

# Trispyrazolymethane piano stool complexes of iron(II) and cobalt(II)

Peter G. Edwards<sup>a,\*</sup>, Andrew Harrison<sup>b</sup>, Paul D. Newman<sup>a</sup>, Wenjian Zhang<sup>a</sup>

<sup>a</sup> School of Chemistry, Cardiff University, Park Place, Cardiff CF10 3AT, United Kingdom

<sup>b</sup> School of Chemistry, the University of Edinburgh, The King's Buildings, West Mains Road, Edinburgh EH9 3JJ, United Kingdom

Received 28 October 2005; received in revised form 9 December 2005; accepted 9 December 2005

Available online 24 January 2006

We dedicate this paper to Professor D.M.P. Mingos in recognition of his substantial contribution to the chemical sciences.

## Abstract

A series of cationic trispyrazolymethane complexes of the general form  $[\text{Tm}^{\text{R}}\text{M}(\text{CH}_3\text{CN})_3]^{2+}$  (Tm = tris(pyrazolyl)methane, **1**, R = 3,5-Me<sub>2</sub>, M = Fe(II); **2**, R = 3-Ph, M = Fe(II); **3**, R = 3,5-Me<sub>2</sub>, M = Co(II); **4**, R = 3-Ph, M = Co(II)) with ‘piano-stool’ structures was prepared by the reaction of the N<sub>3</sub>tripodal ligands (Tm<sup>R</sup>) with  $[(\text{CH}_3\text{CN})_6\text{M}](\text{BF}_4)_2$  in a 1:1 stoichiometric ratio. Magnetic susceptibility measurements indicate that all four complexes with  $\text{BF}_4^-$  counter anions are paramagnetic, high-spin systems in the solid state with  $\mu_{\text{eff}}$  at high temperatures of 5.2 (**1**,  $S = 2$ ), 5.4 (**2**,  $S = 2$ ), 4.9 (**3**,  $S = 3/2$ ) and 4.6 (**4**,  $S = 3/2$ ) BM, respectively. Comparisons of bond lengths from the metal centre to the Tm<sup>R</sup> nitrogen donors, and from the metal centre to the acetonitrile nitrogen donors indicate that the neutral tripodal ligands appear to be more weakly coordinated to the metal centre than are the acetonitrile ligands. Reactions of these tripodal complexes with bidentate phosphine ligands, such as 1,2-diphosphinoethane or 1,2-bis(diallylphosphino)ethane leads to displacement of the tripodal ligand, or to the formation of more thermally stable bis-ligand complexes  $\text{M}(\text{Tm}^{\text{R}})_2$  (R = 3,5-dimethyl).

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Pyrazolymethane complexes; Transition metal piano stool complexes; Tripodal ligands; Iron complexes; Cobalt complexes

## 1. Introduction

Tripodal transition metal complexes stabilised by facially capping ligands in a ‘piano-stool’ type of structure which also contain labile monodentate solvent ligands,  $\text{LML}'_x$  (L = capping ligand; L' = monodentate solvent ligand) are potentially useful precursors in coordination and organometallic chemistry. The lability of the monodentate ligands can be readily exploited such that they may be replaced by other nucleophiles. With appropriate choice of metal (and oxidation state) the ‘LM’ fragment may remain intact during subsequent reactions which are correspondingly localised in sites which are mutually *trans* to the capping ligand. We are interested in structures of this nature in applications such as metal template assisted syntheses of macrocyclic ligands and related, facially coordi-

nated representatives such as  $\text{Cp}^{\text{R}}\text{FeL}_3^+$  [**1**] and  $(\text{CO})_3\text{MoL}_3$  [**2**] (L = CH<sub>3</sub>CN) have been studied in this context and we have demonstrated successful syntheses of 9-, 10- and 12-membered triphosphorus macrocycles by intramolecular hydrophosphinations [**3,4**]. The smaller ring systems are formed upon the kinetically inert  $\eta^5\text{-Cp}^{\text{R}}\text{FeL}_3^+$  template systems and this methodology is limited by difficulties in liberation of the macrocycle. Thus, investigation of alternative facially capping ligands and their complexes remains important.

The tripodal nitrogen chelate ligands, tris(pyrazolyl)borate (Tp) and tris(pyrazolyl)methane (Tm) have been extensively investigated in inorganic, bioinorganic and organometallic chemistry, partly due to their close analogy to cyclopentadienyl ligands [**5–7**]. All these ligands are commonly 6 electron donors (Fig. 1) and occupy three coordination sites as capping ligands when binding a metal. These ligands form a variety of metal complexes that have counterparts in the classic cyclopentadienyl-iron systems

\* Corresponding author.

E-mail address: [edwardspg@cardiff.ac.uk](mailto:edwardspg@cardiff.ac.uk) (P.G. Edwards).

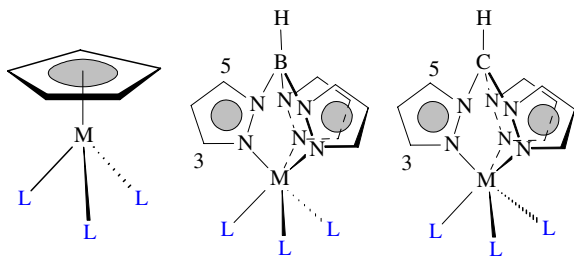


Fig. 1. Analogy between Cp, tris(pyrazolyl)borate and tris(pyrazolyl)methane.

[7]. The Tm or Tp ligands generally form bis-ligand structures for octahedral metal ions in which the two tripodal ligands interdigitate, since the donors are held in a planar fashion roughly in plane with the metal-donor bond. The parent tris(pyrazolyl)borate or tris(pyrazolyl)methane ligands can be modified by introducing substituents such as  $-\text{CH}_3$ ,  $-\text{C}_3\text{H}_7$ ,  $-\text{C}_4\text{H}_9$  or  $-\text{C}_6\text{H}_5$  in the 3- or 3,5- positions of the pyrazole ring resulting in variations of steric bulk. These derivatives, with controlled coordination behaviour, may prevent formation of bis-ligand  $\text{ML}_2$  complexes ( $\text{L} = \text{Tp}$  or  $\text{Tm}$  ligand) [7]. The known tripodal complexes,  $[\text{Tp}^{\text{R}}\text{M}(\text{NCCH}_3)_3]^+$  ( $\text{Tp} = \text{hydrotrispyrazolyl-borate}$ ;  $\text{M} = \text{Ni, Co}$ ), which are very labile in the absence of  $\text{CH}_3\text{CN}$ , were prepared by chloride abstraction from the corresponding chloro complexes,  $\text{Tp}^{\text{R}}\text{M-Cl}$  [8]. The related reported tripodal complex of  $[\text{Fe}(\text{Tm}^{\text{R}})(\text{H}_2\text{O})_3]^{2+}$  ( $\text{R} = 3,5\text{-dimethyl}$ ) shows less solubility in organic solvents [9]. In this paper, we describe the direct and stoichiometric synthesis of iron and cobalt ‘piano-stool’ complexes of substituted tris-pyrazolymethanes, their structural characterisation and selected physical and chemical properties.

## 2. Results and discussion

### 2.1. Synthesis of tripodal complexes

Four tripodal complexes of  $[\text{Tm}^{\text{R}}\text{M}(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  ( $\text{Tm} = \text{tris(pyrazolyl)methane}$ ;  $\text{R} = 3\text{-Ph, 3,5-Me}_2$ ;  $\text{M} = \text{Fe, Co}$ ) were directly prepared by reactions of tripodal  $\text{Tm}^{\text{R}}$  ligands with one equivalent of  $[(\text{CH}_3\text{CN})_6\text{M}](\text{BF}_4)_2$  in acetonitrile solvent (Scheme 1). The products are conveniently crystallised directly from the reaction mixture and are isolated as colourless (Fe) or orange/red (Co) crystals. IR spectra of these complexes confirm the existence of

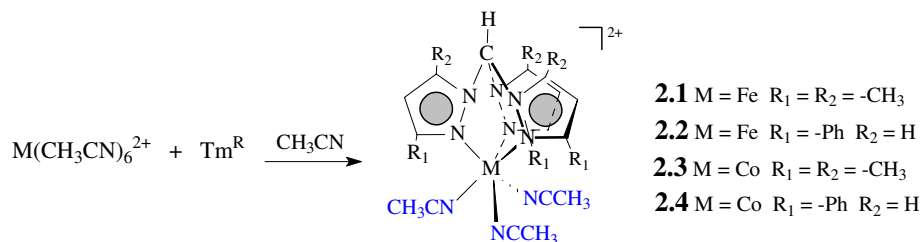
three terminal  $\text{CH}_3\text{CN}$  ligands. The compounds are all air- and moisture-sensitive as the solids or in solution.

The thermally stable bis-ligand complexes,  $[\text{ML}_2]^{2+}$  ( $\text{M} = \text{Fe, Co}$ ;  $\text{L} = \text{Tm}^{\text{R}}$ ), were avoided due to coordination control through the steric hindrance introduced by substituents in the 3- or 3,5-positions of the pyrazole ring. The ratio of the two reagents in the reaction is also important in order to limit formation of the bis-ligand complexes. In the mass spectra of the iron and cobalt complexes **1–4**, the highest ion observed corresponds to the  $[\text{Tm}^{\text{R}}\text{M}]^+$  fragment ( $m/z = 354, 498, 357, 501$  amu for **1–4**, respectively) except when the compound is admitted as a methanol solution in which case complex ions corresponding to the formula,  $[\text{Tm}^{\text{R}}\text{M}(\text{CH}_3\text{CN})_2(\text{CH}_3\text{OH})]^+$  were observed ( $m/z = 468, 612, 471, 615$  amu for **1–4**, respectively) in all cases. Crystalline samples of compounds **1** and **2** are colourless, which is consistent with a paramagnetic high-spin (HS) state for iron complexes at room temperature [10]. In the NMR spectra of all four tripodal complexes in solution, only broad non-diagnostic resonances are observed due to them being paramagnetic. Analytical data for the 3,5-dimethylpyrazolymethane compounds **1** and **3**, were variable and generally low in carbon due to loss of acetonitrile ligands.

### 2.2. Crystal structures

The structures of complexes **1–4** were characterised by X-ray diffraction studies. Their crystal structures are illustrated in Figs. 2–5, respectively. Table 1 gives selected structural parameters for the four tripodal complexes.

The ideal molecular symmetry for these complexes is  $\text{C}_{3v}$  with a 3-fold axis (**1** and **3**) or pseudo 3-fold axis (**2** and **4**) which passes through the metal centre and the apical C atom which links the three pyrazole rings. All four tripodal complexes have a similar structure bearing a distorted octahedral metal centre which is coordinated by tris-pyrazolymethane ligand in a facially capping mode and three acetonitrile supporting ligands *trans* to the  $\text{Tm}^{\text{R}}\text{N}$  donors. The metal centres are sandwiched by two roughly parallel nitrogen planes, one defined by the  $\text{Tm}^{\text{R}}$  nitrogen donors and the other by the acetonitrile nitrogen donors. The average Fe–N bond lengths in **1** {2.165(3) Å} and **2** {2.175(3) Å} are consistent with the high-spin configuration of the Fe centre in both complexes at 150 K. Average bond lengths of ca 1.97 Å are typically observed in low-



Scheme 1. Preparation of tripodal trispyrazolymethane iron and cobalt complexes,  $[(\text{Tm}^{\text{R}})\text{M}(\text{CH}_3\text{CN})_3]^{2+}$ .

Download English Version:

<https://daneshyari.com/en/article/1312961>

Download Persian Version:

<https://daneshyari.com/article/1312961>

[Daneshyari.com](https://daneshyari.com)