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## Mo<sub>6</sub>Br<sub>8</sub>-Cluster-cored organometallic stars and dendrimers

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### Abstract

The octahedral molybdenum cluster  $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_6\text{Br}_8(\text{CF}_3\text{SO}_3)_6]$  undergoes substitution of all six terminal triflate ligands with the organometallic pyridine ligands  $[\text{RuCp}(\text{PPh}_3)_2(\eta^1\text{-C}_2\text{-4-pyridinyl})]$ , **1**, and 1-ferrocenyl-2-(4-pyridinyl) acetylene, **5**, to give the new light and air sensitive hexa-functionalized Mo<sub>6</sub> clusters **4** and **7** respectively, and with the dendronic phenolate ligand  $p\text{-NaO-C}_6\text{H}_4\text{C}\{\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{Me})_2\text{Fc}\}_3$ , **8**, to give the air-sensitive Mo<sub>6</sub>-cluster-cored octadecylferrocenyl dendrimer **9** that discloses a single CV wave in CH<sub>2</sub>Cl<sub>2</sub> and recognizes the biologically important adenosyl triphosphate di-anion (ATP<sup>2-</sup>). The organometallic pyridines **1** and **5** were also coordinated to Ag<sup>+</sup> to give the new trinuclear AgRu<sub>2</sub> and AgFc<sub>2</sub> cationic complexes **2** and **6** respectively for comparison of the structures and electronic delocalization with those of the clusters. **To cite this article:** D. Méry et al., C. R. Chimie 8 (2005).

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### Résumé

L'agrégat octaédrique  $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_6\text{Br}_8(\text{CF}_3\text{SO}_3)_6]$  subit la substitution des six coordinats triflates terminaux avec les ligands pyridiniques organométalliques  $[\text{RuCp}(\text{PPh}_3)_2(\eta^1\text{-C}_2\text{-4-pyridinyl})]$ , **1**, et 1-ferrocenyl-2-(4-pyridinyl) acétylène, **5**, pour donner de nouveaux agrégats hexamolybdène hexafonctionnels **4** et **7**, respectivement. Avec le phénate dendronique  $p\text{-NaO-C}_6\text{H}_4\text{C}\{\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{Me})_2\text{Fc}\}_3$ , **8**, le dendrimère hexamolybdène octadécylferrocényle **9** est obtenu. Ce composé donne une seule vague en voltammétrie cyclique dans CH<sub>2</sub>Cl<sub>2</sub> et reconnaît le dianion de l'ATP, dont l'importance est connue en biologie.

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Les pyridines organométalliques **1** et **5** ont aussi été coordonnées à  $\text{Ag}^+$  pour donner les nouveaux complexes trinocléaires  $\text{AgRu}_2$  et  $\text{AgFc}_2$  **2** et **6** respectivement, afin de comparer leur structure électronique à celles des agrégats. *Pour citer cet article : D. Méry et al., C. R. Chimie 8 (2005).*

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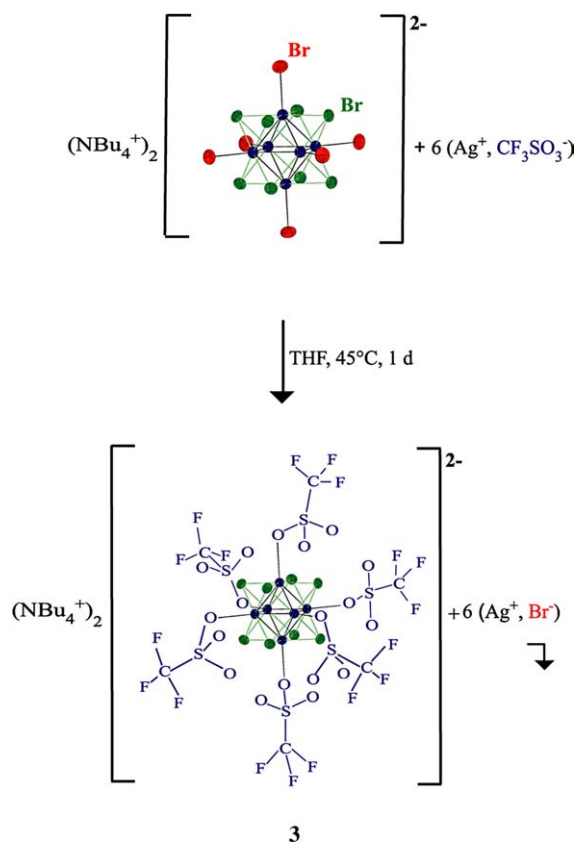
**Keywords:** Cluster; Star; Dendrimer; Organometallics; Assembly; Redox; Anion recognition; ATP

**Mots-clés :** Agrégats ; Étoile ; Organométallique ; Assemblée ; Redox ; Reconnaissance ; ATP ; Dendrimères

## 1. Introduction

There is now an increased effort to focus on the design and assembly of molecular devices that contain nano-clusters [1] given their potential application in catalysis [2], magnetic materials [3] electronics [2] and optics [4,5]. In this context, the bridge between solid-state and molecular materials is an appealing entry into these areas of nanosciences and a starting point towards a broad range of chemistry [6]. Branched molecular architectures [7] also offer another facet to these concepts and allow designing materials with cluster moieties at the core [8] and extremities [9] of dendritic nanostructures [10]. The inorganic clusters  $[\text{Mo}_6\text{X}_{14}]^{2-}$  have been known for 60 years [11,12] and the related superconducting octahedral  $\text{Mo}_6$  clusters  $\text{PbMo}_6\text{S}_8$ , known as Chevrel phases [13], as well as their redox and photo-physical properties [14] added further interest. The  $\text{Mo}(\text{II})$  halide clusters consist of a substitution-resistant core  $[\text{Mo}_6\text{X}_8]^{4+}$  with eight face-bridging inner ligands and semi-labile outer (non-bridging, i.e. terminal) ligands. The outer ligand substitution chemistry has been extensively investigated for almost half a century [15], the substitution of the two apical ligands being easier than that of the four equatorial ones [16]. The hexa-methoxy cluster prepared by Nannelli and Block [17] and the hexa-triflate reported by Shriver's group [18] are the most useful starting materials for further substitution [8b].

Our strategy has consisted in investigating the substitution, *via* the intermediacy of the hexa-triflate (Equation 1), of all six terminal bromide ligands in  $[\text{n-Bu}_4\text{N}]_2[\text{Mo}_6\text{Br}_8\text{Br}^0_6]$  by phenolate and bipyridine ligands connected to redox-active rigid or dendronic organometallic groups. Iron- and ruthenium-centered sandwich and piano-stool structures have been chosen as organometallic connectors, since they have well-known redox properties that can be useful for redox recognition and



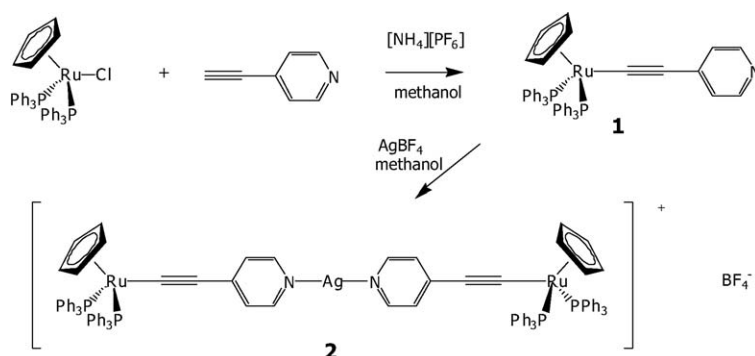
Equation 1.

molecular electronics [19], especially in the dendritic context [20].

## 2. Results

### 2.1. Coordination of a pyridinyl-alcynyl-organoruthenium rod

The rigid organo-ruthenium pyridine ligand **1** was known [21]. We best synthesized it by a different route,



Scheme 1.

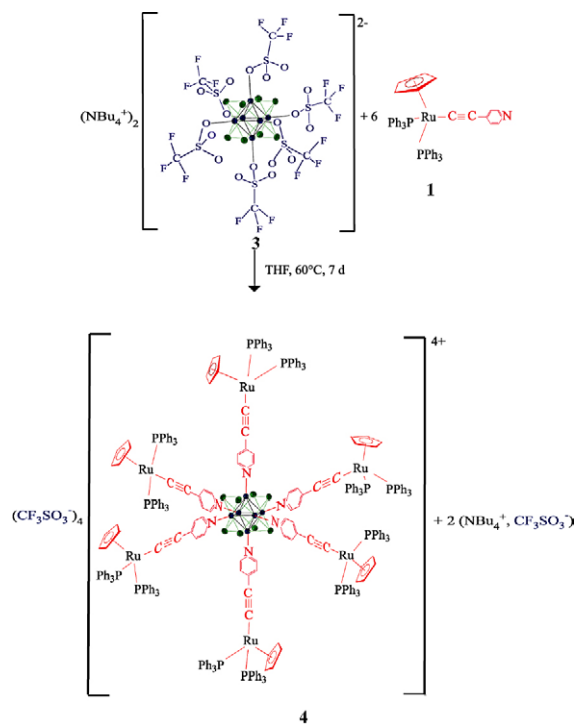
however, involving the reaction of 4-ethynylpyridine with  $[\text{RuCp}(\text{PPh}_3)_2\text{Cl}]$  in the presence of triethylamine and  $[\text{NH}_4][\text{PF}_6]$  in methanol (Scheme 1). This general procedure was reported [22] for the synthesis of the complexes  $[\text{RuCp}(\text{PPh}_3)_2(\eta^1\text{-alkynyl})]$  with ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ). The yellow complex **1** was characterized by standard spectroscopic techniques including  $^{31}\text{P}$  NMR, infrared spectroscopy ( $\nu_{\text{CC}} = 2070\text{ cm}^{-1}$ ) and the MALDI TOF mass spectrum with the dominant molecular peak at 794 Dalton.

In order to compare the coordination of **1** to a single metal center with that in the  $\text{Mo}_6$  cluster, the orange silver complex **2** was synthesized from the ligand **1** and  $\text{AgBF}_4$  in methanol. In the infrared spectrum of the trimetallic complex **2**, the alkynyl CC band was found at  $2016\text{ cm}^{-1}$ . Then, the reaction of **1** with the cluster  $[\text{Mo}_6\text{Br}_8(\text{CF}_3\text{SO}_3)_6][n\text{-Bu}_4\text{N}]_2$ , **3**, was carried out in refluxing THF for a week.

The new hexa-ruthenium hexa-molybdenum compound **4** was recovered by slow precipitation using pentane. A single peak was found in the  $^{31}\text{P}$  NMR spectrum, a single Cp peak was observed in the  $^1\text{H}$  NMR spectrum at  $\delta = 4.42$  ppm, and a single infrared absorption was obtained at  $\nu_{\text{CC}} = 2018\text{ cm}^{-1}$ . This behavior is in accord with the coordination of the cluster by the six organo-ruthenium pyridine ligands and the absence of free pyridine ligand in the sample (Equation 2).

## 2.2. Coordination of a ferrocenyl-alkynyl-pyridine rod

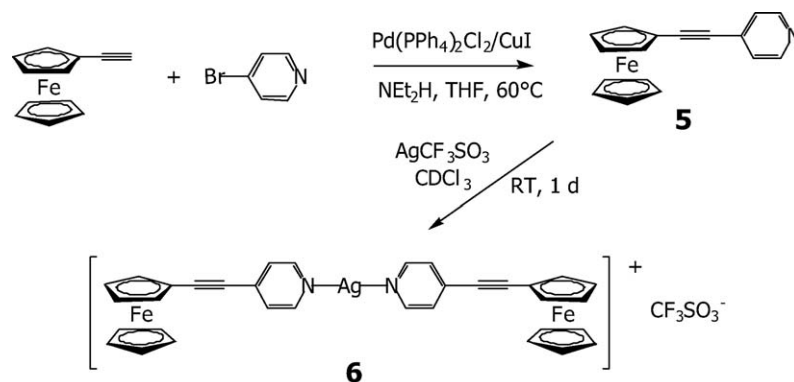
In a similar approach, the red complex 1-ferrocenyl-2-(4-pyridinyl)acetylene, **5**, was synthesized using the reaction of the Vargas' group (Scheme 2) [23]. The reaction of **5** with  $\text{AgSO}_3\text{CF}_3$  or  $\text{AgBF}_4$  at room tempera-



Equation 2.

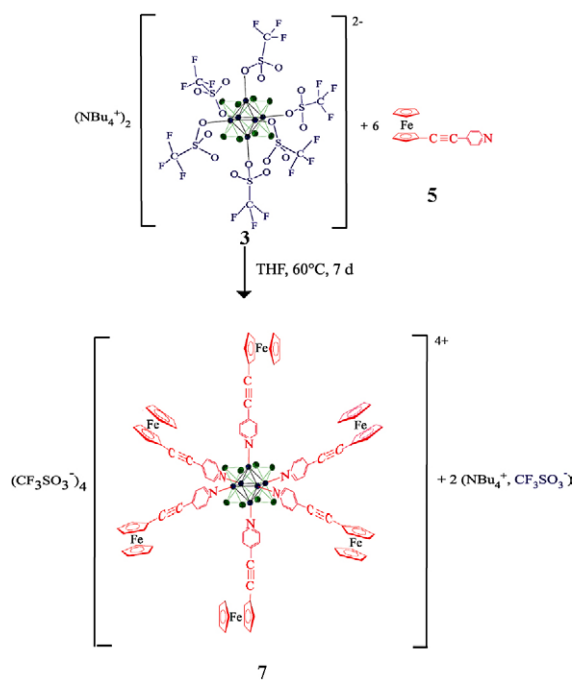
ture in  $\text{CDCl}_3$  gives a red trimetallic complex **6** (shown with the triflate anion) resulting from the coordination of two equivalents of the pyridine nitrogen atom on the silver cation (Scheme 2). The compound **6** is light and air sensitive.

The reaction of the ferrocenyl-containing pyridinyl ligand **5** with the cluster **3** was carried out in refluxing THF for a week to give the new hexasubstituted hexa-ferrocenyl  $\text{Mo}_6$  cluster **7**. The red compound **7** was isolated by precipitation from a THF solution by slow addition of pentane and characterized inter alia by an



Scheme 2.

infrared alkyne absorption at  $2181\text{ cm}^{-1}$ , ferrocene signals including a single Cp signal for the free Cp rings in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Equation 3). This complex **7** is very light and air sensitive. Its CV in  $\text{CH}_2\text{Cl}_2$  shows two close reversible ferrocenyl waves at  $E_{1/2} = 0.800\text{ V}$  vs.  $[\text{FeCp}^*_2]$  with a less intense shoulder at  $E_{1/2} = 0.710\text{ V}$  vs.  $[\text{FeCp}^*_2]$ ; these values compare with the value obtained for the starting monomeric complex **5**,  $E_{1/2} = 0.720\text{ V}$  vs.  $[\text{FeCp}^*_2]$ .



Equation 3.

### 2.3. Coordination of a tri-silylferrocenyl-phenolate dendron

The known tri-silylferrocenyl phenolate dendron  $p\text{-HO-C}_6\text{H}_4\text{C}\{\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{Me})_2\text{Fc}\}_3$ , **8**, has already been used as part of a dendritic gold-nanoparticle-cored device for the recognition of inorganic oxoanions [24]. Its reaction with the  $\text{Mo}_6$  cluster **3** was inspired by previous studies of substitution of the six outer (terminal) halide ligands including Gorman's work that involved dendronic phenolates [8b]. Thus, reaction of **8** with **3** was carried out overnight in THF at  $60\text{ }^\circ\text{C}$ , then in toluene at  $80\text{ }^\circ\text{C}$  for two days which eventually led to completion of the substitution reaction, giving the air-sensitive cluster-cored octadecylsilylferrocenyl dendrimer **9**. The end of the reaction was indicated by the correct ratio of the  $n\text{-Bu}_4\text{N}^+$  cation/dendrion signals in  $^1\text{H}$  NMR of **9** that was obtained only then (Equation 4).

The CV of **9** showed a single oxidation wave for the 18 ferrocenyl redox centers indicating that these 18 ferrocenyl centers are seemingly equivalent as in other polyferrocenyl dendrimers [25]. Addition of  $[n\text{-Bu}_4\text{N}]_2[\text{ATP}]$  to the electrochemical cell leads to the appearance of a new ferrocenyl wave at less positive potential ( $\Delta E = 90\text{ mV}$ ) whose intensity is proportional to the proportion of  $[n\text{-Bu}_4\text{N}]_2[\text{ATP}]$  salt added. This is the indication of an interaction of strong type according to the Kaifer–Echegoyen model [26] as already observed previously with other polyamidoferrocenyl and polysilylferrocenyl dendrimers (Fig. 1). It is noteworthy that the shift of potential (Fig. 1) is much smaller than in gold-nanocluster-cored dendrimers.

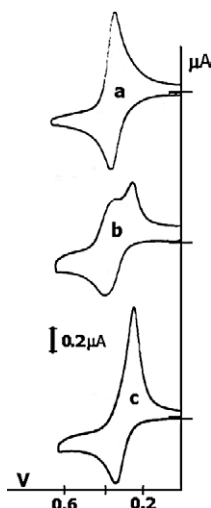
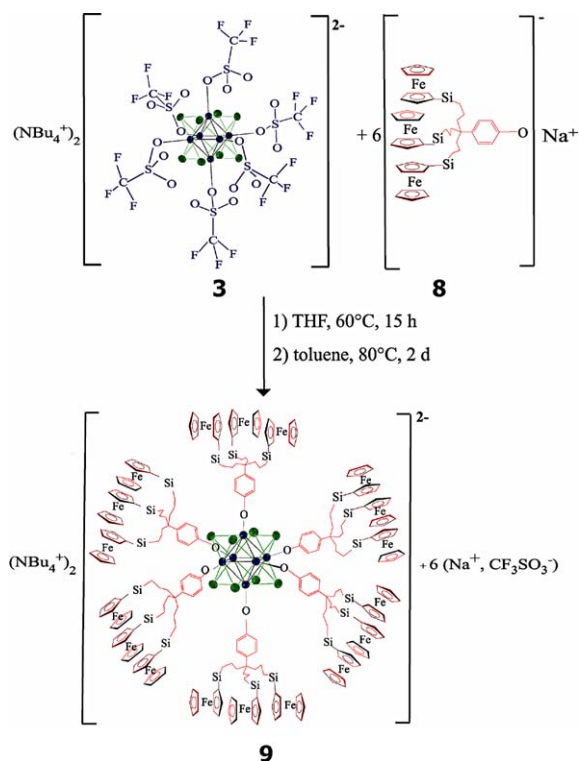


Fig. 1. Titration of  $(\text{Bu}_4\text{N})_2[\text{MoBr}_8(\text{OC}_6\text{H}_4\text{C}(\text{C}_3\text{H}_6\text{Si}(\text{C}_2\text{H}_6\text{Fc})_3)_6)]$  in  $\text{CH}_2\text{Cl}_2$  (Pt,  $[\text{Bu}_4\text{N}][\text{PF}_6]$  0.1 M, 20 °C, reference:  $[\text{FeCp}_2^*]$ , not shown) with  $[\text{Bu}_4\text{N}]_2[\text{ATP}]$ ; a) Before the addition,  $E_{1/2} = 0.40$  V; b) with 0.30 equiv. of anion; c) with an excess of anions,  $E_{1/2} = 0.31$  V. The two methyl substituents on all Si atoms are omitted for clarity.

### 3. Discussion

Precedents showing hexa-substitution of the outer (terminal) halides in the octahedral inorganic clusters such as **3** [8b,18] provided the basis for the new hexa-substitution reactions described in this work. The rigidity and electronic delocalization in the hexa-pyridine-substituted clusters on one hand, and the bulk of the flexible phenolate dendron on the other hand, however, were factors rendering this chemistry challenging. Finally, the two new hexa-substituted pyridine clusters are light- and air-sensitive, and the cluster-cored 18-ferrocenyl dendrimer is air sensitive which made their work-up and use tedious. Thus, parallel reactions with the mononuclear silver salts, although also very light sensitive, were welcome to facilitate assignments and help understand the spectroscopic intricacies. The substitution reactions could indeed be followed by  $^1\text{H}$  NMR using the relative intensity ratio of appropriate signals, and this technique allowed us to confirm the difficulty of hexa-substitution and the long heating time therefore required. We made the choice to follow Shriver's and Gorman's indications involving the hexa-triflates as intermediates for the substitution reactions.

It turned out that the hexa-substituted clusters (in particular the dendritic one) were very difficult to purify in order to obtain correct elemental analyses. These analytical data had to be submitted several times for each product to yield mediocre results, although the  $^1\text{H}$  NMR monitoring clearly showed the end of the substitution reactions. Inorganic impurities were obviously difficult to separate given the low carbon contents systematically obtained. Although this may be partly due to the air and light sensitivity of the compounds, it appears that triflate salts formed in the reactions may be systematic impurities due to the difficulty of their complete separation and detection. The light and air sensitivity of the hexa-alkynyl-pyridine clusters was probably also responsible for our lack of success in obtaining suitable crystals for X-ray crystal structure determinations. Yet, Schriver's group reported the crystal structure of a hexa-ferrocenyl cluster, but with carboxylate ligands [27].

The location of the alkyne C–C band in the infrared spectrum is very sensitive to the coordination and nature of alkyne substituent. For instance, this band is shifted from  $2070\text{ cm}^{-1}$  in the free organoruthenium-pyridine **1** to  $2016$  and  $2018\text{ cm}^{-1}$  in the silver- and cluster com-

plexes **2** and **4** respectively. Likewise, in the ferrocenyl-alkynyl pyridine, the band is shifted from  $2210\text{ cm}^{-1}$  in the free ligand to  $2176$  and  $2181\text{ cm}^{-1}$  in the silver and cluster complexes respectively. These shifts show the decrease of electronic density on the triple bond due to charge transfer from the pyridine ligands to the metals. Likewise, the Cp peak observed in  $^1\text{H}$  NMR, whose singularity is an evidence of complete hexa-substitution, is shifted downfield upon coordination of both organometallic pyridines to the metals. On the other hand, it is remarkable that the change of location of signals of the pyridinyl protons  $\alpha$  to the nitrogen atom is very minute, whereas the shift of that of the meta protons is more important, as in Lindner's pyridine-silver complexes [28]. The substituted Cp ring protons are also slightly more deshielded in the  $\beta$  positions than in the  $\alpha$  one.

The CV of the three cluster-cored poly-organometallic compounds could be recorded in the ferrocenyl and ruthenium regions, but rather little information could be obtained else than a single partially reversible wave for the hexa-ruthenium system as for the monomer. The hexa-ferrocenyl compound **7** shows a major reversible wave and a weak shoulder. This behavior could tentatively be attributable either to small amounts of decoordinated monomeric ferrocene derivative **5** whose potential is the same as that of the shoulder or to the distinction between the two sets of positions (apical and equatorial). Finally, the cluster-cored 18-silylferrocenyl dendrimer appears to share most of the properties of previously reported covalent [25], hydrogen-bonded [29] and gold-nanoparticle cored [24] polyferrocenyl dendrimers except that it is air sensitive due to the nature of the core. As in other polyferrocenyl dendrimers, the apparent equivalence of all the ferrocenyl groups in term of the seemingly unique redox potential allows to use this nanocluster as exo-receptor for the recognition and titration of oxo-anions whose prototype is  $\text{ATP}^{2-}$ . The sensing property by the 18-silylferrocenyl dendrimer is about the same as with the amidoferrocenyl dendrimers [25], but it is of easier access and presents the advantage that the oxidized ferrocenium form is fully stable, contrary to that of amidoferrocenyl moieties [24,25]. The CVs show a rather nice recognition of  $\text{ATP}^{2-}$  in spite of the relatively modest wave shift of 90 mV. The advantages of the golden-nanoparticle-cored polyferrocenyl dendrimers, however, are the air stability and their larger size (up to about 360 ferrocenyl groups) allowing a very easy elec-

trode derivatization [24] that does not work at this time precisely because of the reduced size of this cluster-cored dendritic assembly.

#### 4. Concluding Remarks

Three new hexasubstituted octahedral  $\text{Mo}_6$  clusters with organometallic groups have been synthesized from the precursor  $[\textit{n}\text{-Bu}_4\text{N}]_2[\text{Mo}_6\text{Br}_8(\text{CF}_3\text{SO}_3)_6]$  upon prolonged heating. The substitution reactions of the triflate by the functional pyridine- or phenolate ligands were monitored by  $^1\text{H}$  NMR that showed clean hexasubstitution. The two cluster-cored hexa-pyridine organometallics obtained are light and air sensitive and the 18-Fc dendrimer is air sensitive, which makes their purification, isolation and analysis tedious. Nevertheless,  $^1\text{H}$  NMR is a convenient method to investigate both their synthesis and the electronic changes occurring upon coordination along the organometallic pyridine rods. The  $\text{Mo}_6$ -cluster-cored 18-silylferrocenyl dendrimers resembles, through its periphery, other polyferrocenyl dendrimers assembled by covalent bonds, coordination to gold nanoparticles and hydrogen bonds and, in particular, it behaves as an exo-receptor allowing to recognize and titrate the biologically important anion  $\text{ATP}^{2-}$ .

#### 5. Experimental Section

##### 5.1. General data

Reagent-grade tetrahydrofuran (THF) and pentane were predried over Na foil and distilled from sodium-benzophenone anion under argon immediately prior to use. MeOH was distilled from magnesium just before use. All other chemicals were used as received. All manipulations were carried out using Schlenk techniques or in a nitrogen-filled Vacuum Atmosphere dry lab.  $^1\text{H}$  NMR spectra were recorded at  $25\text{ }^\circ\text{C}$  with a Bruker AC 300 (300 MHz) spectrometer.  $^{13}\text{C}$  NMR spectra were obtained in the pulsed FT mode at 75 MHz with a Bruker AC 300 spectrometer. All chemical shifts are reported in parts per million ( $\delta$ , ppm) with reference to  $\text{Me}_4\text{Si}$  (TMS). The product **1** [21] was synthesized from commercial 4-ethynylpyridine and  $[\text{RuCp}(\text{PPh}_3)_2\text{Cl}]$  according to Bruce's general method

of synthesis of the complexes  $[\text{RuCp}(\text{PPh}_3)_2(\eta^1\text{-alcyanyl})]$  [22]. The precursor cluster **3** was synthesized according to reference [12d]. The reaction conditions used for the syntheses of substituted hexa-pyridine complexes were analogous to those reported in Fréchet's article [1].

Cyclic-voltammetric data were recorded with a PAR 273 potentiostat galvanostat. The reference electrode was an Ag quasi-reference electrode (QRE). The QRE potential was calibrated by adding the reference couple  $[\text{FeCp}_2^*]/[\text{FeCp}_2^*]^+$  ( $\text{Cp}^*$  = pentamethylcyclopentadienyl). The working electrode (platinum) was treated by immersion in 0.1 M  $\text{HNO}_3$ , and then polished before use and between each recording when necessary.

### 5.2. Synthesis of $[\text{RuCp}(\text{PPh}_3)_2(\text{CC-C}_5\text{H}_4\text{N})]$ , **1**

A methanol solution of 4-ethynylpyridine (0.296 g, 2.07 mmol) and 5 ml of triethylamine was added to a suspension of  $[\text{RuCp}(\text{PPh}_3)_2\text{Cl}]$  (1.00 g, 1.38 mmol) and  $\text{NH}_4\text{PF}_6$  (0.449 g, 2.76 mmol) in methanol. The solution was stirred at room temperature for 3 days. The solvent was removed under vacuum and the product was extracted with toluene. The product was precipitated with toluene/pentane. The yellow powder was dried under vacuum. Yield 0.350 g (0.440 mmol) of yellow powder of **1** (32%).

$^1\text{H}$  NMR (MeOD, 300 MHz),  $\delta_{\text{ppm}}$ : 8.06 (d, **NCH**), 7.30 – 7.04 (m,  $\text{PPh}_3$ ), 6.80 (d, **NCCH**), 4.29 (s, Cp).  $^{31}\text{P}$  NMR (MeOD, 100 MHz),  $\delta_{\text{ppm}}$ : 49.60 ( $\text{PPh}_3$ ). Infrared:  $\nu_{\text{CC}} = 2\,070\text{ cm}^{-1}$ . MS (MALDI-TOF; m/z), calcd. for  $\text{C}_{48}\text{H}_{39}\text{NP}_2\text{Ru}$ : 792.85, found: 794.24. CV in  $\text{CH}_2\text{Cl}_2$ :  $E_{1/2} = 0.700\text{ V}$  vs.  $\text{Fc}^*$  at 20 °C (partially chemically reversible:  $i_c/i_a = 0.5$ ).

### 5.3. Synthesis of the trinuclear $\text{AgRu}_2$ complex, **2**

A methanol solution of **1** (0.0530 g, 0.0667 mmol) and  $\text{AgBF}_4$  (0.007 g, 0.0333 mmol) was stirred at room temperature for 12 h. The solvent was removed under vacuum and the product was precipitated with MeOH/pentane. The orange powder was dried under vacuum. Yield: 0.040 g of **2** as an orange powder (67%). Analysis calcd. for  $\text{C}_{96}\text{H}_{78}\text{AgBF}_4\text{N}_2\text{P}_4\text{Ru}_2$ : C: 64.76%, H: 4.42%, found: 64.45%, H: 4.13.

$^1\text{H}$  NMR (MeOD, 300 MHz),  $\delta_{\text{ppm}}$ : 8.08 (d, **NCH**), 7.28 – 7.05 (m,  $\text{PPh}_3$ ), 6.87 (d, **NCCH**), 4.33 (s, Cp). Infrared:  $\nu_{\text{CC}} = 2\,016\text{ cm}^{-1}$ . CV in  $\text{CH}_2\text{Cl}_2$ :  $E_{1/2} =$

0.940 V vs.  $\text{Fc}^*$  at 20 °C (partially chemically reversible  $i_c/i_a = 0.5$ ).

### 5.4. Synthesis of the hexa-substituted cluster $\text{Mo}_6\text{-Ru}_6$ , **4**

A THF solution of **1** (0.131 g, 0.165 mmol) and **3** (0.069 g, 0.0265 mmol) was stirred at 60 °C for 7 days. The solvent was removed under vacuum and the product was precipitated with THF/pentane. The red powder was dried under vacuum. Yield 0.115 g of red powder of **4** (65%). Analysis calcd. for  $\text{Mo}_6\text{Br}_8\text{C}_{292}\text{-H}_{234}\text{F}_{12}\text{S}_4\text{O}_{12}\text{N}_6\text{P}_{12}\text{Ru}_6$  (%): C 53.39, H 3.39, found: C 52.59, H: 2.97.

$^1\text{H}$  NMR (MeOD, 300 MHz),  $\delta_{\text{ppm}}$ : 8.12 (d, **NCH**), 7.23 – 7.08 (m,  $\text{PPh}_3$ ), 7.04 (d, **NCCH**), 4.42 (s, Cp).  $^{31}\text{P}$  NMR (MeOD, 100 MHz),  $\delta_{\text{ppm}}$ : 49.51 ( $\text{PPh}_3$ ). Infrared:  $\nu_{\text{CC}} = 2\,018\text{ cm}^{-1}$ . CV in  $\text{CH}_2\text{Cl}_2$ :  $E_{1/2} = 0.650\text{ V}$  vs.  $\text{Fc}^*$  at 20 °C in  $\text{CH}_2\text{Cl}_2$  (partially chemically reversible  $i_c/i_a = 0.1$ ).

### 5.5. Synthesis of the hexa-ferrocenyl $\text{Mo}_6\text{Fc}_6$ cluster, **7**

A THF solution of **5** (0.054 g, 0.187 mmol) and **3** (0.063 g, 0.029 mmol) was stirred at 60 °C for 7 days. The solvent was removed in vacuum and the product was precipitated with THF/pentane. The red powder was dried under vacuum. Yield 0.073 g of red powder of **7** (63%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz),  $\delta_{\text{ppm}}$ : 8.64 (d, **NCH**), 7.51 (d, **NCCH**), 4.62 and 4.41 (t, **FeCH**), 4.32 (s, Cp).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 63 MHz),  $\delta_{\text{ppm}}$ : 69.9 (**FeC**), 70.2 (**Cp**), 72.0 (**FeC**), 76.95 (**CC**), 125.9 (**NCC**), 147.5 (**NC**). Infrared:  $\nu_{\text{CC}} = 2\,181\text{ cm}^{-1}$ . Elemental analysis calcd (%): C 36.03, H 2.22; found (%): C 35.29, H 1.59. CV in  $\text{CH}_2\text{Cl}_2$  at 20 °C:  $E_{1/2} = 0.800\text{ V}$  vs.  $[\text{FeCp}^*_2]$  in  $\text{CH}_2\text{Cl}_2$ .

### 5.6. Synthesis of the trinuclear $\text{AgFc}_2$ complex, **6**

A chloroform-*d* solution of **5** (0.044 g, 0.0156 mmol) and  $\text{AgSO}_3\text{CF}_3$  (0.020 g, 0.0078 mmol) was stirred at room temperature for 24 h. The solvent was removed under vacuum, and the product was washed with ether and dried under vacuum. Yield: 0.061 g of red powder of **6** (95%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz),  $\delta_{\text{ppm}}$ : 8.54 (d, **NCH**), 7.41 (d, **NCCH**), 4.61 and 4.40 (t, **FeCH**), 4.30 (s, Cp).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 63 MHz),  $\delta_{\text{ppm}}$ : 71.3 (FeC), 72.2 (Cp), 73.5 (FeC), 77.6 (CC), 126.7 (NCC), 137.2 (NCCC), 148.4 (NC). Infrared:  $\nu_{\text{CC}} = 2\,176\text{ cm}^{-1}$ .

Analysis calcd (%): C 50.57, H 3.15; found (%): C 50.28, H 2.91

5.7. *Synthesis of the cluster-cored hexa-tri-silylferrocenylphenolate dendrimer*  
( $\text{Bu}_4\text{N}$ )<sub>2</sub>[ $\text{MoBr}_8(\text{OC}_6\text{H}_4\text{C}\{\text{C}_3\text{H}_6\text{SiC}_2\text{H}_6\text{Fc}\}_3)_6$ ], **9**

A 20-ml THF solution of ( $n\text{-Bu}_4\text{N}$ )<sub>2</sub>[ $\text{MoBr}_8(\text{CF}_3\text{SO}_3)_6$ ], (0.019 mmol, 0.050 g) and  $\text{Na}[\text{OC}_6\text{H}_4\text{C}(\text{C}_3\text{H}_6\text{SiC}_2\text{H}_6\text{Fc})_3]$  (0.23 mmol, 0.222 g) was magnetically stirred at 60 °C overnight. The solvent was removed under vacuum, and 20 ml of toluene were added. The solution was then stirred at 80 °C for two days, then filtered at room temperature over celite. The volume of the filtrate was reduced to 3–5 ml, and 30 ml of anhydrous pentane was added dropwise. An orange powder precipitated and was re-dissolved with 2–3 ml toluene and re-precipitated with pentane. The compound ( $\text{Bu}_4\text{N}$ )<sub>2</sub>[ $\text{MoBr}_8(\text{OC}_6\text{H}_4\text{C}(\text{C}_3\text{H}_6\text{SiC}_2\text{H}_6\text{Fc})_3)_6$ ], **9**, is an orange powder. Yield: 57% 0.080 g.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.85 (m, 12H), 6.45 (m, 12H), 4.12 (s, 12H), 3.91 (s, 30H), 3.86 (s, 12H), 2.72 (m, 16H), 1.40 (m, 36H), 1.07–0.97 (m, 42H), 0.70 (m, 36H), 0.43 (m, 36H), 0.002 (s, 108H).  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  724.65 ( $\text{C}_5\text{H}_4$ ), 72.28 ( $\text{C}_5\text{H}_4$ ), 69.81 ( $\text{C}_5\text{H}_4$ ), 31.34 ( $\text{CH}_2\text{N}$ ), 19.73 ( $\text{CH}_2$ ), 19.20 ( $\text{CH}_2$ ), 15.66 ( $\text{CH}_3$ ), -0.08 ( $\text{CH}_3$ ). CV of the ferrocenyl system:  $E_{1/2} = 0.40\text{ V}$  vs. [ $\text{FeCp}^*_2$ ] in  $\text{CH}_2\text{Cl}_2$  at 20 °C.

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