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Birch Reduction of Aromatic Compounds by Inorganic Electride [Ca₂N]⁺·e⁻ in Alcoholic Solvent; An Analogue of Solvated Electrons

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KEYWORDS : Inorganic Electride, Birch Reduction, Electron Transfer, Solvated Electron

ABSTRACT: Birch reduction of aromatic systems by solvated electrons in alkali metal-ammonia solutions is widely recognized as a key reaction that functionalizes highly stable π -conjugated organic systems. In spite of recent advances in Birch reduction with regards to reducing agent and reaction conditions, there remains an ongoing challenge to develop a simple and efficient Birch reaction under mild conditions. Here, we demonstrate that the inorganic electride $[Ca,N]^+e^$ promotes the Birch reduction of polycyclic aromatic hydrocarbons (PAHs) and naphthalene under alcoholic solvent in the vicinity of room temperature as a solid-type analogy to solvated electrons in alkali metal-ammonia solutions. The anionic electrons from electride [Ca,N]⁺•e⁻ are transferred to PAHs and naphthalene via alcoholysis in a polar co-solvent medium. It is noteworthy that a high conversion yield to the hydrogenated products is ascribed to the extremely high electron transfer efficiency of 98%. This simple protocol utilizing an inorganic electride offers a direct and practical strategy for the reduction of aromatic compounds and provides an outstanding reducing agent for synthetic chemistry.

■ INTRODUCTION

Since the venerated discovery of solvated electrons in alkali metal-ammonia solutions, a variety of organic syntheses and pulse-radiolysis have been widely investigated utilizing the solvated electrons found in diverse solvents such as water and alcohols.^{1,2} Furthermore, the solvated electrons have attracted much attention as a prototype electronic conductor and an intriguing liquid, showing metal-insulator transition and liquid-liquid phase separation.³ In synthetic organic chemistry, the solvated electron, which is the smallest anionic electron and is trapped within surrounding molecules of solvent, is recognized as the most powerful reducing agent that allowed diverse reduction reactions such as Birch and Bouveault-Blanc reactions due to its high redox potential.4,5

From the 1940s, solvated electrons in sodium-ammonia solution have been applied to the reduction of aromatic compounds. In this process, the solvated electrons are transferred to the aromatic rings to form radical anions that are subsequently protonated or hydrogenated.⁶ This is the basic mechanism of the pioneering Birch reduction in synthetic organic chemistry, followed by the application of solvated electron systems (such as alkali metalammonia, -amine and -alcohol solutions) for various reduction reactions.⁷⁻⁹ The reduction of naphthalene is regarded as one of the most representative Birch reductions in organic chemistry.¹⁰ Besides organic synthetic reactions, the Birch reduction is utilized to functionalize materials. For example, a highly hydrogenated graphene was successfully fabricated by reducing graphite oxide or graphite via Birch reduction using sodium-methanol or lithiumethanol solution to impart diverse physical properties to the graphene, such as band gap tuning or ferromagnetism.^{11,12} After the early Birch reduction of naphthalene and benzene, various attempts were made to simplify the reaction procedures and enhance the reduction performance by supplementation with additional reducing agents, proton source additives, photochemical activation, and temperature control.13-21

As widely recognized, there is an urgent need to address the many impediments for practical uses of the Birch reduction.¹⁶ These include extreme reaction conditions (alkali metals induce violent reaction, low temperature: -78 °C), toxicity of reagents, high pressure H₂ gas environment, expensive noble metal catalysts, violent quenching processes, and occurrence of side reactions such as amination due to the nucleophilicity of ammonia.^{6, 17-22} Thus, we are herein proposing that inorganic electride, a solidified crystal of solvated electrons, can ACS Paragon Plus Environment

provide a powerful new reducing agent for simple and mild Birch reduction.²³ It is expected to provide high electron transfer efficiency and environmentally benign processes in universal solvents such as alcohols.

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Electrides are ionic crystals with anionic electrons trapped in the cavity spaces of crystallographic interstitial sites. Similar to solvated electrons, electrides have provided a rich area for theoretical studies of quantum confinement systems and high pressure elements as well as a wide range of applications in synthetic chemistry and electronic devices.²⁴⁻²⁵ The first crystalline organic electride Cs⁺(18-crown-6), •e⁻ was synthesized using solvated electrons of cesium-amine solution as precursors.²⁶ Although the chemical and thermal instability of early organic electrides at room temperature hampered practical room temperature applications, stable organic Na⁺(TriPip222)•e⁻ and inorganic mayenite electrides opened a new epoch in synthetic chemistry.²⁷ In particular, the first room temperature stable inorganic electride $[Ca_{24}Al_{28}O_{64}]^{4+}$ 4e⁻, which has three-dimensionally connected cages, was demonstrated to be a powerful reducing reagent for organic reactions.²⁸⁻³² However, using the electrons trapped in the closed cage structure of $[Ca_{24}Al_{28}O_{64}]^{4+}$ 4e⁻ has several limitations such as insufficient scalability, electron transfer efficiency and yield. In these regards, we have applied newly discovered inorganic two-dimensional (2D) electride $[Ca_2N]^+e^-$ to develop a simple and efficient organic synthetic reaction.

The inorganic electride $[Ca_2N]^+ e^-$ consists of anionic 2D electron gas (2DEG) layer and cationic framework [Ca₂N]⁺ layer. Compared to the closed-cage structure of $[Ca_{24}Al_{28}O_{64}]^{4+}4e^{-}$ (electron concentration 2.33 x 10²¹ cm⁻³), the $[Ca_2N]^+ \cdot e^-$ has an open 2D layer structure and higher electron concentration (1.37 x 10²² cm⁻³). This structural advantage, together with extremely high electron mobility (520 cm^{2} V^{$^{-1}$} s^{$^{-1}$}) and low work function (2.6 eV), allows efficient electron transfer to physically or chemically adsorbed substances.33 Furthermore, diverse organic reactions such as pinacol coupling and trifluoromethylation have been successfully developed utilizing [Ca₂N]⁺•e⁻.^{23, 34-} ³⁶ Here, we report a simple and efficient Birch reduction of PAHs and naphthalene using the electride $[Ca,N]^+ \cdot e^-$ in alcoholic solvents, which is analogous to solvated electrons in alkali-ammonia solutions. The alcoholysis of $[Ca_2N]^+ e^-$ effectively initiates an electron transfer to aromatic substrates, forming radical anions.

RESULTS AND DISCUSSION

Initial investigations into Birch reduction using $[Ca_2N]^* \cdot e^-$ were conducted with anthracene (Table 1). We utilized the hexamethylphosphoramide (HMPA) solvent as an electron transfer media which is known for dissolving alkali metals, generating solvated electrons.³⁷⁻³⁸ First, the reducing reaction of the anthracene was examined in HMPA or co-solvent (HMPA-*i*PrOH) at different reaction temperatures (Table 1, entries 1-4). We observed no reaction using HMPA solvent due to that the $[Ca_2N]^* \cdot e^-$ was hardly decomposed. However, in *i*PrOH solvent, the reaction was preceded by increase of temperatures (

Table 1. Optimization of the reaction conditions for the Birch reduction utilizing $[Ca_2N]^+ \cdot e^-$ electride ^{*a*}



#	Electride Equiv.	Solvent	Time (h)	Temp (°C)	GC Yield (%)
1	1	НМРА	24	rt	N.D.
2	1	HMPA	24	65	N.D.
3	1	HMPA : <i>i</i> PrOH (1:1)	24	rt	N.D.
4	1	HMPA : <i>i</i> PrOH (1:1)	24	65	40
5	1	HMPA : <i>i</i> PrOH (1:1)	48	65	42
6	1.5	HMPA : <i>i</i> PrOH (1:1)	24	65	68
7	1.5	HMPA : <i>i</i> PrOH (1:1)	48	65	71
8	2	HMPA : <i>i</i> PrOH (1:1)	24	65	98 (89) ^b
9	2	HMPA : <i>i</i> PrOH (1:1)	48	65	96
10	2	HMPA : MeOH (1:1)	24	65	93
11	2	Toluene : <i>i</i> PrOH (1:1)	24	65	63
12	3	Toluene : <i>i</i> PrOH (1:1)	24	65	82
13	2	THF : <i>i</i> PrOH (1:1)	24	65	92

^{*a*} General conditions: **1a** (0.5 mmol), $[Ca_2N]^+ e^-$ (0–2 equiv.), Solvent (co-solvent : 2 mL, alcoholic solvent : 2 mL), ^{*b*} Isolated yield

ature. This indicates that the *i*PrOH activates the alcoholysis of the $[Ca_2N]^+ \cdot e^-$ at 65 °C, where the solubility of anthracene in *i*PrOH increases to produce a reduced product. Thus, we used co-solvent system (HMPA:*i*PrOH = 1:1, v/v). Although no reaction occurred at room temperature (3), a distinct reaction was observed at 65 °C. This is ascribed to sufficient decomposition of the $[Ca_2N]^+ \cdot e^-$ via alcoholysis (6) and increased solubility of anthracene. Considering the present results and the reported hydrodehalogenation of organic halides by the $[Ca_2N]^+ \cdot e^-$ in *i*PrOH at room temperature, it is supposed that the reduction potential difference between electride as an electron donor and the reactant as an electron acceptor needs to be controlled by managing reaction conditions such as temperature or acidity of the solvent me

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dia.²³ Therefore, to enhance the alcoholysis of $[Ca_2N]^+ \cdot e^$ for the reduction of anthracene, the solvent temperature was fixed at 65 °C. Although the increase in reaction time is less effective to obtain a higher yield, the higher equivalent of $[Ca_2N]^+ \cdot e^-$ leads to more efficient reaction (6-9). The GC yield of product gradually increased as the equivalents of electride increased, reaching 98%.

Furthermore, we examined the solvent effect by controlling the acidity of the alcoholic solvent and the polarity of the co-solvent (10-13). The increase in the acidity of alcoholic solvent alcohols [pKa; isopropanol (17.1), methanol (15.5)] was not a critical factor 6 and 10. However, when the co-solvent of toluene and *i*PrOH was used, the reaction was hampered, rendering a lower yield (63%) when we used the same 2 equivalent of $[Ca_2N]^+ e^-$ (11). Thus, we optimized the yield by the increase of $[Ca_2N]^+ \cdot e^$ electride equivalents. The yield was increased to 82% when 3 equiv. of $[Ca_3N]^+ \cdot e^-$ electride was used (12). Futhermore, the use of THF and *i*PrOH co-solvent produced a moderately high yield (13). These results indicate that the polarity of solvent media is an important factor for an efficient electron transfer, leading to a high yield of 98%. Thus, it is concluded that the solvation and transfer of anionic electrons was facilitated in the aprotic solvent media. Compared with the Birch reduction by solvated electrons in alkali metal-ammonia solution, it is also notable that the Birch reduction with electride [Ca₂N]⁺•e⁻ occurs smoothly without any side reactions and quenching processes.

29 For the expansion of reaction scope, we applied the cosolvent systems of THF:iPrOH and HMPA:iPrOH. With 30 the established optimal condition $[2 \text{ equiv. of } [Ca_2N]^+ \cdot e^-$, 31 THF: *i*PrOH = 1:1 or HMPA: *i*PrOH = 1:1, v/v), 65 °C], we 32 examined the Birch reduction of various PAHs and two 33 naphthalene derivatives (Table 2) (See the supporting 34 Information). We confirmed the feasibility of the 35 $[Ca_2N]^+ \cdot e^-$ for the Birch reduction with tricyclic aromatic 36 hydrocarbons (2a-2c). The yield for electron-withdrawing 37 group (EWG) (2d) was higher than that for electron-38 donating groups (EDG) (2e-2f). This result is probably 39 attributed to the stabilization of carbanion by the induc-40 tive effect.³⁹ In the case of 9-chloromethylanthracene and 41 9-bromoanthracene (2c-2d), hydrodehalogenation and 42 dearomatization reactions occurred simultaneously. In 43 sequence, we explored the Birch reduction of tetracyclic 44 aromatic hydrocarbons (2g-2h). Two different isomeric 45 neutral tetracyclic aromatic hydrocarbons (tetracene and 46 tetraphene) were well transformed into the partially hy-47 drogenated products with high yields.y 48

On the other hand, it is generally acknowledged that the Birch reduction of naphthalene has been limited due to the instability of naphthalene radical anions. Thus, the Birch reduction of naphthalene could only be induced by a high electron concentration system that is represented by solvated electrons of alkali metal-ammonia solutions. For example, the Birch reduction of naphthalene was conducted with conducted with 2.6 M (2.6 mol L⁻¹) of solvated electrons in sodium-ammonia solution.³ Under

Table 2. Reaction scope of PAHs and naphthalenes
for the Birch reduction utilizing $[Ca_2 N]^{\scriptscriptstyle +} \cdot e^{\scriptscriptstyle -}$ electride a

Substrate	Product	Equiv.	Temp. (°C)	Yield (%)
1a	1a'	2	65	89
2a	2a'	3	65	89
2b	Me 2b'	3	65	86
	Me 2b'	4	65	87
2d	1a'	5	65	84
2e	2e'	5	40	38
		5	65	50
2f 2g	2f' 2g'	4	65	82
2h	2b'	4	65	85
	211 () 2i'	10	65	49
	2i 2j' 2) 10 i'	65	99
	yield = 99%; 21 : 21' : 21' (2k'	4	65	87
	⊘	3	65	68
2m	2k'	3	65	84

^{*a*} General conditions : **1a** (0.5 mmol), $[Ca_2N]^+ \cdot e^-$ (2 equiv.), solvent [THF : 2 mL, *i*PrOH : 2mL, (0.125 M)], 24 h; **2a**, **2b**, **2l**, **2m** (0.5 mmol), $[Ca_2N]^+ \cdot e^-$ (3 equiv.), solvent [THF : 2 mL, *i*PrOH : 2mL, (0.125 M)], 24 h; **2c**, **2g**, **2h**, **2k** (0.5 mmol), $[Ca_2N]^+ \cdot e^-$ (4 equiv.), solvent [THF : 2 mL, *i*PrOH : 2mL, (0.125 M)], 24 h; **2d**, **2e**, **2f** (0.5 mmol), $[Ca_2N]^+ \cdot e^-$ (5 equiv.), solvent [THF : 2 mL, *i*PrOH : 2mL, (0.125 M)], 24 h; **2i**, **2j** (0.5 mmol), $[Ca_2N]^+ \cdot e^-$ (10 equiv.), solvent [HMPA : 2 mL, *i*PrOH : 2mL, (0.125 M)], 24 h. ^{*b*} Determined by NMR spectroscopy.

the optimal condition (**1a**), the Birch reduction of naphthalene derivatives rarely proceeded due to the low electron concentration (0.25 M). To expedite the formation of naphthalene radical anions, we increased the electron concentration from 0.25 M to 1.25 M by adding extra equivalents of electride (**2i-2j**), allowing the reduction of naphthalene and 1-fluoronaphthalene with the yield of 49% and 99%, respectively. In addition, we also examined the Scheme 1. Schematic illustration of a plausible mechanism for the Birch reduction of anthracene by $[Ca_2N]^+ e^-$ electride as the electron transfer agent



Birch-type reduction of alkyne and alkenes (**2k-2m**), also producing corresponding alkanes with a high yield. However, the Birch reductions of both anisole and toluene have not been accomplished under the present optimized condition, requiring a further study for the reductions of monocyclic aromatic hydrocarbons.

To verify the validity of electron transfer via alcoholysis of the $[Ca_2N]^+ e^-$, we carried out experimental mechanisitic studies. The reaction of anthracene was conducted with the existence of radical scavengers under optimized condition to elucidate the radical reaction that facilitates electron transfer from the [Ca₂N]⁺•e⁻ electride via the single electron transfer process. (See the supporting Information) With the presence of radical scavengers such as TEMPO and 1,4-dinitrobenzene, the yields of entry 8 (table 1) was decreased to a level corresponding to the amount of radical scavengers. Also, the alcoholysis of $[Ca,N]^+ \cdot e^-$ electride was proved by the formation of calcium alkoxide and ammonia through the X-ray diffraction and ion chromatography.³² Based on the these results, we propose a plausible mechanism for the present Birch reduction as illustrated in scheme 1. In our process, iPrOH plays vital role of both an activator for anionic electron transfer from [Ca,N]⁺•e⁻ and a hydrogen source for protonation of the reduced anthracene. The iPrOH is responsible for the alcoholysis of [Ca₂N]⁺•e⁻ to produce calcium isopropoxide $(Ca(iPrO)_2)$ and ammonia (NH_2) . The $Ca(iPrO)_2$ and NH₃ was formed by the reaction of 2 $iPrO^$ from *i*PrOH and Ca^{2+} from $[Ca_2N]^+ \cdot e^-$, and reaction of H⁺ from *i*PrOH and N₃ of [Ca₂N]⁺•e⁻, respectively. Consequently, the decomposition of [Ca,N]⁺•e⁻ via alcoholysis released the anionic electrons that are supposed to be solvated in co-solvent media like solvated electrons in alkali metal ammonia solution. Afterward, the released anionic electrons are transferred to anthracene, leading to the formation of radical anions. The radical anions are continuously protonated by proton abstraction from iPrOH. An iterative series of anionic electron transfer, radical anion formation, and protonation completes the Birch reduction of anthracene.

Figure 1 compares the electron transfer efficiency for the Birch reduction of anthracene and naphthalene utilizing $[Ca_2N]^+ e^-$ electride to those for previously reported Birch reductions utilizing various reducing agents in terms of electron concentration. The electron transfer efficiency and concentration were calculated using the ratio of provided and participated electrons (%) and the amount of electrons per volume of solvent (M, mol L^{-1}), respectively. (See the Supporting Information) For the reduction of anthracene, the present Birch reduction showed the highest electron transfer efficiency and completed the reaction with minimal use of the electride reagent; it indicates that this protocol is an economical and practical methodology. Meanwhile, for the reduction of naphthalene, the present electride mediated Birch reduction showed moderately high electron transfer efficiency when compared to that of the Birch reduction using SmI₂/H₂O. However, in spite of the sufficient reduction ability of solvated electrons in alkali metal-ammonia solutions, their practical use is impeded by the harsh reaction conditions such as low reaction temperature (< -30 °C) and violent reactions.



Figure 1. Comparison of electron transfer efficiency and electron concentration in the reduction of anthracene and naph-thalene using typical electron transfer agents and $[Ca_2N]^+ e^-$ electride.

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In contrast, it is noted that the Birch reduction utilizing $[Ca_2N]^+ e^-$ electride was realized in the vicinity of room temperature and in alcoholic solvents, although the optimization for a high transfer efficiency beyond alkali metal-ammonia solutions is further needed.

CONCLUSIONS

In conclusion, we have demonstrated a simple, efficient and mild Birch reduction of PAHs and naphthalene utilizing 2D inorganic electride $[Ca_2N]^+ e^-$ in alcoholic solvents. This protocol can provide a direct and pragmatic synthetic root for the reduction of aromatic compounds. It also can provide a powerful alternative reducing agent for synthetic chemistry as an analogue of solvated electrons in alkali metal-ammonia or amine solutions. Finally, we suspect that, because the electride in alcoholic solvents shows high electron transfer efficiency, it might also be used for electro-catalytic reactions.

EXPERIMENTAL SECTION

1. General Methods. ¹H NMR spectra were recorded at room temperature on a Bruker at 500 MHz in CDCl₃ (δ 7.26 ppm), ¹³C NMR spectral measurements were performed at 125 MHz using CDCl₃ (δ 77.16 ppm). All reported NMR values are given in parts per million (ppm). The terms m, s, d, t, q, quint., and sept. represent multiplet, singlet, doublet, triplet, quadruplet, quintuplet, and septet, respectively, and the term br means a broad signal.

2. Synthesis of dicalcium nitride $[Ca_2N]^+ \cdot e^-$ electride. A stoichiometric polycrystalline $[Ca_2N]^+ \cdot e^-$ electride was synthesized by the solid-state reaction of Ca_3N_2 powders and Ca metal chips. Mixture of Ca_3N_2 powders and Ca chips at a molar ratio of 1:1 were pressed into a pellet form under pressure (20~30 MPa). The pellet was fully covered with molybdenum foil and annealed at 800 °C for 48 hrs under vacuum (~10⁻³ Pa). Then, the sample was quenched into water. To improve homogeneity of $[Ca_2N]^+ \cdot e^-$ electride, the synthesized sample was ground into a powder in an agate mortar in argon-filled glovebox and re-annealed under the same conditions. The synthesized $[Ca_2N]^+ \cdot e^-$ electride is single phase without impurities. The structure of synthesized $[Ca_2N]^+ \cdot e^-$ electride was identified by X-ray diffractometer.

3. General procedures for Birch reduction of Polycyclic aromatic hydrocarbons (PAH) (GP-1) and of **naphthalene** (GP-2). [Ca₂N]⁺•e⁻ electride (94 mg, 1 mmol) was added to a suspension of PAH (0.5 mmol) and naphthalene (0.5 mmol) in 4 ml of dry (THF or HMPA) and *i*PrOH in 1:1 mixture at 65 °C. Because the [Ca₂N]⁺•e⁻ electride is oxidized even in the solvents under ambient atmosphere, the reactions were conducted in inert Ar gas environment until the complete alcoholysis of electride that was observable by the color change of [Ca₂N]⁺•e⁻ electride from black to white. The reaction mixture was quenched with 5% HCl concentrated aqueous solution and then, extracted with Et₂O or n-haxane (20 mL×3). The THF and HMPA were removed by washing with DI water. The combined organic layers were dried over MgSO₄ and concentrated in vacuo.

4. Characterization Data for Products

9,10-dihydroanthracene (1a') According to General Procedure of **GP-1** with 1a (0.05 mmol) and $[Ca_2N]^+ \cdot e^-$ (94 mg, 1 mmol, 2.0 equiv), compound 1a' (83 mg, 92%) was obtained. / According to revised General Procedure of **GP-1** with 2d (0.05 mmol) and $[Ca_2N]^+ \cdot e^-$ (235 mg, 2.5 mmol, 5.0 equiv), compound 1a' (76 mg, 87%) was obtained. ¹H NMR (500 MHz, CDCl₃); 7.29-7.27(m, 4H), 7.19-7.17(m, 4H), 3.93(s, 4H) ; ¹³C[¹H] NMR (125 MHz, CDCl₃) δ : 136.7, 127.4, 126.1, 36.2 ppm. The physical and spectral data were identical to those previously reported for this compound.⁴⁰

9,10-dihydrophenanthrene (2a') According to revised General Procedure of **GP-1** with **2a** (0.05 mmol) and $[Ca_2N]^+e^-$ (141 mg, 1.5 mmol, 3.0 equiv), compound **2a'** (80 mg, 89%) was obtained. ¹H NMR (500 MHz, CDCl₃); 7.75(d, J = 10 Hz, 2H), 7.30-7.27(m, 2H), 7.23-7.20(m, 4H), 2.86(s, 4H) ; ¹³C{¹H} NMR (125 MHz, CDCl₃) δ : 137.4, 134.5, 128.2, 127.4, 127.0, 123.8, 29.1 ppm. The physical and spectral data were identical to those previously reported for this compound.⁴¹

9-methyl-9,10-dihydroanthracene (2b') According to revised General Procedure of **GP-1** with **2b** (0.05 mmol) and $[Ca_2N]^+ \cdot e^-$ (141 mg, 1.5 mmol, 3.0 equiv), compound **2b'** (83 mg, 86%) was obtained. / According to revised General Procedure of **GP-1** with **2c** (0.05 mmol) and $[Ca_2N]^+ \cdot e^-$ (188 mg, 2.0 mmol, 4.0 equiv), compound **2b'** (84 mg, 87%) was obtained. ¹H NMR (500 MHz, CDCl₃); 7.30-7.26(m, 4H), 7.22-7.16(m, 4H), 4.11(d, J = 20 Hz, 1H), 4.03(q, J=5 Hz, 1H), 3.87(d, J = 15 Hz, 1H), 1.42(d, J = 5 Hz, 3H) f; ¹³C[¹H} NMR (125 MHz, CDCl₃) δ : 141.6, 135.9, 127.8, 127.0, 126.5, 126.1, 41.2, 35.2, 23.6 ppm. The physical and spectral data were identical to those previously reported for this compound.⁴⁰

9-ethyl-9,10-dihydroanthracene (**2e**') According to revised General Procedure of **GP-1** with **2e** (0.05 mmol) and $[Ca_2N]^+e^-$ (235 mg, 2.5 mmol, 5.0 equiv), compound **2e**' (40 mg, 38%) was obtained. ¹H NMR (500 MHz, CDCl₃); 7.28-7.20(m, 4H), 7.20-7.18(m, 4H), 4.13-4.09(d, 1H), 3.87-3.79(m, 2H), 1.68-1.65(t, 2H), 0.89-0.86(t, 3H) ; ¹³C{¹H} NMR (125 MHz, CDCl₃) δ : 140.5, 136.1, 128.1, 127.7, 126.0, 125.9, 48.9, 35.3, 30.6, 12.1 ppm. The physical and spectral data were identical to those previously reported for this compound.⁴²

9,10-diphenyl-9,10-dihydroanthracene (**2f**) According to revised General Procedure of **GP-1** with **2f** (0.05 mmol) and $[Ca_2N]^+e^-$ (235 mg, 2.5 mmol, 5.0 equiv), compound **2f** (83 mg, 50%) was obtained. ¹H NMR (500 MHz, CDCl₃); 7.31-7.28(q, 4H), 7.25-7.22(m, 3H), 7.16-7.10(m, 12H), 5.23(s, 2H) ; ¹³C{¹H} NMR (125 MHz, CDCl₃) δ : 143.7, 139.3, 129.3, 128.6, 128.4, 126.5, 126.4, 50.3 ppm. The physical and spectral data were identical to those previously reported for this compound.⁴⁰

5,12-dihydrotetracene (2g') According to revised General Procedure of **GP-1** with **2g** (0.05 mmol) and $[Ca_2N]^+e^-$ (141 mg, 1.5 mmol, 3.0 equiv), compound **2g'** (94 mg, 82%) was obtained. ¹H NMR (500 MHz, CDCl₃); 7.79-7.77(m, 2H), 7.75(s, 2H), 7.42-7.40(m, 2H), 7.34-

7.32(m, 2H), 7.21-7.20(m, 2H), 4.18(s, 4H) ; ${}^{13}C{}^{1}H$ NMR (125 MHz, CDCl₃) δ : 137.1, 135.7, 132.4, 127.3, 127.2, 126.3, 125.3, 125.2, 36.8 ppm. The physical and spectral data were identical to those previously reported for this compound.⁴⁰

7,12-dihydrotetraphene (**2h**') According to revised General Procedure of **GP-1** with **2h** (0.05 mmol) and $[Ca_2N]^+ e^-$ (188 mg, 1.0 mmol, 2.0 equiv), compound **2h**' (97 mg, 85%) was obtained. 'H NMR (500 MHz, CDCl₃); 8.15(d, *J* = 10 Hz, 1H), 7.85(d, *J* = 5 Hz, 1H), 7.72(d, *J* = 5 Hz, 1H), 7.56-7.54(m, 1H), 7.48-7.45(m, 1H), 7.42-7.39(m, 2H), 7.34-7.32(m, 1H), 7.25-7.22(m,2H), 4.41(s, 2H), 4.18(s, 2H); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ : 135.3, 135.2, 132.7, 132.4, 131.5, 130.2, 128.7, 128.2, 127.7, 126.8, 126.5, 126.2, 126.2, 126.1, 125.0, 122.9, 35.8, 31.0 ppm. The physical and spectral data were identical to those previously reported for this compound.⁴³

1,2,3,4-Tetrahydronaphthalene (**2i**') According to General Procedure of **GP-2** with $[Ca_2N]^+ \cdot e^-$ (470 mg, 5 mmol, 10.0 equiv), compound **2i**' (32 mg, 49%) was obtained. / According to revised General Procedure of **GP-2** with **2j** (0.05 mmol) and $[Ca_2N]^+ \cdot e^-$ (470 mg, 5 mmol, 10.0 equiv), compound **2i**' (51%) was obtained. The product was mixture of **2i**, **2j**' and **2i**'. The product was mixture of **2i**, **2j**' and **2i**'. The product was mixture of **2i**, **2j**' and **2i**'. The product was mixture of **2i**, **2j**' and **2i**'. The product was mixture of **2i**, **2j**' and **2i**'. The product was mixture of **2i**, **2j**' and **2i**'. The product was mixture of **2i**, **2j**' and **2i**'. The product was mixture of **2i**, **2i**, and **2i**'. The product was mixture of **2i**, **2i**, and **2i**'. The product was mixture of **2i**, **2i**, and **2i**'. The product was mixture of **2i**, **2i**, and **2i**'. The product was mixture of **2i**, **2i**, and **2i**'. The product was mixture of **2i**, **2i**, and **2i**'. The product was mixture of **2i**, **2i**, and **2i**'. The product was mixture of **2i**, **2i**, and **2i**'. The product was mixture of **2i**, **2i**, and **2i**'. The product was mixture of **2i**, **2i**, and **2i**'. The product was mixture of **2i**, **2i**, and **2i**'. The product was mixture of **2i**, **2i**, and **2i**'. The product was mixture of **2i**, **2i**, and **2i**'. The product was mixture of **2i**, **2i**, and **2i**'. The product was mixture of **2i**, **2i**, and **2i**'. The product was mixture of **2i**, **2i**, and **2i**'. The product was mixture of **2i**, **2i**, and **2i**'. The product was mixture of **2i**, **2i**, and **2i**.

Naphthalene (2i) According to revised General Procedure of **GP-2** with **2j** (0.05 mmol) and $[Ca_2N]^+ \cdot e^-$ (470 mg, 5 mmol, 10.0 equiv), compound **2f**' (18%, determined by 'H NMR spectroscopy) was obtained. The product was mixture of **2i**, **2j**' and **2i**'. 'H NMR (500 MHz, CDCl₃): δ = 7.85-7.83 (m, 4H), 7.48-7.46 (m, 4H) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃) δ : 133.5, 129.1, 125.4 ppm. The physical and spectral data were identical to those previously reported for this compound.²⁰

1,4-Dihydronaphthalene (2j') According to revised General Procedure of **GP-2** with 2j (0.05 mmol) and $[Ca_2N]^+ e^-$ (470 mg, 5 mmol, 10.0 equiv), compound 2i' (30%, determined by 'H NMR spectroscopy) was obtained. The product was mixture of 2i, 2j' and 2i'. 'H NMR (500 MHz, CDCl₃): δ = 7.07–7.01 (m, 4H), 5.92–5.91 (m, 2H), 3.45–3.38 (m, 4H) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃) δ : 133.6, 127.6, 125.8, 123.7, 29.8 ppm. The physical and spectral data were identical to those previously reported for this compound.⁴⁵

1,2-diphenylethane (**2k**') According to revised General Procedure of **GP-1** with **2k** (0.05 mmol) and $[Ca_2N]^+e^-$ (188 mg, 2.0 mmol, 4.0 equiv), compound **2k**' (79 mg, 87%) was obtained. / According to revised General Procedure of **GP-1** with **2l** (0.05 mmol) and $[Ca_2N]^+e^-$ (141 mg, 1.5 mmol, 3.0 equiv), compound **2k**' (62 mg, 68%) was obtained. / According to revised General Procedure of **GP-1** with **2m** (0.05 mmol) and $[Ca_2N]^+e^-$ (141 mg, 1.5 mmol, 3.0 equiv), compound **2k**' (76 mg, 84%) was obtained. ¹H NMR (500 MHz, CDCl₃); 7.29-7.26(m, 4H), 7.10-7.17(m, 6H), 2.92(s, 4H) ; ${}^{13}C{}^{1}H$ NMR (125 MHz, CDCl₃) δ : 141.8, 128.4, 128.3, 126.0, 37.9 ppm. The physical and spectral data were identical to those previously reported for this compound.⁴⁰

ASSOCIATED CONTENT

Supporting Information ¹H NMR and ¹³C NMR Spectra of the Products Reaction scope of PAHs and naphthalenes for the Birch reduction using HMPA Mechanistic Study Electron transferring Efficiency Calculation and Electron Concentration

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