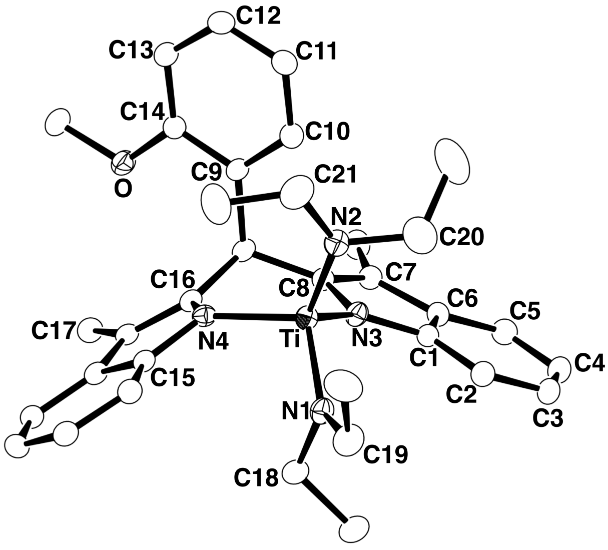


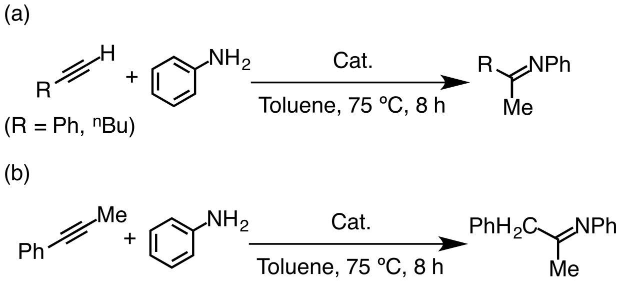
**Figure 2.** ORTEP drawing of **1** with thermal ellipsoids set to 30% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ti–N1 = 1.878(3), Ti–N2 = 1.869(3), Ti–N3 = 1.986(3), Ti–N4 = 1.960(4), Ti–C1 = 3.111(4), Ti–C15 = 3.024(4), Ti–C18 = 2.766(4), Ti–C20 = 2.801(5), N1–Ti–N2 = 108.33(13), N1–Ti–N3 = 110.73(12), N1–Ti–N4 = 107.83(12), N2–Ti–N3 = 114.55(13), N2–Ti–N4 = 118.51(13), N3–Ti–N4 = 96.32(12).

Amido nitrogen atoms coordinated to early transition metals usually exhibit a planar coordination geometry, which has been ascribed to the $p_{\mathrm{N}}\rightarrow d_{\mathrm{M}}$ π-bonding interaction.[16] The N4 atom of **1**, however, is pyramidalized, as evident from its distance from the plane defined by the Ti, C15, and C16 atoms (0.254(3) Å), while the N1, N2, and N3 atoms exhibit planar structures. Most of the indolyl nitrogen atoms with the $\eta^1$-coordination mode adopts a planar geometry,[1,2] but a few pyramidalized examples are known.[1g,1i] We also investigated the geometry of the indolyl nitrogen atoms in **A**[9], and discovered that one nitrogen atom therein is also pyramidalized. The distance from the plane defined by the three binding atoms (0.186 Å) is slightly shorter than that of **1** (0.254(3) Å). Although the possibility of the crystal packing is not excluded, this difference is probably induced by the steric repulsion between the methyl group attached to the N4–containing indolyl ring and the methoxy group of the aromatic ring. Indeed, the O–C17 distance (3.073(4) Å) is less than the sum of the van der Waals radii of the oxygen (1.52 Å) and carbon (1.70 Å) atoms.[17] We also found that the Ti–C15 bond (3.024(4) Å) in **1** is considerably shorter than the Ti–C1 bond (3.111(4) Å). The detailed analysis of these structural differences seems to be essential for an in-depth understanding of the behavior of bis(indolyl)s as ancillary ligands, which are currently in progress in our group.

### Intermolecular hydroamination of alkynes mediated by 1 and A.

Early transition metal complexes supported by indolyl-containing ligands can serve as catalysts for e.g. polymerizations,[9,18–21] hydroaminations,[22] four–component coupling reactions,[1i] hydrophosphonylations,[23] and olefin epoxidations.[24] Thus, we examined the catalytic activity of **1** and **A** for the intermolecular hydroamination of alkynes (Table 1). For that purpose, a mixture of substrates ([alkyne]:[aniline] = 1:3), catalyst (**1**: 8.6 mol%; **A**: 10 mol%), and HCPh$_3$ as an internal standard was stirred for 8 h at 75 °C in toluene. Due to the low solubility of **1** in toluene, the amount of dissolved catalyst is slightly lower than that of **A**. The yields of the produced imines were determined by $^1$H NMR measurements (CDCl$_3$) of the brown solid obtained after evaporation of all volatiles from the reaction mixture.

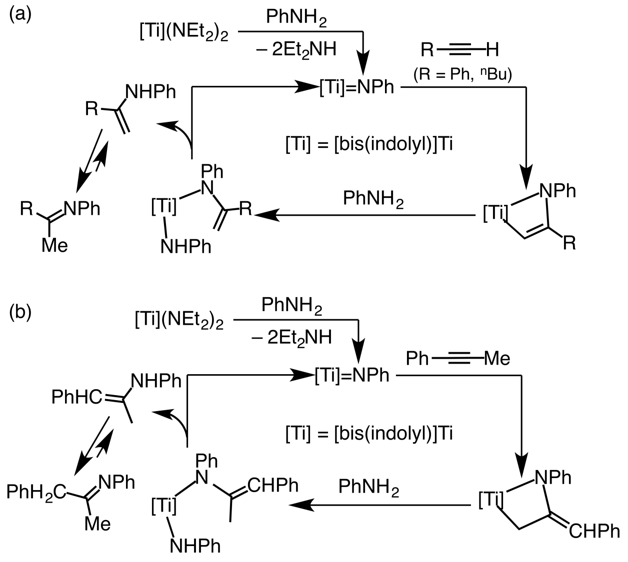
**Table 1.** **1**– or **A**–catalyzed hydroaminations of (a) phenylacetylene or 1–hexyne and (b) 1–phenyl–1–propyne with aniline.[a]



| Entry | Alkyne | Cat. (Content) | Yield[b] |
|---|---|---|---|
| 1 | PhCCH | **1** (8.6 mol%) | 15 |
| 2 | | **A** (10 mol%) | 10 |
| 3 | $^n$BuCCH | **1** (8.6 mol%) | 41 |
| 4 | | **A** (10 mol%) | 27 |
| 5 | PhCCMe | **1** (8.6 mol%) | 18 |
| 6 | | **A** (10 mol%) | 95 |

[a] Reaction conditions: alkyne (1.3 mmol), aniline (4 mmol), 75 °C, 8 h. [b] $^1$H NMR yield.

Reactions with phenylacetylene or 1–hexyne afforded the Markovnikov products, and $^1$H resonances assignable to the anti-Markovnikov products were not observed. When 1–phenyl–1–propyne was used, an imine of phenylacetone was obtained. These regioselectivities are similar to the results obtained when using Ti(NMe$_2$)$_2$(dpma) (dpma = di(pyrrolyl–α–methyl)methylamine) (Scheme 2).[25] For the reactions with phenylacetylene or 1–hexyne (Scheme 2(a)), the active titanium imido species, generated by treating **1** or **A** with aniline, reacts with an alkyne to afford the four-membered metallacycle.[26] In this [2+2] cycloaddition, the Markovnikov regioselectivity is favored based on the electrostatic polarization of the $Ti^{\delta+}=N^{\delta-}$ bond.[27] The resulting metallacycle is protonated by the aniline to yield an enamine, which tautomerizes to the corresponding imine under concomitant regeneration of the active species. In the case of 1–phenyl–1–propyne, the mechanism depicted in Scheme 2(b) could be considered. A reaction of the titanium imido active species with 1–phenyl–1–propyne could induce a 1,3–hydrogen shift, giving rise to the formation of a four-membered metallacycle with an exocyclic C=C bond.[25,28] The ensuing protonation from the intermediate should proceed in a manner similar to that in Scheme 2(a).



**Scheme 2.** A plausible mechanism for the hydroamination of (a) phenylacetylene or 1–hexyne, and (b) 1–phenyl–1–propyne catalyzed by Ti-bis(indolyl) complexes.

In order to assess the validity of the reaction mechanism proposed in Scheme 2(b), the following experiments were performed. When a mixture of **A** and aniline in a 1:1 ratio was heated at 75 ºC, the signals of **A** were weakened, and new signals appeared at $\delta$ 2.46 (s, 6H) and 6.08 (s, 1H) together with the signals of diethylamine. On the other hand, no reaction occurred between **A** and 1–phenyl–1–propyne. These results demonstrate that the **A**-mediated hydroamination of 1–phenyl–1–propyne with aniline initiates from the reaction of **A** and aniline. The new signals could tentatively be assigned to the titanium imido active species. After treating the mixture at 75 ºC for 6 h, 1–phenyl–1–propyne was further added, then the mixed sample was heated at 75 ºC for 1 h. As a result, the signals of the imine product were observed. The observation of the proposed four-membered metallacycle intermediate was failed probably because i) **A** was partially converted into the titanium imido active species by the addition of 1 equiv. of aniline, which remains the unreacted aniline in the reaction mixture, and ii) the remained aniline may react fast with the four-membered metallacycle.

The activities of **1** and **A** were low (10–41% NMR yield) for the hydroamination of phenylacetylene and 1–hexyne (entries 1–4), as well as for the **1**–catalyzed hydroamination of 1-phenyl-1-propyne (18%; entry 5). Surprisingly, the hydroamination of 1–phenyl–1–propyne with **A** proceeded in high yield (95%, entry 6). $Ti(NMe_2)_2(dpma)$ also exhibits a high conversion of 1–phenyl–1–propyne into an imine of phenylacetone (99% GC yield at 75 ºC), albeit that this requires longer reaction times (144 h).[25] The activities of **A** would depend on the reactivities of the tentatively assigned titanium imido species with alkynes. The treatment of the titanium imido species, generated *in situ*, with phenylacetylene gave the unidentified products, which is in contrast to the reaction with 1–phenyl–1–propyne (see above). Although we further examined the **A**-mediated hydroaminations of 1–phenyl–1–propyne with cyclohexylamine or tert-butylamine, low activity for cyclohexylamine (10%) or no activity for tert-butylamine were found in these reaction conditions.

## 4. Conclusion

Herein, we report the coordination chemistry of carbon–bridged bis(indolyl) ligands toward a titanium center. A crystallographic analysis revealed that in such complexes, one of the amido nitrogen atoms of one indolyl group is pyramidalized. Complexes **1** and **A** also act as catalysts for the intermolecular hydroamination of alkynes. Both complexes yield the Markovnikov products when using phenylacetylene or 1–hexyne as alkynes, while the reaction with 1–phenyl–1–propyne affords an imine of phenylacetone. The high activity of **A** for the hydroamination of 1–phenyl–1–propyne is also remarkable. In addition to the substrate scope of such hydroamination reactions, we currently investigate the structures and catalytic activity of relevant zirconium complexes.

**Acknowledgement**

This work was financially supported by the Foundation for Japanese Chemical Research, the Hatakeyama Culture Foundation, the Aomori Support Center for Industrial Promotion, and the Hirosaki University Grant for Exploratory Research by Young Scientists and Newly-appointed Scientists.

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