Mercury(II) Chloride Bridging Two Rhodium Atoms. Preparation and *X*-Ray Crystal Structure of [$Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}HgCl_2)$]

Felice Faraone,* Sandra Lo Schiavo, Giuseppe Bruno, and Gabriella Bombieri

Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, Piazza S. Pugliatti, 98100 Messina, Italy

The title compound has been obtained by treating [$Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)$] [dppm = bis(diphenylphosphino)-methane] with $HgCl_2$, and characterized by spectroscopic and *X*-ray analyses; it represents the first example of mercury(II) chloride bridging two transition metal atoms in a complex.

The reactions of complexes of transition metals in low oxidation states with mercury(II) chloride involve (i) complete displacement of chloride ion to produce metal–mercury–metal bonds,[1] (ii) partial chloride ion displacement to yield complexes in which $HgCl^+$ is bonded to the metal,[2] or (iii) retention of both chlorine atoms to produce simple adducts of $HgCl_2$.[3,4] Recently it was reported[5] that polynuclear metal carbonyl complexes containing bridging CO, CNR, or CS ligands react with an electrophile E, such as $HgCl_2$, to give adducts containing μ–CX–E moieties (X = O, NMe, or S) which were not isolated. Cyclopentadienyl complexes of Co^I, Rh^I, and Ir^I, both mono- and bi-nuclear, generally form simple adducts with $HgCl_2$;[4] in these reactions the metal complex acts as a Lewis base and the mercury(II) chloride as a Lewis acid.

The present report concerns the preparation and the *X*-ray molecular structure of the title compound in which $HgCl_2$ bridges two rhodium atoms. To our knowledge there are no previous reports of transition metal complexes in which $HgCl_2$ is bonded in this way. As the starting material we used the recently prepared[6] compound [$Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)$] (**1**) (dppm = $Ph_2PCH_2PPh_2$). A saturated benzene solution of $HgCl_2$ was added dropwise to a solution of (**1**) in the same solvent until the colour of the solution turned dark green [at this stage (**1**) was still present in solution] and precipitation did not occur. When left a dark green crystalline product (*ca.* 40% yield) was formed from the solution and isolated. After recrystallization from dichloromethane, this was characterized as [$Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}HgCl_2)$] (**2**) by spectroscopic† and *X*-ray analyses.

[$Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)$]
(**1**)

[$Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}HgCl_2)$]
(**2**)

Crystal data: $C_{36}H_{32}Cl_2HgOP_2Rh_2$ at 298 K, M = 1019.9, monoclinic, space group $P2_1/n$, a = 10.720(2), b = 16.062(3), c = 19.817(5) Å, β = 91.3(3)°, D_c = 1.98 g cm^{-3}, Z = 4, $F(000)$ = 1 960. The structure was solved by direct methods and by difference Fourier techniques using 3 127 unique intensities with $I \geqslant 3\sigma(I)$, collected on a Siemens Stoe automated diffractometer with Mo-K_α radiation (λ = 0.7107 Å) for $3 < 2\theta < 50°$, and refined by least-

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† Satisfactory elemental analyses were obtained; m.p. 125 °C (decomp.). I.r. (Nujol mull) ν(CO) 1 780 cm^{-1} [1 730 in (**1**)]; ν(Hg–Cl) 240 cm^{-1}; ^1H n.m.r. ($CDCl_3$, 60 MHz) δ 5.38 [dd, C_5H_5, J(HP) 0.8, J(HRh) 0.5 Hz].

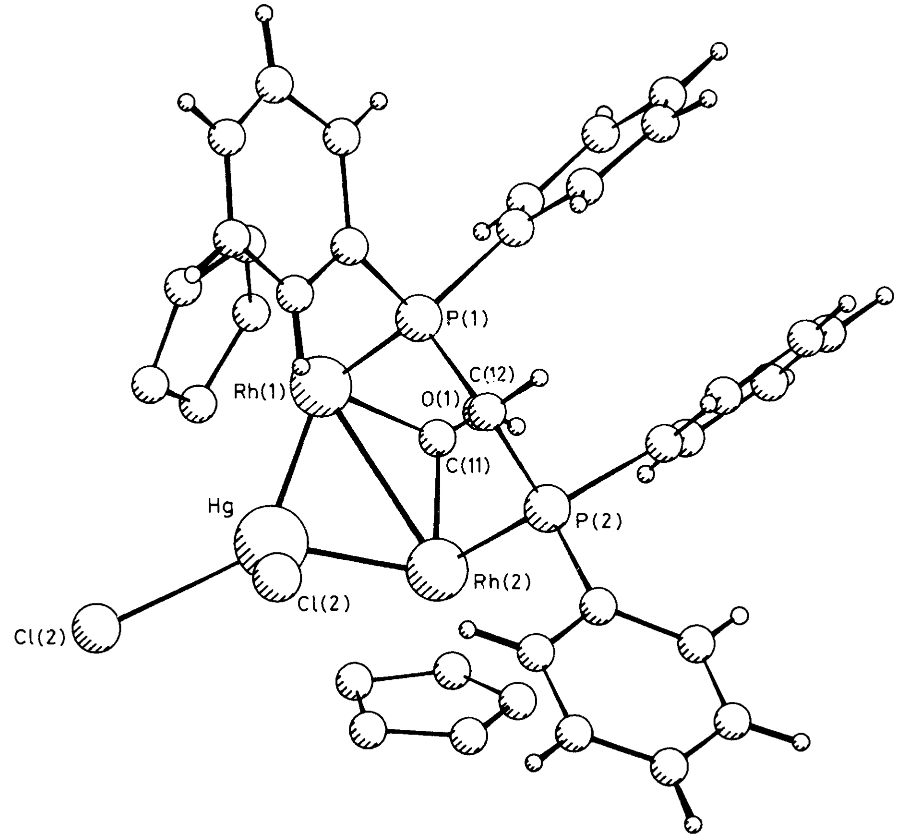

Figure 1. Molecular structure of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}HgCl_2)]$ (**2**). Relevant parameters are: Rh(1)–Rh(2) 2.853(2), Rh(1)–Hg 2.692(1), Rh(2)–Hg 2.744(2), Rh(1)–C(11) 2.00(1), Rh(2)–C(11) 2.00(1), Rh(1)–P(1) 2.260(4), Rh(2)–P(2) 2.270(4), Rh–$(C_5H_5)_{av.}$ 2.25(1), P(1)–C(12) 1.85(2), P(2)–C(12) 1.84(1), Hg–Cl(1) 2.534(3), Hg–Cl(2) 2.581(3) Å; Rh(1)–Hg–Rh(2) 63.3(0), Cl(1)–Hg–Cl(2) 94.1(1), Hg–Rh(1)–C(11) 103.7(4), Hg–Rh(2)–C(11) 101.8(4), Rh(1)–C(11)–Rh(2) 91.0(6), P(1)–C(12)–P(2) 110.3(7)°.

squares. The hydrogen atoms were introduced at calculated positions (C–H 0.95 Å) with isotropic thermal parameters. The phenyl rings were refined without constraints with isotropic thermal parameters; all the remaining atoms were refined anisotropically. Final refinement converged to R_w 0.052.‡ Figure 1 shows a view of the molecular structure.

The Rh(1)–Rh(2) distance of 2.853(2) Å [2.682(1) Å in compound (**1**)], is at the upper limit for a Rh–Rh single bond [range 2.617(3)—2.8415(2) Å].[7] The bridging carbonyl group is symmetrical with distances [Rh(1)–C(11) and Rh(2)–C(11) 2.00(1) Å] of the same order of those reported in the literature.[8] The bridging mercury atom is asymmetrically bonded to the two rhodium atoms with Rh(1)–Hg 2.692(1) and Rh(2)–Hg 2.744(2) Å. These values indicate single bonds. The co-ordination of the mercury atom forms a distorted tetrahedron (within which the angles vary from 63.3 to 135.0°). The bond distances Hg–Cl(1) and Hg–Cl(2), 2.534(3) and 2.581(3) Å, respectively, are significantly larger than the sum of the covalent tetrahedral radii (2.47 Å)[9] but are in the range 2.29—2.56 Å, reported for chloro complexes of Hg^{II} and can be correlated with the formation of Hg–Rh single bonds.

A three-centre, two-electron bridging system probably describes the bonding mode of the Lewis acid $HgCl_2$ to the two rhodium atoms. Other examples, though, are needed fully to define the situation.

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‡ The atomic co-ordinates for this structure 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.