

Synthesis of bridging hydrides of phenyl-functionalized diiron propanedithiolate complexes with 1,2-bis(diphenylphosphine) ethylene or 1,2-bis(diphenylphosphine)ethane ligands

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Abstract Reaction of 2-phenyl-1,3-dibromopropane with in situ generated $(\mu$ -SLi)₂Fe₂(CO)₆ yielded a known complex $[(\mu$ -SCH₂)₂CHC₆H₅]Fe₂(CO)₆ (A). Displacement of two carbonyls from complex A by cis-1,2-bis(diphenylphosphine)ethylene (dppv) or 1,2-bis(diphenylphosphine)ethane (dppe) in the presence of Me₃NO·2H₂O gave two chelate complexes $[(\mu$ -SCH₂)₂CHC₆H₅]Fe₂(CO)₄(κ^2 -dppv), $[A(\kappa^2$ dppv)] and $[(\mu$ -SCH₂)₂CHC₆H₅]Fe₂(CO)₄(κ^2 -dppe), $[A(\kappa^2$ dppe)], respectively. Protonation of the diiron centers of $[A(\kappa^2 - dppv)]$ and $[A(\kappa^2 - dppe)]$ using an excess of HBF₄·Et₂O in dichloromethane at room temperature gave the bridging hydrides $[(\mu-H)A(\kappa^2-dppv)]BF_4$ and $[(\mu-H)A(\kappa^2-dppe)]BF_4$. The complexes $[(\mu-H)A(\kappa^2-dppv)]BF_4$, $[A(\kappa^2-dppe)]$ and $[(\mu-H)A(\kappa^2-dppv)]BF_4$, $[A(\kappa^2-dppe)]$ H)A(κ^2 -dppe)]BF₄ were characterized by elemental analysis and spectroscopic methods, and $[(\mu-H)A(\kappa^2-dppv)]BF_4$ and $[(\mu-H)A(\kappa^2-dppe)]BF_4$ were also characterized by X-ray crystallography. The electrochemical behavior of $[(\mu -$ H)A(κ^2 -dppv)]BF₄ was investigated by cyclic voltammetry, and the catalytic electrochemical reduction in protons from trifluoroacetic acid or p-methylbenzene sulfonic acid to give hydrogen was investigated.

Introduction

In nature, the evolution and oxidation of hydrogen are primarily carried out by hydrogenase (H₂ase) enzymes [1]. According to the metal compositions of their active sites, distinct [NiFe], [FeFe] and [Fe] H₂ases have been identified, among which [FeFe] H₂ase is usually committed to the catalytic production of hydrogen [2-4]. For example, 6000-9000 hydrogen molecules per second are evolved from [FeFe] H₂ase under fermentation conditions [2]. Such high performance is of considerable interest from the point of view of gaining insights into the mechanism of [FeFe] H₂ase and eventually designing robust catalysts for evolution or uptake of hydrogen [5-8]. Indeed, a large amount of investigations have been devoted to structural and functional H₂ase mimics, especially following the characterization of the active sites of [FeFe] H₂ase by X-ray crystallography (Fig. 1) [9-11]. The active site is composed of a [2Fe2S] core, in which two iron atoms are linked by a dithiolate cofactor (SCH₂XCH₂S; X = NH, CH₂ or O) and coordinated by CN⁻ ligands and terminal, bridged or semi-bridged CO ligands. A cubane [4Fe4S] cluster, which relays electrons from and to the [2Fe2S] active site, is tethered to the Fe_p (Fe atom proximal to the [4Fe4S] cluster) of the [2Fe2S] core by the sulfur atom of a cysteine ligand, whereas Fe_d (Fe atom distal from the [4Fe4S] cluster) has an open site at an apical position, where substrates can be combined [12, 13]. During the course of investigations on the synthesis and reactivity of iron hydrides pertinent to the processes of evolution or uptake of hydrogen by [FeFe] H₂ase, many terminal or bridging hydrides have been synthesized [14-21]. In continuation of research into phenyl-functionalized diiron propanedithiolate complexes [22–24], in this paper, we report two bridging hydrides containing chelating 1,2-

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 $\mathbf{X} = \mathbf{CH}_2, \mathbf{O} \text{ or } \mathbf{NH}_2$

Fig. 1 Structure of the active sites of [FeFe] H₂ase

bis(diphenylphosphine)ethylene or 1,2-bis(diphenylphosphine)ethane ligands.

Experimental

Materials and methods

All manipulations were performed using standard Schlenk line and syringe/rubber septa techniques under an argon atmosphere. Solvents were of reagent grade and purified as follows: dichloromethane and acetonitrile were distilled over CaH₂, while *n*-hexane and THF were purified by distillation from sodium/diphenylmethanone. (μ -S₂)Fe₂(CO)₆ [25] and [A(κ^2 dppv)] [26] were prepared according to literature methods. LiBEt₃H (1 M in THF) and Me₃NO·2H₂O were available commercially and used as received. Preparative TLC was carried out on glass plates (25 cm × 20 cm × 0.25 cm) coated with silica gel G (10–40 µm). IR spectra were recorded on a Bruker TENSOR 27 FTIR spectrometer. ¹H and ³¹P NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer. Elemental analyses were obtained on an Elementar Vario EL III analyzer.

Electrochemical measurements were carried out under dry nitrogen using a CHI 620 Electrochemical Workstation (Chen-Hua instrument co., Shanghai, China). *n*-Bu₄NPF₆ (0.1 M in CH₃CN) was used as the electrolyte. CV scans were obtained in a three-electrode cell with a glassy carbon electrode (3 mm diameter) as the working electrode, successively polished with 3- and 1-µm diamond pastes and sonicated in ion-free water for 1 min, a platinum wire as counter electrode, and a nonaqueous Ag/Ag⁺ electrode (1.0 mM AgNO₃ and 0.1 M *n*-Bu₄NPF₆ in CH₃CN) as reference. The potential scale was calibrated against the Fc/Fc⁺ couple and is reported versus this reference system.

X-ray structure determination

Single crystals for X-ray diffraction analysis were grown by slow evaporation of CH_2Cl_2 /hexane solutions of [(μ - H)A(κ^2 -dppv)]BF₄ or [(μ -H)A(κ^2 -dppe)]BF₄ at 5 °C. For each complex, a suitable crystal was selected and analyzed on an Xcalibur, Eos, Gemini diffractometer. The crystal was kept at 291.15 K during data collection. Using Olex2 [27], the structures were solved with the ShelXS structure solution program using direct methods and refined with the ShelXL refinement package using least-squares minimization [28]. The F atoms of the BF₄⁻ anions were disordered over two sets of sites with occupancies of 0.54:0.46 for [(μ -H)A(κ^2 -dppv)]BF₄ and 0.74:0.26 for [(μ -H)A(κ^2 dppe)]BF₄, respectively. Bond (DFIX) and thermal (EADP) restraints were placed on these F atoms. Details of crystal data, data collections, and structure refinement of bridging hydrides [(μ -H)A(κ^2 -dppv)]BF₄ are summarized in Table 1.

Preparation of complex A

A solution of $[(\mu-S)_2Fe_2(CO)_6]$ (0.292 g, 0.85 mmol) in THF (10 ml) was cooled to -78 °C with a liquid nitrogen/ alcohol bath. LiBEt₃H (1 M in THF, 1.70 ml, 1.70 mmol) was added dropwise to this solution by syringe. At the midpoint of the addition, the reaction solution turned from red to dark emerald green and remained green for the rest of addition. After stirring at -78 °C for ca. 15 min, a solution of 2-phenyl-1,3-dibromopropane (0.237 g, 0.85 mmol) in THF (5 ml) was transferred to the reaction solution by a canula. The coolant bath was removed, and the reaction solution was stirred at room temperature for about 3 h. During this period, the color of the solution changed back to red. The solvent was removed on a rotary evaporator, and the residue was subjected to preparative TLC separation using CH_2Cl_2 /petroleum ether (v/v = 1:6) as the eluent. From the second red band, complex A was obtained as a red solid (0.181 g, 46 %). IR (KBr disk, cm⁻¹): $v_{C=0} 2071$ (vs), 2021 (vs), 2006 (vs), 1970 (vs). ¹H NMR (400 MHz, CDCl₃, ppm): 1.82 (t, 2 H, ² $J_{HaHe} = {}^{3}J_{HaHa'} = 13.4$ Hz, 2 SC $H_{a}H_{e}$), 2.35 (m, 1 H, CH), 2.70, 2.74 (dd, 2 H, ${}^{3}J_{\text{HeHa}} = 3.5$ Hz, ${}^{2}J_{\text{HeHa}} = 13.2 \text{ Hz}, 2 \text{ SCH}_{a}H_{e}), 7.10-7.31 \text{ (m, 5 H, C}_{6}H_{5}).$ Anal. Calc. for C₁₅H₁₀Fe₂O₆S₂: C, 39.0; H, 2.2. Found: C, 38.8; H, 2.3 %.

Preparation of $[A(\kappa^2 - dppe)]$

To a solution of complex **A** (0.092 g, 0.20 mmol) and dppe (0.080 g, 0.20 mmol) in MeCN (10 ml) was added Me₃₋NO·2H₂O (0.022 g, 0.20 mmol), and the resulting solution was stirred at 80 °C for 15 h. After removing the solvent on a rotary evaporator, the residue was subjected to preparative TLC separation using CH₂Cl₂/petroleum ether (v/ v = 1:1) as the eluent. From the green band, the complex [A(κ^2 -dppe)] was obtained as a deep green solid (0.040 g, 25 %). IR (KBr disk, cm⁻¹): v_{C=O} 2007 (s), 1929 (vs),

Table 1 Crystal data and structural refinements for [(μ -H)A(κ ²-dppv)]BF₄ and [(μ -H)A(κ ²-dppe)]BF₄

$[(\mu-H)A(\kappa^2-dppv)]BF_4$ $[(\mu-H)A(\kappa^2-dppv)]BF_4$ Empirical formula $C_{39}H_{33}BF_4Fe_2O_4P_2S_2$ $C_{39}H_{35}BF_4Fe_2O_4P_2S_2$ Formula weight 890.22 892.24 Temperature/K 291.15 291.15 Crystal systemTriclinicTriclinicSpace group $P\bar{r}$ $P\bar{r}$ $a/Å$ $10.9839(7)$ $10.2201(6)$ $b/Å$ $14.4739(9)$ $14.5303(10)$ $c/Å$ $26.4000(17)$ $27.750(2)$ $x/°$ $87.738(5)$ $91.727(6)$ $\beta/°$ $70.628(6)$ $104.930(6)$ Volume/Å ³ $3954.3(4)$ $3928.9(5)$ Z 4 4 $\rho_{cabc}mg/mm^3$ 1.495 1.508 u/mm^{-1} 8.141 8.194 $F(000)$ 1816.0 1824.0 Crystal size/mm ³ $0.14 \times 0.12 \times 0.08$ $0.14 \times 0.1 \times 0.05$ 2ℓ range for data collection 6.48 to $127.74°$ 6.32 to 134.16 $-12 \le h \le 12$ $-12 \le h \le 12$ $-12 \le h \le 12$ Index ranges $-10 \le k \le 16$ $-17 \le k \le 14$ $-30 \le l \ge 30$ $-22 \le l \le 33$ $2\ell = 33$ Reflections collected $24,812$ $27,019$ Independent reflections (R_{int}) $12,798 [0.0453]$ $13,829 [0.0484]$ Data/restraints/parameters $12,798/14/1007$ $13,829/2/881$ Goodness-of-fit on F^2 1024 1016 Final R indexes [$I \ log (A)$] $R_1 = 0.0257, wR_2 = 0.1244$ $R_1 = 0.0145, wR_2 = 0.174$ Final R indexes [all data] $R_1 = 0.023, wR_2 = 0.124$			
Empirical formula $C_{30}H_{33}BF_4Fe_2O_4P_2S_2$ $C_{30}H_{35}BF_4Fe_2O_4P_2S_2$ Formula weight 890.22 892.24 Temperature/K 291.15 291.15 Crystal system Triclinic Triclinic Space group PT PT $a/Å$ 10.9839(7) 10.2201(6) $b/Å$ 14.4739(9) 14.5303(10) $c/Å$ 26.4000(17) 27.750(2) $x/°$ 87.738(5) 91.727(6) $\beta/°$ 70.628(6) 104.930(6) Volume/Å ³ 3954.3(4) 3928.9(5) Z 4 4 $\rho_{cabc}mg/mm^3$ 1.495 1.508 u/mm^{-1} 8.141 8.194 $F(000)$ 1816.0 1824.0 Crystal size/mm ³ 0.14 × 0.12 × 0.08 0.14 × 0.1 × 0.05 2ℓ arange for data collection 6.48 to 127.74° 6.32 to 134.16 $-12 \le h \le 12$ $-12 \le h \le 12$ $-12 \le h \le 12$ Index ranges $-10 \le k \le 16$ $-17 < k \le 14$ $-30 \le l \le 30$ $-$		$[(\mu-H)A(\kappa^2-dppv)]BF_4$	$[(\mu-H)A(\kappa^2-dppe)]BF_4$
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$\beta/^{\circ}$ 87.482(5)98.427(6) $\gamma/^{\circ}$ 70.628(6)104.930(6)Volume/Å ³ 3954.3(4)3928.9(5) Z 44 $\rho_{calc} mg/mm^3$ 1.4951.508 u/mm^{-1} 8.1418.194 $F(000)$ 1816.01824.0Crystal size/mm ³ 0.14 × 0.12 × 0.080.14 × 0.1 × 0.05 2θ range for data collection6.48 to 127.74°6.32 to 134.16 $-12 \le h \le 12$ $-12 \le h \le 12$ $-12 \le h \le 12$ Index ranges $-10 \le k \le 16$ $-17 \le k \le 14$ $-30 \le l \le 30$ $-22 \le l \le 33$ Reflections collected24,81227,019Independent reflections (R_{int})12,798 [0.0453]13,829 [0.0484]Data/restraints/parameters12,798/14/100713,829/2/981Goodness-of-fit on F^2 1.0241.016Final R indexes [all data] $R_1 = 0.1023, wR_2 = 0.1244$ $R_1 = 0.1122, wR_2 = 0.1744$ Largest difference in peak/hole/e Å ⁻³ 0.50/-0.360.72/-0.39	x/°	87.738(5)	91.727(6)
$y/^{\circ}$ 70.628(6)104.930(6)Volume/Å33954.3(4)3928.9(5)Z44 $\rho_{ealc}mg/mm^3$ 1.4951.508 u/mm^{-1} 8.1418.194 $F(000)$ 1816.01824.0Crystal size/mm30.14 × 0.12 × 0.080.14 × 0.1 × 0.052 θ range for data collection6.48 to 127.74°6.32 to 134.16 $-12 \le h \le 12$ $-12 \le h \le 12$ $-12 \le h \le 12$ Index ranges $-10 \le k \le 16$ $-17 \le k \le 14$ $-30 \le l \le 30$ $-22 \le l \le 33$ Reflections collected24,81227,019Independent reflections (R_{int})12,798 [0.0453]13,829 [0.0484]Data/restraints/parameters12,798/14/100713,829/2/981Goodness-of-fit on F^2 1.0241.016Final R indexes [$I \ge 2\sigma$ (I)] $R_1 = 0.0557$, $wR_2 = 0.1044$ $R_1 = 0.1122$, $wR_2 = 0.174$ Largest difference in peak/hole/e Å^30.50/-0.360.72/-0.39	β/°	87.482(5)	98.427(6)
Volume/ų3954.3(4)3928.9(5)Z44 $\rho_{calc}mg/mm^3$ 1.4951.508 u/mm^{-1} 8.1418.194F(000)1816.01824.0Crystal size/mm³0.14 × 0.12 × 0.080.14 × 0.1 × 0.052 θ range for data collection6.48 to 127.74°6.32 to 134.16 $-12 \le h \le 12$ $-12 \le h \le 12$ $-12 \le h \le 12$ Index ranges $-10 \le k \le 16$ $-17 \le k \le 14$ $-30 \le l \le 30$ $-22 \le l \le 33$ Reflections collected24,81227,019Independent reflections (R_{int})12,798 [0.0453]13,829 [0.0484]Data/restraints/parameters12,798/14/100713,829/2/981Goodness-of-fit on F^2 1.0241.016Final R indexes [$I \ge 2\sigma$ (I)] $R_1 = 0.0557$, $wR_2 = 0.1044$ $R_1 = 0.0645$, $wR_2 = 0.147$ Final R indexes [all data] $R_1 = 0.1023$, $wR_2 = 0.1244$ $R_1 = 0.1122$, $wR_2 = 0.174$ Largest difference in peak/hole/e Å ⁻³ 0.50/-0.360.72/-0.39	γ / °	70.628(6)	104.930(6)
Z44 $\rho_{calc} mg/mm^3$ 1.4951.508 μ/mm^{-1} 8.1418.194 $F(000)$ 1816.01824.0Crystal size/mm^30.14 × 0.12 × 0.080.14 × 0.1 × 0.05 2θ range for data collection6.48 to 127.74°6.32 to 134.16 $-12 \le h \le 12$ $-12 \le h \le 12$ $-12 \le h \le 12$ Index ranges $-10 \le k \le 16$ $-17 \le k \le 14$ $-30 \le l \le 30$ $-22 \le l \le 33$ Reflections collected24,81227,019Independent reflections (R_{int})12,798 [0.0453]13,829 [0.0484]Data/restraints/parameters12,798/14/100713,829/2/981Goodness-of-fit on F^2 1.0241.016Final R indexes [$I \ge 2\sigma$ (I)] $R_1 = 0.0557$, $wR_2 = 0.1044$ $R_1 = 0.0645$, $wR_2 = 0.147$ Final R indexes [all data] $R_1 = 0.1023$, $wR_2 = 0.1244$ $R_1 = 0.1122$, $wR_2 = 0.174$ Largest difference in peak/hole/e Å ⁻³ 0.50/-0.360.72/-0.39	Volume/Å ³	3954.3(4)	3928.9(5)
$\rho_{calc} mg/mm^3$ 1.4951.508 u/mm^{-1} 8.1418.194 $F(000)$ 1816.01824.0Crystal size/mm^30.14 × 0.12 × 0.080.14 × 0.1 × 0.05 2θ range for data collection6.48 to 127.74°6.32 to 134.16 $-12 \le h \le 12$ $-12 \le h \le 12$ $-12 \le h \le 12$ Index ranges $-10 \le k \le 16$ $-17 \le k \le 14$ $-30 \le l \le 30$ $-22 \le l \le 33$ Reflections collected24,81227,019Independent reflections (R_{int})12,798 [0.0453]13,829 [0.0484]Data/restraints/parameters12,798/14/100713,829/2/981Goodness-of-fit on F^2 1.0241.016Final R indexes [$I \ge 2\sigma$ (I)] $R_1 = 0.0557$, $wR_2 = 0.1044$ $R_1 = 0.0645$, $wR_2 = 0.147$ Final R indexes [all data] $R_1 = 0.1023$, $wR_2 = 0.1244$ $R_1 = 0.1122$, $wR_2 = 0.174$ Largest difference in peak/hole/e Å ⁻³ 0.50/-0.360.72/-0.39	Ζ	4	4
μ/nm^{-1} 8.1418.194 $F(000)$ 1816.01824.0Crystal size/mm³0.14 × 0.12 × 0.080.14 × 0.1 × 0.05 2θ range for data collection6.48 to 127.74°6.32 to 134.16 $-12 \le h \le 12$ $-12 \le h \le 12$ $-12 \le h \le 12$ Index ranges $-10 \le k \le 16$ $-17 \le k \le 14$ $-30 \le l \le 30$ $-22 \le l \le 33$ Reflections collected24,81227,019Independent reflections (R_{int})12,798 [0.0453]13,829 [0.0484]Data/restraints/parameters12,798/14/100713,829/2/981Goodness-of-fit on F^2 1.0241.016Final R indexes [$I \ge 2\sigma$ (I)] $R_1 = 0.0557$, $wR_2 = 0.1044$ $R_1 = 0.0645$, $wR_2 = 0.147$ Final R indexes [all data] $R_1 = 0.1023$, $wR_2 = 0.1244$ $R_1 = 0.1122$, $wR_2 = 0.174$ Largest difference in peak/hole/e Å ⁻³ 0.50/-0.360.72/-0.39	$\rho_{\rm calc} {\rm mg/mm}^3$	1.495	1.508
$F(000)$ 1816.01824.0Crystal size/mm³ $0.14 \times 0.12 \times 0.08$ $0.14 \times 0.1 \times 0.05$ 2θ range for data collection 6.48 to 127.74° 6.32 to 134.16 $-12 \le h \le 12$ $-12 \le h \le 12$ $-12 \le h \le 12$ Index ranges $-10 \le k \le 16$ $-17 \le k \le 14$ $-30 \le l \le 30$ $-22 \le l \le 33$ Reflections collected $24,812$ $27,019$ Independent reflections (R_{int}) $12,798$ [0.0453] $13,829$ [0.0484]Data/restraints/parameters $12,798/14/1007$ $13,829/2/981$ Goodness-of-fit on F^2 1.024 1.016 Final R indexes [$I \ge 2\sigma$ (I)] $R_1 = 0.0557, wR_2 = 0.1044$ $R_1 = 0.0645, wR_2 = 0.147$ Final R indexes [all data] $R_1 = 0.1023, wR_2 = 0.1244$ $R_1 = 0.1122, wR_2 = 0.174$ Largest difference in peak/hole/e Å ⁻³ $0.50/-0.36$ $0.72/-0.39$	μ/mm^{-1}	8.141	8.194
Crystal size/mm³ $0.14 \times 0.12 \times 0.08$ $0.14 \times 0.1 \times 0.05$ 2θ range for data collection 6.48 to 127.74° 6.32 to 134.16 $-12 \le h \le 12$ $-12 \le h \le 12$ $-12 \le h \le 12$ Index ranges $-10 \le k \le 16$ $-17 \le k \le 14$ $-30 \le l \le 30$ $-22 \le l \le 33$ Reflections collected $24,812$ $27,019$ Independent reflections (R_{int}) $12,798$ [0.0453] $13,829$ [0.0484]Data/restraints/parameters $12,798/14/1007$ $13,829/2/981$ Goodness-of-fit on F^2 1.024 1.016 Final R indexes [$I \ge 2\sigma$ (I)] $R_1 = 0.0557, wR_2 = 0.1044$ $R_1 = 0.0645, wR_2 = 0.147$ Final R indexes [all data] $R_1 = 0.1023, wR_2 = 0.1244$ $R_1 = 0.1122, wR_2 = 0.174$ Largest difference in peak/hole/e Å ⁻³ $0.50/-0.36$ $0.72/-0.39$	F(000)	1816.0	1824.0
2θ range for data collection 6.48 to 127.74° 6.32 to 134.16 $-12 \le h \le 12$ $-12 \le h \le 12$ $-12 \le h \le 12$ Index ranges $-10 \le k \le 16$ $-17 \le k \le 14$ $-30 \le l \le 30$ $-22 \le l \le 33$ Reflections collected $24,812$ $27,019$ Independent reflections (R_{int}) $12,798$ [0.0453] $13,829$ [0.0484]Data/restraints/parameters $12,798/14/1007$ $13,829/2/981$ Goodness-of-fit on F^2 1.024 1.016 Final R indexes [$I \ge 2\sigma$ (I)] $R_1 = 0.0557, wR_2 = 0.1044$ $R_1 = 0.0645, wR_2 = 0.147$ Final R indexes [all data] $R_1 = 0.1023, wR_2 = 0.1244$ $R_1 = 0.1122, wR_2 = 0.174$ Largest difference in peak/hole/e Å ⁻³ $0.50/-0.36$ $0.72/-0.39$	Crystal size/mm ³	$0.14\times0.12\times0.08$	$0.14 \times 0.1 \times 0.05$
$-12 \le h \le 12$ $-12 \le h \le 12$ $-10 \le k \le 16$ $-17 \le k \le 14$ $-30 \le l \le 30$ $-22 \le l \le 33$ Reflections collected $24,812$ $27,019$ Independent reflections (R_{int}) $12,798 [0.0453]$ $13,829 [0.0484]$ Data/restraints/parameters $12,798/14/1007$ $13,829/2/981$ Goodness-of-fit on F^2 1.024 1.016 Final R indexes [$I \ge 2\sigma$ (I)] $R_1 = 0.0557, wR_2 = 0.1044$ $R_1 = 0.0645, wR_2 = 0.147$ Final R indexes [all data] $R_1 = 0.1023, wR_2 = 0.1244$ $R_1 = 0.1122, wR_2 = 0.174$ Largest difference in peak/hole/e Å ⁻³ $0.50/-0.36$ $0.72/-0.39$	2θ range for data collection	6.48 to 127.74°	6.32 to 134.16
Index ranges $-10 \le k \le 16$ $-17 \le k \le 14$ $-30 \le l \le 30$ $-22 \le l \le 33$ Reflections collected24,812Independent reflections (R_{int})12,798 [0.0453]Data/restraints/parameters12,798/14/1007Goodness-of-fit on F^2 1.024Final R indexes [$I \ge 2\sigma$ (I)] $R_1 = 0.0557$, $wR_2 = 0.1044$ R_1 = 0.1023, $wR_2 = 0.1244$ $R_1 = 0.1122, wR_2 = 0.174$ Largest difference in peak/hole/e Å ⁻³ 0.50/-0.360.72/-0.39 $0.72/-0.39$		$-12 \le h \le 12$	$-12 \le h \le 12$
$-30 \le l \le 30$ $-22 \le l \le 33$ Reflections collected24,81227,019Independent reflections (R_{int})12,798 [0.0453]13,829 [0.0484]Data/restraints/parameters12,798/14/100713,829/2/981Goodness-of-fit on F^2 1.0241.016Final R indexes [$I \ge 2\sigma$ (I)] $R_1 = 0.0557$, $wR_2 = 0.1044$ $R_1 = 0.0645$, $wR_2 = 0.147$ Final R indexes [all data] $R_1 = 0.1023$, $wR_2 = 0.1244$ $R_1 = 0.1122$, $wR_2 = 0.174$ Largest difference in peak/hole/e Å ⁻³ 0.50/-0.360.72/-0.39	Index ranges	$-10 \le k \le 16$	$-17 \le k \le 14$
Reflections collected24,81227,019Independent reflections (R_{int}) 12,798 [0.0453]13,829 [0.0484]Data/restraints/parameters12,798/14/100713,829/2/981Goodness-of-fit on F^2 1.0241.016Final R indexes $[I \ge 2\sigma (I)]$ $R_1 = 0.0557, wR_2 = 0.1044$ $R_1 = 0.0645, wR_2 = 0.147$ Final R indexes [all data] $R_1 = 0.1023, wR_2 = 0.1244$ $R_1 = 0.1122, wR_2 = 0.174$ Largest difference in peak/hole/e Å ⁻³ 0.50/-0.360.72/-0.39		$-30 \le l \le 30$	$-22 \le l \le 33$
Independent reflections (R_{int}) 12,798 [0.0453]13,829 [0.0484]Data/restraints/parameters12,798/14/100713,829/2/981Goodness-of-fit on F^2 1.0241.016Final R indexes $[I \ge 2\sigma(I)]$ $R_1 = 0.0557, wR_2 = 0.1044$ $R_1 = 0.0645, wR_2 = 0.147$ Final R indexes [all data] $R_1 = 0.1023, wR_2 = 0.1244$ $R_1 = 0.1122, wR_2 = 0.174$ Largest difference in peak/hole/e Å ⁻³ 0.50/-0.360.72/-0.39	Reflections collected	24,812	27,019
Data/restraints/parameters12,798/14/100713,829/2/981Goodness-of-fit on F^2 1.0241.016Final R indexes $[I \ge 2\sigma(I)]$ $R_1 = 0.0557, wR_2 = 0.1044$ $R_1 = 0.0645, wR_2 = 0.147$ Final R indexes [all data] $R_1 = 0.1023, wR_2 = 0.1244$ $R_1 = 0.1122, wR_2 = 0.174$ Largest difference in peak/hole/e Å ⁻³ 0.50/-0.360.72/-0.39	Independent reflections (R_{int})	12,798 [0.0453]	13,829 [0.0484]
Goodness-of-fit on F^2 1.0241.016Final R indexes $[I \ge 2\sigma (I)]$ $R_1 = 0.0557, wR_2 = 0.1044$ $R_1 = 0.0645, wR_2 = 0.147$ Final R indexes [all data] $R_1 = 0.1023, wR_2 = 0.1244$ $R_1 = 0.1122, wR_2 = 0.174$ Largest difference in peak/hole/e Å ⁻³ $0.50/-0.36$ $0.72/-0.39$	Data/restraints/parameters	12,798/14/1007	13,829/2/981
Final R indexes $[I \ge 2\sigma(I)]$ $R_1 = 0.0557, wR_2 = 0.1044$ $R_1 = 0.0645, wR_2 = 0.147$ Final R indexes [all data] $R_1 = 0.1023, wR_2 = 0.1244$ $R_1 = 0.1122, wR_2 = 0.174$ Largest difference in peak/hole/e Å ⁻³ $0.50/-0.36$ $0.72/-0.39$	Goodness-of-fit on F^2	1.024	1.016
Final R indexes [all data] $R_1 = 0.1023, wR_2 = 0.1244$ $R_1 = 0.1122, wR_2 = 0.174$ Largest difference in peak/hole/e Å ⁻³ $0.50/-0.36$ $0.72/-0.39$	Final <i>R</i> indexes $[I \ge 2\sigma (I)]$	$R_1 = 0.0557, wR_2 = 0.1044$	$R_1 = 0.0645, wR_2 = 0.1470$
Largest difference in peak/hole/e $Å^{-3}$ 0.50/-0.36 0.72/-0.39	Final R indexes [all data]	$R_1 = 0.1023, wR_2 = 0.1244$	$R_1 = 0.1122, wR_2 = 0.1744$
	Largest difference in peak/hole/e $Å^{-3}$	0.50/-0.36	0.72/-0.39

1898 (s). ¹H NMR (400 MHz, CDCl₃, ppm): 1.74 (t, 2 H, ² $J_{HaHe} = {}^{3}J_{HaHa'} = 12$ Hz, 2 SC $H_{a}H_{e}$), 1.82 (m, 1 H, CH), 2.43 (d, 2 H, ${}^{2}J_{HeHa} = 12$ Hz, 2 SC $H_{a}H_{e}$), 2.54 (m, 2 H, 2 PC H_{2}), 2.68 (m, 2 H, 2 PC H_{2}), 6.20 (s, 2 H, C₆ H_{5}), 7.02 (s, 3 H, C₆ H_{5}), 7.37–7.51 (m, 16 H, C₆ H_{5}), 7.84 (s, 4 H, C₆ H_{5}). ³¹P NMR (161.9 MHz, CDCl₃, 85 % H₃PO₄, ppm): 91.1 (s, 70 %, basal–apical), 78.2 (s, 30 %, basal–basal). Anal. Calc. for C₃₉H₃₄Fe₂O₄P₂S₂: C, 58.2; H, 4.3. Found: C, 58.1; H, 4.3 %.

Protonation of $[A(\kappa^2 - dppv)]$ and $[A(\kappa^2 - dppe)]$

To a dichloromethane (15 ml) solution of $[A(\kappa^2-dppv)]$ (0.090 g, 0.11 mmol) was added HBF₄·Et₂O (52 %, 40 µL, 0.27 mmol) at room temperature. The resulting solution gradually changed from green to red. After stirring at room temperature for 2 h, the solution was filtered and the volatiles of the filtrate were removed. The resulting solid was washed with diethyl ether (ca. 3 × 1 ml). Subsequently, the solid was redissolved in dichloromethane (ca. 1 ml) and diethyl ether (ca. 10 ml) was added dropwise. After mixing, $[(\mu-H)A(\kappa^2-dppv)]BF_4$ (0.077 g, 79 %) was precipitated and isolated as a dark red solid. IR (KBr disk, cm⁻¹): $v_{C\equiv O}$ 2102 (s), 2043 (vs), 1967 (s). ¹H NMR (400 MHz, CD₂Cl₂, ppm): -14.69 (t, 1 H, $J_{PH} = 20.1$ Hz, μ -H), 2.699 (m, 2 H, 2 SCH_aH_e), 3.180 (m, 3 H, 2 SCH_aH_e, CH), 7.371–7.385 (m, 23 H, C₆H₅), 8.531 (m, 2 H, C₆H₅). ³¹P NMR (161.9 MHz, CD₂Cl₂, 85 % H₃PO₄, ppm): 83.6 (s). Anal. Calc. for C₃₉H₃₃BF₄Fe₂O₄P₂S₂: C, 52.6; H, 3.7. Found: C, 52.9; H, 3.5 %.

Repetition of the above operations using $[A(\kappa^2-dppe)]$ (0.042 g, 0.053 mmol) and HBF₄·Et₂O (52 %, 19 µL, 0.13 mmol) gave $[(\mu-H)A(\kappa^2-dppe)]BF_4$ (0.033 g, 71 %) as a dark red solid. IR (KBr disk, cm⁻¹): $v_{C=O}$ 2099 (s), 2034 (vs), 1946 (m). ¹H NMR (400 MHz, CD₂Cl₂, ppm): -14.30 (t, 1 H, $J_{PH} = 21.2$ Hz, μ -H), 1.80 (m, 1 H), 1.90 (m, 2 H), 2.60 (m, 2 H), 3.24 (m, 2 H), 3.35 (m, 2 H), 7.38–7.85 (m, 25 H, C₆H₅). ³¹P NMR (161.9 MHz, CDCl₃, 85 % H₃PO₄, ppm): 78.1 (s). Anal. Calc. for C₃₉H₃₅BF₄. Fe₂O₄P₂S₂: C, 52.5; H, 4.0. Found: C, 52.7; H, 3.7 %.

Results and discussion

Synthesis and spectroscopic characterization

The known complex A has been prepared previously by the addition of 2-phenyl-1,3-propanedithiol to Fe₃(CO)₁₂ in high yield [22]. However, preparation of 2-phenyl-1,3propanedithiol from 2-phenyl-1,3-propanediol requires at least 72 h. Thus, an alternative synthesis of complex A was designed. 2-Phenyl-1,3-propanediol was readily transformed to 2-phenyl-1,3-dibromopropane at room temperature using CBr₄ and triphenylphosphine. Subsequently, using the in situ generated dianion $[(\mu-S)_2Fe_2(CO)_6]^{2-}$ and 2-phenyl-1,3-dibromopropane, complex A could be readily prepared within 24 h from 2-phenyl-1,3-propanediol in spite of a medium yield [29]. The IR and ¹H NMR spectra of complex A closely matched those of the reported complex $[(\mu$ -SCH₂)₂CHC₆H₅]Fe₂(CO)₆ [22]. In the presence of ca. one equivalent of the decarbonylating agent Me₃₋ NO·2H₂O, the chelate complex $[A(\kappa^2 - dppv)]$ was synthesized in 90 % yield from complex A (Scheme 1) [26]. For the preparation of $[A(\kappa^2-dppe)]$, continuous heating at 80 °C for about 15 h was required but the yield was only 25 % [18, 21]. The inherent *cis*-configuration of the *cis*- dppv ligand may assist in the displacement of the second carbonyl, resulting in ready formation of $[A(\kappa^2 - dppv)]$, whereas dppe will require an internal rotation from *trans* to cis before replacement of the second carbonyl, perhaps hindering the formation of $[A(\kappa^2-dppe)]$. Compared with the IR spectrum of complex A (2071, 2021, 2006, 1970 cm⁻¹), the biggest absorption frequency of the terminal carbonyl of complex $[A(\kappa^2 - dppe)]$ (2007 cm⁻¹) was considerably shifted by about 64 cm⁻¹ toward lower frequency. This is consistent with two CO ligands being replaced by more electron-donating diphosphine ligands in chelating manner [18, 21, 30]. The ¹H NMR spectrum of $[A(\kappa^2-dppe)]$ showed that signals at 1.74, 1.82 and 2.43 ppm for the propanedithiolate protons shifted upfield compared with those of the complex A (1.82, 2.35 and 2.72 ppm), reflecting the increased electron density on the diiron center in [A(κ^2 -dppe)]. Two signals at 2.54 and 2.68 ppm were assigned to the methylene protons of the dppe ligand. The ³¹P NMR spectrum of $[A(\kappa^2 - dppe)]$ showed two signals at 91.1 and 78.2 ppm with different intensities, indicating alternate basal-apical and basalbasal conformations of the diphosphine in solution. Addition of excess HBF₄·Et₂O to a dichloromethane solution of either $[A(\kappa^2 - dppv)]$ or $[A(\kappa^2 - dppe)]$ at room temperature





resulted in a color change of the solution from green to red. Protonation of the diiron center of $[A(\kappa^2-dppv)]$ or $[A(\kappa^2-dppv)]$ dppe)] is indicated by the deserved shifts of 96 or 91 cm^{-1} , respectively, in the IR absorption frequencies of the terminal carbonyls to higher wavenumbers, as those observed for the protonation of $(\mu$ -pdt)Fe₂(CO)₄(κ^2 -dppe) [18], (μ pdt)Fe₂(CO)₄(κ^2 -dppp) [21], (μ -pdt)Fe₂(CO)₄[κ^2 -Ph₂₋ PN(allyl)PPh₂] [20] and $(\mu$ -pdt)Fe(CO)₃Fe(CO)(κ^2 -IMeCH₂IMe) [30]. Protonation of the diiron center or the bridging hydride was further confirmed by the ¹H NMR spectra, which showed a triplet at $\delta - 14.69$ or -14.30 ppm, respectively, at high field as those of analohydrides, $[(\mu-H)(\mu-pdt)Fe_2(CO)_4(\kappa^2$ bridging gous dppe)]BF₄ and $[(\mu-H)Fe_2(CO)_4(\kappa^2-dppp)(\mu-pdt)]BF_4$ [18, 21]. The ³¹P NMR spectra displayed changes from the two signals of the precursor $[A(\kappa^2 - dppv)]$ at 96.0 and 82.1 ppm to one signal for $[(\mu-H)A(\kappa^2-dppv)]BF_4$ at 83.6 ppm or from the two signals of $[A(\kappa^2-dppe)]$ at 91.1 and 78.2 ppm to one signal for $[(\mu-H)A(\kappa^2-dppe)]BF_4$ at 78.1 ppm, consistent with the chemical equivalence of the phosphines of $[(\mu-H)A(\kappa^2-dppv)]BF_4$ or $[(\mu-H)A(\kappa^2-dppe)]BF_4$ in a basal-basal conformation.

X-ray crystal structures

Single crystals of $[(\mu-H)A(\kappa^2-dppv)]BF_4$ and $[(\mu-H)A(\kappa^2-dppv)]BF_4$ dppe)]BF₄ suitable for X-ray diffraction were grown by slow evaporation of hexanes/dichloromethane solutions of $[(\mu-H)A(\kappa^2-dppv)]BF_4$ or $[(\mu-H)A(\kappa^2-dppe)]BF_4$, while all attempts to grow crystals of $[A(\kappa^2-dppe)]$ were unsuccessful. The molecular structures of $[(\mu-H)A(\kappa^2-dppv)]BF_4$ and $[(\mu-H)A(\kappa^2-dppe)]BF_4$ were unambiguously confirmed by X-ray crystallography (Figs. 2, 3) and crystal data, selected bond lengths and angles are listed in Tables 1 and 2. The metric parameters of the [2Fe2S] cluster in the [(μ -H)A(κ^2 -dppv)]⁺ cation vary only slightly from those found in the precursor $[A(\kappa^2 - dppv)]$. For example, the bond lengths of Fe–P (2.2223(14) and 2.2382(15) Å) and the bite angle of P1-Fe₂-P2 (87.03(5)°) are almost the same as those of the precursor $[A(\kappa^2 - dppv)]$ (2.1797(7) and 2.21235(6) Å, 87.31(2)°). Protonation occurs as expected across the Fe-Fe bond and leads to a shortening of this vector by ca. 0.03 Å (from 2.6090(5) Å in [A(κ^2 -dppv)] to 2.5832(10) Å in $[(\mu-H)A(\kappa^2-dppv)]BF_4$, similar to the shortening of the Fe-Fe bond during the protonation processes of $(\mu$ -pdt)Fe₂(CO)₅)(κ^2 -dppe) [18], $(\mu$ -pdt)Fe₂ $(CO)_2(\kappa^2-IMeCH_2IMe)$ [30] and $[Fe_2(CO)_4(\kappa^2-Ph_2PN)]$ $(allyl)PPh_2)(\mu-pdt)$ [20]. Both iron centers in the [(μ -H) $A(\kappa^2$ -dppv)]⁺ cation display distorted octahedral geometries, similar to previously reported bridging hydrides [18, 20, 31]. Each iron atom is displaced from its pyramidal base toward the apical direction, by 0.320(1) Å for Fe2 from the plane S1-S2-P1-P2 and by 0.215(1) Å for Fe1



Fig. 2 Molecular structure of $[(\mu-H)A(\kappa^2-dppv)]BF_4$ with thermal ellipsoids at 30 % probability

from the plane S1-S2-O2-O3. The biggest structural change during the protonation of $[A(\kappa^2 - dppv)]$ is the exchange of positions between a basal carbonyl ligand and an apical phosphine ligand coordinated to atom Fe₂, forming a basal-basal diphosphine complex $[(\mu-H)A(\kappa^2-dppv)]BF_4$. The other structural changes are an increase in the bond angles of Fe2-Fe1-C2 and Fe2-Fe1-C3 by about 6°, and a simultaneous decrease in the bond angles of Fe2-Fe1-C1 by about 4.5°, in order to make room for the hydride. The Fe1-H (1.644 Å) and Fe2-H (1.722 Å) distances are comparable to those of other bridging hydrides [30]. The framework of the $[(\mu-H)A(\kappa^2-dppe)]^+$ cation is similar to that of the $[(\mu-H)A(\kappa^2-dppv)]^+$ cation with the diphosphine of dppe coordinating atom Fe2 in a basal-basal conformation and a hydrogen atom bridging two iron atoms in a geometry close to that of the $[Fe_2(\mu-pdt)(CO)_4(\kappa^2-dppe)(\mu-\mu)]$ H)]⁺ cation [18]. The main difference between [(μ -H)A(κ^2 -dppv)]⁺ and [(μ -H)A(κ^2 -dppe)]⁺ cations is the bond length of C26-C27, which is a single bond of 1.5339(9) Å in $[(\mu-H)A(\kappa^2-dppe)]BF_4$ and double bond of 1.310(3) Å in $[(\mu-H)A(\kappa^2-dppv)]BF_4$. Correspondingly, the bond angle of P1-Fe2-P1 (87.57(6) °) in $[(\mu-H)A(\kappa^2$ dppe)]BF₄ is slightly larger than that of P1-Fe2-P1 $(87.03(5)^{\circ})$ in $[(\mu-H)A(\kappa^2-dppv)]BF_4$.



Fig. 3 Molecular structure of $[(\mu\text{-H})A(\kappa^2\text{-dppe})]BF_4$ with thermal ellipsoids at 30 % probability

Electrochemistry

The CVs of $[(\mu-H)A(\kappa^2-dppv)]BF_4$ and $[A(\kappa^2-dppv)]$ are shown in Fig. 4. The bridging hydride $[(\mu-H)A(\kappa^2-dp$ $pv)]BF_4$ displayed two reduction processes at -1.305 and -1.792 V and one oxidation process at +0.779 V. Compared with redox potentials of $[A(\kappa^2-dppv)]$, positive shifts of 0.75–0.80 V were observed due to protonation of the



Fig. 4 CVs of $[(\mu-H)A(\kappa^2-dppv)]BF_4$ and $[A(\kappa^2-dppv)]$ (1 mM) in 0.1 M *n*-Bu₄NPF₆/MeCN at a scan rate of 0.1 V s⁻¹

Fe-Fe bond and the concomitant reduction in electron density in the diiron center [32]. The oxidation peaks at -0.382, -0.201 and +0.088 V may be ascribed to the intermediate species generated from the reduction processes of $[(\mu-H)A(\kappa^2-dppv)]BF_4$, as these peaks disappeared when the CVs were conducted toward the anode from the initial potential at -0.50 V. On addition of one equivalent of trifluoroacetic acid ($pK_a = 12.7$ in MeCN), the current height at -1.305 V increased slightly, whereas further increases of acid did not show obvious increases in the current heights. The current heights at -1.792 V increased with successive additions of trifluoroacetic acid, but appeared slightly responsive to the increment of acids and only reached 44 μ A in the presence of 10 equivalents of acid (Fig. 5). However, under the same conditions, the current height of the precursor [A(κ^2 -dppv)] reached 135 μ A, larger than that of [(μ -H)A(κ^2 -dppv)]BF₄ [26]. When using a stronger *p*-methylbenzene sulfonic acid (TsOH, $pK_a = 8.7$ in MeCN) as the proton resource, the changes of current intensities around

Table 2 Selected bond lengths (Å) and angles (deg) for $[(\mu-H)A(\kappa^2-dppv)]BF_4$ and $[(\mu-H)A(\kappa^2-dppe)]BF_4$

[(µ-H)A(κ ² -dppv)]BF	F4						
Fe(1)–Fe(2)	2.5832(10)	Fe(1)-S(1)	2.2813(15)	Fe(1)–S(2)	2.2718(14)	Fe(2)–S(1)	2.2613(14)
Fe(2)–P(1)	2.2223(14)	Fe(2)–S(2)	2.2509(14)	Fe(2)–P(2)	2.2382(15)	Fe(1)–C(1)	1.800(6)
Fe(2)–C(4)	1.757(6)	P(1)-C(26)	1.810(5)	P(2)–C(27)	1.812(5)	O(4)–C(4)	1.142(5)
P(1)-Fe(2)-P(2)	87.03(5)	C(27)-P(2)-Fe(2)	107.26(18)	C(26)-P(1)-Fe(2)	107.47(17)	P(2)-Fe(2)-Fe(1)	110.03(5)
C(4)-Fe(2)-P(2)	91.57(17)	P(1)-Fe(2)-Fe(1)	109.10(5)	C(4)-Fe(2)-Fe(1)	148.04(17)	Fe(2)–S(1)–Fe(1)	69.31(4)
Fe(2)-S(2)-Fe(1)	69.66(4)	S(1)-Fe(1)-S(2)	84.12(5)	S(2)-Fe(2)-S(1)	85.06(5)	C(1)-Fe(1)-Fe(2)	139.14(19)
$[(\mu-H)A(\kappa^2-dppe)]BF$	4						
Fe(1)–Fe(2)	2.5783(13)	Fe(1)-S(1)	2.2725(19)	Fe(1)–S(2)	2.2754(16)	Fe(2)–S(1)	2.2491(17)
Fe(2)–P(1)	2.2398(16)	Fe(2)–S(2)	2.2532(16)	Fe(2)–P(2)	2.2523(17)	Fe(1)–C(10)	1.810(8)
Fe(2)–C(13)	1.754(7)	P(1)-C(27)	1.834(6)	P(2)–C(26)	1.837(6)	O(4)–C(13)	1.145(7)
P(1)-Fe(2)-P(2)	87.57(6)	C(27)-P(1)-Fe(2)	107.4(2)	C(26)-P(2)-Fe(2)	105.6(2)	P(1)-Fe(2)-Fe(1)	112.48(5)
C(13)–Fe(2)–P(1)	90.5(2)	P(2)-Fe(2)-Fe(1)	107.00(6)	C(13)-Fe(2)-Fe(1)	148.0(2)	Fe(2)–S(1)–Fe(1)	69.53(6)
Fe(2)-S(2)-Fe(1)	69.41(5)	S(1)-Fe(1)-S(2)	83.75(6)	S(2)-Fe(2)-S(1)	84.79(6)	C(10)-Fe(1)-Fe(2)	139.0(2)



Fig. 5 CVs of $[(\mu-H)A(\kappa^2-dppv)]BF_4$ (1 mM) in 0.1 M *n*-Bu₄NPF₆/MeCN in the presence of CF₃COOH (0–10 mM) at a scan rate of 0.1 V s⁻¹



Fig. 6 CVs of $[(\mu-H)A(\kappa^2-dppv)]BF_4$ (1 mM) in 0.1 M *n*-Bu₄NPF₆/MeCN in the presence of TsOH (0–10 mM) at a scan rate of 0.1 V s⁻¹

-1.305 V were very similar to those in the presence of trifluoroacetic acid, but the current heights at -1.792 V increased substantially on successive additions of TsOH, reaching 121 μ A in the presence of 10 equivalents (Fig. 6) [33, 34]. These observations imply that [(μ -H)A(κ^2 -dppv)]BF₄ can catalyze the reduction in protons and the catalytic efficiency is related to the strength of the acid [35–37]. Both the thermodynamic stability and the basicity of [(μ -H)A(κ^2 dppv)]BF₄ may be relevant to the catalytic process [31].

Conclusions

The complexes $[A(\kappa^2-dppv)]$ and $[A(\kappa^2-dppe)]$ have been prepared and characterized. The inherent configuration of diphosphine ligands has influence on the ease of access of the chelate complexes. Protonation of these precursor complexes yielded the bridging hydrides $[(\mu-H)A(\kappa^2-dp$ pv)]BF₄ and $[(\mu-H)A(\kappa^2-dppe)]BF_4$. These protonation reactions induce a change in coordination model of the diphosphine from apical-basal to basal-basal. The CVs of $[(\mu-H)A(\kappa^2-dppv)]BF_4$ in the presence of acids indicated that the bridging hydride can catalyze the electrochemical reduction of protons, but with different efficiencies depending on the strength of the acid. The relative thermodynamic stability together with the basicity of the bridging hydride may influence the catalytic process.

Supporting information

CCDC 1032305 ([(μ -H)A(κ^2 -dppv)]BF₄) and 1045156 ([(μ -H)A(κ^2 -dppe)]BF₄) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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