Supporting Information

Two-dimensional electride – promoted electron transfer efficiency in transfer hydrogenation of alkynes and alkenes

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General Methods

\(^1\)H NMR spectra were recorded on a Varian at 500 MHz in CDCl\(_3\) (\(\delta\) 7.26 ppm), \(^{13}\)C NMR spectral measurements were performed at 125 MHz using CDCl\(_3\) (\(\delta\) 77.16 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.

The measurement of X-ray diffraction patterns for Ca(O\(_2\)Pr)\(_2\) was made over a 2\(\theta\) range from 5° to 40° along with a step size of 0.02° and scanning speed was set at 1° at 1° min\(^{-1}\) with filtered Cu K\(\alpha\) radiation \(\lambda=0.15418\) nm (Rigaku Smart Lab, Japan).

Ion chromatography was performed on Metrohm 833 IC plus with conductivity detector (solvent: 1.7mM HNO\(_3\) + 0.7mM PDCA in DI water, temperature: room temperature, fluent speed: 0.9mL/min). Analytic sample was prepared by the following procedure: Each sample was taken from the individual reaction mixture using micro-glass filters. To make more accurate analysis, it diluted with deionized water (200 times less than in the original sample).

Synthesis of dicalcium nitride \([\text{Ca}_2\text{N}]^+\cdot\text{e}^-\) electride

A stoichiometric polycrystalline dicalcium nitride ([Ca\(_2\)N]\(^+\)\cdot\text{e}^-) was synthesized by the solid-state reaction of calcium nitride(Ca\(_3\)N\(_2\)) powders and calcium metals. Mixture of Ca\(_2\)N\(_2\) powders and calcium 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 dicalcium nitride [Ca\(_2\)N]\(^+\)\cdot\text{e}^-, the synthesized sample was ground into a powder in an agate mortar in nitrogen-filled glovebox and re-annealed under the same conditions.

General procedure for transfer hydrogenation of aromatic alkynes

Dicalcium nitride [Ca\(_2\)N]\(^+\)\cdot\text{e}^- (235 mg, 2.5 mmol) was added to a suspension of alkyne (0.5 mmol) in 4 mL of dry DMF and \(i\)PrOH in 1:1 mixture at room temperature. The reaction was stirred until color change of electrode(black → white) indicated complete consumption of the starting material, and then the reaction mixture was quenched with water and 5% HCl solution in water and, extracted with Et\(_2\)O (15 mL \times 3), and remove the DMF by washing with DI water. The combined organic layers were dried over MgSO\(_4\) and concentrated in vacuo.

The residue was purified by flash column chromatography on silica gel to furnish the corresponding product.

General procedure for transfer hydrogenation of aromatic alkenes

Dicalcium nitride [Ca\(_2\)N]\(^+\)\cdot\text{e}^- (144 mg, 1.5 mmol) was added to a solution of alkene (0.5 mmol) in 4 mL of dry DMF and MeOH in 1:1 mixture at room temperature. The reaction was stirred until color change of electrode from black to white, indicating that the starting material was completely consumed. Upon completion of the reaction, the reaction mixture was quenched with water and washed with aqueous 5% HCl solution. The reaction mixture was extracted with Et\(_2\)O (15 mL \times 3) and saturated brine. The combined extracts were dried over anhydrous MgSO\(_4\), filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to furnish the corresponding product.
**Characterization Data for Products**

**1,2-diphenylethane (Table 3, Entry 1, 10, 11)**

![1a](image)

The physical and spectral data were identical to those previously reported for this compound.\(^1\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)); 7.29-7.25(m, 4H), 7.19-7.17(m, 6H), 2.92(s, 4H) ; \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 141.9, 128.5, 128.4, 126.0, 38.0 ppm.

**1-methyl-2-(phenylethynyl)benzene (Table 3, Entry 2)**

![1b](image)

The physical and spectral data were identical to those previously reported for this compound.\(^2\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)); 7.30-7.27(m, 2H), 7.21-7.19(m, 3H), 7.14-7.11(m, 4H), 2.89-2.86(m, 4H), 2.94(s, 3H) ; \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 142.1, 140.1, 136.0, 130.3, 128.9, 128.5, 126.2, 126.1, 126.0, 36.8, 35.5, 19.3 ppm.

**1-methoxy-3-phenethylbenzene (Table 3, Entry 3)**

![1c](image)

The physical and spectral data were identical to those previously reported for this compound.\(^3\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)); 7.29-7.26(m, 2H), 7.21-7.17(m, 4H), 6.79(d, \(J = 10\) Hz, 1H), 6.75-6.71(m, 2H), 3.76(s, 3H), 2.90(br s, 4H) ; \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 159.6, 143.5, 141.8, 129.3, 128.5, 128.4, 126.0, 120.9, 114.2, 111.3, 55.1, 38.0, 37.9 ppm.
1-methoxy-4-phenethylbenzene (Table 3, Entry 4)

![Chemical structure of 1-methoxy-4-phenethylbenzene]

The physical and spectral data were identical to those previously reported for this compound.²

$^1$H NMR (500 MHz, CDCl$_3$); 7.27-7.24(m, 2H), 7.17-7.15(m, 3H), 7.08-7.06(m, 2H), 6.81-6.80(m, 2H), 3.75(s, 3H) 2.87-2.83(m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$); 157.9, 141.9, 134.0, 129.4, 128.6, 128.6, 126.0, 126.0, 113.8, 113.8, 55.3, 38.3, 37.1 δ: ppm.

1,2-di-\textit{p}-tolylethane (Table 3, Entry 5, 13)

![Chemical structure of 1,2-di-\textit{p}-tolylethane]

The physical and spectral data were identical to those previously reported for this compound.⁴

$^1$H NMR (500 MHz, CDCl$_3$); 7.14(s, 8H), 2.91(s, 4H), 2.37(s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$); 138.9, 135.3, 129.1, 128.4, 37.7, 21.1 δ: ppm.

1-fluoro-4-phenethylbenzene (Table 3, Entry 6)

![Chemical structure of 1-fluoro-4-phenethylbenzene]

The physical and spectral data were identical to those previously reported for this compound.⁵

$^1$H NMR (500 MHz, CDCl$_3$); 7.29-7.23(m, 2H), 7.20-7.17(m, 1H), 7.15-7.08(m, 4H), 6.96-6.93(m, 2H), 2.88(s, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 162.3(d, $J_F = 242.5$ Hz), 141.5, 137.3(d, $J_F = 2.5$ Hz), 129.9(d, $J_F = 7.5$ Hz), 128.5, 128.4, 126.0, 115.1(d, $J_F = 21.25$ Hz), 38.1, 37.1 ppm.
2,4-difluoro-1-phenethylbenzene (Table 3, Entry 7)

\[
\begin{align*}
\text{F} & \quad \text{1g'} \\
\text{F} & \quad \text{1H} \\
\end{align*}
\]

\(^1\)H NMR (500 MHz, CDCl\(_3\)); 7.28-7.26(m, 2H), 7.20-7.14(m, 3H), 7.05-7.00(m, 1H), 6.78-6.72(m, 2H), 2.91-2.85(m, 4H); \(^1\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 162.46 (d, \(J_F = 12.5\) Hz), 161.98 (d, \(J_F = 12.5\) Hz), 141.22, 131.18 (dd, \(J_F = 8.8, 7.5\) Hz), 128.50, 128.41, 126.12, 124.29 (dd, \(J_F = 16.3, 3.8\) Hz), 103.64 (t, \(J_F = 25\) Hz), 36.49, 30.68 (d, \(J_F = 1.3\) Hz) ppm. HR-MS(EI) \(m/z\) calcd for C\(_{14}\) H\(_{12}\)F\(_2\) 218.0907, founded 218.0902.

1,2-bis(4-fluorophenyl)ethane (Table 3, Entry 8)

\[
\begin{align*}
\text{F} & \quad \text{1h'} \\
\end{align*}
\]

The physical and spectral data were identical to those previously reported for this compound.\(^1\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)); 7.08-7.05(m, 4H), 6.96-6.92(m, 4H), 2.85(s, 4H); \(^1\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 162.3(d, \(J_F = 242.5\) Hz), 137.0(d, \(J_F = 2.5\) Hz), 129.9(d, \(J_F = 20.0\) Hz), 115(d, \(J_F = 21.25\) Hz), 37.2 ppm.

4-ethyl-1,1'-biphenyl (Table 3, Entry 9)

\[
\begin{align*}
\end{align*}
\]

The physical and spectral data were identical to those previously reported for this compound.\(^6\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)); 7.58-7.57(m, 2H), 7.51(d, \(J = 8.2\) Hz, 2H), 7.41(t, \(J = 7.7\) Hz, 2H), 7.33-7.30(m, 1H), 7.28(d, \(J = 10\) Hz, 2H), 2.69(q, \(J = 7.6\) Hz, 2H), 1.27(t, \(J = 7.6\) Hz, 3H); \(^1\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 143.4, 141.23, 138.7, 128.8, 128.3, 127.1, 127.0, 28.6, 15.7 ppm.
Ethane-1,1,2-triyltribenzene (Table 3, Entry 12)

![Ethane-1,1,2-triyltribenzene](image)

The physical and spectral data were identical to those previously reported for this compound.\textsuperscript{7}

\[ ^1\text{H} \text{ NMR (500 MHz, CDCl}_3\text{); 7.23-7.18(m, 8H), 7.15-7.10(m, 5H), 6.99-6.97(m, 2H), 4.21(t, J = 7.8 Hz, 1H), 3.34(d, J = 7.8 Hz, 2H); } ^{13}\text{C} \text{ NMR (125 MHz, CDCl}_3\text{); 144.6, 140.4, 129.2, 128.5, 128.2, 126.3, 126.0, 53.2, 42.2}\delta\text{ ppm.} \]

1,3-dimethoxy-5-phenethylbenzene (Table 3, Entry 13)

![1,3-dimethoxy-5-phenethylbenzene](image)

The physical and spectral data were identical to those previously reported for this compound.\textsuperscript{8}

\[ ^1\text{H} \text{ NMR (500 MHz, CDCl}_3\text{); 7.29-7.26(m, 2H), 7.20-7.18(m, 3H), 6.34-6.33(m, 2H), 6.31-6.30(m, 1H), 3.74(s, 6H), 2.92-2.83(m, 4H); } ^{13}\text{C} \text{ NMR (125 MHz, CDCl}_3\text{); 160.8, 144.2, 141.8, 128.5, 128.4, 126.0, 106.6, 98.0, 55.3, 38.3, 37.8}\delta\text{ ppm.} \]
1,2-diphenylethane (Table 3, Entry1, 10, 11)
1-methyl-2-(phenylethynyl)benzene (Table 3, Entry 2)
1-methoxy-3-phenethylbenzene (Table 3, Entry 3)
1-methoxy-4-phenethylbenzene (Table 3, Entry 4)
1,2-di-p-tolylethane (Table 3, Entry 5, 13)
1-fluoro-4-phenethylbenzene (Table 3, Entry 6)
2,4-difluoro-1-phenethylbenzene (Table 3, Entry 7)
1,2-bis(4-fluorophenyl)ethane (Table 3, Entry 8)
4-ethyl-1,1'-biphenyl (Table 3, Entry 9)
Ethane-1,1,2-triyltribenzene (Table 3, Entry 12)
1,3-dimethoxy-5-phenethylbenzene (Table 3, Entry 13)
**Electron Transferring Efficiency Calculation**

Efficiency = \[\frac{\text{participated electron (equiv.)}}{\text{provided electron (equiv.)}}\] × 100 (%)  

| Reagent       | Participated electron (equiv.) | Provided electron (equiv.) | Efficiency (%) |
|---------------|--------------------------------|---------------------------|----------------|
| Yb\(^{3+}\)  | 1.9                            | 9                         | 21             |
| Mg\(^{2+}\)   | 3.4                            | 10                        | 34             |
| Na-SG         | 3.3                            | 7                         | 47             |
| SmI\(_2\)/H\(_2\)O | 4                              | 5                         | 79             |
| [Ca\(_2\)N\]^+·e\(^-\) | 4                              | 5                         | 80             |

| Reagent       | Participated electron (equiv.) | Provided electron (equiv.) | Efficiency (%) |
|---------------|--------------------------------|---------------------------|----------------|
| Mg\(^{2+}\)   | 1.7                            | 10                        | 17             |
| Yb\(^{3+}\)  | 2                              | 9                         | 22             |
| Na-SG         | 2                              | 7                         | 29             |
| SmI\(_2\)/H\(_2\)O | 2                              | 3                         | 62             |
| TmI\(_2\)     | 2                              | 3                         | 66.7           |
| [Ca\(_2\)N\]^+·e\(^-\) | 2                              | 3                         | 66.7           |

| Reaction       | Participated electron (equiv.) | Provided electron (equiv.) | Efficiency (%) |
|----------------|--------------------------------|---------------------------|----------------|
| Pinacol coupling using C12A7 | 0.7                            | 11.6                      | 6              |
| Pinacol coupling using [Ca\(_2\)N\]^+·e\(^-\) | 1                              | 2                         | 50             |
| Hydrotrifluoromethylation using [Ca\(_2\)N\]^+·e\(^-\) | 0.9                            | 3                         | 30             |
| Transfer hydrogenation using [Ca\(_2\)N\]^+·e\(^-\) | 4                              | 5                         | 80             |
Mechanistic studies (Employment of radical scavengers)

Table S1. Electrides mediated reduction of diphenylacetylene in the presence of radical scavengers

| Additive               | Time | Equiv. | Yield<sup>a</sup> |
|------------------------|------|--------|-------------------|
| None                   | 15h  | -      | 99%               |
| TEMPO                  | 7h   | 1eq    | 64%               |
| Galvioxynol            | 7h   | 1eq    | 58%               |
| 1,4-dinitrobenzene     | 18h  | 1eq    | 48%               |

<sup>a</sup> determined by GC (Using biphenyl as an internal standard)

Mechanistic studies [X-ray diffraction patterns of Ca(OiPr)<sub>2</sub> and reaction time log]

Fig. S1 (a) XRD patterns of Ca(OiPr)<sub>2</sub> standard powders (black line) and resulting Ca(OiPr)<sub>2</sub> product from the reaction mixtures (red line). All measurements are performed under nitrogen atmosphere. (b) Reaction time log; each picture was taken every 3h.
Mechanistic studies [Ion chromatography of NH$_4^+$ (ammonium ion)]

1) NH$_4^+$ cation calibration curve

Function: \[ A = 15.28098B + 0.69722 \times Q \]
Relative standard deviation: 1.115%
Correlation coefficient: 0.99996

| Sample    | Conc. (mg/L) | Volume (μL) | Dilution | Area   |
|-----------|--------------|-------------|----------|--------|
| Standard 1| 0.500        | 1           | 1.0      | 8.155  |
| Standard 2| 1.000        | 1           | 1.0      | 15.8   |
| Standard 3| 5.000        | 1           | 1.0      | 77.77  |
| Standard 4| 10.000       | 1           | 1.0      | 153.2  |
2) Result

![Graph showing conductivity over time](image)

**Sample (THF) - Inset**

| Component                  | Details                                  |
|----------------------------|------------------------------------------|
| Electride                  | [Ca$_2$N]$^+$·e$^-$ (235 mg, 2.5 mmol)    |
| Alkyne                     | diphenylacetylene (90 mg, 0.5 mmol)      |
| Solvent                    | THF 4 mL                                 |
| Washed Solvent             | THF 8 mL                                 |
| Dilution                   | 200 times                                |
| Pressure / Flow            | 7.88 MPa / 0.700 mL/min                  |
| IC value                   | 2.215 mV                                 |
| Final concentration        | 28.4 mg/kg                               |

**Sample (THF+iPrOH)**

| Component                  | Details                                  |
|----------------------------|------------------------------------------|
| Electride                  | [Ca$_2$N]$^+$·e$^-$ (235 mg, 2.5 mmol)    |
| Aldehyde                   | diphenylacetylene (90 mg, 0.5 mmol)      |
| Solvent                    | iPrOH 2 mL / THF 2 mL                    |
| Washed Solvent             | iPrOH 8 mL                               |
| Dilution                   | 200 times                                |
| Pressure / Flow            | 7.88 MPa / 0.700 mL/min                  |
| IC value                   | 0.142 mV                                 |
| Final concentration        | 425.0 mg/kg                               |
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