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Preliminary communication

MONODENTATE PYRIDINE-2-THIOL AND CHELATING AND BRIDGING PYRIDINE-2-THIOLATO COMPLEXES DERIVED FROM RHODIUM(I) CHLORO-CARBONYL DIMER

ANTONY J. DEEMING, M.N. NAFEES MEAH,
Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ (Great Britain)
HELEN M. DAWES and MICHAEL B. HURSTHOUSE
Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS (Great Britain)

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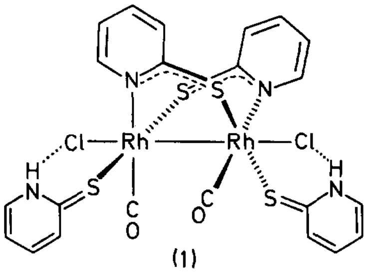
Summary

Dicarbonyl- and monocarbonyl-rhodium(I) compounds formed from $[Rh_2Cl_2(CO)_4]$ and pyridine-2-thiol (NC_5H_4SH) in chloroform slowly give blue-black crystals of the dinuclear rhodium(II) compound $[Rh_2Cl_2(\mu\text{-}NC_5H_4S)_2(\eta^1\text{-}NHC_5H_4S)_2(CO)_2]\cdot2CHCl_3$ (Rh—Rh distance 2.652(4) Å) rather than the much more common tetra-bridged species. Oxidation by air and heat lead to the tris-chelate compound $[Rh^{III}(NC_5H_4S)_3]$.

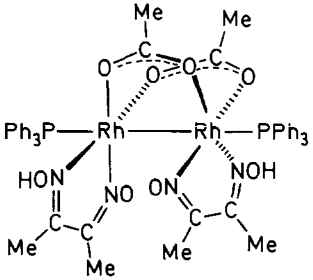
While dinuclear rhodium(II) compounds with four bridging carboxylato, dialkylaminoformamido, 2-pyridinato, or other related organic or inorganic ligands are well-known [1], no such species have been obtained from pyridine-2-thiol LH (LH = NC_5H_4SH). The acetato-dimer gives the adduct $[Rh_2(MeCO_2)_4(LH)_2]$ with LH but the LH ligands do not displace any of the acetato-ligands [2]. Indeed, $[Pt_2(en)_2L_2]Cl_2\cdot3H_2O$ is the only reported dinuclear complex with pyridine-2-thiolate bridges [3], and related pyrimidine-thiolato bridges have been identified in a Mo_2 compound [4]. The free ligand LH exists predominantly as the 2-thiopyridine tautomer [5] and is commonly found to coordinate through sulphur in this way [3] and examples of chelating L are known in spite of the small bite [6,7].

Yellow chloroform solutions of $[Rh_2Cl_2(CO)_4]$ react with LH under nitrogen to give deep-red, air-sensitive solutions. When LH/Rh = 1 the formation of the bridge-cleaved product *cis*-$[RhCl(CO)_2(LH)]$ is indicated (ν(CO)

2083 and 2015 cm^{-1})*, although the removal of solvent gave an intensely coloured solid which could not be properly characterised. When LH/Rh = 2, another neutral *cis*-dicarbonyl compound is formed (ν(CO) 2074 and 2013 cm^{-1}). When LH/Rh = 3 a monocarbonyl (ν(CO) 1978 cm^{-1}) is the major species, but the second *cis*-dicarbonyl is still present (0.75 mol CO displaced/mol Rh atoms) and an atmosphere of CO partially reverses this last step. These rhodium(I) compounds were only characterised by infrared and ^{1}H NMR spectra. However, on leaving a chloroform solution (LH/Rh = 2) to stand under nitrogen for several days deep blue/black insoluble crystals of $[Rh_2Cl_2(LH)_2(L)_2(CO)_2]\cdot 2CHCl_3$, compound (1) (75%), were deposited



(1)



(2)

(ν(CO) (Nujol) 2055s and 2037m cm^{-1}). Analytical data were good but because of its insolubility compound **1** could only be characterised properly by a single crystal X-ray study**.

Molecules of compound **1** (Fig. 1) are of C_2 symmetry and have only two bridging ligands which is very unusual for rhodium(II) dimers. The only other example is $[Rh_2(MeCO_2)_2(dmg)_2(PPh_3)_2]$ (**2**) which contains bridging acetato ligands but the dimethylglyoximato (dmg) ligands chelate as they normally do [8]. In compound **1** the two LH monodentate ligands coordinate through sulphur but also form pseudo-chelate rings through NH. . . .Cl hydrogen bonds (N(21)—Cl(1) 3.003 Å). The octahedral rhodium atoms are more nearly staggered than eclipsed. Whereas in compound **2** there is a twist of 20° out of the eclipsed conformation, compound **1** is much closer to the idealised staggered arrangement (torsional angle N(11)—Rh(A)—Rh—S(1) 37°). Although dehydrochlorination might have given a tetra-bridged structure like that found for the corresponding derivative $[Rh_2(C_6H_6NO)_4]$ where C_6H_6NO is the bridging 6-methylpyridonato ligand [9], this has not occurred in this case.

Air-oxidation of chloroform solutions of $[Rh_2Cl_2(CO)_4]$ and LH (LH/Rh > 3) gave a product (**3**) isolated as orange crystals. Elution of a solu-

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*^{1}H NMR ($CDCl_3$): δ 7.10m (H^5), 7.65m (H^3, H^4), 7.90t (H^6) ppm.

***Crystal data for compound* 1: $C_{24}H_{20}N_4O_2S_4Cl_8Rh_2$, M = 1014.14, monoclinic, space group $C2/c$, a 26.080(3), b 9.319(1), c 16.034(4) Å, β 109.73(2)°, U 3668.32 Å^3, Z = 4, D 1.84 g cm^{-1}, μ(Mo-K_α) 16.01 cm^{-1}, 2725 observed out of 3220 unique reflections [$I > 1.5\sigma(I)$], R = 0.0349, non-hydrogen atoms anisotropic, hydrogens refined freely with individual isotropic temperature parameters. The molecule contains a two-fold rotation axis. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

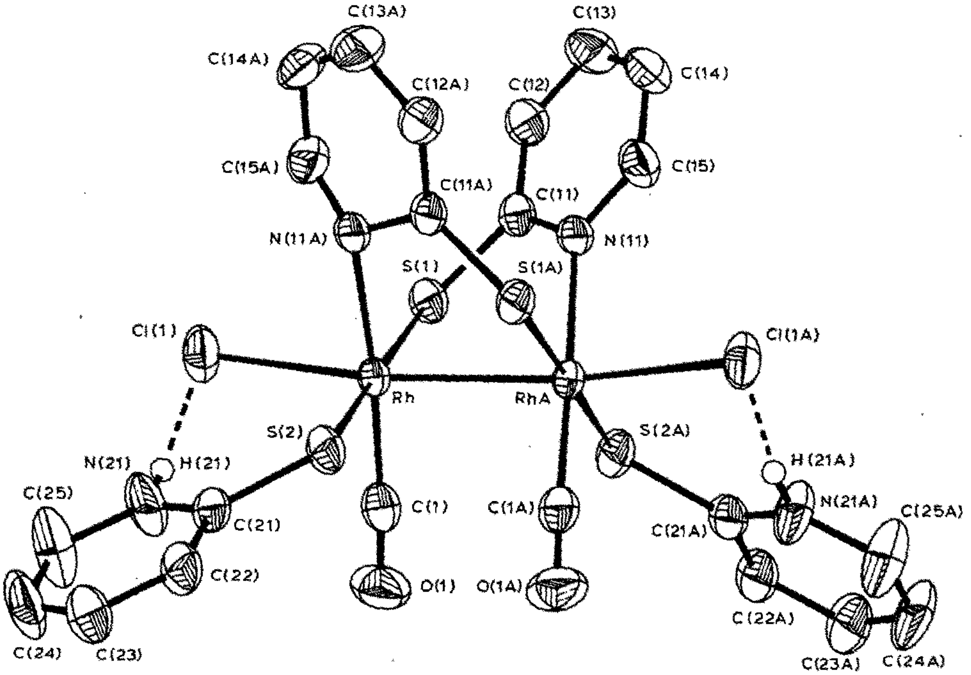
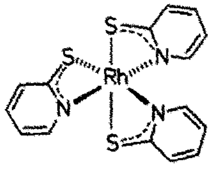


Fig. 1. Molecular structure of $[Rh_2Cl_2(\mu\text{-}L)_2(\eta^1\text{-}LH)_2(CO)_2]$. Selected bond lengths and angles: Rh—Rh(A) 2.652(4), Rh—N(11A) 2.123(4), Rh—S(1) 2.339(3), Rh—S(2) 2.427(3), Rh—C(1) 1.864(7), Rh—Cl(1) 2.547(4), C(21)—S(2) 1.719(6), C(11)—S(1) 1.732(6) Å; Rh(A)—Rh—N(11A) 86.7(1), Rh(A)—Rh—S(1) 82.9(1), Rh(A)—Rh—S(2) 94.1(1), Rh(A)—Rh—C(1) 91.2(1), Cl(1)—Rh—S(1) 83.6(1), Cl(1)—Rh—S(2) 99.4(1), Cl(1)—Rh—N(11A) 92.8(1), Cl(1)—Rh—C(1) 90.0(2)°. All hydrogen atoms were located but only the hydrogen-bonded ones are illustrated. Key to symmetry operations relating designated atoms to reference atoms at (x,y,z): $A = 1.0 - x, y, 0.5 - z$.

tion of 3 through an alumina column gave $[Rh(LH)L_3]$ (4), as red crystals. We are currently studying compounds 3 and 4; both give the same mass spectrum corresponding to $[RhL_3]$ (5) which was shown to be their decomposition product at 180°C. Compound 5, which could not be obtained from



(5)

rhodium trichloride and LH, contains three different ligands L (^{1}H NMR evidence*. Based on a tris-chelate compound of octahedral geometry, only the *mer*-configuration shown for 5 is possible. This was confirmed by an X-ray diffraction study which will be reported later. This is a very unusual example of a tris-chelate transition metal compound with only 4-membered chelate rings.

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* ^{1}H NMR multiplets between δ 6.6 and 8.3 are consistent with three non-equivalent L ligands but these have not been individually assigned.

These results show that pyridine-2-thiol has an unusual flexibility as a ligand, coordinating in at least three modes, although the bridging case we report here is probably relatively unfavourable.

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