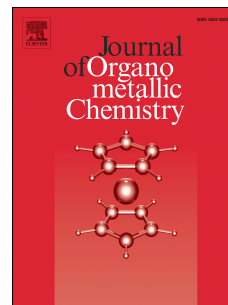


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## Trinuclear clusters containing 2-aminopyridinate/pyrimidinate ligands as electrocatalysts for proton reduction

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### ABSTRACT

Triiron and triruthenium clusters containing capping 2-aminopyridinate/pyrimidinate ligands are developed as functional models of the [FeFe]-hydrogenase for electrocatalytic reduction of protons to hydrogen. The 48-electron clusters  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-pyNH})(\mu\text{-H})$  (**1**),  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-pymNH})(\mu\text{-H})$  (**2**),  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-pyNH})(\mu\text{-H})$  (**3**) and  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-pymNH})(\mu\text{-H})$  (**4**) (pyNH = 2-aminopyridinate, pymNH = 2-aminopyrimidinate) are prepared from reactions of  $\text{M}_3(\text{CO})_{12}$  (M = Fe or Ru) with the corresponding heterocyclic amine at elevated temperatures. Each contains a hydride and a residual amino hydrogen in close proximity (*ca.* 2.8 Å). The triiron 2-aminopyridinate cluster **1** does not protonate by TsOH·H<sub>2</sub>O (used as the proton source during catalysis), whereas its ruthenium analogue **3** undergoes slow protonation across a ruthenium-ruthenium bond. The 2-aminopyrimidinate clusters **2** and **4** undergo rapid protonation at the ring nitrogen. In MeCN, the triiron clusters show a single irreversible reduction wave ( $E_p = -1.61$  V for **1**;  $E_p = -1.47$  V for **2**) in the cathodic region of their CVs, while the triruthenium clusters display a pair of irreversible cathodic waves ( $E_p = -2.01$  and  $-2.15$  V for **1**;  $E_p = -1.93$  and  $-2.09$  V for **2**). All catalyze proton reduction in the presence of TsOH·H<sub>2</sub>O but different mechanisms are proposed. The triiron clusters are more efficient toward proton reduction and operate at reduced overpotentials as compared to their triruthenium analogues. Introduction of a potential proton relay in these clusters neither increases the efficiency nor reduces the overpotential of catalysis which is in sharp contrast with the results observed for hydrogenase biomimetics.

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