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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**.

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], $CNC_6H_4O(O)CC_6H_4OC_{10}H_{21}$-*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 (δ(85% H_3PO_4) = 0.0 ppm), and ^1H NMR (δ(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 Científico-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 $[RhCl(CO)_2(CNC_6H_4O(O)CC_6H_4OC_{10}H_{21})]$ (**1**)*

3.1.1. Method A

A dichloromethane solution (8 ml) of $[Au(C{\equiv}CC_5H_4N)(CNC_6H_4\text{-}O(O)CC_6H_4OC_{10}H_{21})]$ (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 $CNC_6H_4O(O)CC_6H_4OC_{10}H_{21}$-*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.

^1H NMR (298 K, $CDCl_3$): 8.11 (d, *J*(H–H) = 9.0 Hz, 2H, (O)C–C_6H_4–O), 7.57 (d, *J*(H–H) = 8.9 Hz, 2H, CN–C_6H_4–O), 7.33 (d, 2H, CN–C_6H_4–O), 6.97 (d, 2H, (O)C–C_6H_4–O), 4.04 (t, 2H, *J*(H–H) = 6.4 Hz, 2H, CH_2–O–C_6H_4), 1.86–0.87 (m, 19H, C_9H_{19}). FAB(+) *m/z*: 576.0 (M+H$^+$, Calc.: 575.9), 477.0 (M–C_7H_{15}, Calc.: 476.9). IR (KBr, cm^{-1}): 2959 s, 2922 s, 2852 s ν(C–H); 2168 s, ν(C≡N); 2012 m, 1999 s, 1967 s, ν(Rh–C≡O), 1735 s ν(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 $[RhCl(CO)_2(NC_5H_4C{\equiv}CH)]$ (**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%.

^1H 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, ν(C–H); 2112 m, ν(C≡C); 2088 vs, 2074 s, 2017 vs, 1995 s, ν(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 $[RhCl(CO)_2]_2(\mu\text{-}4,4'\text{-bipy})$ (**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%.

^1H 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–$Rh(CO)_2Cl + H_2O$, Calc.: 369.0), 157.1 (4,4′-bipy + H$^+$, Calc.: 157.1). IR (KBr, cm^{-1}): 2098 vs, 2013 vs, ν(C≡O); 1612 s, ν(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 $[RhCl(CO)]_2(\mu\text{-}4,4'\text{-bipy})(\mu\text{-dppb})_2$ (**5**)*

A dichloromethane solution (15 ml) of dppb (31 mg, 0.08 mmol) was added to a solution (20 ml) of $[RhCl(CO)_2](\mu\text{-bipy})$ (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 (^1J(Rh–P) = 158 Hz). ^1H 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 $([RhCl(CO)]_2(\mu\text{-}4,4'\text{-bipy}))_2(\mu\text{-dppm})_4$ (**6**)*

A dichloromethane solution (15 ml) of dppm (28 mg, 0.08 mmol) was added to a solution (20 ml) of $[RhCl(CO)_2](\mu\text{-bipy})$ (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 (^1J(Rh–P) = 121 Hz). ^1H 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 ($[RhCl(CO)(4,4'\text{-bipy})]_2(\mu\text{-dppm}) + H_2O$, Calc.: 1047.1), 803.5 (M–3Cl$^-$, Calc.: 803.5). IR (KBr, cm^{-1}): 2093 s, 2062 s, 1982 vs, ν(C≡O); 1635 s, 1616 s, ν(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 $[Au(C{\equiv}CC_5H_4N)(CNC_6H_4O(O)C\text{-}C_6H_4OC_{10}H_{21})]$ gold complex, in a 1:2 molar ratio in CH_2Cl_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 ν(C≡C) and ν(C≡N) vibration bands were not observed by this technique.

The recorded ^1H 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

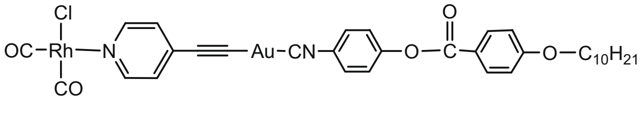

Fig. 1. Drawing of the attempted Rh/Au heterometallic compound.