Preparation and *X*-Ray Structure of a Rhodium(III)–Rhodium(I) Pyrazolate Complex with a Mercury Atom Asymmetrically Bridging the Metal Atoms

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Reaction of $[Rh_2(\mu\text{-}pz)_2(CO)_2(PPh_3)_2]$ (**1**) (pz = pyrazolate) with $HgCl_2$ gives $[(Ph_3P)(CO)ClRh(\mu\text{-}HgCl)(\mu\text{-}pz)_2Rh(CO)(PPh_3)]$ (**2**); the *X*-ray stucture of (**2**) shows the presence of two rhodium atoms in different oxidation states asymmetrically bridged by a mercury atom, so that a unique $Rh^{III}–Hg{\leftarrow}Rh^{I}$ fragment is present.

Recently, dinuclear complexes have been under investigation with respect to reactivity, catalytic activity, and structure.[1] In particular some pyrazolate-bridged iridium(I) or rhodium(I) dimers undergo two-centre oxidative addition reactions with methyl iodide or iodine to give metal–metal bonded iridium(II) or rhodium(II) complexes.[2] Pursuing our interest in pyrazolate rhodium complexes,[3,4] we now report the preparation and characterization of a rhodium(III)–rhodium(I) complex which to the best of our knowledge is the first structurally characterized complex in which a mercury atom asymmetrically bridges two metal atoms in different oxidation states.

Addition of $HgCl_2$ (0.10 mmol) to a dichloromethane solution of $[Rh_2(pz)_2(CO)_2(PPh_3)_2]^3$ (**1**) (0.10 mmol) at room temperature caused the colour of the solution to change from yellow to red. Microanalytical and spectroscopic data for the red solid isolated in 75% yield by addition of hexane suggest the formation[†] of $[(Ph_3P)(CO)ClRh(HgCl)(pz)_2Rh$-

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[†] Similar complexes have been obtained by addition of $HgCl_2$ to $[Rh_2(pz)_2(CO)_2L_2]^3$ [L = $P(OPh)_3$ or $P(p\text{-}MeC_6H_4)_3$]. Further addition of $HgCl_2$ to $[L(CO)ClRh(HgCl)(pz)_2Rh(CO)L]$ complexes produces no fundamental changes.

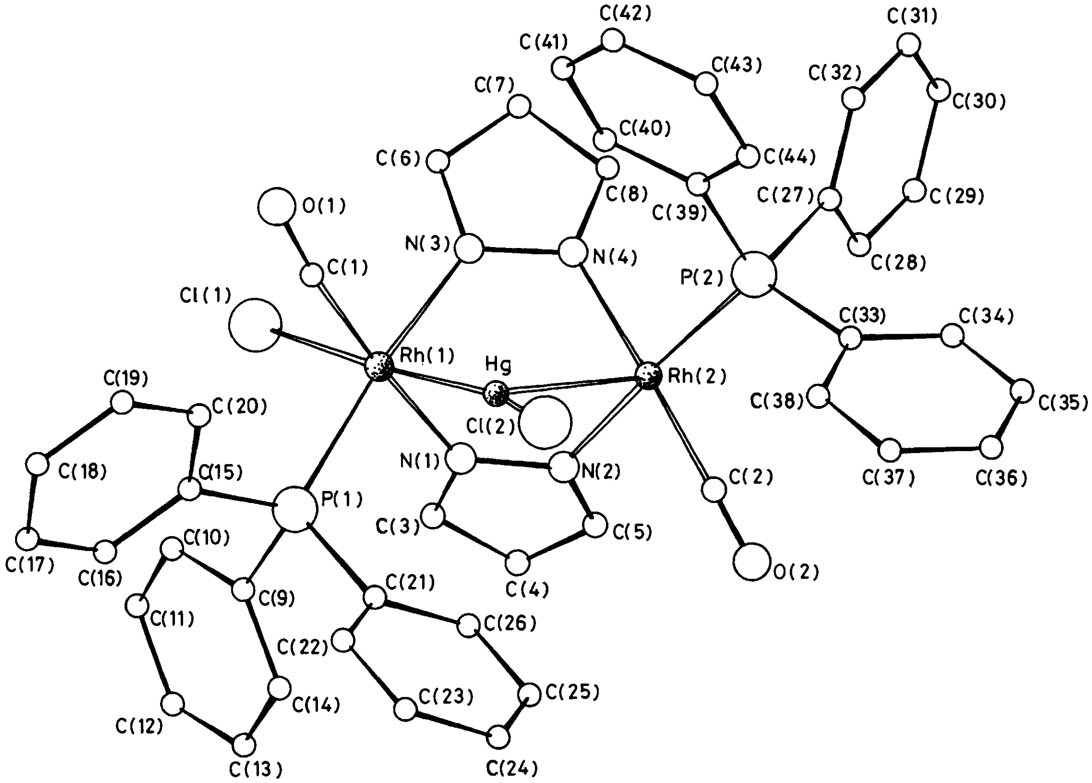

Figure 1. The structure of $[(Ph_3P)(CO)ClRh(HgCl)(pz)_2Rh(CO)(PPh_3)]$ (**2**). Selected bond distances (Å) and angles (°): Hg–Rh(1), 2.586(2); Hg–Rh(2), 2.804(3); Hg–Cl(2), 2.343(6); Rh(1)–Cl(1), 2.474(6); Rh(1)–C(1), 1.82(2); Rh(2)–C(2), 1.87(2); Rh(1)–Hg–Rh(2), 83.1(1); Rh(1)–Hg–Cl(2), 159.2(2); Rh(2)–Hg–Cl(2), 117.8(2); Cl(1)–Rh(1)–Hg, 172.4(2).

$[Rh_2(\mu\text{-}pz)_2(CO)_2(PPh_3)_2]$
(**1**)

$(CO)(PPh_3)]$ (**2**). This formulation has been confirmed by an *X*-ray analysis on a single crystal grown from toluene–hexane.

Crystal data: (**2**) $C_{44}H_{36}Cl_2HgN_4O_2P_2Rh_2$, $M = 1192.05$, monoclinic, space group $P2_1/c$, $a = 20.981(10)$, $b = 12.751(4)$, $c = 18.919(6)$ Å, $\beta = 101.39(3)°$, $Z = 4$, $U = 4962(3)$ Å^3, $D_c = 1.596$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 39.42$ cm^{-1}. The intensities of 7702 independent reflections were collected on a Siemens AED diffractometer (with θ in the range 3—24°) using the θ—2θ scan technique. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares on the basis of 4316 observed reflections $[I \geqslant 2\sigma(I)]$ to an R value of 5.7%.‡

The structure of complex (**2**) is shown in Figure 1 together with the most significant bond distances and angles. This complex may be interpreted as resulting from the oxidative addition of $HgCl_2$ to Rh(1), and simultaneous Lewis acid–base bonding between Hg and Rh(2) in such a way as to form an asymmetrical bridge, Rh–Hg←Rh. The Rh(1) atom has a nearly octahedral arrangement, with an Rh(1)–Hg distance of 2.586(2) Å, in the range previously found for other M–Hg bonds formed by oxidative addition of mercury(II) halides.[5,6] Accordingly, a band at 2070 cm^{-1}, 90 cm^{-1} higher relative to the parent compound (**1**),[3] is attributed to the carbonyl ligand bonded to Rh(1) [Rh(III)]. The Rh(2) atom is in a square-pyramidal arrangement with the mercury occupying the apical position. The Rh(2)–Hg distance is in the expected range for donor–acceptor adducts,[6,7] and the presence of a ν(CO) band at 2020 cm^{-1} [Δν(CO) = 40 cm^{-1}][6,8] supports the proposed interpretation. The Rh(1)–Hg–Cl(2) atoms are not colinear, because of the interaction of Hg with the Rh(2) atom. Although non-linear M–Hg–M (M = transition metal) derivatives have been reported,[9] complex (**2**) is the first example of a mercury atom asymmetrically bridging two rhodium atoms.

We thank Dr. R. D. W. Kemmitt for helpful suggestions.

Received, 10th February 1984; Com. 186

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‡ The atomic co-ordinates 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.