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Cyanide-bridged tetranuclear complexes with T-shaped Pt(CN–M)₃ arrangements

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Dedicated to Professor Stanisław Pasynkiewicz on the occasion of his 70th birthday.

Abstract

Treatment of the trinuclear complex *trans*-[Pt(CN)$_2${CN–Fe(dppe)Cp}$_2$] with Cp(dppe)Fe(MeCN)Br or Cp(PPh$_3$)$_2$RuCl leads to the tetranuclear complexes [Pt(CN){CN–Fe(dppe)Cp}$_3$](SbF$_6$) (**3**) and [Pt(CN){CN–Fe(dppe)Cp}$_2${CN–Ru(PPh$_3$)$_2$Cp}](SbF$_6$) (**4**), containing a T-shaped Pt(CN–Fe)$_3$ or Pt(CN–Fe)$_2$(CN–Ru) skeleton. The electronic communication between the iron and/or ruthenium centers in these complexes was probed by cyclic voltammetry and UV–vis/NIR spectroscopy. Just like in the corresponding trinuclear Pt(CN–M)$_2$ complexes, there is electronic interaction along the linear M–CN chains containing *trans*-configured platinum, but not along the bent chains containing *cis*-configured platinum. © 2000 Elsevier Science S.A. All rights reserved.

1. Introduction

There exists a considerable body of information on the phenomena associated with 'molecular Prussian Blue', i.e. the optical, electrical and magnetic properties of oligonuclear complexes containing transition metal units bridged by cyanide ligands [1–4]. Attractive material properties have been found, and metal–metal charge transfer (MMCT) as a basic feature is well established. But despite the large number of observations, systematic studies are still rare, i.e. those varying the length or shape of (M–CN)$_x$ arrangements or the nature of the metal units contained in them. The reason for this lies in the lack of suitable complexes, which in turn calls for a more serious engagement of preparative chemists.

So far no chain-like (M–CN)$_x$ complex with more than three metal atoms has been fully characterized [1], although investigations of longer chains by optical spectroscopy were reported [5,6]. A number of star-like M(CN–M')$_x$ complexes were reported, some of which have unusually high magnetic moments [1,7]. Information on long-range metal–metal interactions has been obtained for trinuclear complexes by optical spectroscopy [3,4] and cyclic voltammetry [8]. This has included the effects of the orientation of CN–M' units (*cis* versus *trans*) attached to a central ruthenium atom [9]. Altogether these findings are highlights of a field that has yet to be fully exploited.

Our own contributions to this area are based on preparative chemistry yielding oligonuclear complexes suitable for spectroscopic and redox investigations addressing the question of metal–metal interactions in (M–CN)$_x$ arrays. For dinuclear complexes we could evaluate the effects due to cyanide/isocyanide isomerism and to the redox properties of the metal constituents [10]. Initial studies on similar tri- [11] and tetranuclear [12] complexes indicated that long-range electronic communication can exist between metal atoms up to 13 Å apart. A large variability of long-range metal–metal interactions in trinuclear complexes was found depending on the arrangement of the outer

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(CN–M′) units at a central M unit (linear versus tetrahedral and *cis* versus *trans* in square planar or octahedral ligand sets around M) [11–14]. A detailed investigation of trinuclear systems with square planar PtL$_2$ units in the center provided the first unambiguous cases of remote MMCT along a cyanide-linked trimetal chain and showed that this occurs only for a linear Pt(μ-CN–M′)$_2$ arrangement, i.e. for *trans*-configured platinum [14].

This paper presents an extension of the latter work. Two tetranuclear complexes containing a Pt(CN–M′)$_3$ backbone are presented and their spectroscopy and redox chemistry is discussed. The aim of the work was to find out which of the alternative long-range interactions between the external M′ units would be realized.

2. Results and discussion

2.1. Preparation and identification

We previously described the trinuclear complexes **1** and **2** and verified the linear arrangement of M–CN–M′ units in them by spectroscopy and a structure determination [14]. They were constructed from Pt(CN)$_4^{2-}$ by attachment of the electrophilic iron or ruthenium units at the N termini of the cyanide ligands. Complexes **1** and **2** still contain terminal cyanide ligands and thereby offer the possibility of attaching further organometallic units cyanide-bridged to the square-planar Pt(II) center. We found that this is possible for **1**, but only for the attachment of one more cyanometal building block. Treatment of **1** with stoichiometric or excessive quantities of [Cp(dppe)-Fe(CH$_3$CN)]Br or Cp(PPh$_3$)$_2$RuCl yielded the tetranuclear complexes **3** and **4**. Pentanuclear complexes were not obtained, presumably due to steric crowding.

1

2

[3] SbF$_6$

[4] SbF$_6$
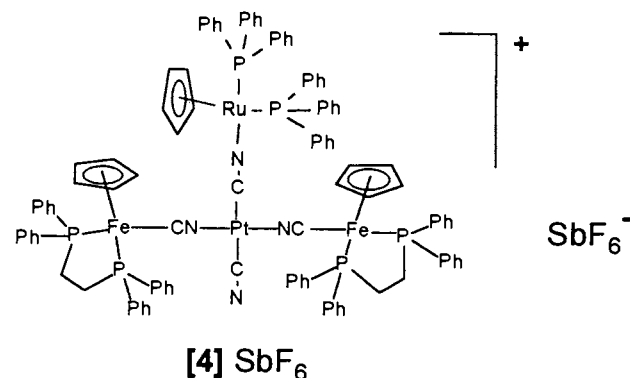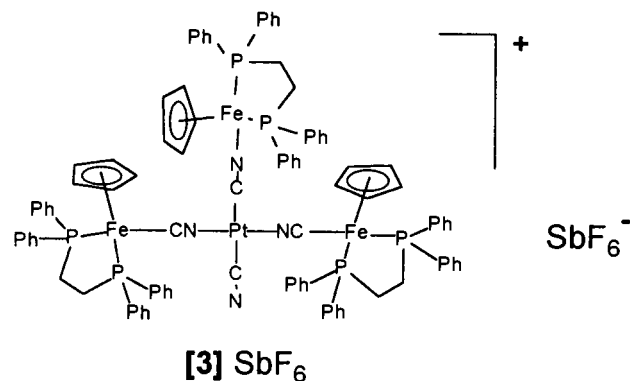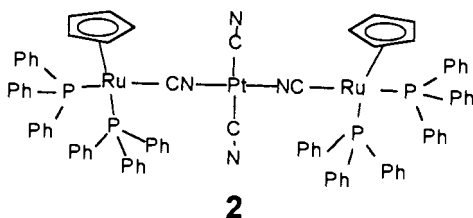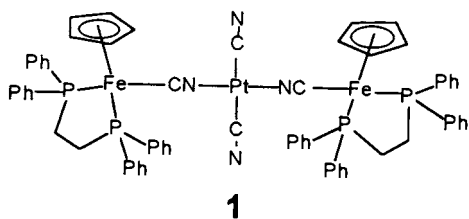
As crystals suitable for an X-ray analysis were not obtained, the structural assignments rest on their NMR spectra (see Section 3) and on the analogy with **1** and **2**. For the unambiguous case of **3** there is the expected 2:1 ratio of signal intensities both for the Cp(^{1}H) and the dppe(^{31}P) resonances. Complex **4** allows two isomers depending on the orientation of the organometallic units which can have the Cp(dppe)Fe groups in the *cis* or *trans* positions at the central platinum. As expected due to the synthesis from **1**, they are *trans*, giving rise to only one Cp(^{1}H) and dppe(^{31}P) resonance of double intensity in comparison with the corresponding resonances of the Cp(PPh$_3$)$_2$Ru group. The ν(CN) IR data gave no information on the structure and bonding of **3** and **4**. Both complexes gave rise to only one CN absorption at the same position (2134 cm^{-1}). As previously observed [14], the CN band positions cannot be used to distinguish *cis* or *trans* orientations of L$_n$M–CN units at square-planar platinum. In the present case there is an additional accidental degeneracy of the band positions for terminal and bridging cyanide.

2.2. Metal–metal interactions

The favorable redox properties of the Cp(dppe)Fe and Cp(PPh$_3$)$_2$Ru units together with the redox-inertness of Pt(II) make electrochemistry an optimal tool to probe electronic interactions along the M–NC–

Pt–CN–M arrays [10,11,14]. This was also found for the present study. Complex **3** shows a broad redox wave with modulations that allow us to assign the reversible transfer of one electron at ca. 0.45 V and of two electrons at ca. 0.53 V (versus Ag/AgCl in CH_2Cl_2). In accordance with the observations for **1** this can be described by initial oxidation of one iron center which has the other one *trans* to it. The second iron center in the *trans* position then 'sees' this redox change and responds with an increase in its own redox potential. The third iron center, which has a terminal cyanide *trans* to it, is slightly less electron-rich than the other two and hence more difficult to oxidize. With the given resolution of cyclic voltammetry its redox potential seems to be identical to that of the second iron center.

While these assignments for **3** are somewhat ambiguous they are not questionable for **4**. Fig. 1 shows the cyclic voltammogram for **4** displaying three reversible one-electron oxidation steps. The first two of these at 0.43 and 0.53 V occur at the Cp(dppe)Fe centers which are mutually *trans*. They can be directly related to the corresponding ones in **1** at 0.36 and 0.47 V. The separate redox wave at 1.02 V is characteristic for the Cp(PPh₃)₂Ru center [14]. Again it is slightly higher than in reference compounds containing two organometallic units linked via cyanide to the central Pt(II), e.g. **2**.
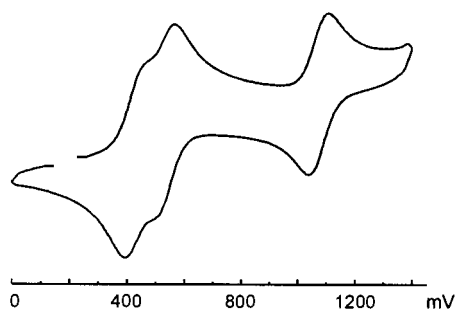

Fig. 1. Cyclic voltammogram of complex **4** (in CH_2Cl_2, potentials vs. Ag/AgCl, electrolyte [TBA]PF₆, sweep rate 100 mV s⁻¹).
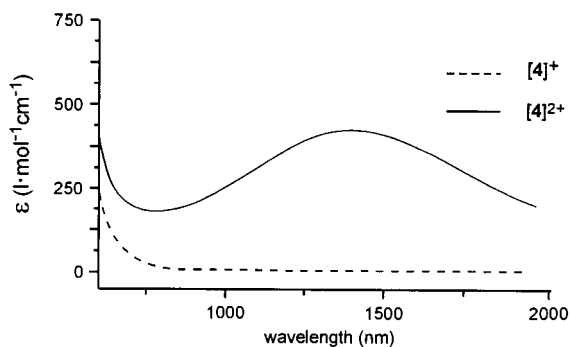

Fig. 2. NIR spectra of dichloromethane solutions containing [Pt(CN){CN–Fe(dppe)Cp}₂{CN–Ru(PPh₃)₂Cp}]⁺ (i.e. **4**⁺, dashed line) and after addition of one equivalent of acetylferrocenium tetrafluoroborate (i.e. **4**²⁺, solid line).

The cyclic voltammogram of **4** demonstrates the iron–iron interaction but it gives no indication as to an iron–ruthenium interaction. NIR spectra of **4** confirm the former and rule out the latter. Fig. 2 shows spectral traces of **4** before and after oxidation with one equivalent of acetylferrocenium tetrafluoroborate whose redox potential of 0.66 V under these conditions is sufficient to oxidize the iron centers but not the ruthenium center. Redox titration of **4** with acetylferrocenium tetrafluoroborate gives rise to a broad absorption in the NIR centered at 1400 nm. This absorption has maximum intensity after the addition of one redox equivalent and has disappeared again after the addition of two redox equivalents, i.e. oxidation of both iron centers. It clearly arises from MMCT between Fe(II) and Fe(III) along the linear Fe–NC–Pt–CN–Fe array of 10 Å length. This corresponds to the observations for **1** after one-electron oxidation where the MMCT band is centered at 1560 nm. In contrast, no MMCT absorption is observed in the spectral range 600–900 nm. This is the range for MMCT between Ru(II) and Fe(III), as observed for [Cp(dppe)Fe–NC–Pt(CN)₂–CN–Ru(PPh₃)₂Cp] after one-electron oxidation at 750 nm [14].

The observations made here confirm the conclusions drawn from the studies of platinum(II) centered trinuclear complexes, e.g. **1** and **2**, and their analogues with *cis*-orientation of the L_nM–CN units. There is electronic communication between the outer organometallic units in linear, but not in bent arrays M–NC–Pt(II)–CN–M. Complexes **3** and **4** have added the information that this is also the case when the linear and bent arrays are present in the same molecule.

3. Experimental

All preparative and measurement techniques and the synthesis of the starting compounds were as described before [10,14]. IR data were recorded from KBr pellets.

3.1. Complex 3

A total of 100 mg (0.075 mmol) of **1** and 96 mg (0.075 mmol) of [Cp(dppe)Fe(CH₃CN)]Br in 20 ml of CH_2Cl_2 were stirred for 3 days. The solvent was then removed in vacuo, the residue picked up in 10 ml of methanol and filtered. To the filtrate was added 19 mg (0.073 mmol) of NaSbF₆, resulting in the immediate formation of a yellowish precipitate. The mixture was evaporated to dryness and the residue extracted with three 10 ml portions of CH_2Cl_2. The combined extracts were filtered and layered with 30 ml of petroleum ether (b.p. 60–70°C), affording after 3 days 20 mg (13%) of **3** as red needles, m.p. 300°C (dec.). Anal. Found: C, 54.05; H, 4.12; N, 2.43. $C_{97}H_{87}F_6Fe_3N_4P_6PtSb\cdot CH_2Cl_2$

(2092.98 + 84.93). Calc.: C, 54.12; H, 4.14; N, 2.57%. IR: v(CN) 2134m. ^{1}H-NMR (CD$_2$Cl$_2$): 7.80–7.00 (m, 60H, Ph), 5.25 (s, 2H, CH$_2$Cl$_2$), 3.92 (s, 10H, Cp), 3.89 (s, 5H, Cp), 2.58–1.97 (m, 12H, dppe). ^{31}P-NMR (CD$_2$Cl$_2$): 97.6 (4P, dppe), 98.4 (2P, dppe).

3.2. Complex 4

A total of 95 mg (0.071 mmol) of **1**, 52 mg (0.070 mmol) of Cp(PPh$_3$)$_2$RuCl and 19 mg (0.073 mmol) of NaSbF$_6$ in 40 ml of 1:1 methanol–dichloromethane were stirred for 3 h. After evaporation to dryness the residue was picked up in 5 ml of dichloromethane, filtered, and the filtrate layered with 10 ml of petroleum ether. After 2 days 80 mg (50%) of **4** had precipitated as red needles, m.p. 300°C (dec.). Anal. Found: C, 54.84; H, 3.95; N, 2.28. C$_{107}$H$_{93}$F$_6$Fe$_2$N$_4$P$_6$PtRuSb·CH$_2$Cl$_2$ (2264.36 + 84.93). Calc.: C, 55,22; H, 4.08; N, 2.39%. IR: v(CN) 2134w. ^{1}H-NMR (acetone-d_6): 7.80–7.07 (m, 70H, Ph), 5.48 (s, 2H, CH$_2$Cl$_2$), 4.11 (s, 5H, Cp), 3.95 (s, 10H, Cp), 2.78–2.17 (m, 8H, dppe). ^{31}P-NMR (acetone-d_6): 98.1 (4P, dppe), 41.7 (2P, PPh$_3$).

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