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Inorganica Chimica Acta 343 (2003) 351–356

Inorganica Chimica Acta

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Note

New dirhodium(II,II) species as building corner connectors for square molecular boxes

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Received 25 March 2002; accepted 30 May 2002

Abstract

The new mixed dirhodium(II,II) complexes, $[Rh_2(form)_2(O_2CC_6H_4CN)_2]$ (**2**) and $[Rh_2(form)_2(O_2CC_5H_4N)_2]$ (**3**) (form = *N*,*N′*-di-*p*-tolylformamidinate) as building corner connectors for heteronuclear molecular boxes, were synthesized. By exploiting the peculiar equatorial reactivity of $[Rh_2(form)_2(O_2CCF3)_2(H_2O)_2]$ (**1**), due to the lability of trifluoroacetates, the synthesis of **2** and **3** was readily achieved by mathematical relations with the *exo*-functionalized 4-cyanobenzoate and isonicotinate carboxylates, respectively. The X-ray diffraction studies performed on the pyridine adduct of **2**, $[Rh_2(form)_2(O_2CC_6H_4CN)_2(Py)_2]$, are reported, together with some preliminary attempts of self-assembly with square-planar platinum(II) and palladium(II) complexes.

Keywords: Dirhodium compounds; Molecular square box; Crystal structures

1. Introduction

Self-assembly by transition metal complexation is recognized today as one of the most promising synthetic strategy of access to well defined and highly ordered molecular architectures [1]. Among others, this method was successfully employed for the rational construction of a large variety of cyclic molecular polygons, the most popular of which is represented by the so called ‘molecular square boxes’. Besides their interesting molecular structures, transition metal incorporating-macrocycles are of interest because they may exhibit a wide variety of physicochemical and functional properties, which make them particularly attractive for applications in the field of material science and nanotechnology [2].

Most of the examples of molecular boxes so far reported mainly involve the use of square-planar or octahedral mononuclear transition metals (Pd, Pt, Re, Os, Ru) [1]. Recently, this synthetic strategy was extended to the use of dimetal units (Mo_2^{4+}, Rh_2^{4+}, etc.) as angular building blocks [3–5], leading to a series of square boxes having the *cis*-$M_2(form)_2$ (form = formamidinate anion) units as angular components and linear or angular dicarboxylates as connectors. Square boxes involving dimetal species as *exo*-bidentate connectors are also accessible by exploiting the classical reactivity of dimetal complexes with lantern structure. By combination of $[Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2]$ (**1**) with *cis*-dipyridyl-diphenyl-porphyrin (*cis*-DPyP), we recently succeeded in preparing the $[Rh_2(form)_2(CF_3CO_2)_2(cis\text{-DPyP})]_4$ molecular square boxes [6]. Due to the well known redox activities of such dimetal complexes as well as of porphyrins, these metallomacrocycles represent, among others, interesting examples of multicomponent redox-systems.

Although such a synthetic approach allows to build square boxes of different sizes and nuclearity depending on the geometry and length of the dicarboxylate connectors [3,4], it leads, in any case, to only neutral and homonuclear boxes, although charges may be potentially introduced, stepwise, by oxidation of the dimetal units.

In order to open new opportunities in the field of dirhodium containing-molecular boxes, we planned the synthesis of new mixed dirhodium(II,II) molecules as

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PII: S0020-1693(02)01171-4

angular building blocks suitable for the self-assembly of macrocyclic squares, neutral or charged, incorporating further transition metals ions.

This aim may be realized by the introduction in the dirhodium lantern structure of two functionalized carboxylates, namely the 4-cyanobenzoate (O_2C-C_6H_4CN) and isonicotinate ($O_2CC_5H_4N$) groups. These, when *cis*-symmetrically bridged to the dirhodium core via the carboxy moieties, are featured by the two dangling cyano-benzoate and pyrydine groups in *cis*-orientation and ready for further coordination.

In the present paper we report on the synthesis and charactherization of $[Rh_2(form)_2(O_2CC_6H_4CN)_2]$ (**2**) and $[Rh_2(form)_2(O_2CC_5H_4N)_2]$ (**3**), together with the X-ray diffraction studies performed on the pyrydine adduct $[Rh_2(form)_2(O_2CC_6H_4CN)_2(Py)_2]$ (**2a**). These unambiguously confirm that the two formamidinate and the functionalized carboxylate groups are symmetrically bridged in a *cisoid* arrangement around the Rh_2^{4+} core, so that the overall molecule displays the wished shape of an angular component for the assembly of square boxes.

Both the species, **2** and **3**, may potentially coordinate, via the two pendant cyano-benzoate and pyrydine groups, to square-planar transition metal complexes affording heteronuclear square macrocycles, neutral or charged, in which the dirhodium moieties are alternated to different metal ions. Depending on the geometry (*cis*- or *trans*-) of the transition metals, square-shaped boxes at different nuclearity could be obtained: (i) macrocycles in which, at the corners, dirhodium units are alternated to different metal ions, or (ii) macrocycles bearing at the corners dirhodium units and transition metals as linear connectors.

Our preliminary attempts of self-assembly of **2** and **3** with *cis*- and *trans*-square-planar transition metal (Pd, Pt) complexes are also reported.

2. Experimental

2.1. Materials and equipment

The starting complex $[Rh_2(form)_2(CF_3COO)_2(H_2O)_2]$ was prepared according to literature data [7]. All other chemicals are commercially available and used as supplied. None of the compounds reported here is air sensitive, but all reactions were carried out under an atmosphere of dry nitrogen. Elemental analyses were performed by REDOX snc Laboratorio di Microanalisi, Cologno Monzese (Milano), Italy.

Infrared spectra were recorded on KBr pellets with a Perkin–Elmer FT 1720X spectrometer. Electronic absorption spectra were recorded on a Perkin–Elmer Lambda 5 UV–Vis spectrophotometer. The NMR measurements were performed with a Bruker AMX 300 spectrometer using standard pulse sequences.

2.2. Syntheses

2.2.1. $[Rh_2(form)_2(O_2CC_6H_4CN)_2]$ (2)

To an acetone–water solution (1:2, 50 ml) of sodium 4-cyanobenzoate ($C_8H_4NO_2Na$) (0.148 g, 0.872 mmol) was added a chloroform–acetone solution (1:2, 40 ml) of **1** (0.200 g, 0.218 mmol) and the resulting mixture left to stir for approximately 24 h. After this time the volatiles were removed by rotavapor and the resulting green solid was collected by filtration, washed several times with warm water and acetone and then dried under vacuum. Yield 90%. $Rh_2C_{46}H_{38}N_6O_4Rh_2$: *Anal.* Calc. C, 58.49; H, 4.05; N, 8.9. Found: C, 58.43; H, 4.15; N, 8.81%. IR (KBr pellet, cm^{-1}): $\nu_{asym}(CO_2)$ 1624 (s), ν(N–C–N) 1591 (s), ν(CN) 2229 (m).

2.2.2. $[Rh_2(form)_2(O_2CC_6H_4\text{–}CN)_2(Py)_2]$ (2a)

To a benzene mixture (20 ml) of **2** (0.100 g, 0.102 mmol) was added 0.5 ml of pyridine (Py). Immediately the starting green solid dissolved affording a red–orange solution. Then *n*-heptane was added and the resulting mixture left on standing for 2 days. During this time **2a** precipitated as dark orange microcrystals. Yield 90%. $C_{56}H_{48}N_8O_4Rh_2$: *Anal.* Calc. C, 60.99; H, 4.39; N, 10.16. Found: C, 60.64; H, 4.51; N, 10.05%. IR (KBr pellet, cm^{-1}): $\nu_{asym}(CO_2)$ 1630 (s); ν(N–C–N) 1593 (s), ν(CN) 2229 (m). ^1H NMR (pyridine-d_5) δ (ppm): 2.11 (s, 12H), 7.1 (dd, 16H, $J = 56.8$ and 7.9 Hz), 7.61 (4H, $J = 8.1$ Hz), 7.72 (t, br, 2H), 8.31 (d, 4H, $J = 8$ Hz).

2.2.3. $[Rh_2(form)_2(O_2CC_5H_4N)_2]$ (3)

Complex **3** was obtained as a green solid by following the same procedure as used for **2**. Sodium isonicotinate ($C_6H_4NO_2Na$) was used as a salt source. The crude solid was recrystallized from chloroform–heptane (3:1) affording **4** as a dark green precipitate. Yield 90%. $C_{42}H_{38}N_6O_4Rh_2$: *Anal.* Calc. C, 56.34; H, 4.32; N, 8.57. Found: C, 56.42; H, 4.34; N, 8.45%. IR (KBr pellet, cm^{-1}): $\nu_{asym}(CO_2)$ 1622 (s); ν(N–C–N) 1596 (s).

2.2.4. $[Rh_2(form)_2(O_2CC_5H_4N)_2(Py)_2]$ (3a)

Complex **3a** was prepared by following the same procedure used as for **2a**. Yield 90%. $C_{52}H_{48}N_8O_4Rh_2$: *Anal.* Calc. C, 59.21; H, 4.59; N, 10.62. Found: C, 59.42; H, 4.61; N, 10.65%. IR (KBr pellet, cm^{-1}): $\nu_{asym}(CO_2)$ 1624 (s); ν(N–C–N) 1594 (s). ^1H NMR (pyridine-d_5) δ (ppm): 2.11 (s, 12H); 7.05 (dd, 16H, $J = 55.1$, 7.8 Hz); 7.72 (t, br, 2H); 8.01 (d, $J = 8$ Hz); 8.60 (d, 4H, $J = 8$ Hz).

2.3. Single-crystal X-ray diffraction studies of [$Rh_2(form)_2(O_2CC_6H_4CN)_2(Py)_2$] (**2a**)

2.3.1. Crystal data

$C_{56}H_{48}N_8O_4Rh_2\cdot C_6H_6$, fw = 1180.95, orthorhombic, $C222_1$ (ITC N. 20), $a = 17.484(7)$ Å, $b = 17.930(6)$ Å, $c = 21.298(9)$ Å, $V = 6677(4)$ Å^3, $Z = 4$, $D_{calc} = 1.175$ mg m^{-3}, $F(000) = 2416$, μ(Mo Kα) = 0.540 mm^{-1}, $R_1 = 0.041/0.049$ and $wR_2 = 0.122/0.134$ for 4065 [$I > 2\sigma(I)$]/all 4560 independent reflections, GOF = 0.839 for 57 restraints and 341 parameters.

Crystals suitable for X-ray analysis were obtained by re-crystallization from a mixture benzene–pyridine–*n*-heptane (30 ml, 1:1:1). Diffraction data were collected at room temperature (r.t.) from a brune 0.35 × 0.40 × 0.46 mm^3 prismatic crystal sample by using a Siemens P4 automated four-circle single-crystal diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Lattice parameters were obtained from least-squares refinement of the setting angles of 37 reflections within $2 \leq 2\theta \leq 31°$ range. Reflections (4692) were measured by the ω scan technique up to $2\theta = 54°$. A crystal decay was evidenced by the 19% decreasing in intensity of the check reflections monitored each 197 measurements. Intensities were evaluated by profile fitting of a 96 steps peak scan among 2q shells procedure [8] and then corrected for Lorentz polarization effects and crystal decay. Absorption correction was applied by integration method. Data-collection and reduction has been performed by XSCANS [9] and SHELXTL package [10]. The structure was solved by a combination of standard Direct Methods [11] and Fourier synthesis, and refined by minimizing the function $\Sigma\, w(F_o^2 - F_c^2)^2$ with the full-matrix least-square technique based on all 4560 independent F^2 [$R_{int} = 0.0176$], by using SHELXL-97 [12]. All non hydrogen atoms were refined anisotropically. Hydrogen atoms were located on the difference Fourier maps and included in the model refinement among the 'riding model' method with the X–H bond geometry and isotropic displacement parameter depending on the parent atom X. One disordered C_6H_6 molecule was found on a twofold axis and was splitted in two staggered positions (with occupancy 0.52 and 0.48, respectively) by using some soft distance restraints. The hydrogen atoms of this co-crystallized solvent unit were not included into the model due to its disorder.

The absolute configuration parameter [13] converged to −0.01(5). The last difference map showed the largest electron density residuals within 1.2 Å from the rhodium atom (max and min range = 0.600 and −0.904 e Å^{-3}). The final geometrical calculations and drawings were carried out with the PARST program [14] and the XPW utility of the Siemens package, respectively.

3. Results and discussion

The present synthetic approach to dirhodium(II,II) based molecular square boxes involves: (i) the synthesis of new dirhodium(II,II) molecules which can act as angular units; (ii) their reactions with square-planar transition metal [palladium(II) and platinum(II)] complexes having *cis*- or *trans*-labile ligands.

3.1. Synthesis and characterization of [$Rh_2(form)_2(O_2CC_6H_4CN)_2$] (**2**) and [$Rh_2(form)_2(O_2CC_5H_4N)_2$] (**3**) dirhodium corner species

The typical equatorial reactivity of [$Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$] (**1**) (form = *N*,*N′*-di-*p*-tolylformamidinate) was exploited to prepare the new dirhodium corner species [$Rh_2(form)_2(O_2CC_6H_4CN)_2$] (**2**) ($O_2CC_6H_4CN$ = 4-cyanobenzoate) and [$Rh_2(form)_2(O_2CC_5H_4N)_2$] (**3**) ($O_2CC_5H_4N$ = isonicotinate) [15]. By treatment of **1** with an excess of sodium 4-cyanobenzoate or isonicotinate, as described in Section 2, complexes **2** and **3** are obtained in high yield. Alternatively, they may be also conveniently prepared by using the partially solvatated [$Rh_2(form)_2(CH_3CN)_6$](BF4)$_2$ as dirhodium starting complex [16], which is more easily accessible than **1**. Complexes **2** and **3** are both stable green solids, which gave satisfactory elemental analyses. Their characterization was accomplished by IR and proton NMR spectroscopic studies while the pyrydine adduct of **2**, [$Rh_2(form)_2(O_2C$–

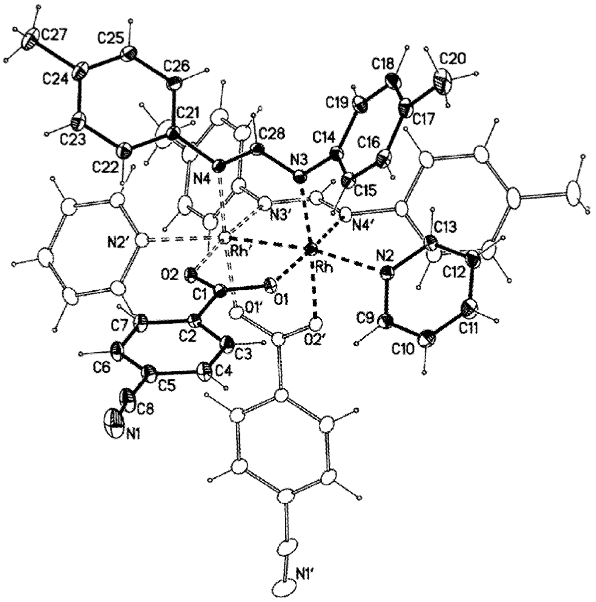

Fig. 1. View of the complex [$Rh_2(form)_2(O_2CC_6H_4CN)_2(Py)_2$] (**2a**) showing the atom numbering scheme of the asymmetric unit denoted by the shaded atoms and solid bonds. The co-crystallized C_6H_6 moiety is omitted for clarity. Thermal ellipsoids are drawn at 10% of probability, while H size is arbitrary.

$C_6H_4CN)_2(Py)_2]$ (**2a**), was analyzed by an X-ray diffraction (Fig. 1). The solid IR spectra of **2** and **3** appear very similar, and experience $v_{asym}(CO_2)$ [1624 and 1622 cm^{-1}, for **2** and **3**, respectively] and v(N–C–N) [1593 and 1596 for **2** and **3**, respectively] absorbtions very close to those of the parent complex **1** [7], indicating that the two formamidinate and carboxylate groups are *cis*-symmetrically bridged across the Rh_2^{4+} core.

In contrast, **2** and **3** differ significantly in solubility. In fact, while **2** is insoluble in the most common solvent, **3** dissolves well in chloroform. Nevertheless the ^1H NMR solution characterization of **3** was prevented as its spectra, ran in a large range of temperatures, exhibit broad signals for all protons, suggesting that some dynamic process is operating in solution Further, from chloroform solution of **3**, left at air on standing for approximately 1 week, a brown solid is recovered. This solid, which is insoluble in the most common solvents, analyzes as **3**. By heating (70 °C, 2–3 h) the brown solid turns green, indicating that **3** is restored.

However, complexes **2** and **3** dissolve well in pyridine affording orange solutions, consistent with the formation of the axial 1:2 dirhodium–pyridine adducts, $[Rh_2(form)_2(O_2CC_6H_4CN)_2(Py)_2]$ (**2a**) and $[Rh_2(form)_2(O_2CC_5H_4N)_2(Py)_2]$ (**3a**), respectively (see Section 2). The proton spectra of **2** and **3**, taken in pyridine, show well resolved signals which are well in agreement with the proposed formulation and the X-ray data of **2a** (Fig. 1). As expected, the presence or benzocyanate or isocotinate groups inside the lantern structure, instead of trifluoroacetates, affects slightly the formamidinate proton patterns as compared with those of **1**. In fact, the formamidinate proton resonances result practically unshifted with respect to those of **1** and consist of a singlet at δ 2.11 for the Me–tolyl protons, in a dd at δ 7.10 for **2** (7.05 for **3**) for tolyl and in a quite broad triplet centered at δ 7.72 for the two methyne ones. In the spectrum of **2** two equally intense doublets are observed for the 2,6 and 3,5 cyanobenzoate protons at δ 8.31 ($J = 8.1$ Hz) and 7.61 ($J = 8.1$ Hz), respectively, and analogously, in the spectrum of **3** two equally intense doublets are observed for the 2,6 and 3,5 pyridyne protons at δ 8.58 ($J = 8$ Hz) and 8.01 (d, $J = 8$ Hz), respectively.

3.2. Crystal structure of $[Rh_2(form)_2(O_2CC_6H_4CN)_2(Py)_2]$ (2a)

A view of complex **2a** showing the atom numbering scheme is reported in Fig. 1. Selected bond lengths (Å) and angles (°) are reported in Table 1.

The crystallographic asymmetric unit contains half part of the dirhodium complex which lies on the twofold axis parallel to cell a. At the solid state, the molecule is perfectly symmetric and shows an homopolar Rh–Rh bond. The dirhodium unit Rh_2^{4+} might be interpreted as constituted by 2 equiv. octahedral rhodium(II) atoms. The coordination of the metal center deviates from the regular geometry due to the expected difference between the equatorial Rh–N and Rh–O bond lengths [2.023(5) vs. 2.082(4) Å mean value, respectively] and, mainly, to the steric hindrance between the axial pyridine and the adjacent two *p*-toluidine fragments of the two bridging formamidinates, coordinated in a *cis* arrangement around the dirhodium core). The pyridine rings minimize such an hindrance by intercalation into the toluidine planes, as evidenced by the corresponding dihedral angles of 28.2(2) and 38.7(2)° with C(14)- and C(21)′-ring, respectively. With respect to the dinuclear axes the pyridine axial ligand appears pushed toward the acetate side(s): in fact, both the N_{eq}–Rh–N_{ax} angles increase up to 98.4(2)° while O_{eq}–Rh–N_{ax} and O_{eq}–Rh–O_{eq} angles are shortened to 86.5(2) and 88.1(2)°, respectively, determining a value of 171.1(1)° for the angle Rh′–Rh–N_{ax} (Table 1). The flat formamidinate fragment shows the usual N–CH–N delocalization not extended to the aryl substituents, whose rings are significantly rotated with respect to the bite mean plane [28.4(2) and 21.4(3)°, respectively]. The same situation was found in the parent complex $[Rh_2(form)_2(CF_3COO)_2(H_2O)_2]$ (**1**) [7], where the axial ligands are water molecules but the –COO– bite of the acetate and benzoate bridges might be considered equivalent (all the O···O distances are is 2.25(1) Å). The title compound shows an alongation of Rh–Rh and Rh–N_{form} bonds [2.469(1) and 2.023(5) vs. 2.426(1) and 1.993(4) Å, respectively] which might be related to the significant steric and electronic differences of the corresponding axial ligands.

Table 1
Selected bond lengths (Å) and angles (°) for $[Rh_2(form)_2(O_2CC_6H_4CN)_2(Py)_2]$ (**2a**)

Bond lengths			
Rh–Rh′	2.469(1)	Rh–N(2)	2.296(5)
Rh–N(4)′	2.016(5)	Rh–N(3)	2.031(5)
Rh–O(1)	2.072(4)	Rh–O(2)′	2.093(4)
N(3)–C(28)	1.311(7)	N(4)–C(28)	1.310(7)
N(3)–C(14)	1.442(7)	N(4)–C(21)	1.418(7)
C(17)–C(20)	1.55(1)	C(24)–C(27)	1.51(1)
O(1)–C(1)	1.275(6)	O(2)–C(1)	1.248(6)
C(1)–C(2)	1.519(8)	C(5)–C(8)	1.42(1)
C(8)–N(1)	1.13(1)		
Bond angles			
N(4)′–Rh–N(3)	90.8(2)	N(3)–Rh–O(1)	90.3(2)
O(1)–Rh–O(2)′	88.1(2)	N(4)′–Rh–O(2)′	90.4(2)
N(3)–Rh–N(2)	98.2(2)	N(4)′–Rh–N(2)	98.6(2)
O(1)–Rh–N(2)	86.2(1)	O(2)′–Rh–N(2)	86.9(2)
N(2)–Rh–Rh′	171.1(1)	N(3)–C(28)–N(4)	123.8(5)
O(2)–C(1)–O(1)	126.7(5)	O(2)–C(1)–C(2)	118.0(5)
O(1)–C(1)–C(2)	115.3(5)	N(1)–C(8)–C(5)	174.0(1)

The atomic equivalent positions are obtained by the symmetry operation x, $-y$, $-z+1$.

By considering the arylacetate bridging ligand, the delocalized $-COO^-$ fragment is not conjugated to the phenyl ring as evidenced by the interconnecting C–C single bond and the dihedral angle of 8.1(3)°.

3.3. Reaction of 3 with palladium and platinum transition metal complexes having *cis*- or *trans*-labile ligands

The spectroscopic as well as the X-ray crystallographic characterization of **2a** and **3a** unambiguously show that, as in their precursor **1**, the carboxylate ligands are *cis*-symmetrically bridged across the dirhodium(II,II). As a consequence the cyanobenzoate and the isocotinate groups appear orthogonally disposed with the two dangling N-binding sites suitable for further coordination. Although the geometrical features make both **2** and **3** ideal angular building blocks capable to produce square boxes by self-assembly with *cis*- or *trans*- square-planar complexes [1], our preliminary attempts to prepare square macrocycles based on **2** and **3** failed.

Complex **2**, as previously pointed out, is only soluble in pyridine and in chloroform or benzene–pyridine mixtures. Pyridine competes with the dirhodium complex N-binding sites in the reaction with palladium and platinum complexes preventing the study of such reactions.

We, therefore, turned our attention to the possibility to realize square boxes by using **3** as angular precursor component. Following a largely employed procedure [1], we studied the 1:1 reaction of **3** with a series palladium and platinum complexes, bearing two *cis*- or *trans*-labile ligands, of the type $[M(L-L)]X_2$ [L–L = 1,2-bisbis(diphenylphosphino)ethane, ethylenediamine] or $[M(P\{C_6H_5\}_3)_2]X_2$ ($X = CF_3SO_3$, BF_4, PF_6 etc.) and $[Pd(C_6H_5CN)_2Cl_2]$. By the addition of an equivalent of such palladium or platinum complexes to a solution of **3**, solids with a 1:1 dirhodium–palladium or platinum stoichiometry were isolated, but, they did not afford significant NMR and the ESI mass spectra. The NMR spectra, as already observed for their precursor **3**, consist of broad signals at any temperature, while the ESI mass spectra, were more in agreement with the presence in solution of a mixture of oligomers. No evidence of insoluble solid, indicating the formation of polymeric species, were observed.

Such results combined with the fact the characterization of **2** and **3** was reached in pyridine solvent, where they transform in the corresponding axial bis-adducts **2a** and **3a**, may be reasonably explained taking in account the axial reactivity of dirhodium(II,II) species.

The solution behavior of **2** and **3**, which significantly differ from that of their corresponding pyridine adducts as well as the formation of the insoluble brown solid formed from chloroform solution of **3** (see above), led us to suggest that, when the axial binding sites on **2** or **3** are free, some polymerization process occurs leading to insoluble polymeric solids. It is well known the dirhodium(II,II) axial reactivity towards N–Lewis bases, so that such a process may be promoted by N-coordination of CN or Py groups to the free axial sites on dirhodium. In pyridine such a polymerization process is prevented as, consistently to X-ray findings, pyridine results axially coordinated.

Recently, an analogous dirhenium complex bearing two isocotinate groups *cis*-symmetrically bridged to the dirhenium core, $[Re_2Cl_2(dppm)_2(O_2C-C_5H_4N)_2]$ (dppm = bis(diphenylphosphino)methane) [17], was reported. Differently from **3**, this complex, which bears two chlorine axially coordinated, did not display a similar solution behavior. Further, such a dirhenium complex resulted a successful angular precursor affording a dirhenium-platinum square box by self assembly with the square-planar transition complex *cis*-$Pt(dbbpy)(O_3SCF_3)_2$ [dbbpy = 4,4′-di-ter-butyl-2,2′-bipyridine]. This allows to retain that in **3** the absence of axially ligated molecules not only affects its solution behavior but even its reactivity.

Further attempts are in progress in our laboratory to prepare square macrocycles incorporating **2** and **3** as angular units. The recent large number of reports in the context of square boxes based on dimetal units prompts us the communication of these preliminary results.

4. Supplementary material

Details of the crystal structure of $[Rh_2(form)_2(O_2C-C_6H_4-CN)_2(Py)_2]$ (**2a**) have been deposited with the Cambridge Crystallographic Data Centre under CCDC no. 181807. Copies of this data can be obtained, free of charge, on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http//www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by MURST and Italian CNR.

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