Supplementary Materials

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

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Fig. S2. ^{31}P NMR spectrum of $\text{Pt}(\text{PPh}_3)_2\text{Cl}_2$ in CDCl_3 .

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Pt(PPh₃)₂Cl₂ (green), and 9.32 μM Pt(PPh₃)₂(L)Cl (violet) in DMF (0.10 M [n-Bu₄N]ClO₄) under -1.45 V versus Ag/AgNO₃.

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Fig. S13. (a) GC traces after a 1-h controlled-potential electrolysis at -1.45V vs Ag/AgCl of $2.33\text{ }\mu\text{M}$ $\text{Pt}(\text{PPh}_3)_2(\text{L})\text{Cl}$ 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

$$\text{pH} = 14 + \lg \frac{\sum It}{FV} \quad \text{where } I = \text{current (A)}, t = \text{time (s)}, F = \text{Faraday constant (96485 C/mol)}, V = \text{solution volume (0.05 L)}.$$

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C/mol), $V = \text{solution volume (0.05 L)}$.

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 ($\text{pH } 7.0$). 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 $pH = 14 + \lg \frac{\sum It}{FV}$ 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(PPh₃)₂Cl₂ 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.

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

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

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

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

$$TOF = \frac{\Delta C}{F \cdot n_1 \cdot n_2 \cdot t} = \frac{1.55C \times 3600}{96485C \cdot mol^{-1} \times 2 \times 0.373 \times 10^{-6} mol \times 120} = 651.87 h^{-1}$$

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

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

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

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

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(PPh ₃) ₂ (L)Cl 1
Empirical formula	C ₁₂ H ₁₂ N ₄ O	C ₅₂ H ₅₁ ClN ₄ O ₃ P ₂ Pt
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/Å ³	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 F ²	0.940	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0520 wR2 = 0.1302	R1 = 0.0664 wR2 = 0.1664
R indices (all data)	R1 = 0.1278 wR2 = 0.1817	R1 = 0.0828 wR2 = 0.1726

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

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