Rhodium-Catalysed Carbonylation of Methanol Using a New Multifunctional Ligand − Isolation and Structural Characterisation of the Macrocycle $[Rh_2I_6(CO)_2(C_6H_4N_3CH_2CO_2C_4H_2SCO_2CH_2C_6H_4N_3)]_2$

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Dedicated in profound gratitude to Professor Max Herberhold on the occasion of his 65th birthday

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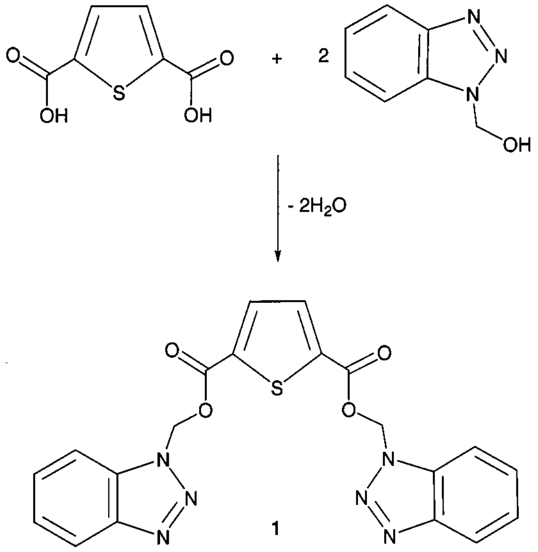
The new multifunctional ligand thiophene-2,5-bis(carboxylatomethylenebenzotriazole) (**1**) reacts with $[RhCl(CO)_2]_2$ to give the rhodium complex $[RhCl(CO)(\mathbf{1})]_2$ (**2**), which was found to catalyse efficiently the iodide-mediated carbonylation of methanol. The macrocyclic carbonyliodorhodium complex $[Rh_2I_6(CO)_2(\mathbf{1})]_2$ (**3**) was isolated from the catalytic mixture and structurally characterised.

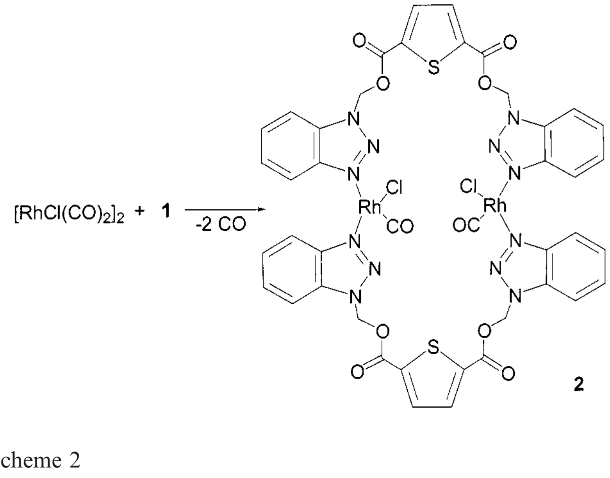
The carbonylation of methanol to give acetic acid is one of the most important homogeneously catalysed industrial processes.[1] The catalytic reaction requires the use of iodide promoters which convert methanol, prior to carbonylation, into the actual substrate methyl iodide.[2] The classical Monsanto process is based on soluble rhodium catalysts.[3] It is well established that the anion $[RhI_2(CO)_2]^-$ is the active species in the catalytic process, the rate-determining step of which is the oxidative addition of CH_3I to give $[RhI_3(CH_3)(CO)_2]^-$.[4] There have been many attempts to modify the complex $[RhI_2(CO)_2]^-$ with suitable ligands which can increase the susceptibility of the Rh^I centre towards oxidative addition of methyl iodide.[5] Our approach consisted in developing multifunctional ligands based on benzotriazole and thiophene units in order to improve the catalytic activity of the rhodium catalyst.

The multifunctional ligand thiophene-2,5-bis(carboxylatomethylenebenzotriazole) (**1**) is easily accessible by classical condensation methods[6] from hydroxymethylbenzotriazole and 2,5-thiophene dicarboxylic acid (Scheme 1). It can be isolated in 62% yield as a white microcrystalline powder.

Compound **1** was found to coordinate easily to rhodium through the 3-N atom of the triazole unit. The reaction of **1** with $[RhCl(CO)_2]_2$ in toluene at room temperature gives the rhodium(I) complex $[RhCl(CO)(\mathbf{1})]_2$ (**2**) quantitatively as an air-stable yellow solid (Scheme 2). This compound is moderately soluble in acetone and toluene, but only sparingly soluble in alcohols and insoluble in alkanes. Microanalytical and NMR spectroscopic data are consistent with the composition proposed, the dimeric nature of the molecule clearly follows from the ESI mass spectrum which shows the molecular peak at m/z = 1220. Complex **2** exhibits two



Scheme 1



Scheme 2

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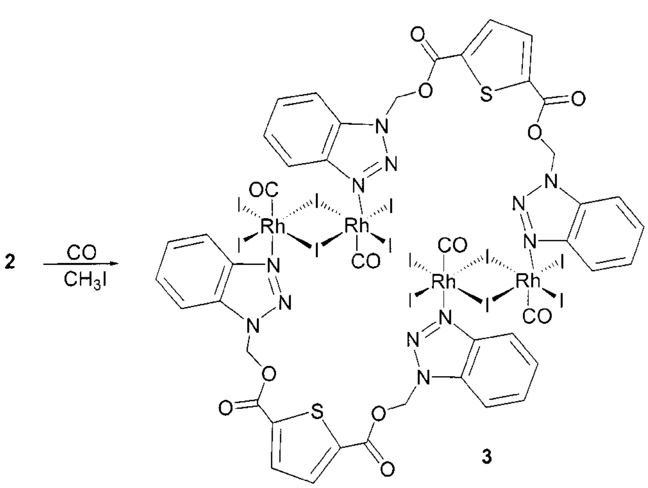
strong ν(CO) absorptions in the IR spectrum, as expected for a *cisoid* arrangement of the two terminal carbonyl ligands.[7] The yellow colour is indicative of square-planar, noninteracting rhodium centres.[8] Macrocycles of similar types, for example $[Rh_2Cl_2(CO)_2\{\mu\text{-}(Ph_2P)_2py\}_2]$[9] and $[Rh_2(CO)_2Cl_2\{Ph_2P(CH_2)P(S)Ph_2\}_2]$,[7] have been reported previously for rhodium but never used as catalysts.

Complex **2** catalyses the iodide-promoted carbonylation of methanol to give acetic acid and methyl acetate with much higher catalytic activities than that of the classical $[RhCl(CO)_2]_2$ catalyst. The catalytic reaction is performed with a methanol/methyl iodide/water (58%, 26%, 16%) mixture at 170 °C under a CO pressure of 25 bar, the catalyst/substrate ratio being 1:2000. After 20 min., the catalytic turnover number (mol CH_3COOH plus mol CH_3COOCH_3 per mol **2**) is found to be 700 (catalytic turnover frequency 35 min^{-1}). $[RhCl(CO)_2]_2$ gives a catalytic turnover number of 400 (catalytic turnover frequency 20 min^{-1}) under the same conditions. A similar increase of the catalytic activity with respect to that of $[RhCl(CO)_2]_2$ has been observed for the triethylphosphane complex $[RhCl(CO)(PEt_3)_2]$.[5f]

From the reaction mixture of the catalytic reaction we isolated the red-brown complex **3** by crystallisation of the organometallic residue from acetone. Compound **3** is directly accessible in high yield from the reaction of **2** with methyl iodide and carbon monoxide (1 bar) in acetone solution. It contains iodo ligands and a *transoid* dicarbonyl arrangement, giving rise to a single ν(CO) absorption in the infrared spectrum. It was suggested for complexes containing phosphane ligands that the dissociation of the phosphane may occurred during the catalytic process. In our case there is clearly a Rh−N bond cleavage. The facile conversion of **2** into **3** under ambient conditions demonstrates that fragmentation, ligand dissociation and rearrangement occur easily.

In the single-crystal X-ray structure analysis[10] **3** turns out to be a macrocycle containing two dinuclear iodo-bridged Rh^{III} units (Scheme 3). The four rhodium atoms have a distorted octahedral coordination geometry: they are coordinated to the 3-N atoms of the benzotriazole units of **1** (Figure 1). The four rhodium−nitrogen bonds are almost equal in length. The two planar $Rh_2(\mu_2\text{-}I)_2$ rings are arranged perpendicular with respect to the cycle formed by the four rhodium atoms and the two ligands, Rh(1)−**1**−Rh(2)−Rh(3)−**1**−Rh(4). The bond lengths and angles for each Rh_2I_6 unit are similar to those reported by Forster[11] for $[Rh_2I_6(MeCO)_2(CO)_2]^{2-}$ and by Dilworth[12] for $[Rh_2I_6(Ph_2PC_6H_4SMe)_2]$.



Scheme 3

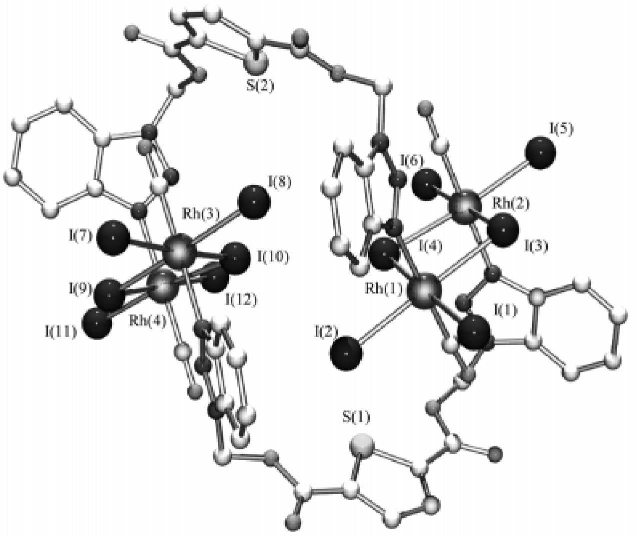


Figure 1. Molecular structure of complex **3** (hydrogen atoms and solvent molecules omitted for clarity); selected bond lengths [Å]: Rh(1)−N(12) 2.128(11), Rh(2)−N(1) 2.139(10), Rh(3)−N(6) 2.091(11), Rh(4)−N(7) 2.102(11), Rh(1)-(C1) 1.864(16), Rh(2)−C(2) 1.851(14), Rh(3)−C(3) 1.867(16), Rh(4)−C(4) 1.840(12), Rh(3)−I(8) 2.6056(14), Rh(3)−I(10) 2.6922(13), Rh(1)−Rh(2) 3.8854, Rh(3)−Rh(4) 3.9098

In contrast to the rhodium(I) macrocycle **2**, the rhodium(III) macrocycle **3** does not catalyse the carbonylation of methanol: the low catalytic activity observed (TON 100 after 20 min., TOF 5 min^{-1}) when **3** is used as the catalyst precursor is due to a partial decomposition of **3** to give $[RhI_2(CO)_2]^-$. This is in line with what has been observed for other iodo-bridged dirhodium(III) complexes.[13]

To the best of our knowledge, **2** is the first macrocyclic dirhodium complex involved in the carbonylation of methanol. It is possible that the better catalytic performance of **2** with respect to that of the classical species $[RhI_2(CO)_2]^-$ is due to its macrocyclic nature.

Experimental Section

General: Solvents were dried and distilled under nitrogen prior to use. All reactions were carried out under nitrogen, using standard Schlenk techniques. All other reagents were purchased (Fluka) and used as received. Nuclear magnetic resonance spectra were recorded using a Varian Gemini 200 BB instrument or a Bruker AMX 400 spectrometer and referenced to the signals of the residual protons in the deuterated solvents. ^1H NMR: internal standard solvent, external standard TMS; ^{13}C NMR: internal standard solvent, external standard TMS. Infrared spectra were recorded with a Perkin−Elmer 1720X FT-IR spectrometer as KBr pellets. Microanalyses were carried out by the Laboratory of Pharmaceutical Chemistry, University of Geneva, Switzerland.

1: A solution of 2,5-thiophenedicarboxylic acid (1.72 g, 10 mmol), *N*,*N*-dicyclohexylcarbodiimide (2.3 g, 11 mmol), 4-(dimethylamino)pyridine (122 mg, 1 mmol), 4-pyrrolidinopyridine (148 mg, 1 mmol) and hydroxymethylbenzotriazole (3.3 g, 22 mmol) in CH_2Cl_2 (40 mL) was allowed to stand at room temperature under nitrogen, until the esterification was complete. The resulting solution was filtered to remove *N*,*N*-dicyclohexyl urea and the filtrate was concentrated under reduced pressure. The residue was chromatographed on silica gel (80 g), eluting with hexane/ether (1:1) to afford 2.7 g (62%) of **1** as a white solid. $C_{20}H_{14}N_6O_4S$ (434.4): calcd. C 55.29, H 3.25, N 19.35; found C 55.25, H 3.27, N 19.31. − FT-IR (4000−400 cm^{-1}): $\tilde{\nu}$ = 3029vw, 2979w, 1749s, 1709vs, 1532m, 1452m, 1280s, 1240s, 1159m, 1069s, 989m, 743s, 543m, 493m cm^{-1}. − FAB-MS (positive ion): *m*/*z* = 435 [M^+]. − ^1H NMR ([D_6]acetone): δ = 8.07 (m, 4 H), δ = 7.87 (s, 2 H), δ = 7.68 (t, 2 H), δ = 7.37 (t, 2 H), δ = 6.99 (s, 4 H). − ^{13}C NMR ([D_6]acetone): δ = 160.46, 146.31, 138.28, 134.73, 132.95, 128.94, 124.97, 120.44, 110.17, 68.82.

2: A solution of $[RhCl(CO)_2]_2$ (100 mg, 0.26 mmol) and **1** (248 mg, 0.57 mmol) in toluene (20 mL) was stirred at room temperature for 2 h. The solution was filtered then evaporated to dryness. The resulting yellow solid was washed with ether (10 mL) and dried under vacuum (240 mg, 77%). $C_{42}H_{28}Cl_2N_{12}O_{10}Rh_2S_2$ (1201.6): calcd. C 41.98, H 2.35, N 13.99; found C 42.25, H 2.27, N 13.81. − FT-IR (4000−400 cm^{-1}): $\tilde{\nu}$ = 3035vw, 2975w, 2086s, 2013vs, 1727vs, 1529m, 1455m, 1237s, 1159m, 1070s, 984m, 746s, 493m cm^{-1}. − ESI-MS: *m*/*z* = 1220 [M + H_2O]. − ^1H NMR ([D_6]acetone): δ = 8.35 (d, 4 H), δ = 8.20 (d, 4 H), δ = 7.91 (s, 4 H), δ = 7.80 (m, 4 H), δ = 7.67 (m, 4 H), δ = 7.09 (s, 8 H). − ^{13}C NMR ([D_6]acetone): δ = 183.52, 160.35, 145.89, 138.18, 135.74, 133.42, 129.58, 125.98, 120.09, 111.66, 70.16.

3: Complex **2** (100 mg, 0.08 mmol), ethanoic acid (1 mL) and iodomethane (1 mL) were dissolved in acetone (20 mL) under an atmosphere of carbon monoxide. After heating at reflux for 1 h, the resulting brownish solution was filtered and then the solvent was evaporated to dryness. The remaining red-brown solid was washed with ether and dried in vacuo (388 mg, 59%). Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of an acetone solution. FT-IR (4000−400 cm^{-1}): $\tilde{\nu}$ = 3035vw, 2975w, 2059s, 1729vs, 1524m, 1455m, 1246s, 1076s, 746s, 519m cm^{-1}. − ^1H NMR ([D_6]DMSO): δ = 8.65 (d, 4 H), δ = 8.53 (d, 4 H), δ = 8.01−7.88 (m, 12 H), δ = 7.15 (s, 8 H). − ^{13}C NMR ([D_6]DMSO): δ = 192.53, 160.26, 147.04, 138.56, 134.93, 133.40, 129.21, 125.50, 120.11, 111.66, 70.28.

Catalytic Runs: In a typical experiment, $[RhCl(CO)_2]_2$ (24 mg, 0.06 mmol) and **1** (53 mg, 0.12 mmol) were dissolved in methanol (4.46 mL). Iodomethane (11 mmol) and water (200 mmol) were added to this solution, and the mixture was placed in a 100 mL stainless steel autoclave. After purging three times with CO, the autoclave was pressurised with carbon monoxide (25 bar) and heated to 170 °C with vigorous stirring of the reaction mixture (900 rpm). After 20 min., the autoclave was cooled to room temperature, and the pressure was released. The solution was filtered and analysed by GC.

Crystal Structure Determination of 3:[10] A black crystal of compound **1** was mounted on a Stoe Imaging Plate Diffractometer System (Stoe & Cie, 1995) equipped with a one-circle goniometer and a graphite-monochromator. Data collection was performed at −120 °C using Mo-K_α radiation (λ = 0.71073 Å). 190 exposures (3 min. per exposure) were obtained at an image plate distance of 70 mm with $0 < \theta < 190°$ and with the crystal oscillating through 1° in θ. The resolution was $D_{min} - D_{max}$ 12.45−0.81 Å. Crystallographic data are reported in Table 1. The structure was solved by direct methods using the program SHELXS-97[14] and refined by full-matrix least-squares on F^2 with SHELXL-97.[15] The hydrogen atoms were included in calculated positions and treated as riding atoms using the SHELXL-97 default parameters. The compound crystallises with 7.5 molecules of acetone per asymmetric unit. The solvent molecule with an occupancy of 0.5 is strongly disordered and therefore all atom positions have been refined isotropically. An absorption correction using DIFABS in PLATON99[16] was applied (T_{min} = 0.185, T_{max} = 0.656). The figures were drawn with ORTEP-32.[17]

Table 1. Crystallographic data for **3**

Empirical formula	$C_{66.5}H_{73}I_{12}N_{12}O_{19.5}Rh_4S_2$
Molecular mass	3350.93
Temperature [K]	153(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	27.693(2)
b [Å]	14.3087(13)
c [Å]	13.6096(11)
α [°]	103.300(10)
β [°]	80.091(10)
γ [°]	79.420(10)
Volume [Å^3]	5027.9(7)
Z	2
D_c [g cm^{-3}]	2.213
Wavelength [Å]	0.71073(Mo-K_α)
μ [min^{-1}]	4.434
F (000)	3120
θ range [°]	1.84−25.83
Unique refl. with $I > 2\sigma(I)$	11752
Final *R*1, *wR*2 (observed data)[a]	0.0578, 0.1600
No. of variables	740
GOF	1.009
Residual density (max/min) [eÅ^{-3}]	2.941/-2.508

[a] $R1 = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|]$; $wR^2 = \{[\Sigma(w(F_o^2 - F_c^2)^2]/\Sigma(wF_o^4)]^{1/2}\}$

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[10] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-160381 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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