Dalton Transactions

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ARTICLE

A potential role of substrate as a base for deprotonation pathway in Rh-catalysed C-H amination of heteroArenes: DFT insights

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Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

The possibility of direct introduction of a new functionality through C–H bond activation is an attractive strategy in covalent synthesis. Here, we investigated the mechanism of Rh-catalysed C–H amination of the hetero-aryl substrate (2-phenylpyridine) using phenyl azide as nitrogen source by density functional theory (DFT). For the deprotocyclometallation and protodecyclometallation processes of the title reaction, we propose a stepwise base-assisted mechanism (pathway I) instead of previously reported concerted mechanism (pathway II). In the new mechanism proposed here, 2-phenylpyridine acts as a base in the initial deprotonation step (C–H bond cleavage) and transports the proton towards the final protonation step. In fact, the N–H bond of the strong conjugate acid (formed during initial C–H bond cleavage) considered in pathway I (via **TS4**) is more acidic than the C–H bond of the neutral substrate considered in pathway II (via **TS5**). The higher activation barrier of **TS5** mainly originates from the ring strain of the four membered cyclic transition state. The vital role of base, as disclosed here, can potentially have broader mechanistic implications for the development of reaction conditions of transition metal catalysed reactions.

Introduction

Transition metal-catalysed direct conversion of C–H bonds into C–C, C–O, and C–N bonds has emerged as a powerful method for the construction of functionalized aromatic compounds.^{1–4} Among them, the direct aryl amination reactions have attracted much attention from the synthetic chemistry community because aryl and hetero aryl amines are ubiquitous in a large number of natural products, pharmaceuticals, and functional organic materials.⁵ The use of substrates containing ‘directing groups’ that coordinate to a transition metal catalyst,

followed by proximal C–H bond activation, has become a common strategy to control the site selectivity. In current synthetic methodologies for the construction of C–N bonds, azides have been widely used as convenient aminating reagents in C–H activation protocols.^{6–9} Recently, one of authors developed a process of transition metal-catalysed direct intermolecular C–H amination of arenes and alkenes using various azides as nitrogen sources including sulfonyl, aryl, alkyl, and acyl variants.^{10–12} Different catalytic systems of Rh, Ru, and Ir have also been reported for this versatile reaction.^{12–15}

It is assumed that the α -N atom of the azide approaches the metallacycle intermediate, generating a reactive metal-nitrenoid intermediate that subsequently inserts into the C–metal bond with the liberation of an N₂ molecule. Although transition metal-catalysed C–H activation reactions are likely to occur via the formation of metallacycle intermediate complex, the mechanism leading to its formation may be different depending on the metal catalysts and the reaction conditions employed. For the metallacycle formation that initiated via deprotonation from a C–H bond by a coordinated ligand, Macgregor and co-workers coined the term “ambiphilic metal-ligand assistance” (AMLA)^{16, 17}, whereas Fagnou and co-workers have termed it the “concerted metallation–deprotonation” (CMD) process.^{18–20}

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[†] Electronic supplementary information (ESI) available: [Optimized geometries, and various energy parameters]. See DOI: 10.1039/c000000x/

Scheme 1 C-H amination using azides as nitrogen source.

Herein, the title reaction lacks a deprotonating ligand coordinated to the catalytic system (Scheme 1). However, it has already been reported that a solvent/base can assist proton transfer in several reactions.^{21–24} In this paper, we propose, in an alternative mechanism, the potential involvement of a hetero-aryl substrate as a deprotonating agent in the initial C-H bond activation step, followed by the formation of a strong conjugate acid that delivers a proton in the final protonolysis step.

The catalytic cycle for the Rh-catalysed reaction is concisely shown in Scheme 2. The addition of AgSbF_6 to the RhCp^*Cl_2 complex brings $\text{RhCp}^*(\text{SbF}_6)_2$ as the active species of the catalyst and initiates the reaction. The interaction of a substrate lone pair with the rhodium atom of the catalyst, followed by C-H deprotonation, leads to a rhodacycle. The rhodacycle then interacts with an aryl azide molecule to form an Rh(V)-nitrenoid species complex with simultaneous elimination of nitrogen molecule. In fact, metal-nitrenoid species are known to be generated in such reactions and a few examples of C-N bond formation upon treatment of the corresponding metal-nitrenoid species with hydrocarbons have also been reported.^{25–29} The

Scheme 2. Possible mechanism of C-H amination using phenyl azide as the nitrogen source.

higher oxidation state of rhodium in the Rh-nitrenoid species has been theoretically verified using NBO analysis.³⁰ The imido group attached to the rhodium atom then inserts into the Rh-C bond and forms Rh(III)-amido species, followed by regeneration of the catalyst, together with amine formation, make the catalytic cycle active.

Methodology

The preferred mechanistic pathway is identified by locating the intermediates and transition states at the B3LYP/Gen level using the Gaussian 09 quantum chemistry package, in which Gen stands for the 6-311+G** basis set for all atoms except for Rh and Sb, which are treated with the SDDAll basis set.^{31–33} Energies are further refined by adding Grimme's gCP-D3 correction.^{34,35} Single point solvation energy correction (solvent is 1,2 dichloroethane) is added using the solvation model based on density (SMD).³⁶ The temperature used for obtaining thermodynamic parameters is 358.15 K (consistent with the experiment). Complete details of the calculations are given in the SI. Transition states are characterized by one and only one imaginary frequency pertaining to the desired reaction coordinates and further confirmed by IRC calculations. The discussions are presented on the basis of relative Gibbs energies with respect to infinitely separated reactants unless otherwise specified as shown in Figure 1. We note that, to check the functional and basis set dependence of the results, we also additionally obtained the energy profiles using M06-2X/6-31+G* and M06-2X/6-311+G**. As shown in the Supporting Information, different levels of DFT calculations did not change the conclusions.

It should be noted that metal-catalysed reactions are often associated with variation in the oxidation state of the metal atom as well as of the total charge of intermediates appearing in the reaction, which is neutralized by the counter-ions present in the system. The recently reported explicit use of counter-ions in the non-heme iron catalyst reaction mechanism suggests that it helps to avoid the irregularities associated with self-interaction problem inherent in DFT.^{37–39} Hence, we have also used SbF_6^- ions along with all intermediates and transition states (after extensive site sampling) to get rid of the charge inconsistency associated with the reaction steps as well as to account for the effect of non-bonding interactions induced by the counter ions in the reaction environment.

Results and Discussion

The mechanism can be considered as beginning with the interaction of a nitrogen lone pair of the substrate (2-phenylpyridine or 2pb) with an active catalyst $(\text{Cp}^*)\text{Rh}^{\text{III}}(\text{SbF}_6)_2$

Fig. 1 Gibbs energy profiles for the Rh-catalysed C-H activation reaction. Numerical values are relative Gibbs energy in kcal/mol. Grey solid line indicates pathway II. Geometries of the TSs are given in Fig. 2.

Fig. 2. Optimised geometries of the selected transition states. Distances are given in Å. Colour code: grey—C, blue—N, white—H, yellow—Sb, ivory—F, and red—Rh. Non-critical hydrogen atoms are omitted for clarity. Values in parenthesis are ΔG[‡] in kcal/mol.

to form a weakly bound pre-reacting complex **a**, leading to C-H activation (Fig. 1). A base-assisted deprotonation step (here, the base is 2pb) is modelled for the cyclometallation (rhodacycle formation), in which a second substrate (basic) molecule acts as a base to abstract the proton; this step is similar to the CMD mechanism reported by Fagnou¹⁸⁻²⁰ (or the AMLA mechanism reported by Macgregor^{16, 17}) in which deprotonation occurs from a coordinated ligand (e.g., CH_3COO^-).⁴⁰ The pre-reactant complex **b** ($\Delta G_{\text{rel}} = -0.3$ kcal/mol) undergoes base-assisted deprotocyclometallation with a Gibbs activation energy barrier ($\Delta G^\ddagger$) of 24.8 kcal/mol (via **TS₁**; Fig. 2) to form the intermediate complex **c** ($\Delta G_{\text{rel}} = -0.9$ kcal/mol). Jutand et al. suggested that intermolecular proton abstraction by an acetate ligand for the C-H bond activation of functional arenes by Ru(II) complexes is facilitated either by agostic M(C-H) bond or by the formation of a Wheland intermediate.^{41, 42} To validate this, we have conducted natural bond orbital (NBO) analysis and Bader's atoms in molecules (AIM) analysis of complexes **a**, **b** and **TS₁**.^{43, 44} The possibility of an agostic Rh(C-H) bond is not observed in the above-mentioned complexes. However, the NBO charge analysis of complexes **a** and **b** shows that the carbon atom from which the proton leaves has a more negative charge (-0.29 and -0.30 in complexes **a** and **b** respectively) than other carbon atoms of the same aromatic ring (-0.13 to -0.19) which suggests that complexes **a** and **b** are Wheland type intermediates. Similar charge depletion from the activated carbon is enhanced in the case of **TS₁** (NBO charge is -0.38 at the activated carbon) and this strongly supports the idea that the formation of Wheland type intermediate can facilitate C-H bond activation.

The TS search for the counter ion (SbF_6^-) assisted deprotonative cyclometallation has also been extensively tried but has so far failed. The metal centre of the stable rhodacycle **d** ($\Delta G_{\text{rel}} = -6.7$ kcal/mol) coordinates with the phenyl azide and the resulting intermediate complex **e** has a little higher energy ($\Delta G_{\text{rel}} = 2.1$ kcal/mol). The phenyl addition to the metal centre happens with the simultaneous elimination of the nitrogen molecules via **TS₂** ($\Delta G_{\text{rel}} = 21.0$ kcal/mol). This step demands an activation barrier of 27.7 kcal/mol of Gibbs energy to form a stable nitrenoid intermediate **f** ($\Delta G_{\text{rel}} = -22.3$ kcal/mol). Previous mechanistic study of this type of reaction mechanism has indicated that a concerted insertion of an amido group into the M-C bond, accompanied by N_2 elimination without the formation of metal-nitrenoid intermediate **f**, is less favourable and hence such process is not considered here.³⁰ The Rh-N(imido) bond length is found to decrease from 2.31 Å in complex **e** to 1.90 Å in complex **f**, indicating the formation of a metal-nitrenoid complex. We also observed that in complex **e**, the Hirschfield charge at rhodium centre is 0.22 (NBO charge is 0.18), which increases to 0.29 in complex **f** (NBO charge is

0.24).⁴⁵ The NBO charge analysis also shows that the Wiberg bond index (resembles the number of covalent bonds each atom forms) for Rh is 3.51 in complex **e**, whereas it increases to 4.01 in complex **f**, suggesting a higher oxidation state for rhodium atom (V) in complex **f**. The imido group coordinated to the metal atom in complex **f** then undergoes a migratory insertion (or rearrangement) between the metal centre and the activated phenyl carbon atom via a three-membered cyclic transition state (**TS₃**; $\Delta G^\ddagger = 6.5$ kcal/mol) to form a highly stable Rh (III)-amido species **g** ($\Delta G_{\text{rel}} = -55.6$ kcal/mol). The Wiberg bond index of the rhodium metal atom in intermediate complex **g** is reduced to 3.38, suggesting a lower oxidation state of the metal. The reason for the exothermic migratory insertion of the imido group into the Rh-C bond can be attributed to the reduction in oxidation state of the rhodium metal atom from V in complex **f** to III in complex **g**. Very recently, Zhang et al. isolated Ru-metallacycles corresponding to **d** and **g**, which also support the above reaction sequences.⁴⁶

Li et al. suggested that the proton used for the protonolysis step in the catalytic cycle (catalyst regeneration with product formation) can be provided by an in situ generated H^+ produced in the first stage of the C-H bond cleavage.⁴⁷ Hence, we have considered the abstraction of a proton from the protonated substrate ($2\text{pbH}^+\text{SbF}_6^-$; conjugate acid formed in the initial cyclometallation step) with a simultaneous decomplexation of the product (base-assisted protodemetalation pathway; pathway I) for catalyst regeneration. The association of a protonated base gives rise to an intermediate complex **h** ($\Delta G_{\text{rel}} = -51.1$ kcal/mol), which undergoes a base-assisted protodemetalation via **TS₄** with an activation barrier of 10.5 kcal/mol of energy. Catalyst regeneration seems to be favourable by 1.8 kcal/mol of energy. Overall, the reaction seems to be exergonic by 54.9 kcal/mol of Gibbs energy.

Previous computational studies of the title reaction have suggested a mechanism in which the final protonation of the developing amino group occurs by C-H deprotonation of the second substrate (even though C-H proton of the substrate is less acidic compared to that of any protonated base); there was no indication of deprotonation during the initial rhodacycle formation.^{30, 48, 49} Therefore, we have also modelled this previously reported mechanism (pathway II). We found that the pathway II requires an activation barrier of 34.5 kcal/mol of energy (via **TS₅**) to form the rhodacycle, **d*** and the amino product in a concerted process (**k** is the associated complex of rhodacycle and the product; $\Delta G_{\text{rel}} = -56.7$ kcal/mol). In fact, the C-H proton of the substrate in pathway II is less acidic for protonation of the amido group of complex **g** via decyclometallation, than the N-H proton of the pyridinium ion in pathway I. The higher activation barrier of **TS₅** mainly originates

from the higher strain in the four-membered cyclic transition state than that of **TS**₄ for an intermolecular proton shuttling. The large energy difference between **TS**₄ and **TS**₅ indicates that the reaction prefers to follow pathway I (via **TS**₄; which has a very low energy barrier) as soon as **g** encounters a protonated base (conjugate acid). Moreover, a lower energy barrier of base-assisted deprotonation in the second cycle (via **TS**₁*; $\Delta G^\ddagger = 25.2$ kcal/mol) compared to that of pathway II via **TS**₅ ($\Delta G^\ddagger = 34.5$ kcal/mol) drives the catalyst cycle towards pathway I (Curtin-Hammett principle). Hence, the presence of a base or a basic substrate makes the catalytic cycle following a stepwise base-assisted deprotonation/protonation pathway more feasible.

Conclusions

The role of a hetero-aryl substrate as a base has been considered in the Rh-catalysed C-H amination reaction. A stepwise base-assisted cyclometallation of the C-H bond cleavage and a protonated base-assisted decyclometallation to generate the product is identified as a plausible mechanism of the title reaction. The rate-determining step was calculated to be the formation of a rhodium–nitrenoid intermediate ($\Delta G^\ddagger = 27.7$ kcal/mol) rather than the presupposed C-H activation step, which is in agreement with the earlier conclusion based on the computational and KIE mechanistic studies.³⁰ The crucial role of the basic substrate, as disclosed here, could potentially has broader mechanistic implications for the development of reaction conditions of transition metal-catalysed reactions.

Acknowledgements

This work was supported by the National Research Foundation of Korea Grant (NRF-2015R1A2A1A15055539) funded by Korean Government. The generous support from computation facilities at the KAUST IT and Supercomputing Lab as well as KISTI is also acknowledged.

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Graphical abstract:

DFT studies suggest that basic substrates assist C-H activation step in Rh-catalysed reaction and transport protons towards the protodemetalation step.