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# Models of the iron-only hydrogenase: Synthesis and protonation of bridge and chelate complexes $[\text{Fe}_2(\text{CO})_4\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}(\mu\text{-pdt})]$ ( $n = 2-4$ ) – evidence for a terminal hydride intermediate

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## Abstract

Reactions of  $[\text{Fe}_2(\text{CO})_6(\mu\text{-pdt})]$  ( $\text{pdt} = \text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$ ) and diphosphines,  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 2-4$ ) and *trans*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$ , have been carried out under different conditions. For all, at room temperature in MeCN with added  $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$  the diphosphine-linked complexes  $[\{\text{Fe}_2(\text{CO})_5(\mu\text{-pdt})\}_2(\mu, \kappa^1, \kappa^1\text{-diphosphine})]$  result. For *trans*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$  this is the only product under all conditions. It has been crystallographically characterised revealing a  $C_2$  symmetric structure with apical substitution at the diiron centres. In refluxing toluene, reactions with *dippe* and *dppp* lead to the formation of a mixture of diphosphine-bridged and chelate isomers  $[\text{Fe}_2(\text{CO})_4(\mu\text{-diphosphine})(\mu\text{-pdt})]$  and  $[\text{Fe}_2(\text{CO})_4(\kappa^2\text{-diphosphine})(\mu\text{-pdt})]$ , respectively, while with *dppb* the bridged complex  $[\text{Fe}_2(\text{CO})_4(\mu\text{-dppb})(\mu\text{-pdt})]$  is the only product. In MeCN at 60–70 °C (with added  $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ ) similar products result although the ratios differ providing evidence for the conversion of chelate to bridge isomers. Three complexes,  $[\text{Fe}_2(\text{CO})_4(\mu\text{-dippe})(\mu\text{-pdt})]$ ,  $[\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dppp})(\mu\text{-pdt})]$  and  $[\text{Fe}_2(\text{CO})_4(\mu\text{-dppb})(\mu\text{-pdt})]$ , have been crystallographically characterised and are compared to the previously reported *dppm* ( $n = 1$ ) complexes  $[\text{Fe}_2(\text{CO})_4(\mu\text{-dppm})(\mu\text{-pdt})]$  and  $[\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dppm})(\mu\text{-pdt})]$ . Diphosphine-bridged complexes are structurally superficially similar although significant differences are noted in some key bond lengths and angles, while chelate complexes  $[\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dppp})(\mu\text{-pdt})]$  and  $[\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dppm})(\mu\text{-pdt})]$  differ in adopting basal–apical and dibasal coordination geometries, respectively, in the solid state. A number of protonation studies have been carried out. Addition of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  to  $[\text{Fe}_2(\text{CO})_4(\mu\text{-dippe})(\mu\text{-pdt})]$  affords a bridging hydride complex with poor stability, while in contrast with  $[\text{Fe}_2(\text{CO})_4(\mu\text{-dppb})(\mu\text{-pdt})]$  the stable hydride  $[(\mu\text{-H})\text{Fe}_2(\text{CO})_4(\mu\text{-dppb})(\mu\text{-pdt})][\text{BF}_4]$  results. This difference is partially ascribed to the greater flexibility of the diphosphine backbone in *dppb*. With  $[\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dppp})(\mu\text{-pdt})]$  the bridging hydride complex  $[(\mu\text{-H})\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dppp})(\mu\text{-pdt})][\text{BF}_4]$  is the final product, in which the diphosphine occupies two basal sites. Monitoring by NMR at low temperature shows the initial formation of a terminal hydride, which rapidly rearranges to a bridged isomer in which the diphosphine adopts a basal–apical geometry and this in turn rearranges in a slower process to the dibasal isomer. This behavior is similar to that recently communicated for  $[\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dippe})(\mu\text{-pdt})]$ . [S. Ezzaher, J.-F. Capon, F. Gloaguen, F. Y. Pétilion, P. Schollhammer, J. Talarmin, R. Pichon, N. Kervarec, *Inorg. Chem.* 46 (2007) 3426–3428.] **To cite this article: F. I. Adam et al., C. R. Chimie 11 (2008).**  
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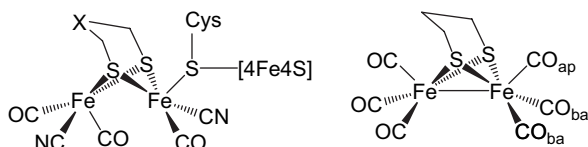
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## 1. Introduction

There is currently intense interest in the chemistry of dithiolate-bridged diiron complexes,  $[\text{Fe}_2(\text{CO})_6(\mu\text{-SXS})]$ , resulting from the realisation that they closely resemble the two-iron unit of the H-cluster active site of iron-only hydrogenases. A key step in the electrocatalytic conversion of protons to hydrogen at the active centre is the coordination of the proton(s). The hexacarbonyls themselves are generally not basic enough to bind a proton and the main approach adopted to circumvent this problem is to substitute one or more carbonyls for more basic phosphine ligands. In this way a large number of phosphine-substituted derivatives of  $[\text{Fe}_2(\text{CO})_6(\mu\text{-pdt})]$  (pdt =  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$ ) have been prepared.



Recent theoretical studies have suggested that the asymmetry of the diiron centre may be a desirable feature of biomimetic models of iron-only hydrogenases [1]. One way to build in both steric and electronic asymmetries is to coordinate diphosphines in a chelating manner. With this in mind, we [2–4] and others [5–8] have begun exploring the reactivity of  $[\text{Fe}_2(\text{CO})_6(\mu\text{-pdt})]$  (**1**) and related dithiolate-bridged complexes with a range of bidentate phosphines. From these studies it is becoming clear that formation of bridge and chelate isomers  $[\text{Fe}_2(\text{CO})_4(\mu\text{-diphosphine})(\mu\text{-pdt})]$  and  $[\text{Fe}_2(\text{CO})_4(\kappa^2\text{-diphosphine})(\mu\text{-pdt})]$  can occur, the latter existing as a mixture of dibasal and basal–apical isomers. The nature of products formed and their relative amounts depend upon the reaction conditions employed and the nature of the diphosphine backbone. For example with dppm, the formation of monodentate  $[\text{Fe}_2(\text{CO})_5(\kappa^1\text{-dppm})(\mu\text{-pdt})]$  initially results [4,8]. This in turn converts under more forcing conditions into the bridged tetracarbonyl complex  $[\text{Fe}_2(\text{CO})_4(\mu\text{-dppm})(\mu\text{-pdt})]$  with only very small amounts of the chelate isomer  $[\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dppm})(\mu\text{-pdt})]$  being formed [4]. Further, since the latter subsequently converts rapidly to the bridged isomer upon heating this precludes its development as a biomimetic model.

We thus sought to probe the use of other diphosphines towards preparation of asymmetric chelate complexes  $[\text{Fe}_2(\text{CO})_4(\kappa^2\text{-diphosphine})(\mu\text{-pdt})]$ . In this

context, *cis*- $\text{Ph}_2\text{PCH}=\text{CHPh}_2$  [4,5] and 1,2- $(\text{Ph}_2\text{P})_2\text{C}_6\text{H}_4$  [4] have been shown to react with **1** to exclusively yield the desired chelate complexes and both are currently under investigation as models. As an extension of our work in this area we sought to probe the coordination to **1** with the widely utilized diphosphines,  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 2$ , dppe;  $n = 3$ , dppp;  $n = 4$ , dppb), which have much more flexible backbones than dppm ( $n = 1$ ). While this work was in progress two independent reports appeared covering aspects of this work. Thus, Sun and co-workers reported that addition of dppe to **1** under mild conditions affords tetranuclear  $[\{\text{Fe}_2(\text{CO})_5(\mu\text{-pdt})\}_2(\mu,\kappa^1,\kappa^1\text{-dppe})]$  [8], while under more forcing conditions Schollhammer detailed the isolation of the chelate complex,  $[\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dppe})(\mu\text{-pdt})]$  [6]. This latter work is particularly relevant to ours since it is also shown that low-temperature protonation of  $[\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dppe})(\mu\text{-pdt})]$  affords terminal hydride complexes, which rearrange to give the more stable bridged hydride  $[(\mu\text{-H})\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dppe})(\mu\text{-pdt})]^+$  [6]. This discovery may be important since, in context of biomimetic models, it is widely accepted that terminal hydride species are key intermediates in the electrocatalytic proton reduction.

## 2. Results and discussion

### 2.1. Diphosphine-linked tetranuclear complexes $[\{\text{Fe}_2(\text{CO})_5(\mu\text{-pdt})\}_2(\mu,\kappa^1,\kappa^1\text{-diphosphine})]$ (**2a–d**)

Hexacarbonyl  $[\text{Fe}_2(\text{CO})_6(\mu\text{-pdt})]$  (**1**) is unreactive towards phosphines at room temperature in the absence of either the carbonyl-activating reagent  $\text{Me}_3\text{NO}$  or UV–visible irradiation. Addition of diphosphines  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 2–4$ ) and *trans*- $\text{Ph}_2\text{PCH}=\text{CHPh}_2$  to **2** equiv of **1** in acetonitrile with added  $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$  resulted in the immediate formation of the diphosphine-linked tetranuclear complexes  $[\{\text{Fe}_2(\text{CO})_5(\mu\text{-pdt})\}_2(\mu,\kappa^1,\kappa^1\text{-diphosphine})]$  (**2a–d**) in high yields. If 1 equiv of **1** is employed then formation of **2a–d** is again clean leaving some unreacted **1**. Formation of **2a–d** is readily seen by changes in the IR spectrum the characteristic low frequency carbonyl vibration of **1** at  $2074\text{ cm}^{-1}$  being replaced by a band at *ca.*  $2045\text{ cm}^{-1}$ . All display a singlet in the  $^{31}\text{P}$  NMR spectra consistent with a symmetric structure, while  $^1\text{H}$  NMR data are generally not very informative. While this work was in progress, Sun, Akermark and co-workers reported an analogous synthesis of the dppe complex **2a** [8].

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