Supplementary Materials

Function of triazenido compound for electrocatalytic hydrogen production catalyzed by platinum complex

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**Fig. S15.** (a) GC traces after a 1-h controlled-potential electrolysis at −1.45 V vs Ag/AgCl of 2.33 μM HL in 0.25 M phosphate buffer (pH 7.0). A standard of CH₄ was added for calibration purposes. (b) Measured (red) and calculated (black) pH changes assuming a 100% Faradic efficiency of complex during electrolysis. (the theoretical pH change over time can be calculated by the equation of \( pH = 14 + \lg \sum \frac{I_t}{FV} \) where \( I \) = current (A), \( t \) = time (s), \( F \) = Faraday constant (96485 C/mol), \( V \) = solution volume (0.05 L).

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**Eq. S1.** The calculation of TOF for Pt(PPh₃)₂Cl₂ (in DMF)

**Eq. S2.** The calculation of TOF for Pt(PPh₃)₂(L)Cl (in DMF)

**Eq. S3.** The calculation of TOF for Pt(PPh₃)₂(L)Cl (in buffer, pH 7.0)

**Eq. S4.** The calculation of TOF for (Pt(PPh₃)₂Cl₂ (in buffer, pH 7.0).

**Eq. S5.** The calculation of TOF for HL (in buffer, pH 7.0)
Table S1. Crystallographic data for HL and Pt(PPh₃)₂(L)Cl 1

Table S2. Selected bond lengths (Å) and angles (°) for HL and Pt(PPh₃)₂(L)Cl 1

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Fig. S7. (a) Scan rate dependence of precatalytic waves for a 0.76 mM solution of complex 1 with 0.10 M [n-Bu4N]ClO4, at scan rates from 50 to 300 mV/s. (b) Scan rate dependence of precatalytic waves for a 1.26 mM solution of Pt(PPh3)2Cl2 with 0.10 M [n-Bu4N]ClO4, at scan rates from 50 to 300 mV/s.
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**Fig. S10.** Charge buildup versus time from electrolysis of blank (black), 9.32 μM HL (red), 9.32 μM Pt(PPh₃)₂Cl₂ (blue), the mixture of 9.32 μM HL and 9.32 μM
Pt(PPh$_3$)$_2$Cl$_2$ (green), and 9.32 µM Pt(PPh$_3$)$_2$(L)Cl (violet) in DMF (0.10 M [n-Bu$_4$N]ClO$_4$) under -1.45 V versus Ag/AgNO$_3$.

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\[ pH = 14 + \lg \left( \frac{I}{F} \right) \]

where I = current (A), t = time (s), F = Faraday constant (96485 C/mol), V = solution volume (0.05 L).
Fig. S14. (a) GC traces after a 1-h controlled-potential electrolysis at −1.45 V vs Ag/AgCl of 2.33 μM Pt(PPh₃)₂Cl₂ in 0.25 M phosphate buffer (pH 7.0). A standard of CH₄ was added for calibration purposes. (b) Measured (red) and calculated (black) pH changes assuming a 100% Faradic efficiency of complex during electrolysis. (the theoretical pH change over time can be calculated by the equation of
\[ pH = 14 + \log \left( \frac{\sum I t}{FV} \right) \]

where \( I = \) current (A), \( t = \) time (s), \( F = \) Faraday constant (96485 C/mol), \( V = \) solution volume (0.05 L).

**Fig. S15.** (a) GC traces after a 1-h controlled-potential electrolysis at \(-1.45 \text{ V vs Ag/AgCl}\) of 2.33 \( \mu \text{M} \) HL in 0.25 M phosphate buffer (pH 7.0). A standard of CH\(_4\) was added for calibration purposes. (b) Measured (red) and calculated (black) pH changes assuming a 100% Faradic efficiency of complex during electrolysis. (the theoretical
pH change over time can be calculated by the equation of \( pH = 14 + \lg \frac{\sum I}{FV} \) where \( I \) = current (A), \( t \) = time (s), \( F \) = Faraday constant (96485 C/mol), \( V \) = solution volume (0.05 L).
**Fig. S16.** (a) Charge buildup versus time from 2.33 μM complex 1 in a 0.25 M buffer (pH 7.0) under -1.45 V vs Ag/AgCl. (b) Charge buildup versus time from 2.33 μM Pt(PPh$_3$)$_2$Cl$_2$ in a 0.25 M buffer (pH 7.0) under -1.45 V vs Ag/AgCl. (c) Charge buildup versus time from 2.33 μM HL in a 0.25 M buffer (pH 7.0) under -1.45 V vs Ag/AgCl.

\[
TOF = \frac{\Delta C}{F \cdot n_1 \cdot n_2 \cdot t} = \frac{0.0234C \times 3600}{96485C \cdot \text{mol}^{-1} \times 2 \times 0.373 \times 10^{-6} \text{mol} \times 120} = 9.84\text{h}^{-1}
\]

**Eq. S1.** The calculation of TOF for Pt(PPh$_3$)$_2$Cl$_2$ (in DMF)

\[
TOF = \frac{\Delta C}{F \cdot n_1 \cdot n_2 \cdot t} = \frac{0.0603C \times 3600}{96485C \cdot \text{mol}^{-1} \times 2 \times 0.373 \times 10^{-6} \text{mol} \times 120} = 25.36\text{h}^{-1}
\]

**Eq. S2.** The calculation of TOF for Pt(PPh$_3$)$_2$(L)Cl (in DMF)
\[ \text{TOF} = \frac{\Delta C}{F \cdot n_1 \cdot n_2 \cdot t} = \frac{1.55C \times 3600}{96485C \cdot \text{mol}^{-1} \times 2 \times 0.373 \times 10^{-6} \text{mol} \times 120} = 651.87 \text{h}^{-1} \]

\[ \text{Eq. S3. The calculation of TOF for Pt(PPh}_3^2\text{)(L)Cl (in buffer, pH 7.0)} \]

\[ \text{TOF} = \frac{\Delta C}{F \cdot n_1 \cdot n_2 \cdot t} = \frac{0.583C \times 3600}{96485C \cdot \text{mol}^{-1} \times 2 \times 0.373 \times 10^{-6} \text{mol} \times 120} = 245.18 \text{h}^{-1} \]

\[ \text{Eq. S4. The calculation of TOF for (Pt(PPh}_3^2\text{Cl}_2 (in buffer, pH 7.0).} \]

\[ \text{TOF} = \frac{\Delta C}{F \cdot n_1 \cdot n_2 \cdot t} = \frac{0.226C \times 3600}{96485C \cdot \text{mol}^{-1} \times 2 \times 0.373 \times 10^{-6} \text{mol} \times 120} = 95.06 \text{h}^{-1} \]

\[ \text{Eq. S5. The calculation of TOF for HL (in buffer, pH 7.0)} \]
Table S1. Crystallographic data for HL and Pt(PPh₃)₂(L)Cl 1

| Parameter                        | HL                | Pt(PPh₃)₂(L)Cl 1 |
|----------------------------------|-------------------|------------------|
| Empirical formula                | C₁₂H₁₂N₄O        | C₅₂H₅₁ClN₄O₃P₂Pt|
| Formula weight                   | 228.26            | 1072.45          |
| λ (Å)                            | 0.71073           | 0.71073          |
| Crystal system                   | monoclinic        | monoclinic       |
| Space group                      | P2(1)/c           | P2(1)/c          |
| a/Å                              | 18.961(4)         | 23.331(3)        |
| b/Å                              | 5.3302(11)        | 10.0888(13)      |
| c/Å                              | 25.673(10)        | 22.298(2)        |
| α°                               | 90                | 90               |
| β°                               | 115.89(2)         | 116.786(3)       |
| γ°                               | 90                | 90               |
| V/Å³                             | 2334.2(11)        | 4685.5(10)       |
| Z                                | 8                 | 4                |
| Dc/Mgm⁻³                         | 1.299             | 1.520            |
| F(000)                           | 960               | 2160             |
| θ range for data collection     | 3.19 to 27.46°    | 3.28 to 27.48°   |
| Reflections collected/unique    | 20901/5246        | 23259/10452      |
| Data/restraints/parameters       | 5246/0/307        | 10452/0/538      |
| Goodness-of-fit on F²            | 0.940             | 1.070            |
| Final R indices [I>2sigma(I)]    | R1 = 0.0520       | R1 = 0.0664      |
|                                  | wR2 = 0.1302      | wR2 = 0.1664     |
| R indices (all data)             | R1 = 0.1278       | R1 = 0.0828      |
|                                  | wR2 = 0.1817      | wR2 = 0.1726     |
**Table S2.** Selected bond lengths (Å) and angles (°) for HL and Pt(PPh₃)₂(L)Cl 1

|        | HL               | Complex 1         |
|--------|------------------|-------------------|
|        |                  |                   |
| N(1)-N(2) | 1.269(3)          | Pt(1)-N(2) | 2.038(7)       |
| N(2)-N(3) | 1.336(3)          | Pt(1)-P(1) | 2.238(2)       |
| N(4)-C(8) | 1.333(3)          | Pt(1)-P(2) | 2.270(2)       |
| N(1)-N(2)-N(3) | 110.6(2) | Pt(1)-Cl(1) | 2.363(2)       |
|        | N(1)-C(1) | 1.422(3)          |                   |
|        | N(3)-C(8) | 1.388(3)          |                   |
|        | N(3)-C(8)-N(4) | 113.6(2) | N(3)-N(1)-N(2) | 112.9(7)       |