ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

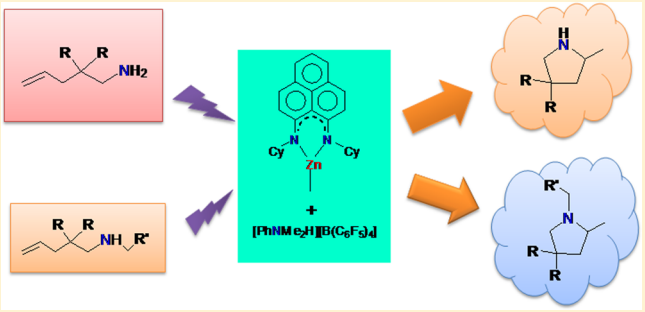
Organozinc Catalyst on a Phenalenyl Scaffold for Intramolecular Hydroamination of Aminoalkenes

Arup Mukherjee, Tamal K. Sen, Pradip Kr. Ghorai, and Swadhin K. Mandal*

Department of Chemical Sciences, Indian Institute of Science Education and Research-Kolkata, Mohanpur 741252, Nadia, West Bengal, India

Supporting Information

ABSTRACT: The syntheses and characterization of two organozinc compounds were accomplished by reacting phenalenyl (PLY)-based ligands with $ZnMe_2$. Reactions of [HN(Cy),O-PLY] and [HN(Cy),N(Cy)-PLY] ligands with $ZnMe_2$ led to the formation of the dimeric orange-colored organozinc compound $[N(Cy),O\text{-}PLY\text{-}ZnMe]_2$ (**1**) and red-colored monomeric organozinc compound [N(Cy),N(Cy)-PLY-ZnMe] (**2**) under evolution of methane. Both **1** and **2** were characterized by NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction study. The organozinc compound **2** was tested as a catalyst for intramolecular hydroamination of both unactivated primary and secondary aminoalkenes in the presence of an externally added activator, which generated the zinc-based cation *in situ*. The catalytic result obtained from the present catalyst **2** was compared with the catalysts having similar structure from previous studies. The DFT calculation indicates that the stability of the *in situ* generated cation plays a significant role in the catalytic activity in the hydroamination reaction.



INTRODUCTION

Nitrogen-containing heterocycles, such as amines, enamines, and imines, have attracted significant interest among synthetic and medicinal chemists over the years, since they are the key synthetic intermediates of natural products.[1] Among the several synthetic routes, hydroamination, the catalytic addition of the N−H bond across a C−C multiple bond, is of particular importance.[2] The reaction offers an atom economical pathway for the synthesis of nitrogen-containing molecules in a more environmental friendly way than the conventional reaction pathway. Over the last decades, there have been an enormous number of efforts to develop an efficient catalyst for this demanding transformation including those based on main group elements,[3] rare earth metals,[4] and transition metals.[5,6] In this regard, the most recent trend is the use of low-cost, nontoxic metal based catalysts for carrying out hydroamination catalysis. The hydroamination reaction has been routinely used in the production of many pharmaceutically important and biologically relevant drug molecules and natural products.[7] It is important that the product of the hydroamination catalysis is not contaminated with any toxic metal residue. As a result, the development of hydroamination catalysts based on nontoxic metals such as calcium,[3a−f] magnesium,[3b,f] and zinc[8,9] has been a growing topic in the past few years. In particular, the use of zinc-based catalysts and their performance in the hydroamination reaction have been promising in recent years, which started with the report by Roesky, Blechert, and co-workers on the development of organozinc catalysts based on aminotroponiminate ligands.[8,9a−d,g,h] Thiel and co-workers have recently isolated and crystallographically demonstrated formation of a metal alkyl intermediate in the zinc-mediated intramolecular hydroamination reaction of an aminoalkene.[10]

As part of our ongoing search for hydroamination catalysts,[11] we started using a new class of ligands based on the phenalenyl moiety for carrying out hydroamination catalysis.[12] Phenalenyl is a well-known odd alternant hydrocarbon with high symmetry (D_{3h}), having the ability to exist in three redox states, namely, closed shell cation, open shell neutral radical, and closed shell anion. Haddon and co-workers have earlier used the open shell phenalenyl unit as a building block to prepare organic magnetic semiconductors exhibiting simultaneous bistability in multiple physical channels and the highest room-temperature conductivity among any neutral organic solids.[13] Previous articles by Morita, Takui, and Hicks document the status of phenalenyl-based open shell chemistry.[14] Recently, we started developing the organometallic chemistry using phenalenyl (PLY) ligands leading to the closed shell cationic phenalenyl moiety.[12,15] Very recently, we reported that an organozinc phenalenyl compound bearing the closed shell cationic phenalenyl unit can act as a building block for organometallic spintronics materials.[16] Apart from the organometallic spintronics application of phenalenyl-based compounds, in our recent studies, we have reported the synthesis of a series of ethylzinc and methylaluminum catalysts based on phenalenyl ligands for ring-opening polymerization of ε-caprolactone and *rac*-lactide.[15b,c] Herein,

Received: September 11, 2013
Published: November 11, 2013

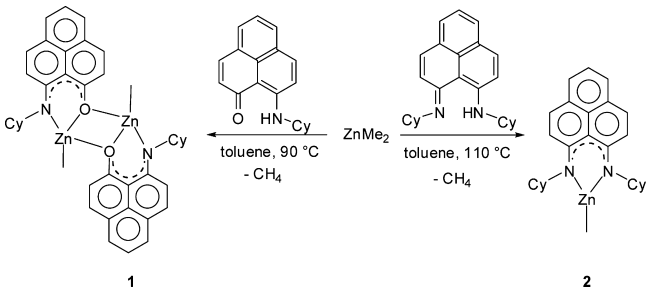
   dx.doi.org/10.1021/om400906u | *Organometallics* 2013, 32, 7213−7224

we report the syntheses and characterization of two organozinc complexes, [N(Cy),O-PLY-ZnMe]$_2$ (**1**) and [N(Cy),N(Cy)-PLY-ZnMe] (**2**), containing a phenalenyl ligand backbone. The catalyst [N(Cy),N(Cy)-PLY-ZnMe] (**2**) was used for hydroamination of unactivated primary and secondary aminoalkenes in the presence of an externally added activator. NMR spectroscopy, kinetic studies, and DFT calculations were employed to understand the activity of this class of catalyst. Although early studies[8,9,12] considered that the coordinatively unsaturated zinc cation acts as catalyst, no study has considered the correlation between the stability of the zinc cation and the outcome of the hydroamination catalysis. In the present study, we have demonstrated that the stability of the *in situ* generated cationic species is responsible for the different rates of hydroamination reaction observed for different catalysts. The catalytic activity can be correlated with the HOMO−LOMO energy gap of the *in situ* generated cationic species, which is an indicator of their stability.

RESULTS AND DISCUSSION

Syntheses of the Organozinc Compounds 1 and 2. The syntheses of [N(Cy),O-PLY-ZnMe]$_2$ (**1**) and [N(Cy),N(Cy)PLY-ZnMe] (**2**) were accomplished by reacting 9-*N*-cyclohexyl-1-oxophenalene, [HN(Cy),O-PLY], and 9-*N*-cyclohexyl-1-*N*′-cyclohexylphenalene, [HN(Cy),N(Cy)-PLY], with $ZnMe_2$ at 90 and 110 °C, respectively (Scheme 1). A solution

Scheme 1. Syntheses of Organozinc Compounds 1 and 2 with Phenalenyl Ligands



of [HN(Cy),O-PLY] or [HN(Cy),N(Cy)-PLY] in toluene was added drop-by-drop to a solution of $ZnMe_2$ in 1:1.2 stoichiometric ratio in toluene at −50 °C and heated at 90 °C for 12 h or at 110 °C for 24 h to yield **1** or **2**. The ^{1}H NMR spectra of both reaction mixtures reveal clean and nearly quantitative conversions of the reactants to products as exhibited by the absence of any characteristic N−H proton resonance (δ 13.5 ppm in [HN(Cy),O-PLY] or δ 14.05 ppm in [HN(Cy),N(Cy)-PLY] in C_6D_6) of the free phenalenyl ligands.

Both **1** and **2** were characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analyses, and single-crystal X-ray diffraction studies. The ^{1}H NMR spectra of **1** in THF-d_8 and **2** in C_6D_6 exhibited a singlet at δ −0.65 and 0.09 ppm, respectively, attributed to the proton resonance arising from the methyl group bound to the zinc ion. The ^{13}C NMR spectra of **1** and **2** revealed a resonance at δ −13.1 ppm in THF-d_8 and −5.1 ppm in C_6D_6, respectively, which are assigned to the Zn-CH_3 carbon resonance.

X-ray Crystal Structures of 1 and 2. Suitable crystals of **1** were obtained from slow cooling of a hot toluene solution at 25 °C, while those of **2** were obtained from a cold toluene solution at 0 °C. Molecular structures of both **1** and **2** were determined unambiguously by single-crystal X-ray diffraction studies (Figure 1). Complexes **1** and **2** were crystallized in the monoclinic space group $P2_1/n$ and $C2/c$, respectively, with one molecule in the asymmetric unit cell in both cases. The X-ray structures of **1** and **2** reveal a distorted tetrahedral and trigonal planar geometry, respectively, around the zinc center. The molecular structure of **1** revealed a dimeric structure with oxygen atoms bridging between two zinc centers, which results in the formation of a nearly flat Zn1−O1−Zn1^i−O1^i four-membered heterocycle. The Zn1−Zn1^i distance is 3.25 Å in **1**, which can be compared with the literature data reported earlier for a similar oxygen-bridged organozinc dimer bearing an aminotroponimate ligand (3.1283(8) Å)[9f] and a phenalenyl ligand (3.1 Å).[15c] The Zn(1)−N bond distances observed in **2** [Zn(1)−N(1), 1.964(2) Å and Zn(1)−N(2), 1.9536(19) Å] are comparable with that of the Zn−N bond distance determined (1.968 Å) in the methylzinc complex of the *N*-cyclohexyl-2-(cyclohexylamino)troponiminate ligand.[9g] The Zn−N bond length observed in **1** [2.0291(19) Å] is longer when compared with that of **2** (av 1.958 Å). The Zn−C bond distances observed in **1** [Zn(1)−C(20), 1.959(2) Å] and **2** [Zn(1)−C(26), 1.966(3) Å] are comparable with that of the Zn−C bond distance observed (1.944 Å) in a previously characterized organozinc complex, *N*-cyclohexyl-2-(cyclohexylamino)troponiminate methylzinc.[9g] The N−Zn−C bond angles in **2** [N(1)−Zn(1)−C(26), 132.89(10)°; N(2)−Zn(1)−C(26), 133.66(10)°] are smaller than the bond angles found in the complex [*N*-isopropyl-2-(isopropylamino)troponiminato]methylzinc (N−Zn−C, 138.5−139.6°), making the N(1)−Zn(1)−N(2) bond angle in **2** [93.37(8)°] wider as compared with that observed in the [*N*-isopropyl-2-(isopropylamino)troponiminato]methylzinc complex (N−Zn−N, 81.94°).[8a]

Catalytic Intramolecular Hydroamination Reactions. Previous studies have demonstrated that organozinc compounds can catalyze the intramolecular hydroamination reaction of aminoalkenes in the presence of a boron-based Lewis acceptor.[8,9,12] Earlier, we have shown that the organozinc compounds developed with the phenalenyl ligands exhibited good to excellent catalytic activity in the case of the intramolecular hydroamination reaction of unactivated primary and secondary aminoalkenes.[12] Previously, Roesky, Blechert, and co-workers have shown that the introduction of the cyclohexyl substituents on the aminotroponiminate ligand enhances the catalytic activity of the resulting organozinc complex dramatically in the case of the intramolecular hydroamination reaction of secondary aminoalkenes.[9g] In this study, the catalytic activity of complex **2**, having two cyclohexyl substituents on the donor phenalenyl unit, was tested for the intramolecular hydroamination reaction of unactivated primary and secondary aminoalkenes.

The study started with the unactivated primary aminoalkenes. First, the intramolecular hydroamination reaction of (1-allylcyclohexyl)methylamine (**3**) with complex **2** was performed in C_6D_6 maintaining the bath temperature at 120 °C without adding any activator. After heating for 24 h, we found <10% of the hydroamination product (**4**) with complex **2**, as revealed by the ^{1}H NMR spectrum of the catalytic reaction mixture. To increase the catalytic activity of complex **2** toward cyclization of primary aminoalkenes, the reaction was carried out with an equimolar amount (with respect to the catalyst) of the activator [$PhNMe_2H$][$B(C_6F_5)_4$], whereupon we found that catalyst **2** afforded 93% conversion after 7.5 h in C_6D_6 maintaining the bath temperature at 120 °C.

dx.doi.org/10.1021/om400906u | *Organometallics* 2013, 32, 7213−7224

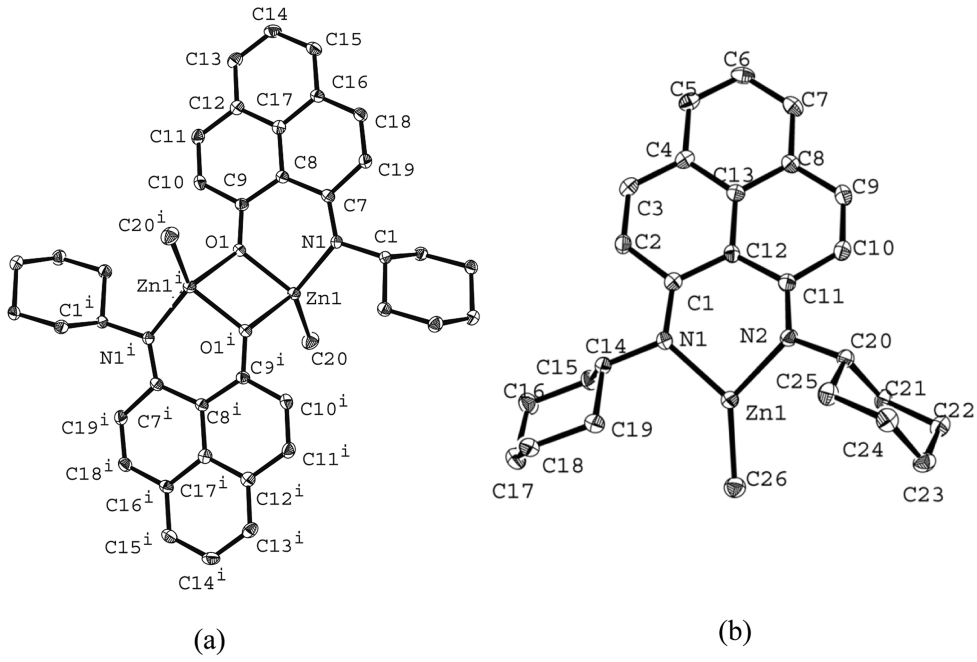


Figure 1. Molecular structures of organozinc complexes (a) **1** and (b) **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg) in (a) **1**: Zn(1)−C(20) 1.959(2), Zn(1)−O(1) 1.9814(16), Zn(1)−N(1) 2.0291(19), O(1)−C(9) 1.311(3); C(20)−Zn(1)−O(1) 130.88(9), C(20)−Zn(1)−N(1) 127.84(10), O(1)−Zn(1)−N(1) 89.87(7), O(1)−Zn(1)−O(1) 77.88(7); and (b) **2**: Zn(1)−N(1) 1.964(2), Zn(1)−N(2) 1.9536(19), Zn(1)−C(26) 1.966(3), N(1)−C(1) 1.347(3), N(2)−C(11) 1.340(3), N(1)−C(14) 1.484(3), N(2)−C(20) 1.481(3); N(1)−Zn(1)−C(26) 132.89(10), N(2)−Zn(1)−C(26) 133.66(10), N(1)−Zn(1)−N(2) 93.37(8), C(1)−N(1)−Zn(1) 123.57(16), C(11)−N(2)−Zn(1) 120.51(16).

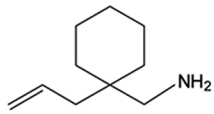
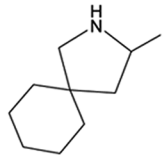
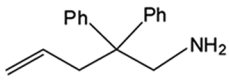
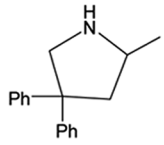
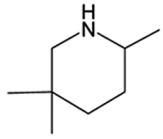
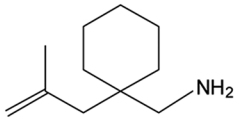
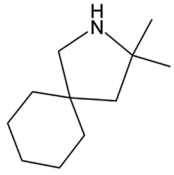
Next, the catalytic efficacy of catalyst **1** was also tested for the hydroamination reaction of substrate **3** in the presence of this activator (Table 1, entry 1). The catalytic result suggests that **1** is not an efficient catalyst (Table 1, entry 1). Thus we proceeded with catalyst **2** for cyclization of various primary aminoalkene substrates, and the results were compared with the activity of two structurally related organozinc-based catalysts, [N(Me),N(Me)-PLY-ZnMe] (**5**) and [N(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**), bearing phenalenyl ligands reported earlier.[12] A careful observation of Table 1 suggests that the catalytic activity of this newly synthesized organozinc complex **2** is much higher as compared to the previously reported phenalenyl-based organozinc complex [N(Me),N(Me)-PLY-ZnMe] (**5**) and comparable or slightly better when compared with organozinc compound [N(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**).[12] Compounds **2**, **5**, and **6** differ from each other in terms of the substituents attached to the donor N-center. Furthermore, examination of the data in Table 1 emphasizes that catalyst **2** cyclizes the primary aminoalkenes at different rates depending upon the substituents at the *β*-position of the aminoalkenes with respect to the amine moiety (Thorpe−Ingold effect). The NMR spectroscopic measurements were used to monitor the progress of the cyclization process of (1-allylcyclohexyl)methylamine (**3**) with catalyst **2** in C_6D_6 maintaining the bath temperature at 120 °C, which revealed a clean conversion of the aminoalkene substrate into the heterocyclic hydroamination product (**4**, Figure 2). Figure 2 reveals that the characteristic resonances of the olefinic protons of the aminoalkene moiety disappear with the gradual progress of the reaction, while those of the hydroamination product evolve with time.

Furthermore, detailed kinetic studies were performed to gain insight into the cyclization process catalyzed by **2** using the primary aminoalkene (1-allylcyclohexyl)methylamine (**3**) in C_6D_6. Kinetic studies of the representative cyclization of **3** to **4** were carried out with catalyst **2** and $[PhNMe_2H][B(C_6F_5)_4]$ in equimolar amounts by ^1H NMR spectroscopic monitoring experiments. The evolution of the specific resonances of the heterocyclic products was monitored by ^1H NMR spectroscopy relative to an internal standard over the course of the first 7 h. To check the order of the cyclization process, the reaction was carried out with 5.92 mM **2** and 118.4 mM **3**. A plot of $\ln(C/C_0)$ versus time provided a straight line with negative slope, as shown in Figure 3a, revealing a pseudo-first-order rate of reaction. To determine the order of the reaction with respect to the catalyst concentration, the cyclization of **3** was carried out with varied concentrations of **2** (from 6.16 to 9.89 mM) keeping the concentration of substrate **3** fixed at 117.5 mM. A plot of k_{obs} versus different catalyst concentrations reveals a linear increase of the reaction rate with catalyst concentration, confirming the first-order dependency of the reaction rate with respect to the catalyst concentration (Figure 3b). This was further confirmed by the van't Hoff plot (Figure 3c).[17] A plot of $\ln k_{obs}$ versus ln[Cat] provided a linear graph (Figure 3c), and the value of the slope was determined to be 1.03 (slope = order of the reaction).[17] The order of the reaction with respect to the substrate concentration was determined by varying the concentrations of **3** (113.8 to 448.6 mM) and keeping the concentration of catalyst **2** fixed at 5.89 mM (Figure 3d). A plot of k_{obs} versus different substrate concentrations indicated a gradual decrease of the reaction rate, revealing the inverse order of the reaction with respect to the substrate concentration. This result complies with the inverse order of intramolecular hydroamination reaction with respect to substrate concentration that was reported previously by Michael and Cochran.[18]

Moreover, we carried out the H/D kinetic isotope effect (KIE) experiment using **3** and **3**-d_2 with 5 mol % of catalyst **2**

dx.doi.org/10.1021/om400906u | *Organometallics* 2013, 32, 7213−7224

Table 1. Intramolecular Hydroamination of Unactivated Primary Aminoalkenes[a]

Entry	Substrate	Product	Catalyst	Time (h)	Conv.(%)[b]
1	 **3**	 **4**	[N(Cy),O–PLY-ZnMe]$_2$ (**1**)	7.5	12[c]
2			[N(Cy),N(Cy)-PLY-ZnMe] (**2**)	7.5	93[c]
3			[N(Me),N(Me)-PLY-ZnMe] (**5**)	8.5	15[12]
4			[N(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**)	8.5	91[12]
5			[N(Cy),N(Cy)-PLY-ZnMe] (**2**)	6.3	98[c]
6			[N(Me),N(Me)-PLY-ZnMe] (**5**)	7.5	12[12]
7			[N(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**)	7.5	98[12]
8			[N(Cy),N(Cy)-PLY-ZnMe] (**2**)	20	96[c]
9			[N(Me),N(Me)-PLY-ZnMe] (**5**)	24	2[12]
10			[N(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**)	24	97[12]
11			[N(Cy),N(Cy)-PLY-ZnMe] (**2**)	90	97[c]
12			[N(Me),N(Me)-PLY-ZnMe] (**5**)	110	14[12]
13			[N(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**)	110	97[12]

[a] Reaction conditions: amine (20 μL), catalyst (5 mol %) and activator, $[PhNMe_2H][B(C_6F_5)_4]$ (5 mol %) in 0.6 mL C_6D_6 by maintaining the reaction bath temperature at 120 °C. [b] Determined by ^{1}H NMR spectroscopy against an internal standard. [c] Present work.

and 5 mol % of $[PhNMe_2H][B(C_6F_5)_4]$ under the same reaction conditions (Scheme 2). The first-order plots of the cyclization of **3** and **3**-d_2 under the reaction conditions result in k_{obs} = 0.341 h^{-1} and k_{obs} = 0.101 h^{-1}, respectively, which translate into a primary KIE of 3.38 (Figure 4). This observation indicates that the amino group of **3** is involved in the key step of the primary aminoalkene activation process, which is reminiscent of our earlier observation, where we reported an alkene

dx.doi.org/10.1021/om400906u | *Organometallics* 2013, 32, 7213−7224

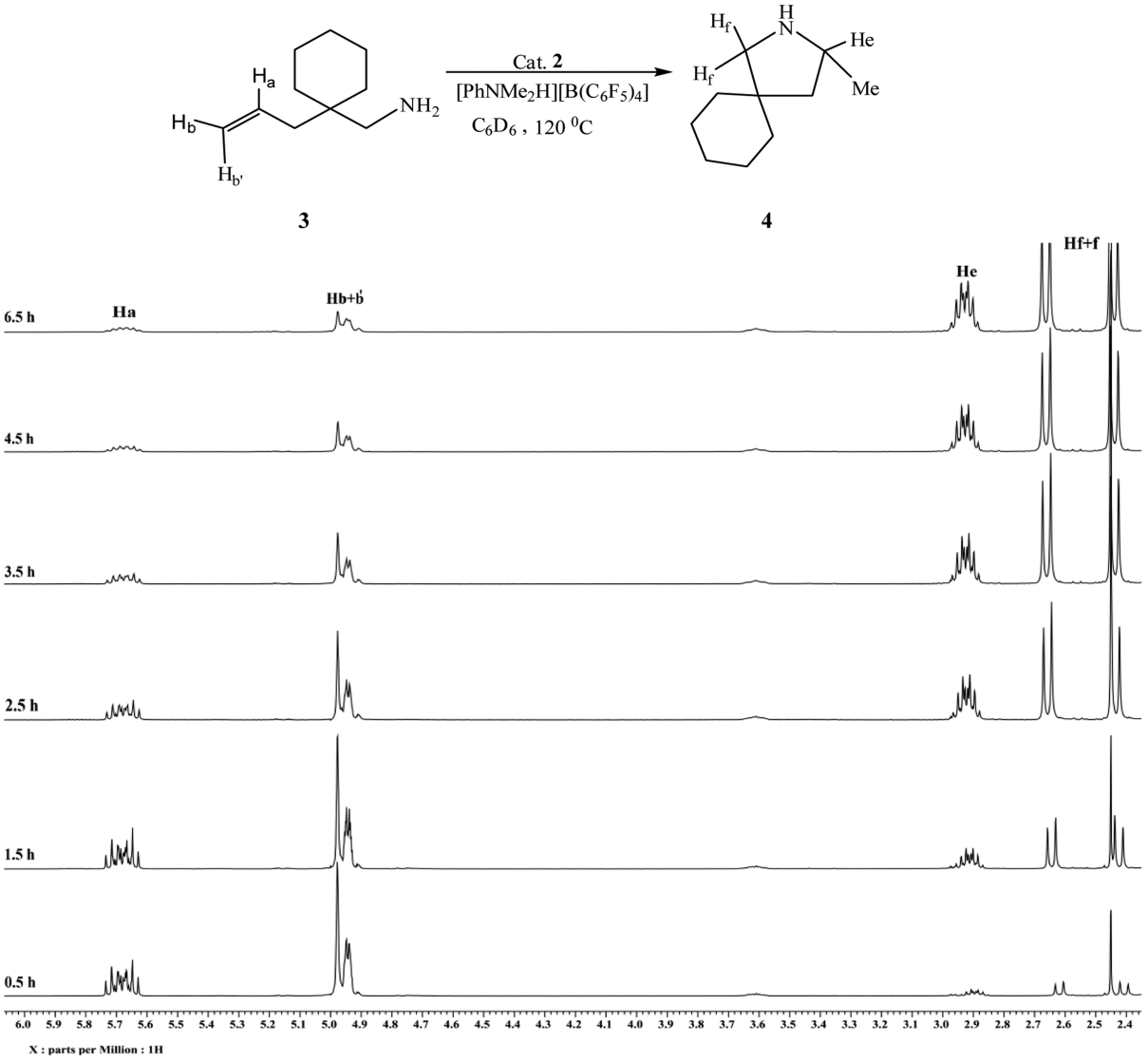


Figure 2. Stack plots of ^{1}H NMR spectrum for the reaction of (1-allylcyclohexyl)methylamine (**3**) with **2** as catalyst at different time intervals.

activation pathway for cyclization of secondary aminoalkenes with an organozinc phenalenyl-based catalyst in which the cleavage of the N−H bond takes part in the slowest step of the mechanistic cycle.[12]

On the basis of the promising reactivity displayed by catalyst **2** toward cyclization of primary aminoalkenes, the activity of **2** in intramolecular hydroamination of unactivated secondary aminoalkenes was checked. To evaluate the generality of the catalytic activity of **2** on secondary aminoalkene substrates, the reaction was investigated with a number of secondary aminoalkenes in the presence of 5 mol % of catalyst under a 5 mol % activator loading at 80 °C in C_6D_6 (Table 2). Inspection of Table 2 suggests that catalyst **2** is tolerable to the different functional groups present in the substrate molecules, and the catalytic activity of **2** is much higher than the activator alone.[19] The secondary aminoalkene substrate bearing a thiophene moiety shows a higher reaction rate than the corresponding aminoalkene with a furan moiety for catalyst **2** (Table 2, entries 11 and 14). This may be attributed to a more effective chelation of the zinc catalysts by the aminofuran. In this case also, we found that the catalytic activity of catalyst **2** is much higher as compared to the previously reported phenalenyl-based organozinc complex [N(Me),N(Me)-PLY-ZnMe] (**5**) and comparable or slightly better when compared with organozinc compound [N(*i*Pr),N-(*i*Pr)-PLY-ZnMe] (**6**).[12]

Trends in Catalytic Activity. Tables 1 and 2 list the comparative reactivity of the present catalyst with that of previously reported catalysts [N(Me),N(Me)-PLY-ZnMe] (**5**) and [N-(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**).[12] A closer look at the catalyst structure reveals that **2** differs from **5** and **6** only in terms of the substituents attached to the donor nitrogen center. The catalytic results presented in Tables 1 and 2 indicate that there is a dramatic difference between the catalytic activity of **5** and that of **2** and **6**, while that of **2** and **6** is appreciably higher than that of **5**. The catalytic activity of **2** is comparable to that of **6** or slightly better. To understand this trend in the catalytic activity, we carried out DFT calculations on the active catalyst generated *in situ* by addition of externally added activator $[PhNMe_2H][B(C_6F_5)_4]$.

Previous studies have demonstrated that addition of $[PhNMe_2H][B(C_6F_5)_4]$ as an activator in the solution of the methylzinc complex generates the coordinatively unsaturated zinc cation *in situ*, which functions as a catalytically active species.[8,9,12] The activator abstracts the methyl group attached

dx.doi.org/10.1021/om400906u | *Organometallics* 2013, 32, 7213−7224

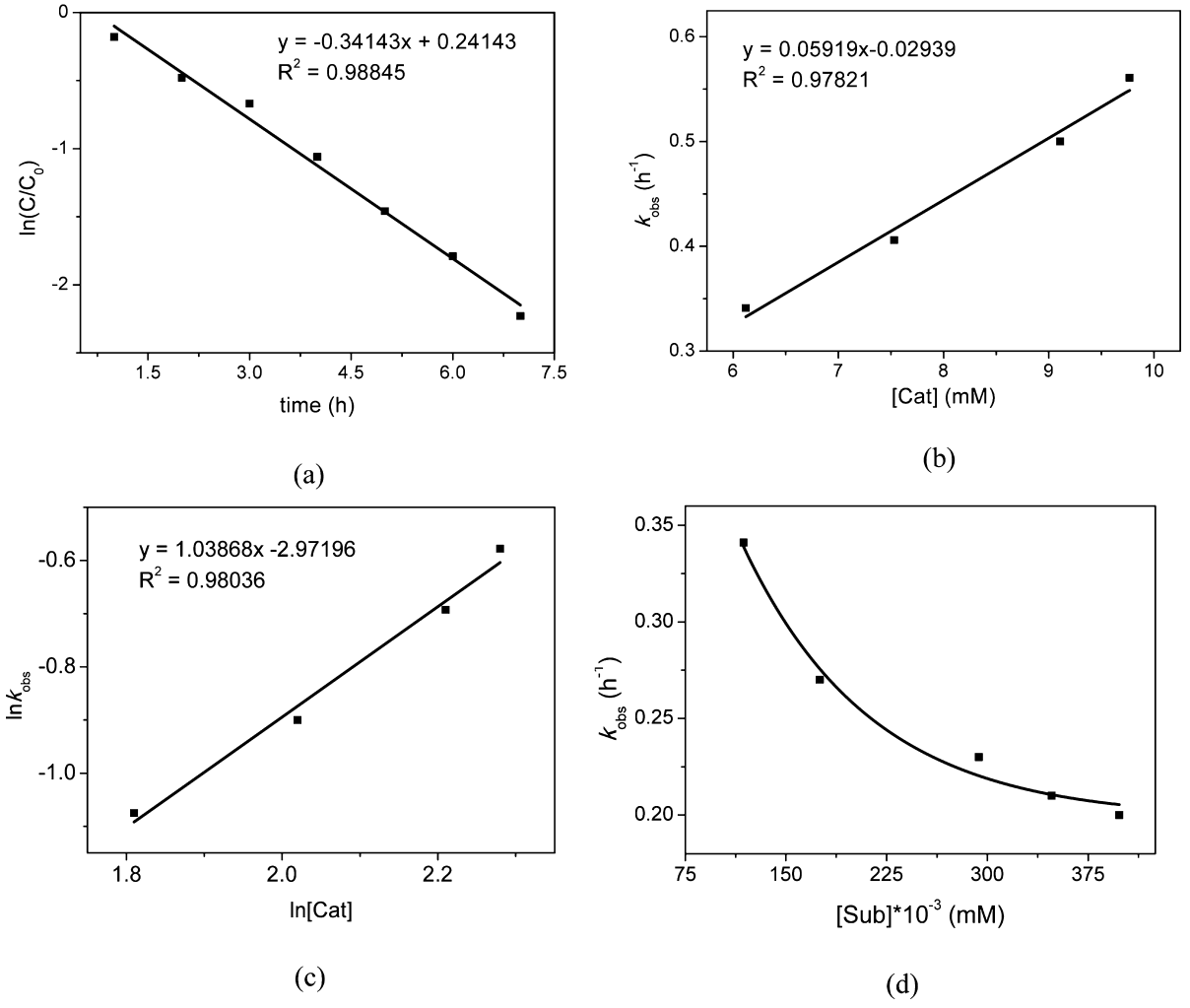
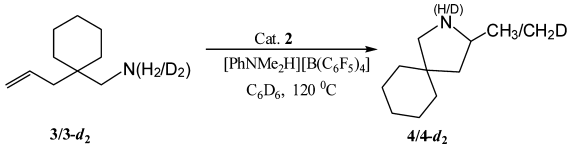


Figure 3. Kinetic studies of primary aminoalkene cyclization process monitored by ^{1}H NMR spectroscopy in C_6D_6: (a) plot of $\ln(C/C_0)$ versus time for the cyclization of **3**; (b) plot of k_{obs} versus [Cat] for the cyclization of **3**; (c) van't Hoff plot of ln k_{obs} versus ln[Cat]; (d) plot of k_{obs} versus [Sub] for the cyclization of **3** using catalyst **2**.

Scheme 2. Cyclization of (1-Allylcyclohexylmethyl)amine (3) and (1-Allylcyclohexylmethyl)amine-d_2 (3-d_2) Using 2 as Catalyst in C_6D_6, Maintaining the Bath Temperature at 120 °C



to the zinc center to generate the zinc cation *in situ*. The ^{1}H NMR experiment in the present work also supports formation of a zinc-centered cation on addition of a stoichiometric amount of activator (Scheme 3). The ^{1}H NMR spectroscopy of the reaction mixture reveals the complete disappearance of the zinc methyl resonance of **2** at δ 0.09 ppm and appearance of two new resonances at δ 0.15 and 2.5 ppm due to the generation of CH_4[20] and $PhNMe_2$, respectively (see Supporting Information Figure S2). This observation confirms the role of the activator as a methyl abstractor and the generation of a zinc cation, which is in accordance with earlier reports.[8b,9g,12]

Furthermore, in order to understand the catalytic activity trend of catalysts **2**, **5**, and **6** in the intramolecular hydroamination reaction of primary and secondary aminoalkenes

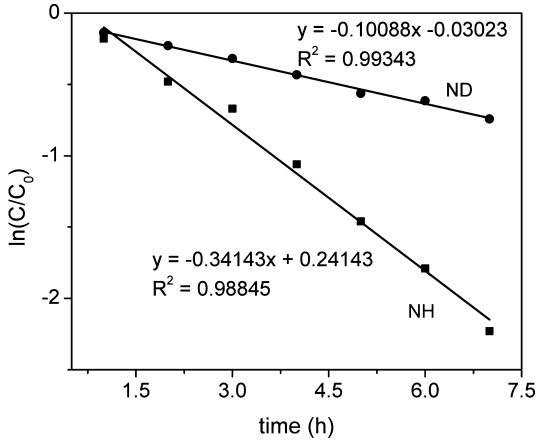
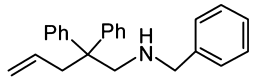
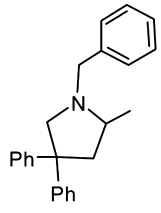
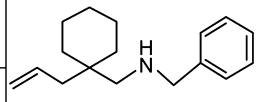
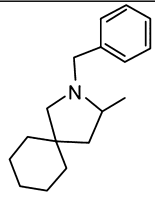
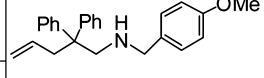
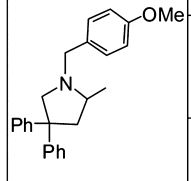
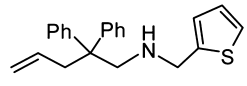
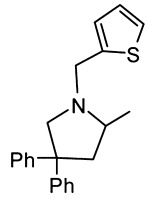
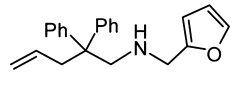
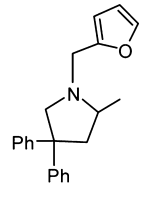


Figure 4. H/D KIE study for the formation of **3** and **3**-d_2 using catalyst **2** in C_6D_6.

(Tables 1 and 2), we carried out a computational study on the active catalyst, zinc-centered cation. In particular, the DFT calculation was utilized to calculate the HUMO−LUMO energy gap of the zinc cation to assess their stability.[21] The computed frontier orbitals (HOMO and LUMO of zinc-centered cation **7**

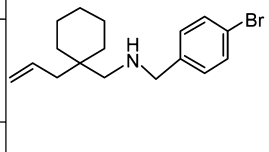
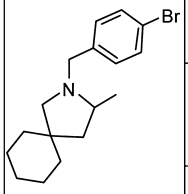
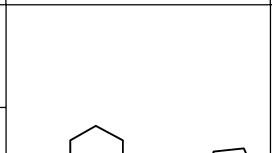
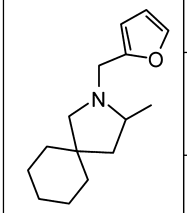
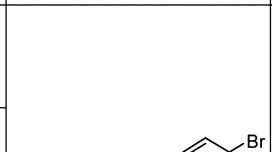
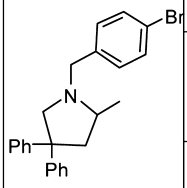
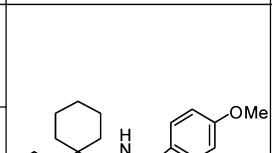
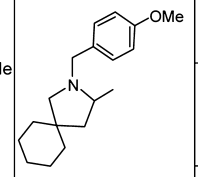
dx.doi.org/10.1021/om400906u | *Organometallics* 2013, 32, 7213−7224

Table 2. Intramolecular Hydroamination of Unactivated Secondary Aminoalkenes[a]

Entry	Substrate	Product	Catalyst	Time (h)	Conv.(%)[b]
1			[N(Cy),O–PLY-ZnMe]$_2$ (**1**)	2.5	15[c]
2			[N(Cy),N(Cy)-PLY-ZnMe] (**2**)	2.5 h	96[c]
3			[N(Me),N(Me)-PLY-ZnMe] (**5**)	4.0	8[12]
4			[N(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**)	4.0	96[12]
5			[N(Cy),N(Cy)-PLY-ZnMe] (**2**)	2.0	97[c]
6			[N(Me),N(Me)-PLY-ZnMe] (**5**)	3.2	9[12]
7			[N(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**)	3.2	98[12]
8			[N(Cy),N(Cy)-PLY-ZnMe] (**2**)	2.0	96[c]
9			[N(Me),N(Me)-PLY-ZnMe] (**5**)	2.5	6[12]
10			[N(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**)	2.5	98[12]
11			[N(Cy),N(Cy)-PLY-ZnMe] (**2**)	0.4	93[c]
12			[N(Me),N(Me)-PLY-ZnMe] (**5**)	0.5	3[12]
13			[N(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**)	0.5	99[12]
14			[N(Cy),N(Cy)-PLY-ZnMe] (**2**)	2.0	96[c]
15			[N(Me),N(Me)-PLY-ZnMe] (**5**)	2.5	5[12]
16			[N(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**)	2.5	99[12]

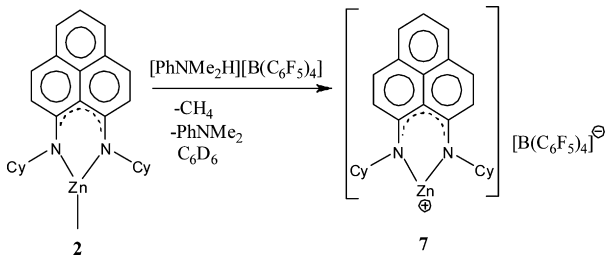
dx.doi.org/10.1021/om400906u | *Organometallics* 2013, 32, 7213−7224

Table 2. continued

Entry	Substrate	Product	Catalyst	Time (h)	Conv.(%)[b]
17			[N(Cy),N(Cy)-PLY-ZnMe] (**2**)	3.0	98[c]
18			[N(Me),N(Me)-PLY-ZnMe] (**5**)	3.5	12[12]
19			[N(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**)	3.5	97[12]
20			[N(Cy),N(Cy)-PLY-ZnMe] (**2**)	1.0	99[c]
21			[N(Me),N(Me)-PLY-ZnMe] (**5**)	1.0	8[12]
22			[N(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**)	1.0	97[12]
23			[N(Cy),N(Cy)-PLY-ZnMe] (**2**)	2.0	97[c]
24			[N(Me),N(Me)-PLY-ZnMe] (**5**)	2.5	5[12]
25			[N(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**)	2.5	99[12]
26			[N(Cy),N(Cy)-PLY-ZnMe] (**2**)	1.5	98[c]
27			[N(Me),N(Me)-PLY-ZnMe] (**5**)	2.5	2[12]
28			[N(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**)	2.5	97[12]

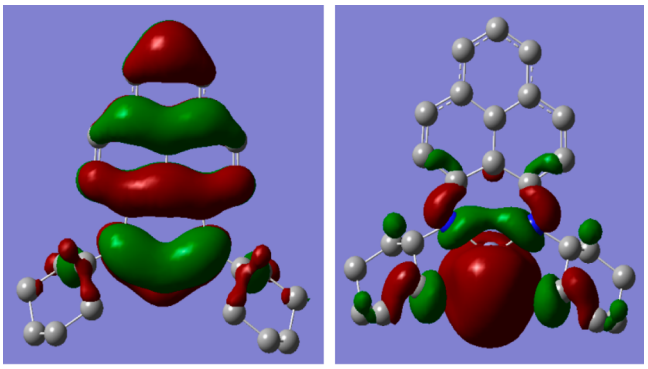
[a]Reaction conditions: amine (20 μL), catalyst (5 mol %), and activator, $[PhNMe_2H][B(C_6F_5)_4]$ (5 mol %), in 0.6 mL of C_6D_6 at 80 °C. [b]Determined by ^1H NMR spectroscopy against an internal standard. [c]Present work.

Scheme 3. Generation of Zinc-Centered Cation 7



generated from **2**) as ascertained by DFT calculations are presented in Figure 5. The LUMO of cation **7** clearly indicates that it is a primarily zinc-centered one. Furthermore, the computed HOMO−LUMO energy gap of the zinc-centered cation **7** is 73.3 kcal/mol. This value is higher as compared to the previously reported value for zinc-centered cation **8** (64.6 kcal/mol), generated from [N(Me),N(Me)-PLY-ZnMe] (**5**), and slightly higher than the zinc-centered cation **9** (70.6 kcal/mol), generated from [N(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**).[12] This reveals comparatively higher stability for the cation **7** over that of **8** and **9**.[12] Figure 6a displays the HOMO−LUMO energy gap calculated in the cations **7**, **8**, and **9**, which indicates the formation of the most stable cation from the present catalyst **2**. Furthermore, the catalytic reactions using substrate (1-allylcyclohexyl)-methylamine (**3**) were performed under identical conditions

dx.doi.org/10.1021/om400906u | *Organometallics* 2013, 32, 7213−7224



(a) (b)

Figure 5. Computed (a) HOMO and (b) LUMO of the zinc-centered cation **7**.

using catalysts [N(Cy),N(Cy)-PLY-ZnMe (**2**), [N(Me),N-(Me)-PLY-ZnMe] (**5**), and [N(*i*Pr),N(*i*Pr)-PLY-ZnMe] (**6**). The catalytic result reveals that the catalyst **2** is the most efficient one. Under identical conditions, catalyst **5** led to only 8% conversion, while the catalysts **2** and **6** led to nearly 87% and 80% conversion, respectively. This catalytic trend can grossly be correlated with the HOMO−LUMO energy gap of the corresponding *in situ* generated cations as reflected from Figure 6b. The cation **7** with highest HOMO−LUMO energy gap results in the best activity, while the cation **8** with the lowest HOMO−LUMO energy gap results in the worst catalytic activity.

To further examine the stability of the catalytically active zinc-centered cation and its longevity in the catalytic cycle, we have investigated the catalytic activity of **2** in the successive catalytic cycles continuously. The cation **7** generated *in situ* from **2** by addition of a stoichiometric amount of activator was used to carry out this experiment. In this case, the longevity of catalyst **2** was monitored by performing several catalytic runs within the same reaction vessel to test whether the catalyst remained live for several catalytic cycles.[22] Five successive catalytic runs were carried out in two different reactions by using 5 mol % of catalyst **2** and an equimolar amount of $[PhNMe_2H][B(C_6F_5)_4]$ with primary aminoalkene substrate **3** in one reaction and with secondary aminoalkene substrate benzyl(2,2-diphenylpentenyl)amine (**10**) in another reaction in C_6D_6 maintaining the bath temperature at 120 and 80 °C, respectively, by *in situ* recycling methodology.[22] The ^{1}H NMR integration was used to calculate the conversion with respect to a known amount of an internal standard (hexamethylbenzene). After full consumption of the substrates, fresh batches of new substrates were added without introducing any additional catalyst. After each 7.5 h (for reaction with primary aminoalkene substrate) and 2.5 h (for reaction with secondary aminoalkene substrate) interval, the conversions into the products were checked by recording ^{1}H NMR spectra of the reaction mixtures. The catalytic runs were repeated for five successive cycles. It was found that **2** remained catalytically active up to five consecutive runs (Figure 7); however, a gradual decrease in the activity was noted by NMR spectroscopy. Nevertheless, this result clearly indicates that the catalytically active species (cation **7** in the present case) remains live for several consecutive runs of the catalytic cycles, indicating good cation stability in the reaction medium.

SUMMARY AND CONCLUSION

The present study reports the development of a nontoxic metal-based hydroamination catalyst containing phenalenyl ligands. Reactions of phenalenyl ligands with $ZnMe_2$ led to the formation of organozinc complexes $[N(Cy),O\text{-}PLY\text{-}ZnMe]_2$ (**1**) and [N(Cy),N(Cy)-PLY-ZnMe] (**2**) under evolution of methane. The solid-state structures of both complexes **1** and **2** were determined by single-crystal X-ray diffraction study. Complex **2** was used as a catalyst for intramolecular hydroamination of unactivated primary and secondary aminoalkenes in the presence of an externally added activator. The activator *in situ* generates the catalytically active cation, and the DFT calculation was employed to understand the stability of the active cation. The performance of the catalyst **2** was further compared with the activity of earlier reported organozinc catalysts bearing phenalenyl-based ligands. The DFT calculation indicated that the stability of the catalytically active zinc-centered cations is primarily responsible for the observed catalytic activity. The more stable cation leads to better catalytic activity in the intramolecular hydroamination reaction of both primary and secondary aminoalkene substrates.

EXPERIMENTAL SECTION

All manipulations were performed under a dry and oxygen-free atmosphere (N_2) using standard Schlenk techniques or inside a

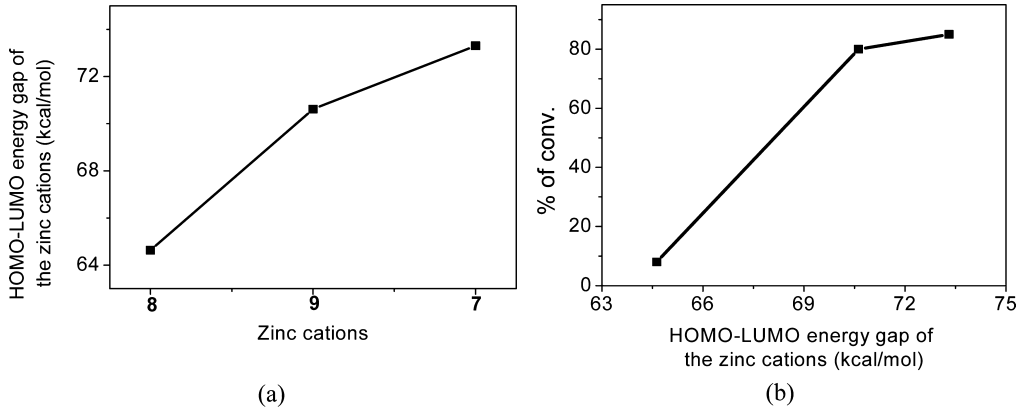


Figure 6. (a) Plot of the computed HOMO and LUMO energy gap of the zinc-centered cations **7**, **8**, and **9** generated from the methylzinc complexes **2**, **5**, and **6**, respectively. (b) Plot of the % of conversion of **3** to the corresponding cyclic product **4** after 6 h with the HOMO−LUMO energy gap of the zinc-centered cations **7**, **8**, and **9** (for the catalytic conditions see Table 1).

dx.doi.org/10.1021/om400906u | *Organometallics* 2013, 32, 7213−7224

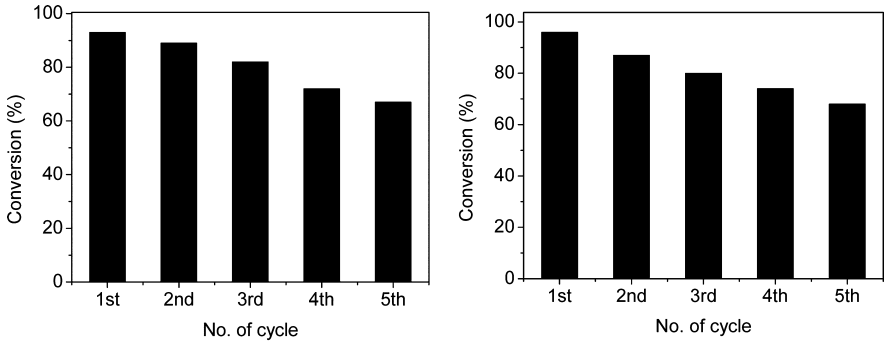


Figure 7. Catalyst longevity test for the cyclization of (a) (1-allylcyclohexyl)methylamine (**3**) with catalyst **2** in C_6D_6 maintaining the reaction bath at 120 °C and (b) benzyl(2,2-diphenyl-4-pentenyl)amine (**10**) with catalyst **2** in C_6D_6 at 80 °C.

nitrogen-filled MBraun glovebox maintained at below 0.1 ppm of O_2 and H_2O level, utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use. All solvents were distilled from Na/benzophenone prior to use. Other chemicals were purchased commercially and used as received. Deuterated benzene was purchased from Cambridge Isotope Laboratories, dried by sodium potassium alloy, and stored over 4 Å molecular sieves prior to use. Dimethyl zinc solution and $[PhNMe_2H][B(C_6F_5)_4]$ were purchased from Acros Organics. ^1H and ^{13}C NMR spectra were recorded with a JEOL-ECS 400 MHz and Bruker Avance 500 MHz spectrometers using C_6D_6 as solvent at 298 K unless otherwise stated. Elemental analyses were performed using a Perkin-Elmer 2400 CHN analyzer. Melting points were measured in sealed glass tubes with a Büchi melting point B 540 instrument. 9-*N*-Cyclohexyl-1-oxophenalene[13b] and 9-*N*-cyclohexyl-1-*N*′-cyclohexylphenalene[15c] were synthesized according to the literature procedures. The aminoalkene substrates 2,2-diphenylpent-4-en-1-amine,[6e] (1-allylcyclohexyl)methylamine,[23] 2,2-dimethylhex-5-enylamine,[4e] 4-methyl-2,2-diphenylpent-4-en-1-amine,[24] 4-methyl-(1-allylcyclohexyl)-methylamine,[24] benzyl(2,2-diphenyl-4-pentenyl)amine,[6e] (4-bromobenzyl)-(2,2-diphenyl-4-pentenyl)amine,[6e] (4-methoxybenzyl)-(2,2-diphenyl-4-pentenyl)amine,[25] (2,2-diphenylpent-4-enyl)furan-2-ylmethylamine,[8b] (2,2-diphenylpent-4-enyl)thiophen-2-ylmethylamine,[8b] (1-allylcyclohexylmethyl)benzylamine,[6e] (1-allylcyclohexylmethyl)-(4-bromobenzyl)amine,[26] 2-Furan-2-ylmethyl-3-methyl-2-aza-spiro[4.5]-decanamine,[9g] (1-allylcyclohexylmethyl)(4-methoxybenzyl)amine,[26] and benzyl(2,2-dimethyl-4-pentenyl)amine[6e] were prepared as reported previously and dried by distilling twice from CaH_2. The hydroamination products are known compounds and were identified by comparison to the literature NMR spectroscopic data.[4e,8b,9g,6e,24−26]

Synthesis of [N(Cy),O-PLY-ZnMe]$_2$ (1). A solution of [HN-(Cy),O-PLY] (0.277 g, 1 mmol) in toluene (20 mL) was added dropwise to a $ZnMe_2$ solution (1.2 M in toluene; 1.0 mL, 1.2 mmol) in toluene (20 mL) at −50 °C. The reaction mixture was slowly warmed to ambient temperature and heated at 90 °C for 12 h. The solution was filtered through a Celite pad under hot conditions and kept at 25 °C. Suitable orange-colored crystals of the title compound were developed from the reaction mixture within 2 h. Yield: 0.220 g (62%). ^1H NMR (THF-d_8, 500 MHz, 298 K): δ 7.79 (4H, d, J = 8.5 Hz, Ar−*H*), 7.69−7.67 (4H, m, Ar−*H*), 7.39 (2H, d, J = 10.0 Hz, Ar−*H*), 7.28 (2H, t, J = 7.5 Hz, Ar−*H*), 7.04 (2H, d, J = 9.0 Hz, Ar−*H*), 3.99−3.95 (2H, m, N−C*H*−$(CH_2)_2$), 1.92−1.72 (14H, m, Cy−*H*), 1.53−1.45 (4H, m, Cy−*H*), 1.31−1.25 (2H, m, Cy−*H*), −0.65 (6H, s, Zn−*Me*) ppm. ^{13}C NMR (THF-d_8, 125 MHz, 298 K): δ 177.2 (Ar), 163.1 (Ar), 138.0 (Ar), 135.9 (Ar), 131.6 (Ar), 130.7 (Ar), 130.2 (Ar), 129.3 (Ar), 126.0 (Ar), 125.9 (Ar), 121.2 (Ar), 119.1 (Ar), 111.3 (Ar), 59.8 (NCH−$(CH_2)_2$), 35.3 (CH_2), 26.4 (CH_2), 25.4 (CH_2), −13.0 (Zn−*Me*) ppm. Melting point: 310−312 °C. Anal. Calcd for $C_{40}H_{42}N_2O_2Zn_2$: C, 67.28; H, 5.89; N, 3.92. Found: C, 67.18; H, 5.79; N, 3.87.

Synthesis of [N(Cy),N(Cy)-PLY-ZnMe] (2). A solution of [HN(Cy),N(Cy)-PLY] (0.358 g, 1.0 mmol) in toluene (25 mL) was added dropwise to the $ZnMe_2$ solution (1.2 M in toluene; 1.0 mL, 1.2 mmol) in toluene (20 mL) at −50 °C. The reaction mixture was slowly warmed to ambient temperature and heated at 110 °C for 24 h. The resulting deep red solution was then passed through an activated Celite pad, concentrated to approximately 10 mL under reduced pressure, and kept at 0 °C. After 1 day, suitable red-colored crystals of the title compound were developed from the reaction mixture. Yield: 0.280 g (64%). ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 7.59 (2H, d, J = 7.3 Hz, Ar−*H*), 7.46 (2H, d, J = 9.1 Hz, Ar−*H*), 7.26 (2H, d, J = 9.8 Hz, Ar−*H*), 7.14 (1H, t, J = 7.3 Hz, Ar−*H*), 3.69−3.71 (2H, m, N−C*H*−$(CH_2)_2$), 1.59−1.92 (12H, m, Cy−*H*), 1.24−1.36 (8H, m, Cy−*H*), 0.09 (3H, s, Zn−*Me*) ppm. ^{13}C NMR (C_6D_6, 100 MHz, 298 K): δ 160.5 (Ar), 135.1 (Ar), 130.1 (Ar), 129.3 (Ar), 125.5 (Ar), 120.2 (Ar), 119.0 (Ar), 108.9 (Ar), 60.3 (NCH−$(CH_2)_2$), 35.8 (CH_2), 26.3 (CH_2), 26.2 (CH_2), −5.1 (Zn−*Me*) ppm. Melting point: 143−144 °C. Anal. Calcd for $C_{26}H_{32}N_2Zn$: C, 71.30; H, 7.36; N, 6.40. Found: C, 71.86; H, 7.41; N, 6.37.

General Procedure for the Intramolecular Hydroamination of Primary Aminoalkenes. All NMR tube scale reactions were performed in a N_2-filled glovebox. A predried NMR tube was charged with a solution of the catalyst (5 mol %), $[PhNMe_2H][B(C_6F_5)_4]$ (5 mol %), and hexamethylbenzene (measured amount used as internal standard) in 0.6 mL of C_6D_6 under a nitrogen atmosphere. Thereafter, the ^1H NMR of the reaction mixture was checked to make sure the abstraction of the Zn−Me protons was complete. Aminoalkene (20 μL) was added to the solution, the NMR tube was sealed, and the reaction mixture was heated in a preheated oil-bath maintained at 120 °C for the stated duration of time. The progress of the reaction was monitored by ^1H NMR spectroscopy. The NMR yields were determined by comparing the integration of the internal standard with a well-resolved signal of the heterocyclic product.

General Procedure for the Intramolecular Hydroamination of Secondary Aminoalkenes. All NMR tube scale reactions were performed in a N_2-filled glovebox. A predried NMR tube was charged with a solution of the catalyst (5 mol %), $[PhNMe_2H][B(C_6F_5)_4]$ (5 mol %), and hexamethylbenzene (measured amount used as internal standard) in 0.6 mL of C_6D_6 under a nitrogen atmosphere. Thereafter, the ^1H NMR of the reaction mixture was checked to make sure the abstraction of the Zn−Me protons was complete. Aminoalkene (20 μL) was added to the solution, the NMR tube was sealed, and the reaction mixture was heated at 80 °C in a preheated oil-bath for the stated duration of time. The progress of the reaction was monitored by ^1H NMR spectroscopy. The NMR yields were determined by comparing the integration of the internal standard with a well-resolved signal of the heterocyclic product.

General Procedure for Kinetic Experiments. All manipulations were performed in a N_2-filled glovebox. Kinetic experiments were performed using NMR techniques on a JEOL-ECS 400 MHz and Bruker Avance 500 MHz spectrometers. A standard solution of catalyst was made by weighing the complex **2** into a vial and adding deuterated solvent. The detailed kinetic experiments were carried out on the

dx.doi.org/10.1021/om400906u | *Organometallics* 2013, 32, 7213−7224

cyclization of **3**. Stock solutions containing substrate **3**, an internal standard (hexamethylbenzene), and activator were prepared by dissolving in deuterated solvent in a similar fashion as described above. The activator, internal standard, and catalyst were added to a predried screw cap NMR tube. Thereafter, the ^{1}H NMR of the reaction mixture was checked to ensure the complete abstraction of the Zn−Me protons. A measured amount of aminoalkene substrate was added to this solution, the NMR tube was sealed and placed at the appropriate temperature, and the progress of the catalysis was monitored by ^{1}H NMR spectroscopy after described time intervals. The concentrations of substrate and product were determined by relative integration to a known concentration of hexamethylbenzene dissolved in deuterated solvent.

Computational Details. Geometry optimizations and vibrational frequency analyses were carried out without any symmetry constraints at the level of density functional theory (DFT) based methods as implemented in the electronic structure program Gaussian 03.[27] We used Beck's three-parameter hybrid exchange functional[28] combined with the Lee−Yang−Parr nonlocal correlation function[29] abbreviated as B3LYP. The split-valence basis set with diffuse functions, namely, 6-311++G, has been employed for all atoms. Vibrational frequencies were calculated for optimized molecular structures to verify that no negative frequencies were present for minimum energy structures.

X-ray Crystallographic Studies. The data of **1** and **2** were collected from a shock-cooled crystal at 100(2) K[30] on a Bruker SMART-APEX II diffractometer with a D8 goniometer equipped with a fine-focus INCOATEC Mo microsource.[31] The data sets of the compounds were integrated with SAINT,[32] and an empirical absorption correction (SADABS) was applied.[33] The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[34] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically at calculated positions using a riding model. CCDC-911744 (**1**) and CCDC-805581 (**2**) 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.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete ref 27, NMR of the stoichiometric reaction mixture, NMR characterization data of the complexes, and X-ray crystallographic details. This information is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: swadhin.mandal@iiserkol.ac.in.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

A.M. and T.K.S. are thankful to IISER-Kolkata and CSIR, India, respectively for research fellowships. S.K.M. thanks SERB (DST), New Delhi, India, for financial support.

■ REFERENCES

(1) O'Hagan, D. *Nat. Prod. Rep.* **2000**, *17*, 435−446.

(2) (a) Müller, T. E.; Hultzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. *Chem. Rev.* **2008**, *108*, 3795−3892. (b) Hartwig, J. F. *Nature* **2008**, *455*, 314−322. (c) Roesky, P. W.; Müller, T. E. *Angew. Chem.* **2003**, *115*, 2812−2814; *Angew. Chem., Int. Ed.* **2003**, *42*, 2708−2710. (d) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673−686. (e) Hultzsch, K. C. *Adv. Synth. Catal.* **2005**, *347*, 367−391. (f) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673−686.

(3) (a) Dunne, J. F.; Fulton, D. B.; Ellern, A.; Sadow, A. D. *J. Am. Chem. Soc.* **2010**, *132*, 17680−17683. (b) Crimmin, M. R.; Arrowsmith, M.; Barrett, A. G. M.; Casely, I. J.; Hill, M. S.; Procopiou, P. A. *J. Am. Chem. Soc.* **2009**, *131*, 9670−9685. (c) Barrett, A. G. M.; Brinkmann, C.; Crimmin, M. R.; Hill, M. S.; Hunt, P.; Procopiou, P. A. *J. Am. Chem. Soc.* **2009**, *131*, 12906−12907. (d) Crimmin, M. R.; Casely, I. J.; Hill, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 2042−2043. (e) Datta, S.; Roesky, P. W. *Organometallics* **2007**, *26*, 4392−4394. (f) Zhang, X.; Emge, T. J.; Hultzsch, K. C. *Angew. Chem.* **2012**, *124*, 406−410; *Angew. Chem., Int. Ed.* **2012**, *51*, 394−398. (g) Brinkmann, C.; Barrett, A. G. M.; Hill, M. S.; Procopiou, P. A. *J. Am. Chem. Soc.* **2012**, *134*, 2193−2207. (h) Koller, J.; Bergman, R. G. *Chem. Commun.* **2010**, *46*, 4577−4579. (i) Khandelwal, M.; Wehmschulte, R. J. *J. Organomet. Chem.* **2012**, *696*, 4179−4183.

(4) (a) Stubbert, B. D.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 6149−6167. (b) Stubbert, B. D.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 4253−4271. (c) Hong, S.; Tian, S.; Metz, M. V.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 14768−14783. (d) Arredondo, V. M.; Tian, S.; McDonald, F. E.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 3633−3639. (e) Gribkov, D. V.; Hultzsch, K. C.; Hampel, F. *J. Am. Chem. Soc.* **2006**, *128*, 3748−3759.

(5) (a) Manna, K.; Xu, S.; Sadow, A. D. *Angew. Chem.* **2011**, *123*, 1905−1908; *Angew. Chem., Int. Ed.* **2011**, *50*, 1865−1868. (b) Wood, M. C.; Leitch, D. C.; Yeung, C. S.; Kozak, J. A.; Schafer, L. L. *Angew. Chem.* **2007**, *119*, 358−362; *Angew. Chem., Int. Ed.* **2007**, *46*, 354−358. (c) Leitch, D. C.; Payne, P. R.; Dunbar, C. R.; Schafer, L. L. *J. Am. Chem. Soc.* **2009**, *131*, 18246−18247. (d) Allan, L. E. N.; Clarkson, G. J.; Fox, D. J.; Gott, A. L.; Scott, P. *J. Am. Chem. Soc.* **2010**, *132*, 15308−15320. (e) Knight, P. D.; Munslow, I.; O'Shaughnessy, P. N.; Scott, P. *Chem. Commun.* **2004**, 894−895. (f) Bexrud, J. A.; Beard, J. D.; Leitch, D. C.; Schafer, L. L. *Org. Lett.* **2005**, *7*, 1959−1962. (g) Payne, P. R.; Bexrud, J. A.; Leitch, D. C.; Schafer, L. L. *J. Am. Chem. Soc.* **2011**, *133*, 15453−15463. (h) Julian, L. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 13813−13822.

(6) (a) Liu, Z.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 1570−1571. (b) Liu, Z.; Yamamichi, H.; Madrahimov, S. T.; Hartwig, J. F. *J. Am. Chem. Soc.* **2011**, *133*, 2772−2782. (c) Hesp, K. D.; Tobisch, S.; Stradiotto, M. *J. Am. Chem. Soc.* **2010**, *132*, 413−426. (d) Cochran, B. M.; Michael, F. E. *J. Am. Chem. Soc.* **2008**, *130*, 2786−2792. (e) Bender, C. F.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 1070−1071. (f) Wang, Z. J.; Benitez, D.; Tkatchouk, E.; Goddard, W. A., III; Toste, F. D. *J. Am. Chem. Soc.* **2010**, *132*, 13064−13071. (g) Nettekoven, U.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 1166−1167. (h) Chong, E.; Qayyum, S.; Schafer, L. L.; Kempe, R. *Organometallics* **2013**, *32*, 1858−1865.

(7) (a) Jiang, T.; Livinghouse, T. *Org. Lett.* **2010**, *12*, 4271−4273. (b) McGrane, P. L.; Livinghouse, T. *J. Am. Chem. Soc.* **1993**, *115*, 11485−11489. (c) McGrane, P. L.; Livinghouse, T. *J. Org. Chem.* **1992**, *57*, 1323−1324. (d) Patil, N. T.; Pahadi, N. K.; Yamamoto, Y. *Tetrahedron Lett.* **2005**, *46*, 2101−2103. (e) Jones, T. H.; Blum, M. S.; Fales, H. M.; Thompson, C. R. *J. Org. Chem.* **1980**, *45*, 4778−4780. (f) Arredondo, V. M.; Tian, S.; McDonald, F. E.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 3633−3639.

(8) (a) Zulys, A.; Dochnahl, M.; Hollmann, D.; Löhnwitz, K.; Herrmann, J.-S.; Roesky, P. W.; Blechert, S. *Angew. Chem.* **2005**, *117*, 7972−7976; *Angew. Chem., Int. Ed.* **2005**, *44*, 7794−7798. (b) Dochnahl, M.; Löhnwitz, K.; Pissarek, J.-W.; Biyikal, M.; Schulz, S. R.; Schön, S.; Meyer, N.; Roesky, P. W.; Blechert, S. *Chem.−Eur. J.* **2007**, *13*, 6654−6666. (c) Dochnahl, M.; Löhnwitz, K.; Lühl, A.; Pissarek, J. W.; Biyikal, M.; Roesky, P. W.; Blechert, S. *Organometallics* **2010**, *29*, 2637−2645. (d) Jenter, J.; Lühl, A.; Roesky, P. W.; Blechert, S. *J. Organomet. Chem.* **2011**, *696*, 406−418. (e) Biyikal, M.; Porta, M.; Roesky, P. W.; Blechert, S. *Adv. Synth. Catal.* **2010**, *352*, 1870−1875. (f) Pews-Davtyan, A.; Beller, M. *Chem. Commun.* **2011**, *47*, 2152−2154. (g) Duncan, C.; Biradar, A. V.; Asefa, T. *ACS Catal.* **2011**, *1*, 736−750. (h) Luehl, A.; Nayek, H. P.; Blechert, S.; Roesky, P. W. *Chem. Commun.* **2011**, *47*, 8280−8282.

(9) (a) Pissarek, J.-W.; Schlesiger, D.; Roesky, P. W.; Blechert, S. *Adv. Synth. Catal.* **2009**, *351*, 2081−2085. (b) Löhnwitz, K.; Molski, M. J.; Lühl, A.; Roesky, P. W.; Dochnahl, M.; Blechert, S. *Eur. J. Inorg. Chem.* **2009**, 1369−1375. (c) Biyikal, M.; Löhnwitz, K.; Meyer, N.; Dochnahl,

M.; Roesky, P. W.; Blechert, S. *Eur. J. Inorg. Chem.* **2010**, 1070−1081. (d) Dochnahl, M.; Löhnwitz, L.; Pissarek, J.-W.; Roesky, P. W.; Blechert, S. *Dalton Trans.* **2008**, 2844−2848. (e) Yin, Y.; Ma, W.; Chai, Z.; Zhao, G. *J. Org. Chem.* **2007**, *72*, 5731−5736. (f) Meyer, N.; Löhnwitz, K.; Zulys, A.; Roesky, P. W.; Dochnahl, M.; Blechert, S. *Organometallics* **2006**, *25*, 3730−3734. (g) Dochnahl, M.; Pissarek, J.-W.; Blechert, S.; Löhnwitz, K.; Roesky, P. W. *Chem. Commun.* **2006**, 3405−3407. (h) Li, T.; Schulz, S.; Roesky, P. W. *Chem. Soc. Rev.* **2012**, *41*, 3759−3771.

(10) Sarish, S. P.; Schaffner, D.; Suna, Y.; Thiel, W. R. *Chem. Commun.* **2013**, *49*, 9672−9674.

(11) (a) Mukherjee, A.; Nembenna, S.; Sen, T. K.; Sarish, S. P.; Ghorai, P. K.; Ott, H.; Stalke, D.; Mandal, S. K.; Roesky, H. W. *Angew. Chem.* **2011**, *123*, 4054−4058; *Angew. Chem., Int. Ed.* **2011**, *50*, 3968−3972. (b) Mukherjee, A.; Sen, T. K.; Mandal, S. K.; Maity, B.; Koley, D. *RSC Adv.* **2013**, *3*, 1255−1264.

(12) Mukherjee, A.; Sen, T. K.; Ghorai, P. K.; Samuel, P. P.; Schulzke, C.; Mandal, S. K. *Chem.—Eur. J.* **2012**, *18*, 10530−10545.

(13) (a) Haddon, R. C. *Nature* **1975**, *256*, 394−396. (b) Itkis, M. E.; Chi, X.; Cordes, A. W.; Haddon, R. C. *Science* **2002**, *296*, 1443−1445. (c) Pal, S. K.; Itkis, M. E.; Tham, F. S.; Reed, R. W.; Oakley, R. T.; Haddon, R. C. *Science* **2005**, *309*, 281−284. (d) Mandal, S. K.; Itkis, M. E.; Chi, X.; Samanta, S.; Lidsky, D.; Reed, R. W.; Oakley, R. T.; Tham, F. S.; Haddon, R. C. *J. Am. Chem. Soc.* **2005**, *127*, 8185−8196. (e) Mandal, S. K.; Samanta, S.; Itkis, M. E.; Jensen, D. W.; Reed, R. W.; Oakley, R. T.; Tham, F. S.; Donnadieu, B.; Haddon, R. C. *J. Am. Chem. Soc.* **2006**, *128*, 1982−1994.

(14) (a) Morita, Y.; Suzuki, S.; Sato, K.; Takui, T. *Nat. Chem.* **2011**, *3*, 197−204. (b) Hicks, R. G. *Nat. Chem.* **2011**, *3*, 189−191.

(15) (a) Mukherjee, A.; Sen, T. K.; Mandal, S. K.; Kratzert, D.; Stalke, D.; Döring, A.; Schulzke, C. *J. Chem. Sci.* **2011**, *123*, 139−144. (b) Sen, T. K.; Mukherjee, A.; Modak, A.; Ghorai, P. K.; Kratzert, D.; Granitzka, M.; Stalke, D.; Mandal, S. K. *Chem.−Eur. J.* **2012**, *18*, 54−58. (c) Sen, T. K.; Mukherjee, A.; Modak, A.; Mandal, S. K.; Koley, D. *Dalton Trans.* **2013**, *42*, 1893−1904. (d) Mukherjee, A.; Sen, T. K.; Ghorai, P. K.; Mandal, S. K. *Sci. Rep.* **2013**, *3*, 2821.

(16) Raman, K. V.; Kamerbeek, A. M.; Mukherjee, A.; Atodiresei, N.; Sen, T. K.; Lazić, Caciuc, P. V.; Michel, R.; Stalke, D.; Mandal, S. K.; Blügel, S.; Münzenberg, M.; Moodera, J. S. *Nature* **2013**, *493*, 509−513.

(17) Seo, S. Y.; Marks, T. J. *Chem.—Eur. J.* **2010**, *16*, 5148−5162.

(18) Cochran, B. M.; Michael, F. E. *J. Am. Chem. Soc.* **2008**, *130*, 2786−2792.

(19) Ackermann, L.; Kaspar, L. T.; Althammer, A. *Org. Biomol. Chem.* **2007**, *5*, 1975−1978.

(20) Koller, J.; Bergman, R. G. *Organometallics* **2010**, *29*, 3350−3356.

(21) (a) Parr, R. G.; Zhou, Z. *Acc. Chem. Res.* **1993**, *26*, 256−258. (b) Burdett, J. K.; Coddens, B. A.; Kulkarni, G. V. *Inorg. Chem.* **1988**, *27*, 3259−3261.

(22) (a) Santra, S.; Ranjan, P.; Ghorai, P. K.; Mandal, S. K. *Inorg. Chim. Acta* **2011**, *372*, 47−52. (b) Sau, S. C.; Santra, S.; Sen, T. K.; Mandal, S. K.; Koley, D. *Chem. Commun.* **2012**, *48*, 555−557. (c) Narayanan, R.; El-Sayed, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 8340−8347.

(23) Horrillo Martínez, P.; Hultzsch, K. C.; Hampel, F. *Chem. Commun.* **2006**, 2221−2223.

(24) Molander, G. A.; Dowdy, E. D. *J. Org. Chem.* **1998**, *63*, 8983−8988.

(25) Hesp, K. D.; Stradiotto, M. *Org. Lett.* **2009**, *11*, 1449−1452.

(26) Bender, C. F.; Hudson, W. B.; Widenhoefer, R. A. *Organometallics* **2008**, *27*, 2356−2358.

(27) Frish, M. J.; Trucks, G. W.; Chlegel, H. B.; et al. *Gaussian 03*; Gaussion, Inc.: Wallingford, CT, 2004.

(28) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(29) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(30) (a) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171−178. (b) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615−619.

(31) Schulz, T.; Meindl, K.; Leusser, D.; Stern, D.; Graf, J.; Michaelsen, C.; Ruf, M.; Sheldrick, G. M.; Stalke, D. *J. Appl. Crystallogr.* **2009**, *42*, 885−891.

(32) *SAINT-NT*; Bruker AXS Inc.: Madison, WI, 2000.

(33) Sheldrick, G. M. *SADABS 2.0*; Universität Göttingen: Göttingen, Germany, 2000.

(34) (a) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473. (b) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112−122.