A coordinatively saturated nickel complex supported by triazenido ligands, a new electrocatalyst for hydrogen generation via ligandcentered proton-transfer

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Calculated methods

According to Eqs. (1) 41 and (2) 42 (Eq. S1), electrocatalytic activities are estimated, and the results are listed in Fig. S8. For example, at an OP of 941.6 mV, this electrocatalytic system can afford 76.31 moles of hydrogen per mole of catalyst.

$$TOF = \frac{\Delta C}{F \cdot n_1 \cdot n_2 \cdot t}$$
(1)

Overpotential = Applied potential $-E^{\circ}_{HA}$

= Applied potential – $(E^{\circ}_{H^+}-(2.303RT/F)pK_{aHA})$ (2)

41 J. P. Cao, T. Fang, Z. Q. Wang, Y. W. Ren and S. Z. Zhan, *J. Mol. Cata. A: Chem.*, 2014, **391**, 191–197.

42 G. A. N. Felton, R. S. Glass, D. L. Lichtenberger and D. H. Evans, *Inorg. Chem.*, 2006, **45**, 9181-9184.

Where, ΔC is the charge from the catalyst solution during CPE minus the charge from solution without catalyst during CPE; F is Faraday's constant, n_1 is the number of moles of electrons required to generate one mole of H₂, n_2 is the number of moles of catalyst in solution, and t is the duration of electrolysis.

Physical measurements for this paper

Elemental analyses for C, H, and N were conducted on a Perkin-Elmer analyzer model 240. UV-Vis spectra were measured on a Hitachi U-3010. ESI-MS experiments were performed on a Bruker Daltonics Esquire 3000 Spectrometer by introducing samples directly into the ESI source using a syringe pump. The energy dispersive spectrometer (EDS) measurement was carried out on a Shimadzu EPMA-1600 electron probe X-ray microanalyser. Cyclic voltammograms (CVs) were obtained on a CHI-660E electrochemical analyzer under N2 using a three-electrode cell in which a glassy carbon electrode, 1 mm in diameter) was the working electrode, a saturated Ag/AgNO₃ electrode was the reference electrode, and platinum wire was the auxiliary electrode. A ferrocene/ferrocenium (1+) couple was used as an internal standard. 0.10 M [(n-Bu)₄N]ClO₄ was used as the supporting electrolyte. Acetic acid was added by syringe. Controlled-potential electrolysis (CPE) in CH₃CN was conducted using an air-tight glass double compartment cell separated by a glass frit. The working compartment was fitted with a glassy carbon plate and an Ag/AgNO₃ reference electrode. The auxiliary compartment was fitted with a Pt gauze electrode. The working compartment was filled with 50 mL of acetic acid in a 0.10 Μ

[(n-Bu₄N)]ClO₄ CH₃CN solution, while the auxiliary compartment was filled with 35 mL of 0.10 M [(n-Bu₄N)]ClO₄ CH₃CN solution, resulting in equal solution levels in both compartments. CPE in aqueous media was also conducted using an air-tight glass double compartment cell separated by a glass frit. The working compartment was fitted with a glassy carbon plate and an Ag/AgCl reference electrode. The auxiliary compartment was fitted with a Pt gauze electrode. The working compartment was filled with 50 mL of 0.25 M phosphate buffer solution (CH₃CN:H₂O = 2:5 as solvent), while the auxiliary compartment was filled with 35 mL buffer solution. After addition of complex **1**, both compartments were bubbled for 60 min with N₂ and CVs were recorded as controls. After electrolysis, a 0.5 mL aliquot of the headspace was removed and replaced with 0.5 mL of CH₄. A sample of the headspace was injected into the gas chromatograph (GC). GC experiments were carried out with an Agilent Technologies 7890A gas chromatography instrument.

Crystal structure determination

The X-ray analysis of **1** was carried out with a Bruker P4 X-ray diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 113 K. All empirical absorption corrections were applied by using the SADABS program.⁵⁰ The structure was solved using direct methods and the corresponding non-hydrogen atoms are refined anisotropically. All the hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL-2014 computer program.⁵¹ Details of the crystal parameters, data collection and refinement for the nickel complex are listed in Table S1, and selected bond distances are given in Table S2. CCDC 1547901 contains the supplementary crystallographic data of **1**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

- 50 G. M. Sheldrick, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Göttingen, Germany, (1996).
- 51 G. M. Sheldrick, Acta Cryst., 2015, C71, 3-8.

Supplementary Materials

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Fig. S1. ESI-MS of the nickel complex, 1 in methanol.



Fig. S2. UV-Vis spectra of the nickel complex, 1 and the related components in CH_3CN .



Fig. S3. Cyclic voltammogram of 1.71 mM ligand in 0.10 M of [n-Bu₄N]ClO₄ CH₃CN solution at a glassy carbon electrode and a scan rate of 100 mV/s.



Fig. S4. Cyclic voltammogram of 1.71 mM Ni $(CH_3CO_2)_2$ in 0.10 M of $[n-Bu_4N]ClO_4$ CH₃CN solution at a glassy carbon electrode and a scan rate of 100 mV/s.



Fig. S5. Scan rate dependence of catalytic wave for a 1.71 mM solution of complex **1** (0.10 M [n-Bu₄N]ClO₄), at scan rates from 50 to 300 mV/s.



Fig. S6. Cyclic voltammograms of 1.71 mM **1** in 0.10 M of [n-Bu₄N]ClO₄ CH₃CN solution (black), when addition of 4.64 mM of acetic acid (red); further addition of 4.64 mM triethylamine (TEA). Conditions: 0.10 M [n-Bu₄N]ClO₄ as supporting electrolyte, scan rate: 100 mV/s, glassy carbon working electrode (1.0 mm diameter), Pt counter electrode, Ag/AgNO₃ reference electrode, Fc internal standard (*).



Fig. S7. Cyclic voltammograms of a 1.71 mM solution of ligand, with varying concentrations of acetic acid in CH₃CN. Conditions: 0.10 M [n-Bu₄N]ClO₄ as supporting electrolyte, scan rate: 100 mV/s, glassy carbon working electrode (1.0 mm diameter), Pt counter electrode, Ag/AgNO₃ reference electrode, Fc internal standard (*).



Fig. S8. (a) Charge buildup versus time from electrolysis of a 3.68 μ M complex **1** in CH₃CN (0.10 M [n-Bu₄N]ClO₄) under various applied potentials. All data have

been deducted blank. (b) Charge buildup versus time from electrolysis of a 0.10 M [n-Bu₄N]ClO₄.



Fig. S8. Turnover frequency (mol H_2 /mol catalysts h^{-1}) for electrocatalystic hydrogen production by complex **1** (3.68 μ M) under a series of overpotentials.



Fig. S10. Cyclic voltammograms (CVs) of complex **l** in different concentration. Conditions: 0.25 M phosphate buffered solution (pH 7.0), glassy carbon working electrode (1.0 mm diameter), Pt wire counter electrode, Ag/AgCl reference electrode.



Fig. S11. CVs of ligand (0.295 μ M) in different pH values. Conditions: 0.25 M phosphate buffered solution, glassy carbon working electrode (1.0 mm diameter), Pt wire counter electrode, Ag/AgNO₃ reference electrode.





Fig. S12. (a) GC traces after a 1 h controlled-potential electrolysis at -1.45 V versus Ag/AgCl of 3.68 μ M complex **1** 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 **1** during electrolysis. (the theoretical pH change over time can be calculated by the equation of $pH = 14 + log \sum_{FV}^{It}$ where I = current (A), t = time (s), F = Faraday constant (96485)

C/mol), V = solution volume (0.05 L)).



Fig. S13. Turnover frequency (mol H_2 /mol catalysts/h) for electrocatalystic hydrogen production by complex 1 under a series of overpotentials.



Fig. S14. (a) Charge buildup versus time from electrolysis of a 0.25 M buffer solution (pH 7.0) under -1.45 V versus Ag/AgCl. (b) Charge buildup versus time from electrolysis of a 3.68 μ M HL in a 0.25 M buffer solution (pH 7.0) under various applied potentials. All data have been deducted blank.



Fig. S15. Turnover frequency (mol H_2 /mol catalysts/h) for electrocatalystic hydrogen production by HL under a series of overpotentials.



Fig. S16. CV of acetic acid (19.0 μ M). Glassy carbon working electrode (1.0 mm diameter), Pt counter electrode, Ag/AgNO₃ reference electrode, scan rate 100 mV/s.



Fig. S17. Extended controlled potential electrolysis of 5.38 μ M complex **1**, showing charge buildup versus time with an applied potential of -1.45 V versus Ag/AgCl. Conditions: 0.25 M aqueous buffer solution (pH 7.0), glassy carbon working electrode (1.25 cm²), Ag/AgCl reference electrode, Pt wire counter electrode.



Fig. S18. UV-vis spectra of complex **1** before and after a 72 h electrolysis in phosphate buffer solutions (pH 7.0).



Fig. S19. 20 cycles of cyclic voltammograms of 1.71 mM complex **1** in 0.25 M phosphate buffer solutions (pH 7.0), glassy carbon working electrode, Pt counter electrode, Ag/AgCl reference electrode, scan rate 100 mV/s.





Fig. S20. Energy Dispersive Spectrometer (EDS) of a glassy carbon electrode after a 4 hours electrolysis. There was no significant change in the EDS after electrolysis.

$$TOF = \frac{\Delta C}{F \cdot n_1 \cdot n_2 \cdot t} = \frac{0.0724C \times 3600}{96485C \cdot mol^{-1} \times 2 \times 0.1475 \times 10^{-6} mol \times 120} = 76.31h^{-1}$$

Eq. S1. The calculation of TOF for H_2 generation by the nickel complex from acetic acid.

$$TOF = \frac{\Delta C}{F \cdot n_1 \cdot n_2 \cdot t} = \frac{0.625C \times 3600}{96485C \cdot mol^{-1} \times 2 \times 0.1475 \times 10^{-6} mol \times 120} = 658.76h^{-1}$$

Eq. S2. The calculation of TOF for H_2 generation by the nickel complex from aqueous buffer.

$$TOF = \frac{\Delta C}{F \cdot n_1 \cdot n_2 \cdot t} = \frac{0.0686C \times 3600}{96485C \cdot mol^{-1} \times 2 \times 0.1475 \times 10^{-6} mol \times 120} = 72.30h^{-1}$$

Eq. S3. The calculation of TOF for H_2 generation by the ligand (HL) from aqueous buffer.

Empirical formula	$C_{28}H_{16}N_{10}S_4N_1$		
Formula weight	679.46		
Temperature/K	113.15		
Crystal system	tetragonal		
Space group	I-4		
a/Å	10.256(8)		
b/Å	10.256(8)		
c/Å	13.160(10)		
α/°	90		
β/°	90		
γ/°	90		
Volume/Å ³	1384(2)		
Z	2		
$\rho_{calc}g/cm^3$	1.630		
μ/mm^{-1}	1.044		
F(000)	692.0		
Crystal size/mm ³	$0.12 \times 0.08 \times 0.06$		
Radiation	MoKa ($\lambda = 0.71073$)		
2Θ range for data collection/°	5.036 to 49.94		
Index ranges	$-12 \le h \le 12, -12 \le k \le 11, -15 \le l \le 14$		
Reflections collected	5830		
Independent reflections	1221 [$R_{int} = 0.2740, R_{sigma} = 0.1433$]		
Data/restraints/parameters	1221/0/99		
Goodness-of-fit on F^2	1.031		
Final R indexes [I>= 2σ (I)]	$R_1 \!=\! 0.0678, wR_2 \!= 0.1619$		
Final R indexes [all data]	$R_1 = 0.0713, wR_2 = 0.1654$		
Largest diff. peak/hole / e Å ⁻³	1.36/-0.49 21		

 Table S1 Crystal data and structure refinement for the nickel(II) complex 1

Table S2 Selected bond lengths (Å) for the nickel(II) complex 1

Ni1-N1 ¹	2.092(8)	Ni1-N1 ²	2.092(8)
Ni1-N1 ³	2.092(8)	Ni1-N1	2.092(8)
Ni1-N3	2.051(9)	Ni1-N3 ¹	2.051(9)