Synthesis and structural analysis of a *exo*-ditopic macrocyclic ligand bearing 2,2′-bipyridine units interconnected by silane spacers and of its binuclear ruthenium complex

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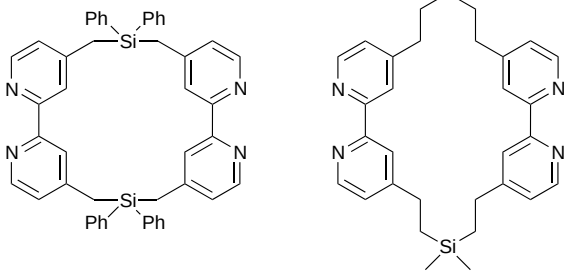
The synthesis and structural analysis of a macrocyclic *exo*-ditopic ligand bearing two 2,2′-bipyridine units interconnected at the 4 and 4′ positions by two $-(CH_2)_2Si(CH_2)_2-$ spacers and of its acyclic analogue is achieved; for both compounds ruthenium homobinuclear complexes were prepared; for the complex obtained with the cyclic ligand, both diastereoisomers were separated and the structure of the *meso* form was elucidated by X-ray analysis.

Whereas considerable effort has been invested in designing *endo*-di- and poly-topic ligands affording discrete *endo* complexes in which metal centres are located in close proximity, over the last few years much interest seems to be focused on *exo* ligands in which the coordination sites are outwardly oriented.[1] This increase in interest is related to the development of coordination polymers in which *exo*-ditopic ligands play the role of connectors between metallic centres. Although many examples of coordination polymers are available, most of the reported cases deal with bis-monodentate ligands.[2] Only few coordination polymers based on bridging of metallic centres by bis-tridentate ligands have been published so far.[3] Our approach to the formation of coordination polymers is based on the use of bis-bidentate ligands. 2,2′-Bipyridine derivatives are the most widely used chelates for metal binding.[4] We have previously reported *exo*-ditopic ligands based on two 2,2′-bipyridine units interconnected at the 4 and 4′ positions imposing the divergent orientation of the binding sites either by $(CH_2)_n$[5] or by CH_2SiCH_2 fragments (compound **1**).[6] In the latter case, probably owing to the presence of fragile benzylic positions, we were unable to prepare the ruthenium binuclear complexes.



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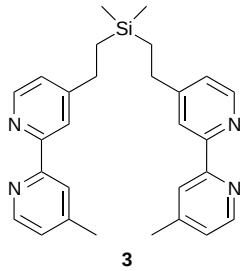

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In order to overcome this problem, ligand **2**, in which the two 2,2′-bipy chelates are interconnected at the 4 and 4′ positions by two $(CH_2)_2Si(CH_2)_2$ fragments was designed. Introduction of two silicon atoms within the macrocyclic framework has been previously reported for silacrown ether derivatives.[7] The silane moieties might be used either as connecting groups or as reactive centres allowing further structural modification. Prior to elaboration of coordination polymers using ligand **2**, a detailed structural analysis of discrete binuclear complexes based on such a ligand is needed. Here, we present the synthesis of both the free ligand **2** and its acyclic analogue **3** and of their homobinuclear ruthenium(II) complexes **2**-Ru_2 and **3**-Ru_2. For the **2**-Ru_2 complex, we also report a solid state structural analysis. The synthesis of ligand **2** was achieved by reacting the dilithium derivative of 4,4′-dimethyl-2,2′-bipyridine,[8] prepared by treating at 0 °C the latter with lithium diisopropyl amide (LDA) in dry THF, with bis(chloromethyl)dimethylsilane in dry THF at 25 °C (slow addition, 4–5 h and further stirring at room temp. overnight). To the blue–violet solution thus obtained a few drops of MeOH were added to quench the excess LDA before it was evaporated to dryness. In order to separate polymeric species, the residue was taken up in $CHCl_3$ and filtered. The solid was further washed with $CHCl_3$. The filtrate and washes were combined and evaporated to dryness affording a mixture of ten different products. Both compound **2** and **3** were obtained as a mixture after chromatography [SiO_2, CH_2Cl_2–MeOH (0–3%)]. Their separation (3% yield for compound **2**) appeared to be only feasible upon crystallisation from a hexane–CH_2Cl_2 mixture. However, compound **3** was also prepared in 50% yield by treating the monolithium derivative of 4,4′-dimethyl-2,2′-bipyridine with bis(chloromethyl)dimethylsilane in dry THF at 25 °C.

The X-ray analysis (Fig. 1) of the free ligand **2** revealed the following features:† (*i*) the two bipy units, both in *transoid* conformation, were almost parallel to each other leading thus to a cyclophane type situation (box dimension of 2.9 × 11.6 Å); (*ii*) the coordination geometry around both silicon atoms was tetrahedral with an average Si–C distance of 1.86 Å and C–Si–C angle of 109.5°; (*iii*) on each silane moiety, both methyl groups were pointing towards the exterior of the macrocycle.

The homobinuclear complexes $(\mathbf{2}\text{-}Ru_2)^{4+}4PF_6^-$ and $(\mathbf{3}\text{-}Ru_2)^{4+}4PF_6^-$ were obtained upon treatment under reflux of **2** or **3** with $Ru(bipy)_2Cl_2\cdot 2H_2O$ in degassed EtOH followed by addition of NH_4PF_6 which caused the precipitation of both

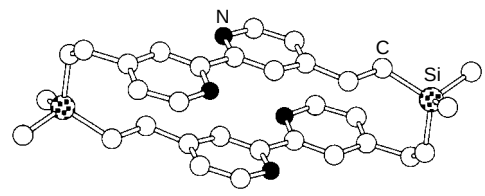
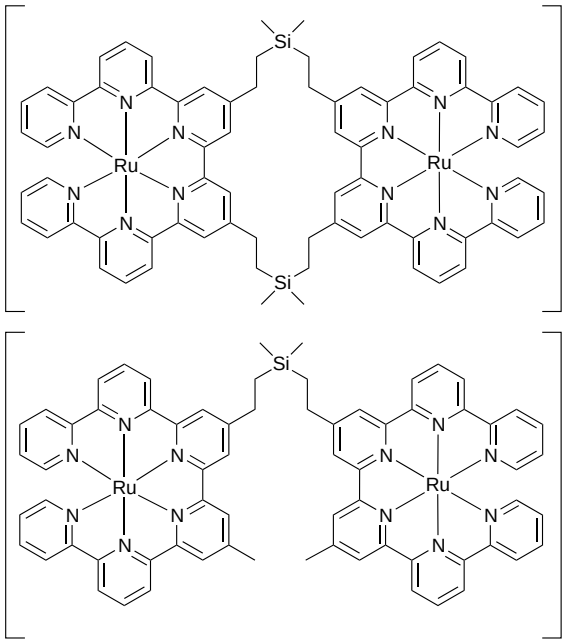


Fig. 1 X-Ray crystal structure of ligand **2**; H atoms are not shown for clarity (for distances and angles see text)



stereoisomeric (Δ,Δ; Λ,Λ) and *meso* (Δ, Λ) complexes in a 1 : 1 mixture. The latter was further recrystallised from acetone–ether. For (**2**-Ru_2)$^{4+}$4PF_6^-, the 1 : 1 ratio of stereoisomers was deduced from the ^{1}H NMR spectrum (300 MHz, CD_3CN, 25 °C) of the mixture which revealed that among the signals present, three singlets corresponding to MeSi fragments were the most differentiated. The diastereomeric separation of the mixture was achieved by crystallisation of the *meso* form by slow diffusion of benzene into a nitromethane solution. The assignment of singlets corresponding to MeSi groups was based on the ^{1}H NMR study of both the pure *meso* form which showed two singlets at δ 0.02 and 0.1 and of the remaining mixture of enantiomers which revealed only one singlet at δ 0.06.

In the solid state (Fig. 2), the structure of the *meso* form of (**2**-Ru_2)$^{4+}$4PF_6^- was studied by X-ray diffraction† which revealed the following features: (*i*) in addition to (**2**-Ru_2)$^{4+}$4PF_6^- complex, six MeCN and two MeOH molecules are present in the solid state but without any interaction with the metallic centres; (*ii*) in marked contrast with the free ligand **2**, both bipy units in the complex adopt a *cisoid* conformation allowing, as expected, the chelation of Ru^{II} cations; (*iii*) the cationic moiety of the complex possesses a centre of symmetry; (*iv*) the coordination geometry around Si atoms was tetrahedral with an average Si–C distance and C–Si–C angle of 1.86 Å and 109.4° respectively; (*v*) owing to the conformation of the $(CH_2)_2Si(CH_2)_2$ fragments (CCCSi, and CSiCC dihedral angles of 171.0 and −87.2 °, respectively), in marked contrast with the free ligand adopting a cyclophane type conformation, the two bipy units oppositly oriented are almost parallel but not coplanar; (*vi*) both Me groups of both silane moieties are, as in the case of the free ligand, outwardly oriented; (*vii*) for both Ru^{II} centres, the coordination sphere is composed of six nitrogen atoms amongst which four are belonging to the two auxiliary bipy units and the remaining two are part of the macrocyclic ligand **2**. The coordination geometry around each Ru^{II} was almost octahedral with an average Ru–N distance of 2.05 Å; (*viii*) the two Ru^{II} centres were separated by 13.58 Å; (*ix*) quite interestingly and unexpectedly, among the four PF_6^- anion present, two of them were localised below and above the mean plane of the macrocyclic core and pointing almost towards the centre of the macrocycle.

It is worth noting that a systematic Cambridge Database search revealed that only three homobinuclear ruthenium complexes bearing three bipyridine type ligands have been structurally characterised (KIKHOB,[9] ZADLAR,[5a] ZELCIC[1d]). Preparation of linear coordination polymers based on compound **2** is under current investigation.

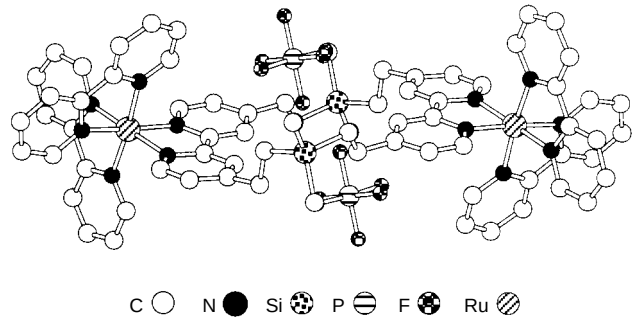


Fig. 2 Crystal X-ray structure of the *meso* form of the ruthenium binuclear complex obtained with ligand **2**; solvent molecules as well as H atoms are not shown for clarity (for distances and angles see text)

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Footnotes and References

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† *Crystallographic data*: **2** (slightly yellow crystals, 294 K): $C_{32}H_{40}N_4Si_2$, M = 536.87, monoclinic, space group $P2_1/c$, a = 9.408(2), b = 12.506(2), c = 12.651(3) Å, β = 90.31(2)°, U = 1488.5 Å^3, Z = 2, D_c = 1.20 g cm^{-3}, Mo-Kα graphite-monochromated radiation (λ = 0.7103 Å), 17.36 data with $I > 3\sigma(I)$, R = 0.047, R_w = 0.068.

(**2**-Ru_2)$^{4+}$4PF_6^- (orange crystals, −173 K): $C_{72}H_{72}N_{12}Si_2Ru_2$·4$PF_6$·$CH_3CN$·2$CH_3OH$, M = 2254.03, triclinic, space group $P\bar{1}$, a = 12.1109(8), b = 13.486(1), c = 18.456(2) Å, α = 103.678(7), β = 95.143(6), γ = 111.723(7)°, U = 2667(1) Å^3, Z = 1, D_c = 1.40 g cm^{-3}, Mo-Kα graphite-monochromated radiation (λ = 0.7103 Å), 7379 data with $I > 3\sigma(I)$, R = 0.049, R_w = 0.080. CCDC 182/634.

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