

Article

Integrating Organic Lewis Acid and Redox Catalysis: The Phenalenyl Cation in Dual Role

Jasimuddin Ahmed, Soumi Chakraborty, Anex Jose, Sreejyothi P, and Swadhin K. Mandal

J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.8b04786 • Publication Date (Web): 08 Jun 2018

Downloaded from http://pubs.acs.org on June 8, 2018

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Integrating Organic Lewis Acid and Redox Catalysis: The Phenalenyl Cation in Dual Role Jasimuddin Ahmed, Soumi Chakraborty, Anex Jose, Sreejyothi P and Swadhin K. Mandal*

*E-mail: <u>swadhin.mandal@iiserkol.ac.in</u>

Department of Chemical Sciences, Indian Institute of Science Education and Research-Kolkata, Mohanpur-741246, India.

ABSTRACT: In recent years, merging different types of catalysis in a single pot has drawn considerable attention and these catalytic processes have mainly relied upon metals. However, development of a completely metal free approach integrating organic redox and organic Lewis acidic property into a single system has been missing in the current literature. This study establishes that a redox active phenalenyl (PLY) cation can activate one of the substrates by single electron transfer (SET) process while the same can activate the other substrate by a donor–acceptor type interaction using its Lewis acidity. This approach has successfully achieved light and metal-free catalytic C-H functionalization of unactivated arenes at ambient temperature (39 entries; including core moiety of a top-selling molecule boscalid), an economically attractive alternative to the rare metal-based multi-catalysts process. A tandem approach involving trapping of reaction intermediates, spectroscopy along with DFT calculations unravels the dual role of phenalenyl cation.

INTRODUCTION

In recent years, there have been emerging trends in integrating multiple catalysts in one pot. In this way, concepts of "tandem", "merged", "cascade", or "relay" catalysis were introduced.¹⁻⁷ MacMillan and co-workers have reported merging photoredox catalysis with organocatalysis for direct asymmetric alkylation of aldehydes where two different catalysts in a same reaction pot act on two different substrates.⁴ These catalytic combinations frequently exploit Lewis acidity (inorganic Lewis acids, mostly metal based) and/or redox activity (by metal based catalysts) and/or nucleophilicity (predominantly metal-free catalyst). In this regard, development of a completely metal free catalyst integrating such properties into a single metal free system might overcome these shortcomings, however such approach has been missing in the current literature. For example, role of a Lewis acid in a variety of catalytic transformations is well-established and traditionally it takes advantage of various readily available inorganic Lewis acids. The classic Lewis acid AlCl₃ activates the aromatic ring in Friedel-Craft reaction by formation of a charge transfer complex with aromatic π -electron cloud.⁸ On the other hand, redox activity of a typical transition metal based catalyst is the basis of most of the transition metal mediated catalytic processes. Integrating these two important features namely Lewis acidity with redox activity might lead to an unprecedented catalytic outcome. For example, Glorius and co-workers have introduced a pioneering catalytic protocol combining redox active ruthenium catalyst stimulated by light and Lewis acidic gold catalyst where 1-pentene-5-ol reacted with aryldiazonium salt to afford oxyarylated product.⁹ Using the combination of Ru or Ir based photoredox catalyst and Lewis-acidic gold catalyst, a series of organic transformations has been accomplished and the area was reviewed recently.^{10, 11}



Figure 1. (a, b) Summary of past and present work. (c) Molecular drawings of phenalenyl cations (I and II) showcasing that the redox active property originates from their low-lying empty NBMO.

At the same time Yoon has reviewed the topic of photochemical stereocontrolled organic transformations by using tandem photoredox–chiral Lewis acid catalyst.¹² Very recently, Lee and co-workers have utilized this dual Au/Ru catalytic protocol in the arylation of arenes under light stimulation (Figure 1a).¹³ Despite this success, these multicatalytic combinations suffer from the following major drawbacks: a) use of expensive and rare metals, b) chance of catalyst poisoning of one catalyst by another; a common issue with merging two different catalysts in one pot.

To achieve the goal of merging redox catalysis with Lewis acidic catalysis without using expensive and rare metals, we resorted to the phenalenyl cation which is known from entirely different perspective since almost six decades.^{14, 15} The early Hückel calculations^{14, 15} showed that the phenalenyl cation consisting of odd number (13) of carbon atoms has an empty nonbonding molecular orbital (NBMO), which can readily accept electron(s); an observation also revealed experimentally by the cyclic voltammograms (CVs) of the phenalenyl cations I and II (Figure 1c) recently.¹⁶ This property of phenalenvl cation in fact inspired Haddon to pioneer the idea of creating phenalenyl radical based conductors.¹⁷⁻²⁰ The singly populated phenalenyl radicals (generated from phenalenyl cation) heralded a new era in designing organic magnets, conductors, molecular switch, molecules with elusive Resonating Valence Bond (RVB) ground state as postulated by Pauling and Anderson, molecular battery, quantum spin simulators, spin electronic device etc.¹⁹⁻²⁸ During the last two decades, a handful of phenalenyl based radicals were isolated and characterized in solid-state by Haddon^{18-20, 23}, Nakasuzi²⁴⁻²⁵, Takui²¹, Kubo²⁶, Morita²⁹ and co-workers. The relevance of phenalenyl based radicals in catalysis is emerging only in recent years and the topic has been very recently reviewed.³⁰ As the second advantage, by virtue of the same empty NBMO of phenalenyl cation, it can act as an organic Lewis acid. We envisage that the major advantage associated with phenalenyl cation as an organic Lewis acid as

well as redox active catalyst might originate from easy accessibility of its empty NBMO (Figure 1c), which does not compromise the stability of the associated transition state owing to its minimal reorganization energy required in populating the empty NBMO as also proposed by Haddon in different perspective long back.¹⁷

In this work, we have integrated the redox activity of phenalenyl cation along with its organic Lewis acidity. The phenalenyl cation on reduction by a single electron can generate the phenalenyl based radical, which in turn can participate in a single electron transfer process (SET) to activate the aryl diazonium coupling partner into a highly reactive aryl radical. On the other hand, upon the SET process, it produces back the phenalenyl cation which subsequently can act as a Lewis acid to activate the unbiased arene coupling partner just like the classic Lewis acid AlCl₃ in Friedel-Craft reaction by forming a charge transfer complex.⁸ This dual mode of activation through phenalenyl cations (I and II) opens up possibility of an alternative yet very effective strategy for replacing the existing expensive and rare metals based catalytic combination. Herein, we report for the first time, light and metal free C-H arylation of a diverse range of arenes at room temperature resulting in excellent yield *(upto 91%, 39 examples)* using the phenalenyl based cation (Figure 1b).

RESULTS AND DISCUSSION

The phenalenyl based cations **I** and **II** (Figure 1c) were synthesized according to literature method.^{31, 32} The current investigation was started with direct C-H arylation of arenes which has drawn considerable attention in recent years.^{13, 33-36} At first, metallic potassium (K) was considered as the reducing agent and benzene was taken as an electronically unbiased arene to proceed with our reaction optimization study in the presence of 4-chlorophenyl diazonium salt

coupling partner (see ESI, Table S1). Subsequently, an organic electron donor tetrakis(dimethylamino)ethylene (TDAE) was used instead of metal (K) to carry out the same reaction which resulted in the formation of desired product with almost similar efficiency. After optimizing with different combinations (see ESI, Table S1), we found that 2.5 mol % of catalyst I in the presence of 5 mol % of TDAE in DMSO for 12h is the most productive conditions for arylation of benzene (1a) with diazonium coupling partner 2a to afford 73% yield of the biarylated product **3a** at room temperature (ESI, Table S1, entry 4). Two sets of blank reactions were carried out: one is without catalyst, which does not afford biarylated product and another is without TDAE, which affords <5% arylated product (ESI, Table S1, entries 10 and 11). To check the effect of light (if there any), the reaction was also performed under dark condition. This reaction led to 75% yield of **3a**, which clearly discarded the possibility of any light stimulation (ESI, Table S1, entry 12). Before proceeding towards general scope of this protocol using various arene and diazonium coupling partner combinations, our previously reported protocol³⁸ was tested using a neutral phenalenyl ligand PLY(N,O) and KO'Bu. Three different reactions were performed with three arenes (benzene, anisole and nitrobenzene) using the neutral phenalenyl ligand PLY(N,O) and KO^tBu under the same conditions reported earlier³⁷ and these reactions afforded the desired biarylated product only in trace quantity (<5% conversion, see SI, Scheme S1). These unsuccessful reactions clearly demonstrate the advantage of the present catalytic protocol using PLY cation as catalyst over previously reported method³⁸ and validate our current catalytic results.

Next, arylation of benzene (1a) was carried out with five different aryldiazonium salt coupling partners (2a-f) under the optimized metal free catalytic conditions (ESI, Table S1, entry 4), which resulted in 49-82% yield of corresponding biarylated products (3a-f, Scheme 1).

Moderate to excellent yields (58-82%) of para, ortho, meta-functionalized biarylated products (4a-f) were observed when toluene (1b) was used as the arene partner. Further, this protocol was utilized in ortho-selective (other regioisomers were formed in less than 5% yield) arylation of anisole (1c) with different aryldiazonium salt coupling partners (2a-d, 2g), resulting in good to excellent yield (64-91%) of the C2 arylated products of anisole (5a-d, 5g). Successful arylation of these two arenes (toluene and anisole) at ambient conditions shows efficiency of our catalytic protocol for electron rich aromatic systems. Additionally, we started investigating the applicability of this protocol towards electron deficient aromatic systems such as nitrobenzene or benzonitrile. Arylation of nitrobenzene (1d) resulted in moderate to excellent yield (43-91%) of biarylated products (6b, 6e-g) of nitrobenzene at preferably ortho-position (Scheme 1). Subsequently, chlorobenzene (1e) was taken as the arene partner for arylation under metal free conditions at room temperature. Biarylated products of chlorobenzene (7b, 7f) were obtained as the mixture of ortho and para arylated products with 82% and 63% overall yield, respectively. Whereas benzonitrile (1f) shows an ortho selectivity in this arylation process with less than 10%other regio-isomers, affording biarylated products 8a, 8f-g with 50-64% yields. Additionally, the preparation of a biologically active biarylated product was carried out by arylation of methylbenzoate (1g) under metal free catalytic protocol at room temperature.



Scheme 1. Aromatic C-H arylation of different arenes (1) at room temperature with various diazo coupling partners. ^[a] [a] Reaction conditions: 1a-b (2.4 mmol)/1c-i (1.2 mmol), 2a (0.24 mmol), catalyst (0.006 mmol), solvent (1 mL), rt = room temperature. [b] With lower equivalent of arenes and potassium as electron donor. [c] With 3 equiv. (0.72 mmol) arene. [d] NMR conversion.

Ortho-position selective arylation of methylbenzoate was accomplished (Scheme 1) with four different aryl diazonium salts (2c, d, f, g), which resulted in 53-76% yield of biarylated products (9c, d, f, g). Almost similar yield was obtained when 3 equivalent of methyl benzoate was taken (Scheme 1). Next, these reactions were carried out with 1, 3, 5 substituted benzene with different aryldiazonium salt coupling partners. When mesitylene (1h) was the coupling partner, 84-65% yield of the arylated products (10a-f) was obtained and earlier similar yield with meitylene was achieved using Ru/Au dual photoredox catalysts (Scheme 1).¹³ Arylation of 1, 3, 5-trimethoxy benzene shows a good reactivity towards the arylation with different arydiazonium salt coupling partners (2a, b) to afford 84 and 89% yield of arylated products 11a and 11b, respectively. However, this shows poor reactivity towards any attion with coupling partners 2d, **2f-h** affording 28-50% yield of arylated products **11d**, **11f-h** (Scheme 1). An alternative strategy of this arylation protocol using an inorganic reducing agent (metallic potassium) for toluene (1a, 5 equiv.), nitrobenezene (1d, 3 equiv.), mesitylene (1h, 3 equiv.) and 1, 3, 5 trimethoxybenzne (1i, 2 equiv.) successfully resulted in similar yield of the arylated products. This study further revalidate underlying concept of this protocol (Scheme 1). It may be noted that the product 6a is the core part of a very important fungicide boscalid (marketed by BASF with over 150 million euro turnover per year³⁸), has been prepared by the arylation of nitrobenzene with 4-chloro aryldiazonium salt coupling partner in 84% yield, and there has been no report of such metal free catalytic reaction at room temperature, which promises cost-effective preparation of a high value product such as boscalid.

Keeping this elegant catalytic protocol in hand, the mechanistic investigation of this reaction was initiated. When this reaction was carried out in the presence of higher equivalence

of a radical scavenger 2.2.6.6-tetramethylpiperidinoxyl (TEMPO) the reaction was almost completely arrested (Scheme 2a). This experiment indicates a radical mediated mechanistic path.³⁹ Additionally, we have been able to trap the arvl radical formed from the arvl diazo coupling partner by TEMPO to unequivocally establish the involvement of the aryl radical as an intermediate (Scheme 2b). The trapped product was characterised by spectroscopy (¹H and ¹³C NMR) and matched the data with the earlier report.³⁹ Furthermore, an EPR spectrum of catalyst I has been recorded before and after the addition of TDAE. This EPR experimental result clearly indicates that catalyst I (PLY cation) is EPR silent before addition of TDAE and upon TDAE addition, it undergoes a sharp colour change from orange to deep green resulting in an EPR active compound (g = 2.002), which suggests formation of a phenalenvl based radical³⁷ by taking an electron from the organic reducing agent TDAE (Scheme 2c). Such electron transfer capability of TDAE to cationic phenalenyl generating phenalenyl based radical compound is well-established in literature.⁴⁰ All these experiments (Scheme 2) confirm the formation of a phenalenyl based radical. Next we became curious to explore the insight of the activation process of electronically unbiased arenes by the present phenalenyl cations. It was envisaged that the phenalenyl cation as an organic Lewis acid,¹⁶ can form a donor-acceptor type complex on interaction with the aromatic π -electron cloud of the arenes. This type of interaction between aromatic π -electron donor and acceptor molecule bearing NDI (naphthalene diimide) containing moieties has been reported previously⁴¹⁻⁴³ and effect of molecules having varied electron donating capacity has been investigated by estimating quenching of absorbance as well as fluorescence.⁴³ This area of catalyst designing by non-covalent π -interaction has been reviewed recently by Sigman, Toste and co-workers.⁴⁴ Herein, to understand the π -electronic displacement



Scheme 2. Mechanistic investigation: (a) Reaction inhibition on benzene arylation by TEMPO.(b) Trapping of reaction intermediate by TEMPO, (c) A schematic representation of phenalenyl radical generation by electron transfer from TDAE in DMSO and the EPR spectrum of radical species A

This study was carried out with strongly luminescent phenalenyl cation **II**. At first, 2.5 mL of 18 μ M solution of **II** in acetonitrile was subjected for absorbance and fluorescence measurements. Next, maintaining the same concentration of II in 2.45 mL of acetonitrile, 50 µL of different arenes were added. UV-vis spectroscopy revealed a clear quenching in absorbance of phenalenyl cation II (Figure 2a). Further, it unambiguously establishes that the relative quenching efficiency is higher for stronger electron donating arenes (benzene < toluene < mesitylene). Similar trend in relative quenching was also noted in emission spectra of \mathbf{II} , where luminescence intensity of \mathbf{II} diminished most effectively by mesitylene as compared to toluene and benzene (Figure 2b). This type of quenching in both the UV and emission spectra can be attributed to the π -electronic charge transfer from arene to the NBMO of phenalenyl cation II. CD spectra of the same samples eliminated the possibility of such quenching originating from other effect such as Cotton effect or monochromophoric effect (see ESI, Figure S3). Furthermore, appearance of a new absorption peak near 350 nm in the UV-vis spectra (Figure 2c) can be considered as the signature for such charge transfer from aromatic π to NBMO of phenalenyl cation. From the normalized UV-vis spectra (Figure 2c), it can be clearly observed that this peak (near 350 nm) becomes gradually prominent on moving from benzene to mesitylene. Subsequently, the Time-Correlated Single Photon Counting (TCSPC) measurement displays a steady decrease in fluorescence lifetime of **II** in the presence of arenes. The gradual decrease in life-time of **II** from 2.41 ns (in neat acetonitrile) to 2.31 ns in benzene to 0.53 ns in toluene was noted (Figure 2d). In case of mesitylene, this life-time decreased as low as 0.43 ns (Figure 2d). Furthermore, the ¹H NMR spectrum of II in presence of benzene-d₆ in CD₃CN (relative arene concentration is $\sim 15\%$) shows a clear up-field shift of the proton peak positions when compared with that of free phenalenyl



Figure 2: Spectroscopic measurements. (a) Absorption spectra of phenalenyl cation II in CH_3CN , (b) Emission spectra of phenalenyl cation II with different arenes in CH_3CN , (c) Normalized UV spectra, (d) TCSPC spectra of phenalenyl cation II with different arenes in

CH₃CN, (e) Stack plot of ¹H NMR spectra of phenalenyl cation II in absence and presence of benzene- d_6 in CD₃CN.

cation **II** in acetonitrile-d₃ (Figure 2e). Such ¹H NMR spectra at various concentrations of arene (benzene or toluene or mesitylene) in CD₃CN were also measured. For example, at ~2 % concentration of arene as well as at ~7% concentration of arene in CD₃CN, we have noticed a similar up-field ¹H NMR shift of the PLY(O,O) cation (see SI, Figures S7-S8). Recently, a similar ¹H NMR spectroscopic investigation was carried out to understand π -cation interaction in silylation reaction of heteroarenes.⁴⁵ Further to investigate the intermolecular interaction between the PLY(O,O) cation (catalyst **II**) and arene molecule, Nuclear Overhauser Effect (NOE) experiments were performed. These experiments were carried out with different arenes (50 µL of benzene or toluene or mesitylene) in 600 µL acetontrile-d₃ (see SI, Figures S9-12) and clearly revealed a significant NOE interaction between PLY cation and arene. This result clearly supports a strong intermolecular interaction between PLY cation and arene molecule. Combining all these spectroscopic results, it may be concluded that the aromatic π -electron is transferred from arenes to phenalenyl cation **II** establishing Lewis acidic property of phenalenyl cation.

To further understand the nature of interaction between the phenalenyl cation and arenes, we resorted to DFT calculations. Figure 3a shows the binding energy of such arene-phenalenyl cation complex, intermolecular distance between aromatic planes and Mulliken charge distributions for three complexes studied. In all the cases, the intermolecular distances were calculated (3.26 to 3.17 Å) to be well-below the sum of Van der Waal's radii of carbon atoms



59

Figure 3: a) Optimized geometry of charge transfer complexes between phenalenyl cation **II** and different arenes revealing strong interaction. b) Frontier molecular orbitals of the optimized species.

(3.42 Å). Such distance below the sum of Van der Waal's radii is hallmark of non-classical bonding interaction that has been demonstrated in several phenalenyl based compounds earlier based on experimental findings as well as from theoretical calculations.^{19, 20, 25, 46} It may be interesting to note that, in the present phenalenyl cation-arene complexes, the intermolecular bond distance gradually decreases from 3.26 Å in case of complex with benzene to 3.22 Å (with toluene) to 3.17 Å (with mesitylene). This trend clearly correlates with the relative electron donation ability of benzene to mesitylene forming gradually stronger charge transfer complex with phenalenyl cation. Accordingly, the complex of cation II with mesitylene has the highest binding energy (-11.54 kcal mol⁻¹) followed by toluene- (-9.34 kcal mol⁻¹) and benzene-complex (-7.95 kcal mol⁻¹). Furthermore, Mulliken charge analysis clearly indicated the charge transfer from arene to phenalenyl cation in all these complexes. The extent of charge transfer is maximum for mesitylene-complex and lowest for benzene-complex. All these parameters obtained from calculations corroborate well with the observation noted from our photophysical studies as discussed above (Figure 2). Thus it is evident that the arene acts as donor while phenalenyl cation serves as an acceptor due to its π -acidity. Figure 3b depicts the frontier molecular orbital analysis. In all complexes, HOMO is delocalized on arene and LUMO is delocalized over phenalenyl cation, which is indicative of a charge transfer from arene to phenalenyl cation. Thus, the computational studies clearly indicate that mesitylene forms the strongest charge transfer interaction with phenalenyl cation and binding interaction between the

Page 17 of 26

donor and acceptor within the charge transfer complexes increases gradually in the following order: benzene<toluene<mesitylene. This conclusion correlates very well with the trend observed for quenching of absorbance and luminescence of phenalenyl cation in presence of different arenes. Most electron rich arene among the series namely mesitylene forms complex with maximum charge transfer and thus it results the quenching of the absorbance and luminescence of phenalenyl cation to the highest among the three arenes studied (Figure 2). In addition to this, owing to this donor acceptor type interaction between the phenalenyl cation and arene, the arene develops a net +(ve) charge because of some of its π -electron cloud is drained out. Theoretical studies calculate a net charge of +0.130 on benzene, +0.176 on toulene and +0.212 on mesitylene moieties in these complexes, respectively. This +(ve) charge generated on the arene coupling partners (such as benzene or toluene or mesitylene) on forming a donor-acceptor type complex activates them towards the attack by the in situ generated aryl radical having predominant nucleophilic feature⁴⁷ (see below). Combining all these observations and evidences, we propose a mechanistic cycle (Figure 4a) where the phenalenyl based radical (A) is formed *in situ* by accepting an electron from TDAE. Subsequently, this phenalenyl radical transfers an electron via a SET process to the aryl diazonium coupling partner. To further establish the redox role of PLY radical, the relative rate of electron transfer for the SET process was measured using UV-vis spectrometry at -20 °C. From this study, it was revealed that the electron transfer from TDAE to PLY cation is five times faster $(0.0592 \text{ Sce}^{-1})$ than that of TDAE to diazonium salt $(0.0113 \text{ Sce}^{-1})$. This result indicates that the electron transfer from PLY radical to aryl diazonium partner is more feasible than that of direct electron transfer from TDAE. This SET (SET 1) from the phenalenyl based radical (A) to the aryl diazonium coupling partner produces an aryl radical (III)³⁷ and regenerates the phenalenyl cation (I or II). The generation of anyl radical has been proved by trapping it using TEMPO and



Figure 4. a) Proposed reaction mechanism, b) Schematic presentation of the different single electron transfer process with relative frontier molecular orbital energy calculated by DFT at B3LYP/6-31g+(d) level (E_I: energy of catalyst I and E_{II}: energy of catalyst II).

characterized by NMR spectroscopic measurements. Further, the PLY radical was isolated and reacted it with any diazonium partner to generate the any radical. This any radical was also trapped with TEMPO to establish that the PLY radical is involved in the SET process to generate the aryl radical (see SI, Scheme S2). However, the possibility of direct electron transfer from TDAE to the diazonium salt cannot be completely excluded. Subsequently, this regenerated phenalenyl cation can interact with the other substrate (arene) of this reaction via formation of species IV. Formation of IV is evident from spectroscopic and theoretical studies (vide supra, Figures 2 and 3). The formation of species IV facilitates a π -electron transfer from area (π -bonding orbital) to the non-bonding orbital of phenalenyl cation, which creates a deficiency of electron on the arene carbon centers making it susceptible towards nucleophilic attack by arvl radical formed in situ generating a radical species V. Following this, the species V undergoes another SET process (SET 2) to regenerate the phenalenyl based radical species A and a cationic biaryl species VI. Highly acidic proton of VI is next taken up by BF₄⁻ to form HBF₄ affording the desired biarylated product. In such radical mechanism a chain propagation process will always be there, which has been shown by SET 3 process.³⁹ In such process, the electron transfers from V to aryl diazonium salt coupling partner 2 to produce any radical which subsequently can attack to the activated carbon center of arenes to afford the biaryl coupled product. Further, the electronic structure calculations on species V (with benzene as arene partner and in situ generated phenyl radical from phenyl diazonium salt partner) unraveled the optimized geometry (Figure 4a). Binding energy of species V was found to be -8.72 kcal/mol. The registry of the diarene intermediate by forming a complex with phenalenvl cation in complex V facilitates the SET 2 process where an electron is transferred from diarene intermediate to the LUMO of phenalenyl cation. Thus the phenalenyl radical species A can be regenerated, and the catalytic cycle continues. The frontier molecular orbital (FMO) energy calculations using DFT at B3LYP/6-31g+(d) level authenticates the feasibility of the energy landscape involving various proposed single electron transfer processes involved during the catalysis. The relative FMO energies of the active species involved in these SET processes are presented schematically in Figure 4b.

CONCLUSIONS

In conclusion, for the first time without employing any metals, we have been able to integrate two important features widely used in catalyst design namely redox activity and Lewis acidity within a molecule. The empty NBMO of phenalenyl cation can induce a SET process after it is filled with a single electron by a chemical reductant thus it uses its redox activity to activate one of the coupling partners. On the other hand, the same empty NBMO of the phenalenyl cation plays a key role as a purely organic Lewis acceptor in activating the unbiased arene, which is another coupling partner of this reaction. We have developed a metal free catalytic protocol yet efficient and versatile method as a replacement of expensive metal based catalysis in C-H arylation of arenes at room temperature without any light stimulations.

Methods

All solvents and arenes were distilled from Na/benzophenone or calcium hydride under inert condition prior to use. All chemicals were purchased and used as received. The ¹H and ¹³C {¹H} NMR spectra were recorded on 400 and 500 MHz spectrometers in CDCl₃ with residual undeuterated solvent (CDCl₃, 7.26/77.0) as an internal standard. Chemical shifts (δ) are given in ppm, and *J* values are given in Hz. All chemical shifts were reported in ppm using tetramethylsilane as a reference. Chemical shifts (δ) downfield from the reference standard were

assigned positive values. Open-column chromatography and thin-layer chromatography (TLC) were performed on silica gel (Merck silica gel 100-200 mesh). Evaporation of solvents was performed under reduced pressure using a rotary evaporator.

Reaction procedure for optimization study on C-H arylation of benzene.

Catalyst of required amount was taken with 1 mL DMSO solvent in 25 mL pressure tube, reducing agent of required amount was added to the catalyst solution. Benzene (2.4 mmol) and diazo coupling partner (**2a**, 0.24 mmol) were added to the resulting solution of catalyst inside a nitrogen filled glovebox. The final reaction mixture was allowed to stir for required time at room temperature. After completion of the reaction, product was extracted in 25 mL dichloromethane (DCM) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and crude product was purified by column chromatography on silica gel (100-200 mesh) using hexane/EtOAc mixture to yield the pure desired products.

General procedure for C-H arylation of arenes

Catalyst I/catalyst II (0.006 mmol) was taken with 1 mL DMSO solvent in a 25 mL pressure tube, TDAE (0.012 mmol) was added to the catalyst solution. Arene (1a-b 2.4 mmol/1c-I 1.2 mmol) and diazo coupling partner (2, 0.24 mmol) were added to the resulting solution of catalyst inside a nitrogen filled glovebox. The final reaction mixture was allowed to stir for required time at room temperature. After completion of the reaction, product was extracted in 25 mL dichloromethane (DCM) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and crude product was purified by column chromatography over silica gel (100-200 mesh) using hexane/EtOAc mixture to yield the pure desired products.

ACKNOWLEDGEMENTS

We thank SERB, India (Grant No. SR/S1/IC-25/2012) for financial support. J. A, S. C and A. J thank IISER-Kolkata for fellowship. IISER-Kolkata computation facility. JA thanks Mr Shantanu Pattanayak for his help in measuring rate of electron transfer. Authors thank anonymous reviewers for their constructive suggestions.

ASSOCIATED CONTENT

Supporting Information. Tables, figures and details of the experiments. "This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>."

Competing financial interests

The authors declare no competing financial interests.

References

1. Goldman, A. S.; Roy, A. H.; Huang, Z.; Ahuja, R.; Schinski, W.; Brookhart, M. Science, **2006**, *312*, 257-261.

2. Ye, Y.; Sanford. M. S. J. Am. Chem. Soc. 2012, 134, 9034-9037.

3. Dong, G.; Teo, P.; Wickens, Z. K.; Grubbs, R. H. Science, 2011, 333, 1609-1612.

4. Nicewicz, D. A.; MacMillan, D. W. C. Science, 2008, 322, 77-80.

5. David C.; Fabry, D. C.; Rueping, M. Acc. Chem. Res., 2016, 49, 1969-1979.

6. Morris, S. A.; Wang, J.; Zheng, N. Acc. Chem. Res. 2016, 49, 1957-1968.

1 ว

|) |
|--|
| 4 |
| 4 |
| 5 |
| 6 |
| 7 |
| 8 |
| 9 |
| 10 |
| 11 |
| 12 |
| 12 |
| 13 |
| 14 |
| 15 |
| 16 |
| 17 |
| 18 |
| 19 |
| 20 |
| 21 |
| רב בי |
| 22 |
| 23 |
| 24 |
| 25 |
| 26 |
| 27 |
| 28 |
| 29 |
| 30 |
| 30 21 |
| 51 |
| 32 |
| 33 |
| 34 |
| 35 |
| 36 |
| 37 |
| 38 |
| 30 |
| 10 |
| 40 |
| 4.1 |
| 41 |
| 41 42 |
| 41 42 43 |
| 41 42 43 44 |
| 41 42 43 44 45 |
| 41 42 43 44 45 46 |
| 41 42 43 44 45 46 47 |
| 41 42 43 44 45 46 47 48 |
| 41 42 43 44 45 46 47 48 40 |
| 41 42 43 44 45 46 47 48 49 |
| 41 42 43 44 45 46 47 48 49 50 |
| 41 42 43 44 45 46 47 48 49 50 51 |
| 41 42 43 44 45 46 47 48 49 50 51 52 |
| 41 42 43 44 45 46 47 48 49 50 51 52 53 |
| 41 42 43 44 45 46 47 48 49 50 51 52 53 54 |
| 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 |
| 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 |
| 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 |
| 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 |

7. Corcoran, E. B.; Pirnot, M. T.; Lin, S.; Dreher, S. D.; DiRocco, D. A.; Davies, I. W.; Buchwald, S. L.; MacMillan, D. W. C. *Science* **2016**, *353*, 279-283.

- 8. Tarakeshwar, P.; Lee, J. Y.; Kim, K. S. J. Phys. Chem. A, 1998, 102, 2253-2255.
- 9. Sahoo, B.; Hopkinson, M. N.; Glorius, F. J. Am. Chem. Soc. 2013, 135, 5505-5508.
- 10. Hopkinson, M. N.; Tlahuext-Aca, A.; Glorius, F. Acc. Chem. Res. 2016, 49, 2261-2272.
- 11. 4. Shu, X.-Z.; Zhang, M.; He, Y.; Frei, H.; Toste, F. D. J. Am. Chem. Soc. 2014, 136, 5844-5847.
- 12. Yoon, T. P. Acc. Chem. Res. 2016, 49, 2307–2315.
- 13. Gauchot, V.; Sutherland, D. R.; Lee. A.-L. Chem. Sci. 2017, 8, 2885-2889.
- 14. Reid, D. H. Tetrahedron 1958, 3, 339-352.
- 15. Reid, D. H. Quart. Rev. 1965, 19, 274-302.

16. RahaRoy, S.; Nijamudheen, A.; Pariyar, A.; Ghosh, A.; Vardhanapu, P. K.; Mandal, P. K.;Datta, A.; Mandal. S. K. ACS Catal. 2014, 4, 4307–4319.

- 17. Haddon, R. C. Nature 1975, 256, 394-396.
- 18. Haddon, R. C. Aust. J. Chem. 1975, 28, 2343-2351.
- 19. Itkis, M. E.; Chi, X.; Cordes, A. W.; Haddon, R. C. Science 2002, 296, 1443-1445.

20. Pal, S. K.; Itkis, M. E.; Tham, F. S.; Reed, R. W.; Oakley, R. T.; Haddon R. C. Science 2005, 309, 281–284.

21. Morita, Y.; Nishida, S.; Murata, T.; Moriguchi, M.; Ueda, A.; Satoh, M.; Arifuku, K.; Sato,
K.; Takui, T. *Nat. Mater.* 2011, *10*, 947-951.

23

- 22. Raman, K. V.; Kamerbeek, A. M.; Mukherjee, A.; Atodiresei, N.; Sen, T. K.; Lazic, P.;
- Caciuc, V.; Michel, R.; Stalke, D.; Mandal, S. K.; Blugel, S.; Munzenberg, M.; Moodera, J. S. *Nature* **2013**, *493*, 509–513.
- 23. Koutentis, P. A.; Chen, Y.; Cao, Y.; Best, T. P.; Itkis, M. E.; Beer, L.; Oakley, R.T.; Cordes,
- A. W.; Brock, C. P.; Haddon, R. C. J. Am. Chem. Soc. 2001, 123, 3864-3871.
- 24. Ueda, A.; Suzuki, S.; Yoshida, K.; Fukui, K.; Sato, K.; Takui, T.; Nakasuji, K.; Morita, Y. *Angew. Chem. Int. Ed.* **2013**, *52*, 4795–4799.
- 25. Goto, K.; Kubo, T.; Yamamoto, K.; Nakasuji, K.; Sato, K.; Shiomi, D.; Takui, T.; Kubota,
- M.; Kobayashi, T.; Yakusi, K. J. Am. Chem. Soc. 1999, 121, 1619-1620.
- 26. Uchida, K.; Mou, Z.; Kertesz, M.; Kubo, T. J. Am. Chem. Soc. 2016, 138, 4665-4672.
- 27. Morita, Y.; Suzuki, S.; Sato, K.; Takui, T. Nat. Chem. 2011, 3, 197–204.
- 28. Hicks, R. G. Nat. Chem. 2011, 3, 189-191.
- 29. Ikabata, Y.; Wang, Q.; Yoshikawa, T.; Ueda, A.; Murata, T.; Kariyazono, K.; Moriguchi, M.;
- Okamoto, H.; Morita, Y.; Nakai, H. npj Quantum Materials 2017, 2, 27 (page no. 1-7).
- 30. Mukherjee, A.; Sau, S. C.; Mandal, S. K. Acc. Chem. Res. 2017, 50, 1679-1691.
- 31. Franz, K. D.; Martin, R. L. Tetrahedron 1978, 34, 2147-2152.
- 32. Haddon, R. C.; Rayford, R.; Hirani, A. M. J. Org. Chem. 1981, 46, 4587-4588.
- 33. Crisstomo, F. P.; Martin, T.; Carrillo, R. Angew. Chem. Int. Ed. 2014, 53, 2181-2185.
- 34. Shirakawa, E.; Itoh, K.-I.; Higashino, T.; Hayashi, T. J. Am. Chem. Soc. 2010, 132, 15537– 15539.
- 35. Sun, C.-L.; Li, H.; Yu, D.-G.; Yu, M.; Zhou, X.; Lu, X.-Y.; Huang, K.; Zheng, S.-F.; Li, B.-J.; Shi, Z.-J. *Nat. Chem.* 2010, *2*, 1044–1049.

| 2 |
|----------|
| 3 |
| 4 |
| 5 |
| 6 |
| 7 |
| / 0 |
| 8 |
| 9 |
| 10 |
| 11 |
| 12 |
| 13 |
| 14 |
| 15 |
| 16 |
| 17 |
| 18 |
| 10 |
| קו 20 |
| 20 21 |
| 21 |
| 22 |
| 23 |
| 24 |
| 25 |
| 26 |
| 27 |
| 28 |
| 29 |
| 30 |
| 21 |
| 21 |
| 32 |
| 33 |
| 34 |
| 35 |
| 36 |
| 37 |
| 38 |
| 39 |
| 40 |
| 41 |
| רד ⊿ר |
| ד∠ ⊿כ |
| 40 44 |
| 44 |
| 45 |
| 46 |
| 47 |
| 48 |
| 49 |
| 50 |
| 51 |
| 52 |
| 52 |
| 57 |
| 54 55 |
| 55 |
| 56 |
| 57 |
| 58 |
| 59 |
| 60 |

36. Barham, J. P.; Coulthard, G.; Emery, K. J.; Doni, E.; Cumine, F.; Nocera, G.; John, M. P.; Berlouis, L. E. A.; McGuire, T.; Tuttle, T.; Murphy, J. A. *J. Am. Chem. Soc.* **2016**, *138*, 7402–7410.

- 37. Ahmed, J.; Sreejyothi P; Vijaykumar, G.; Jose, A.; Raj, M.; Mandal. S. K. *Chem. Sci.* **2017**, *8*, 7798-7806.
- 38. Gooßen, L. J.; Deng, G.; Levy, L. M. Science 2006, 333, 662-664.

39. Hari, D. P.; Schroll, P.; König, B. J. Am. Chem. Soc. 2012, 134, 2958-2961.

40. 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.

41. Takashima, Y.; Martínez, V.; Furukawa, S.; Kondo, M.; Shimomura, S.; Uehara, H.; Nakahama, M.; Sugimoto, K.; Kitagawa, S. *Nat. Commun.*, **2011**, *2*, 168-175.

42. Kulkarni, C., Periyasamy, G., Balasubramanian, S., George, S. J. *Phys. Chem. Chem. Phys.* 2014, *16*, 14661-14664.

43. Basak, S.; Bhattacharya, S.; Datta, A.; Banerjee, A. Chem. Eur. J. 2014, 20, 5721-5726.

44. Neel, A. J.; Hilton, M. J.; Sigman, M. S.; Toste, F. D. Nature 2017, 543, 637-646.

45. Banerjee, S.; Yang, Y-F.; Jenkins, I. D.; Liang, Y.; Toutov, A. A.; Liu, W-B.; Schuman, D.
P.; Grubbs, R. H.; Stoltz, B. M.; Krenske, E. H.; Houk, K. N.; Zare, R. N. J. Am. Chem. Soc.
2017, 139, 6880–6887.

46. Dreuw, A.; Head-Gordon. M. J. Am. Chem. Soc. 2004, 126, 4007-4016.

47. Vleeschouwer, F. D.; Speybroeck, V. V.; Waroquier, M.; Geerlings, P.; Proft, F. D. *Org. Lett.*, **2007**, *9*, 2721-2724.

TOC GRAPHIC

Integrating Organic Lewis Acid and Redox Catalysis: The Phenalenyl Cation in Dual Role

Jasimuddin Ahmed, Soumi Chakraborty, Anex Jose, Sreejyothi P and Swadhin K. Mandal*

