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Electrocatalytic proton reduction by  $[\text{Fe}(\text{CO})_2(\kappa^2\text{-dppv})(\kappa^1\text{-SAr})_2]$  (dppv = *cis*-1,2-bis(diphenylphosphino)ethylene; Ar =  $\text{C}_6\text{F}_5$ ,  $\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_4\text{CH}_3\text{-}p$ )

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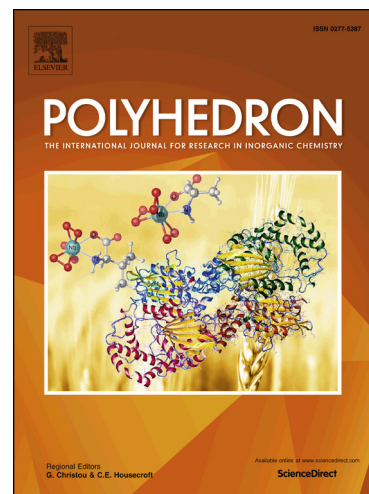
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**ABSTRACT**

Electrocatalytic reduction of protons to hydrogen by mononuclear iron complexes which are developed as models of the distal iron center of [FeFe]-hydrogenase active site are described. A series of iron(II) bis(thiolate) complexes  $[\text{Fe}(\text{CO})_2(\kappa^2\text{-dppv})(\kappa^1\text{-SAr})_2]$  (**1**, Ar =  $\text{C}_6\text{F}_5$ ; **2**, Ar =  $\text{C}_6\text{H}_5$ ; **3**, Ar =  $\text{C}_6\text{H}_4\text{CH}_3\text{-}p$ ; dppv = *cis*-1,2-bis(diphenylphosphino)ethylene) have been prepared from direct reactions between the corresponding hexacarbonyl  $[\text{Fe}_2(\text{CO})_6(\mu\text{-SAr})_2]$  and dppv at elevated temperatures. Structurally they are similar being coordinated by a chelating dppv, two carbonyls and two thiolato ligands bonded in an all *cis*-arrangement. Solution spectroscopic data indicate that they exist in two isomeric forms in solution. All reversibly protonate at sulphur atom(s) upon addition of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  and lose a thiolate ligand as thiol. They show a common quasi-reversible reductive feature (attributed to the  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}}$  couple) in their CVs in addition to other redox responses and are able to catalyze reduction of protons to hydrogen at their Fe(I) oxidation state in presence of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ . Complex **1** is the

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