New rhodium(I) supramolecular structures containing pyridyl and bipyridyl ligands

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ABSTRACT

The use of dimeric $[RhCl(CO)_2]_2$ as acceptor unit in the construction of mono-, bi- and three-dimensional metallosupramolecular structures is reported.

The reaction of the dimer with the alkynylgold complex $[Au(C\equiv CC_5H_4N)(CNC_6H_4O(O)CC_6H_4OC_{10}H_{21})]$ resulted in the mononuclear rhodium complex **1**, through an unexpected transfer of the isonitrile ligand from the gold to the rhodium centres.

The reaction of the linear unit $[RhCl(CO)_2]_2(\mu\text{-}4,4'\text{-bipy})$ (**3**) with the diphosphine 1,4-bis(diphenylphosphino)butane (dppb) yielded the simultaneous formation of both metallomacrocycles $[RhCl(CO)(dppb)]_2$ (**4**) and $\{[RhCl(CO)]_2(\mu\text{-}4,4'\text{-bipy})\}_2(\mu\text{-dppb})_2$ (**5**). The use of a diphosphine with smaller bite angle, 1,1'-bis-(diphenylphosphino)methane, (dppm) formed the three-dimensional $\{[RhCl(CO)]_2(\mu\text{-}4,4'\text{-bipy})\}_2(\mu\text{-dppm})_4$ complex (**6**) that incorporates four diphosphine units connecting two $[RhCl(CO)_2]_2(\mu\text{-bipy})$ linear edges. PM3 semi-empirical method has been used to calculate the optimised geometry of compound **6**.

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1. Introduction

The self-assembly of finite structures via the application of the directional bonding approach has become a very topical field of research. The use of transition metal centres and coordination bonds has been proved to be an efficient method to obtain a great variety of discrete molecular architectures with different shapes and sizes that depends on the wide range of the species involved in the assembly process [1–12].

Square-planar Pd(II) and Pt(II) complexes have been commonly used to prepare metallosupramolecules which contain square or near orthogonal angles in their geometry [13–22]. However, other metals have also been used in these reactions. In particular, Rh(I) and Ir(I) units have been explored in the synthesis of bi- [23–27] and three-dimensional compounds [28,29] and they are of great interest due to their potential catalytic activity and luminescent behaviour, that could be very useful in host–guest studies [30–35].

Although diverse donor bridging linkers have been employed in the construction of supramolecular architectures, the use of bipyridyl-based ligands as organic edges has been proved to be very convenient due to the ability of N-donating ligands to coordinate to metal centres. It is interesting to remark that phosphorus donor linkers, in contrast with nitrogen donor groups, are not very common and only a limited number of metallomacrocycles and polymers have been reported [22].

We report herein the synthesis of new mono-, bi- and three-dimensional rhodium complexes via self-assembly reactions involving the $[RhCl(CO)_2]_2$ dimer. The use of this metallic carbonyl dimer as acceptor unit in self-assembly reactions is here reported for the first time.

2. Experimental

2.1. General

All manipulations were performed under prepurified N_2 using standard Schlenk techniques. All solvents were distilled from appropriate drying agents. Compounds $[RhCl(CO)_2]_2$ [35], 1,1'-bis-diphenylphosphinomethane (dppm) [36], 1,4-bis(diphenylphosphino)butane (dppb) [36], $CNC_6H_4O(O)CC_6H_4OC_{10}H_{21}\text{-}p$ [37], [AuCl(tht)] [38], 4-ethynylpyridine [39], $[Au(C\equiv Cpy)(CNC_6H_4O(O)CC_6H_4OC_{10}H_{21})]$ [40] and $[PPh_4][Au(acac)_2]$ [41] were synthesised as described previously. Compound 4,4'-bipyridine (Avocado, 98%) was used as received.

2.2. Measurements

Infrared spectra were recorded on an FT-IR 520 Nicolet spectrophotometer. $^{31}P\{^1H\}$ NMR ($\delta(85\%\ H_3PO_4) = 0.0$ ppm), and ^1H NMR ($\delta(TMS) = 0.0$ ppm) spectra were obtained on a Bruker DXR 250, Varian Inova 300 and Varian Mercury 400 spectrometers. Elemental analyses of C, H and N were carried out at the Serveis Científic-Tècnics of the Universitat de Barcelona. ESI-MS and FAB

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mass spectra were recorded on a LC/MSD-TOF spectrometer and on a Fisons VG Quattro spectrometer at the Universitat de Barcelona. Microscopy studies were carried out using a Leica DMRB microscope provided with a Mettler FP82HT hot stage and a Mettler FP90 central processor, at a heating rate of 10 °C min^{-1}.

2.2.1. Molecular modelling and semi-empirical calculations

Electronic structure was calculated with PM3 semi-empirical methods in structures previously optimised with MM+ molecular mechanics method, both methods included in the software package Spartan'04 V1.0.0.

3. Synthesis and characterisation

3.1. Synthesis of [RhCl(CO)$_2$(CNC$_6$H$_4$O(O)CC$_6$H$_4$OC$_{10}$H$_{21}$)] (1)

3.1.1. Method A

A dichloromethane solution (8 ml) of [Au(C≡CC$_5$H$_4$N)(CNC$_6$H$_4$-O(O)CC$_6$H$_4$OC$_{10}$H$_{21}$)] (40 mg, 0.06 mmol) was added to a solution (8 ml) of [RhCl(CO)$_2$]$_2$ (12 mg, 0.03 mmol) in the same solvent. After 1 h of stirring the dark orange suspension was concentrated to dryness and the violet solid residue was dissolved in the minimum quantity of acetone and kept at −10 °C for 2 h. A dark purple solid was obtained in 45% yield.

3.1.2. Method B

A dichloromethane solution (8 ml) of CNC$_6$H$_4$O(O)CC$_6$H$_4$OC$_{10}$-H$_{21}$-p (78 mg, 0.21 mmol) was added to a solution (10 ml) of [RhCl(CO)$_2$]$_2$ (40 mg, 0.10 mmol) in the same solvent. After 30 min of stirring the yellow solution became dark orange. The solution was concentrated to dryness and the solid residue was dissolved in the minimum quantity of acetone and kept at −10 °C for 2 h. A dark purple solid was obtained in 40% yield.

^{1}H NMR (298 K, CDCl$_3$): 8.11 (d, J(H–H) = 9.0 Hz, 2H, (O)C–C$_6$H$_4$–O), 7.57 (d, J(H–H) = 8.9 Hz, 2H, CN–C$_6$H$_4$–O), 7.33 (d, 2H, CN–C$_6$H$_4$–O), 6.97 (d, 2H, (O)C–C$_6$H$_4$–O), 4.04 (t, 2H, J(H–H) = 6.4 Hz, 2H, CH$_2$–O–C$_6$H$_4$), 1.86–0.87 (m, 19H, C$_9$H$_{19}$). FAB(+) m/z: 576.0 (M+H$^+$, Calc.: 575.9), 477.0 (M–C$_7$H$_{15}$, Calc.: 476.9). IR (KBr, cm^{-1}): 2959 s, 2922 s, 2852 s v(C–H); 2168 s, v(C≡N); 2012 m, 1999 s, 1967 s, v(Rh–C≡O), 1735 s v(O–C≡O). Anal. Calc. C, 54.23; H, 5.43; N, 2.43. Found: C, 54.28; H, 5.48; N, 2.48.

3.2. Synthesis of [RhCl(CO)$_2$(NC$_5$H$_4$C≡CH)] (2)

A dichloromethane solution (5 ml) of 4-ethynylpyridine (53 mg, 0.52 mmol) was added to a solution (5 ml) of [RhCl(CO)$_2$]$_2$ (100 mg, 0.26 mmol) in the same solvent. After 1 h of stirring at room temperature the resulting orange solution was concentrated to ca. 2 ml and hexane (8 ml) was added. An orange solid was obtained, filtered, washed with hexane, and vacuum dried. Yield: 90%.

^{1}H NMR (298 K, CDCl$_3$): 8.65 (d, J(H–H) = 6.5 Hz, 2H, H$_{\alpha\text{-pyr}}$), 7.43 (d, 2H, H$_{\beta\text{-pyr}}$), 3.45 (s, 1H, C≡CH). FAB(+) m/z: 301.0 (M+H$^+$, Calc.: 300.5), 243.6 (M–2 CO, Calc.: 243.5). IR (KBr, cm^{-1}): 3217 m, v(C–H); 2112 m, v(C≡C); 2088 vs, 2074 s, 2017 vs, 1995 s, v(C≡O). Anal. Calc. C, 36.44; H, 1.68; N, 4.72. Found: C, 36.49; H, 1.69; N, 4.70.

3.3. Synthesis of [RhCl(CO)$_2$]$_2$(μ-4,4′-bipy) (3)

Solid 4,4′-bipyridine (40 mg, 0.26 mmol) was added to a dichloromethane solution (10 ml) of [RhCl(CO)$_2$]$_2$ (100 mg, 0.26 mmol). After 1 h of stirring at room temperature a red solid was obtained that was filtered, washed with hexane and vacuum dried. Yield: 85%.

^{1}H NMR (298 K, CDCl$_3$): 8.94 (d, J(H–H) = 6.8 Hz, 4H, H$_{\alpha\text{-pyr}}$), 7.71 (d, 4H, H$_{\beta\text{-pyr}}$). FAB(+) m/z: 547.3 (M+H$^+$, Calc.: 547.1), 369.0 (M–Rh(CO)$_2$Cl + H$_2$O, Calc.: 369.0), 157.1 (4,4′-bipy + H$^+$, Calc.: 157.1). IR (KBr, cm^{-1}): 2098 vs, 2013 vs, v(C≡O); 1612 s, v(C≡N). Anal. Calc.: C, 30.84; H, 1.47; N, 5.14. Found: C, 30.86; H, 1.50; N, 5.17.

3.4. Synthesis of [RhCl(CO)]$_2$(μ-4,4′-bipy)(μ-dppb)$_2$ (5)

A dichloromethane solution (15 ml) of dppb (31 mg, 0.08 mmol) was added to a solution (20 ml) of [RhCl(CO)$_2$]$_2$(μ-bipy) (40 mg, 0.08 mmol) in the same solvent. After 1 h of stirring the orange solution turned orange. The solution was concentrated to ca. 4 ml and hexane (10 ml) was added. The obtained red solid was filtered, washed with hexane and vacuum dried. Yield: 10%.

^{31}P NMR (298 K, CDCl$_3$): 38.6 ppm (^{1}J(Rh–P) = 158 Hz). ^{1}H NMR (298 K, CDCl$_3$): 9.14 (s, br, 8H, H$_{\alpha\text{-pyr}}$), 7.74–7.28 (m, 48H, Ph+H$_{\alpha\text{-pyr}}$), 2.57–2.42 (m, br, 8H, P-CH$_2$–CH$_2$–), 1.77–1.63 (m, br, 8H, P-CH$_2$–CH$_2$). ESI-MS(+) m/z: 1803.2 (M–CO + H$^+$, Calc.: 1803.0), 1747.2 (M–3CO + H$^+$, Calc.: 1746.9) and 1719.1 (M–4CO + H$^+$, Calc.: 1719.0). Anal. Calc.: C, 52.37; H, 4.18; N, 3.05. Found: C, 52.39; H, 4.19; N, 3.08.

3.5. Synthesis of ([RhCl(CO)]$_2$(μ-4,4′-bipy))$_2$(μ-dppm)$_4$ (6)

A dichloromethane solution (15 ml) of dppm (28 mg, 0.08 mmol) was added to a solution (20 ml) of [RhCl(CO)$_2$]$_2$(μ-bipy) (40 mg, 0.08 mmol) in the same solvent. After 1 h of stirring the orange solution turned bright yellow. The solution was concentrated to ca. 4 ml and hexane (10 ml) was added. The obtained pale orange solid was filtered, washed with hexane and vacuum dried. Yield: 80%.

^{31}P NMR (298K, CDCl$_3$): 19.5 ppm (^{1}J(Rh–P) = 121 Hz). ^{1}H NMR (298 K, CDCl$_3$): 8.83 (d, J(H–H) = 8.4 Hz, 8H, H$_{\alpha\text{-pyr}}$), 7.63–7.38 (m, 88H, Ph+H$_{\beta\text{-pyr}}$), 3.95–3.91 (m, br, 8H, P-CH$_2$-P). ESI-MS(+) m/z: 2131.1 (M–dppm + H$^+$, Calc.: 2131.1), 1047.0 ([RhCl(CO)(4,4′-bipy)]$_2$(μ-dppm) + H$_2$O, Calc.: 1047.1), 803.5 (M–3Cl$^-$, Calc.: 803.5). IR (KBr, cm^{-1}): 2093 s, 2062 s, 1982 vs, v(C≡O); 1635 s, 1616 s, v(C≡N). Anal. Calc.: C, 59.20; H, 4.14; N, 2.23. Found: C, 59.25; H, 4.17; N, 2.26.

4. Results and discussion

4.1. Use of [RhCl(CO)$_2$]$_2$ as building block in self-assembly reactions

In order to obtain a Rh/Au heterometallic compound (Fig. 1), [RhCl(CO)$_2$]$_2$ was reacted with the [Au(C≡CC$_5$H$_4$N)(CNC$_6$H$_4$O(O)C-C$_6$H$_4$OC$_{10}$H$_{21}$)] gold complex, in a 1:2 molar ratio in CH$_2$Cl$_2$ solution.

The resulting violet compound was spectroscopically characterised. The IR spectrum shows the presence of a strong C≡N band and the bands corresponding to the carbonyl ligands coordinated to the rhodium metal atom and those of the carboxylic group of the isonitrile ligand. The expected v(C≡C) and v(C≡N) vibration bands were not observed by this technique.

The recorded ^{1}H NMR spectrum of the compound shows four distorted doublets attributed to the aromatic hydrogens of the isonitrile rings in the range 8.11–6.97 ppm. The first methylene
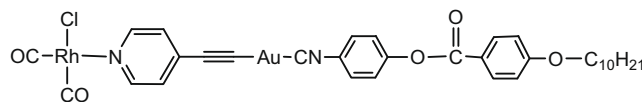

Fig. 1. Drawing of the attempted Rh/Au heterometallic compound.

proton of the alkoxy chain of the isonitrile group appears as a triplet at 4.04 ppm and the remaining alkoxy chain hydrogens appear in the range 1.86–0.87 ppm. The peaks corresponding to the pyridine protons were not displayed by this technique.

These results are indicative of the lack of the alkynylpyridine group in the obtained compound and agree with the formation of a rhodium complex containing only the corresponding isonitrile ligand directly coordinated to the rhodium metal atom (compound **1**). The IR spectrum of the residue of the reaction shows a C≡C stretch band at 2126 cm^{-1} that evidences the presence of the [Au(C≡CC$_5$H$_4$N)]$_n$ gold polymer as secondary product (see Scheme 1, method A).

The FAB(+)-MS spectrum detected peaks at m/z 576.0 (M+H$^+$) and 477.0 (M–C$_7$H$_{15}$) that are also indicative of the formation of **1**.

In order to check this hypothesis, the isonitrile CNC$_6$H$_4$O(O)C-C$_6$H$_4$OC$_{10}$H$_{21}$-p was allowed to react with the [RhCl(CO)$_2$]$_2$ dimer in CH$_2$Cl$_2$ solution at room temperature and the formation of compound **1** was observed (Scheme 1, method B).

The results show that the obtention of **1** following method A takes place by means of an unexpected isonitrile transfer reaction where the organic ligand is transferred from the gold compound to the rhodium(I) derivative. This reaction seems to be favoured by the formation of the [Au(C≡CC$_5$H$_4$N)]$_n$ polymer as secondary product.

Similar processes involving alkynyl ligands and gold(I) metal atoms are known but still scarce [42–45]. In particular, the trans-metallation reaction where an ethynylpyridine group is transferred from a gold(I) metal centre to a rhenium (I) complex, has been previously reported by us and being favoured by the formation of the same [Au(C≡CC$_5$H$_4$N)]$_n$ polymer [45]. As observed for the rhenium

complex, the process is clean, since no traces of metallic gold were deposited in this reaction.

It is interesting to notice that to our knowledge, there is no precedent in the literature for the reaction where an isonitrile ligand is transferred from a gold(I) to a rhodium(I) metal atom.

The mesogenic behaviour of the free isonitrile ligand has been previously studied and has been seen to display smectic A and nematic mesophases [37]. The isonitrile gold(I) derivative also presents liquid crystalline properties (SmA mesophase) [40]. For this reason the potential properties of compound **1** as a liquid crystal were carefully investigated. Unfortunately, the rhodium isonitrile complex decomposes upon heating at 355 °C without melting and consequently compound **1** does not exhibit mesogenic behaviour.

This high decomposition temperature suggests very strong intermolecular interactions in the solid state, which is not compatible with formation of liquid crystalline assemblies. A similar behaviour is found in some cis-[RhCl(CO)$_2$(L)] (L = 4′-alkoxy-4-stilbazole)] [46]. In contrast, the structurally related cyanobiphenyl complex cis-[RhCl(CO)$_2$(NC-C$_6$H$_4$C$_6$H$_4$OC$_9$H$_{19}$)] that exhibits relatively low melting temperatures and consequently lower intermolecular interactions than **1**, displays a nematic mesophase at 79 °C [47].

A second attempt of using the [RhCl(CO)$_2$]$_2$ unit in self-assembly processes was explored by means of its reaction with 4-ethynylpyridine in a 1:2 ratio, in order to obtain **2** (Scheme 2) which was thought to be an excellent precursor for the synthesis of heterometallic supramolecular complexes.

A red solid was obtained after addition of hexane to the previously concentrated dichloromethane solution. Evidence for the
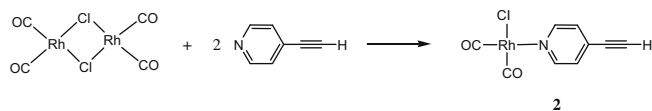
Method A


1

Method B

1
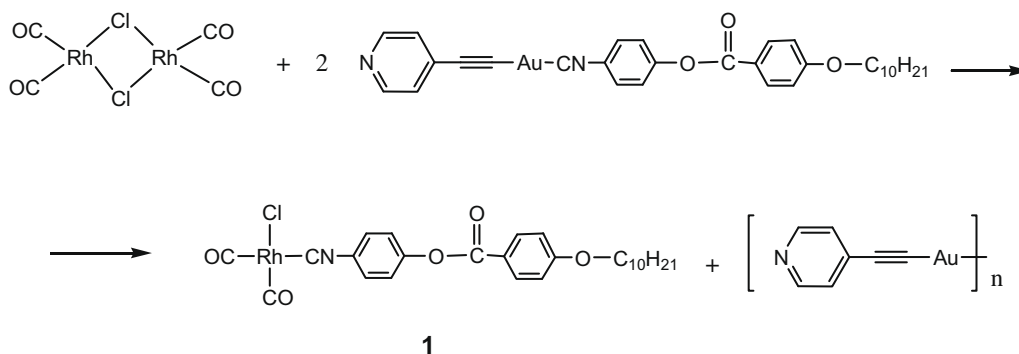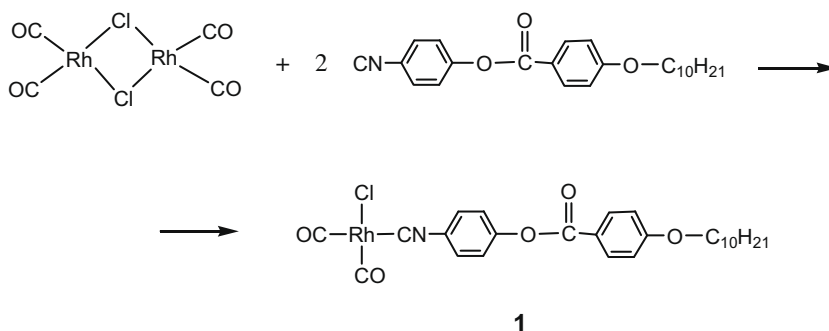
Scheme 1.

Scheme 2.

proposed structure was obtained from IR, and ^{1}H NMR spectroscopies, FAB-MS spectrometry and elemental analysis. The IR spectrum of **2** shows a band at 3217 cm^{-1} that corresponds to the presence of a terminal acetylenic proton. There is also observed a C≡C vibration band at 2112 cm^{-1} that is shifted about 15 cm^{-1} to higher frequencies with respect to the corresponding free 4-ethynylpyridine ligand and the v(C≡O) stretching vibrations from the carbonyl ligands bonded to rhodium are observed between 2088 and 1995 cm^{-1}. The presence of two only v(C≡O) stretching bands in dichloromethane solution (at 2088 and 2014 cm^{-1}), lead us to attribute a *cis*-geometry for **2**, according to literature [46].

The ^{1}H NMR spectrum confirms the coordination of the ligand since the H$_\alpha$ of the pyridine ring shifted 0.4 ppm downfield relative to the same signals of the free organic ligand. Furthermore, the terminal acetylene protons shifted *ca.* 0.5 ppm upfield with respect to the non-coordinated ligand. The incorporation of only one 4-ethynylpyridine group was confirmed by elemental analysis and FAB-MS mass spectrometry that displays the protonated molecular peak at *m/z* 301.0 and the signal corresponding to the loss of the two carbonyl ligands at *m/z* 243.6.

This compound is particularly interesting due to the presence of a potentially removable acetylene proton located at terminal position that makes compound **2** a good candidate to behave as a building block for the construction of more complex metallosupramolecular structures. Specifically, **2** was assumed to be able to react with the gold complex (PPh$_4$)[Au(acac)$_2$], according to the "acac method" [48], yielding heterobimetallic structures where the gold centre should coordinate to two equivalents of **2** by means of the formation of Au–C≡C bonds. Unfortunately, the latter reaction gave intractable solids that we were not able to characterise.
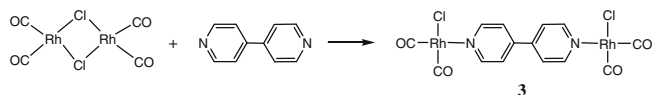
The great stability of the [Au(C≡CC$_5$H$_4$N)]$_n$ polymer could be considered as a possible driving force for the formation of this insoluble compound in front of the pre-designed heterobimetallic supramolecular squares.

Our third attempt to use [RhCl(CO)$_2$]$_2$ as precursor for metallosupramolecular species involved its reaction with the 4,4′-bipyridine ligand (Scheme 3) to give **3**, which was thought to be an interesting metallosupramolecular edge in self-assembly processes.

The ^{1}H NMR spectrum of the obtained dark red solid shows the H$_\alpha$ and H$_\beta$ signals due to the coordinated 4,4′-bipyridine ligand that have shifted 0.2 ppm downfield with respect to the free organic ligand. IR spectroscopy and FAB-MS(+) spectrometry also confirm the formation of the product.

Compound **3** was reacted with the diphosphine dppb in an attempt to obtain a bidimensional supramolecular rectangle constituted by two units of **3** as edges linked by two dppb groups (compound **5**, scheme 4). Both reactants were mixed in dichloromethane at room temperature. After 1h of stirring the red reaction solution turned orange. After concentration under vacuum, hexane was added to precipitate a solid whose characterisation shows the presence of a mixture of two different macrocyclic compounds [RhCl(CO)(dppb)]$_2$ (**4**) and {[RhCl(CO)]$_2$(μ-4,4′-bipy)}$_2$(μ-dppb)$_2$ (**5**) in a 2:1 molar ratio (scheme 4). ^{31}P NMR spectrum in deuterated chloroform displays two doublets centred at 38.5 and 22.5 ppm with Rh–P coupling constants of 158 and 123 Hz attributed to **4** and **5**, respectively. ^{1}H NMR is in agreement with the formation of a mixture of different compounds since two different sets of signals are obtained for both bipyridine protons and methylene groups of the diphosphine. One of the bipyridine sets are attributed to the free 4,4′-bipyridine ligand, what is indicative that this compound precipitates together with both macrocycles. The H$_\alpha$ protons of the bipyridine unit of **5** are displayed at 9.14, 0.2 ppm downfield shifted with respect to the precursor **3**, whilst the H$_\beta$ protons are observed in the same region of the phenyl protons (7.74–7.28 ppm).

ESI-MS(+) mass spectrometry was very helpful in the identification of the resulting compounds of the reaction. Peaks at *m/z* 1149.1 and 557.4 corresponding to ([RhCl(CO)(dppb)]$_2$–Cl) and ([RhCl(CO)(dppb)]$_2$–2 Cl) evidence the formation of a small macrocycle constituted by two RhCl(CO) units connected by two dppb ligands as major product (Scheme 4, compound **4**). Moreover, peaks at *m/z* 1803.2, 1747.2 and 1719.1 are attributable to {[RhCl(CO)]$_2$(μ-4,4′-bipy)}$_2$(μ-dppb)$_2$ (**5**) with the loss of one, three and four carbonyl ligands. Compound **4** was previously reported in the literature [49] and recently investigated by Lamb et al. [30,50].
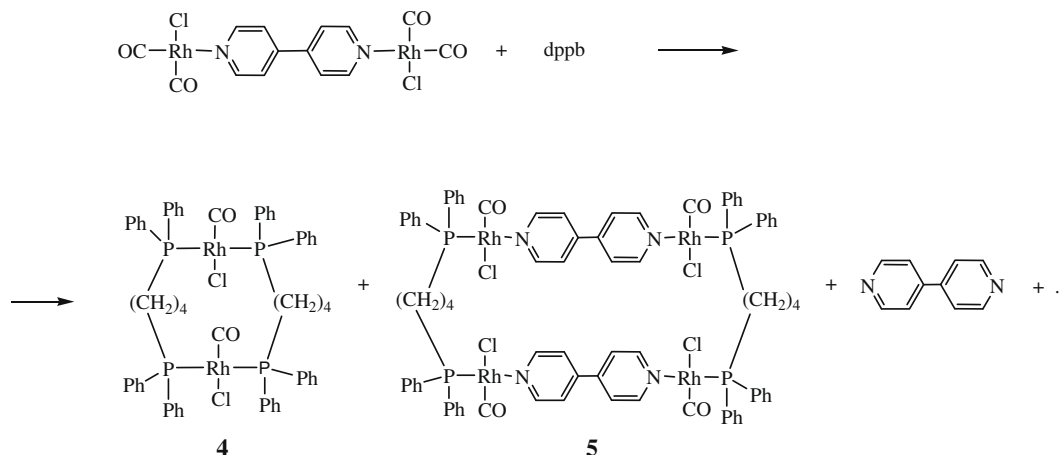
Scheme 3.
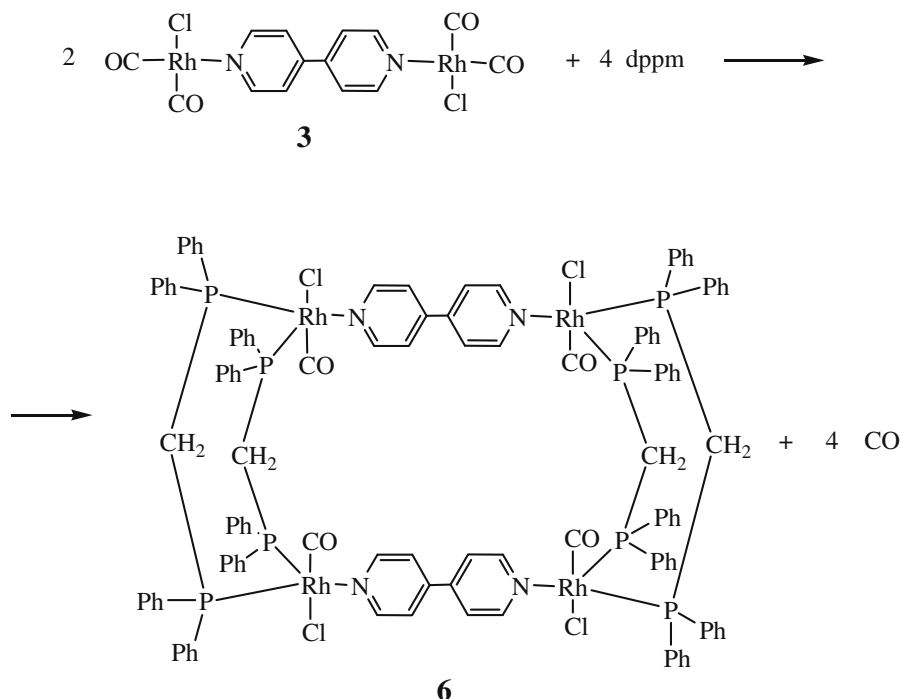
Scheme 4.

Scheme 5.

The authors demonstrated that this compound presents a high thermodynamic stability that could be the reason for the favoured formation of this macrocycle compared with that of **5**. The great stability of this compound made difficult the formation of the desired compound **5** in pure form in the reaction medium and it was only obtained after several recrystallisation processes.

In order to test the effect of the bite angle of the diphosphine, the same reaction was investigated by using dppm instead of dppb and a more soluble pale orange solid was obtained. Surprisingly, the characterisation of the solid indicated the formation of the unexpected compound {[RhCl(CO)]$_2$(μ-4,4'-bipy)}$_2$(μ-dppm)$_4$ (compound **6**, scheme 5) with three-dimensional structure which incorporates four dppm units connecting two [RhCl(CO)]$_2$(μ-4,4'-bipy) edges. In spite of numerous attempts, we were not able to grow single crystals of **6**. However, its proposed structure is strongly supported spectroscopically. Thus, ^{1}H NMR spectrum recorded in deuterated chloroform at 298 K shows only one signal for the H$_\alpha$ of the bipyridine at 8.83, 0.1 ppm upfield shifted with respect to the precursor **3** (Fig. 2, top). H$_\beta$ resonance together with the corresponding to the phenyl protons and are displayed in the range 7.63–7.38 ppm. ^{1}H NMR integration confirms the incorporation of four dppm in the structure of the compound since the H$_\alpha$ and the CH$_2$ groups of the diphosphine are observed to be in a 1:1 ratio instead of expected 2:1 for the rectangular bidimensional complex.

The signal corresponding to the methylene protons of the diphosphine is unexpectedly broad (298 K) and could be indicative of a dynamic process that involves the diphosphine ligand.

Interestingly, the ^{1}H NMR spectrum recorded at 220 K shows the splitting of the broad CH$_2$ signal into two broad peaks centred at 4.15 and 3.40 ppm (Fig. 2, below) that coalesce into a single band at *ca.* 3.90 ppm at room temperature. All these facts are indicative of the unequivalence of the methylene protons of the carbon chains. gCOSY-NMR spectroscopy shows cross peaks, that confirm the vicinity of both unequivalent CH$_2$ protons.

^{31}P NMR spectrum shows one broad doublet centred at *ca.* 20 ppm with a Rh–P coupling constant of *ca.* 120 Hz. This coupling
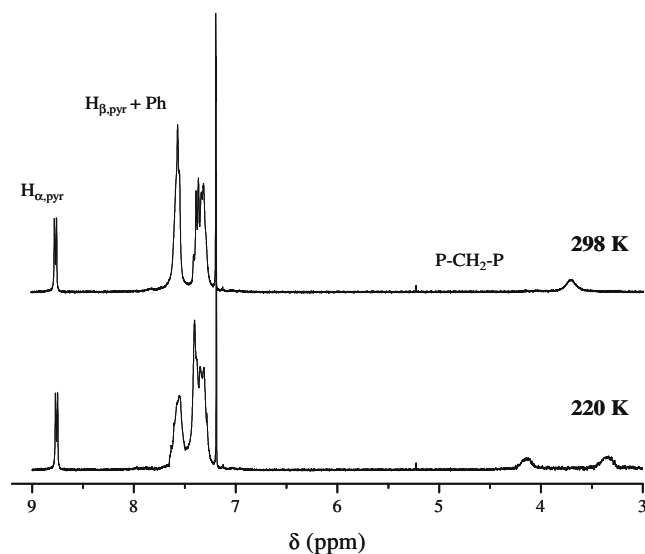

Fig. 2. ^{1}H NMR spectrum of compound **6** in CDCl$_3$ recorded at 298 K (up) and at 220 K (down).

constant is in the same range than the corresponding to two phosphorus atoms bonded to a rhodium centre, as the obtained for **4**. The ^{31}P NMR broad doublet recorded at room temperature becomes sharp and perfectly defined (^1J(Rh–P) = 114 Hz) when the spectrum is registered at 220 K (Fig. 3). From these results we suggest that the observed broad signals are due to a dynamic process that involves the coordination of the diphosphines in **6**.

Characterisation by IR spectroscopy shows the presence of a unique v(C≡O) vibration at 1982 cm^{-1}, shifted 30 and 115 cm^{-1} to lower wavenumbers with respect to the two IR bands recorded for the [RhCl(CO)$_2$]$_2$(μ-4,4'-bipy) precursor. This shift is in agreement with a higher retrodonation effect from the rhodium centre
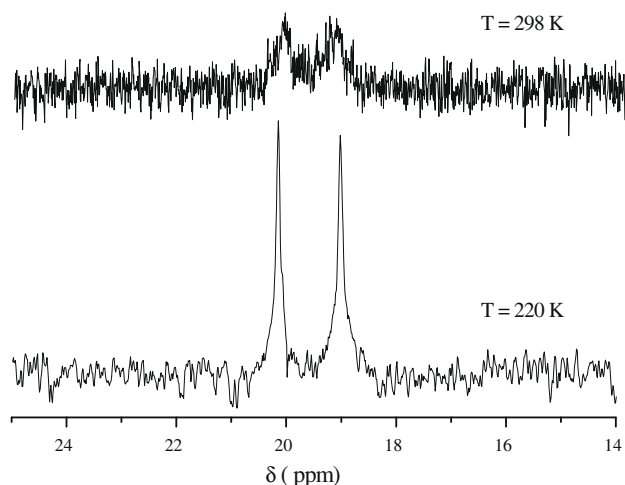
Fig. 3. ^{31}P NMR spectrum of compound **6** in CDCl$_3$ at 298 K (top) and 220 K (down).

Fig. 5. Space filling model of the optimised equilibrium geometry of compound **6**.

to the antibonding molecular orbital of the carbonyl ligand as a consequence of the loss of one of these ligands when the phosphorus coordination occurs.

ESI-MS spectrum was also recorded and peaks at *m/z* 2131.1 and 803.5 corresponding to {([RhCl(CO)]$_2$(μ-bipy)}$_2$(μ-dppm)$_4$–dppm) and {([RhCl(CO)]$_2$(μ-bipy)}$_2$(μ-dppm)$_4$–3Cl), respectively were detected. The assignation of these peaks clearly evidences the formation of **6** (Scheme 5) as the resulting product of the process.

4.2. PM3. and MM+ geometry optimisation

Due to the lack of crystal structure of **6**, PM3 and MM+ calculations were undertaken to optimise the minimum energy geometry of this complex and visualise its expected shape. The calculated molecule is shown in Fig. 4.

It is clearly shown that both dppm ligands coordinate to two rhodium metals forming a three-dimensional structure with one diphosphine above and the other below the plane determined by the four rhodium atoms.

Carbonyl and chloride ligands and some of the phenyl rings are expected to be located outside the cavity. Furthermore, the two pyridine rings of both bipyridines are observed to be twisted approximately 35°.
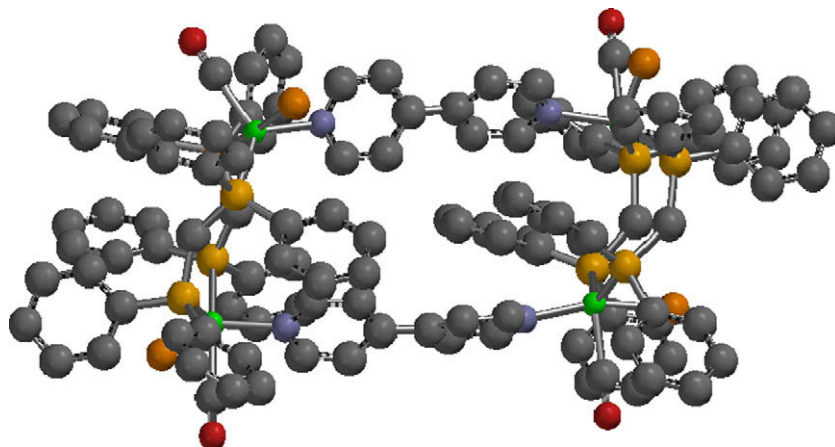
The symmetry plane delimited by the four rhodium centres makes equivalent the protons of the methylene units from different dppm ligands. This graphical model has been very useful to understand the unequivalence of the CH$_2$ protons observed in the ^1H NMR spectrum since it could be observed that one of the protons is located outside the cavity and the other one inside.

As could be observed in the space filling model representation (Fig. 5), compound **6** presents an empty inner cavity that makes the compound potentially active in molecular recognition processes and catalysis. The size of the cavity (5.2 × 13.9 Å) has been calculated by means of distances between the opposite atoms of both edges.

Preliminary luminescence and molecular calculations studies of the compound seem to indicate that compound **6** is a good candidate to be used as a sensor in host/guest processes.

All these results encourage us to extend our investigations to other diphosphines or bipyridine bridging units in order to construct new three-dimensional supramolecular assemblies with different inner cavity sizes. The effect of the different bridging ligands on the nature of the corresponding empty inner cavity should be studied in order to develop new supramolecular systems that could be potentially used in luminescence and molecular recognition applications.

5. Conclusions

The [RhCl(CO)$_2$]$_2$ compound has been used as acceptor in self-assembly reactions with different pyridine derivatives for the construction of mono-, bi- and three-dimensional novel rhodium(I)

Fig. 4. Minimum energy geometry calculated for compound **6** (hydrogens are omitted for clarity). Green: rhodium; orange: phosphorous; grey: carbon; blue: nitrogen and red: oxygen. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
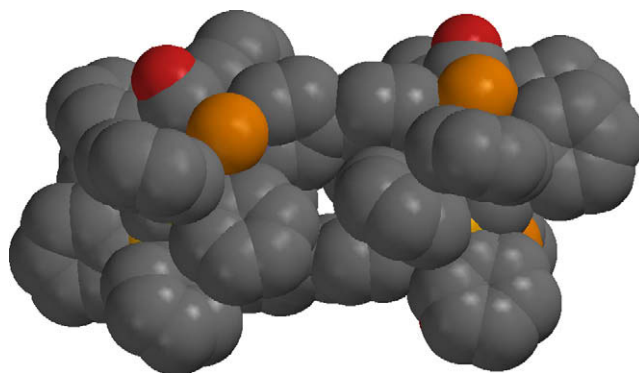
derivatives. Attempts to obtain a Rh/Au heterobimetallic [RhCl(CO)$_2$(NC$_5$H$_4$C$\equiv$C)Au(CNC$_6$H$_4$O(O)CC$_6$H$_4$OC$_{10}$H$_{21}$)] compound, lead to an unexpected isonitrile transfer process of the isonitrile organic ligand from the gold(I) precursor to the rhodium(I) metal complex giving the unexpected homometallic rhodium derivative [RhCl(CO)$_2$(CNC$_6$H$_4$O(O)CC$_6$H$_4$OC$_{10}$H$_{21}$)] (**1**). The study of the mesogenic behaviour of **1** shows that the compound decomposes upon heating at 355 °C.

Whilst the reaction of [RhCl(CO)$_2$]$_2$(μ-bipy) (**3**) and dppm has allowed the obtention of the three-dimensional derivative {[RhCl(CO)]$_2$(μ-bipy)}$_2$(μ-dppm)$_4$ (**6**), the reaction with the larger dppb conduces to a bi-dimensional rectangular structure, fact that clearly indicates the influence of the bite angle of the diphosphine on the structure of the final product of the reaction.

The calculated optimised geometry of **6** has been shown to present an empty inner cavity that makes the compound potentially useful in molecular recognition and catalytic processes.

Acknowledgements

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