Synthesis and Characterization of an Unusual Tetranuclear Rhodium Complex; *X*-Ray Molecular Structure of $[Rh_4(\mu\text{-}Cl)_2(\mu\text{-}az)_2(\mu\text{-}CO)_2(CO)_2(nbd)_2]$ (az = 7-azaindolate; nbd = norborna-2,5-diene)

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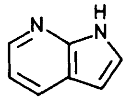
The complex [RhCl(nbd)(Haz)] (nbd = norborna-2,5-diene, Haz = 7-azaindole) reacts with $[Rh(acac)(CO)_2]$ (acac = MeCOCHCOMe) to give the tetranuclear compound $[Rh_4(\mu\text{-}Cl)_2(\mu\text{-}az)_2(\mu\text{-}CO)_2(CO)_2(nbd)_2]$, whose structure, determined by an *X*-ray analysis, contains a novel planar Rh_4Cl_2 framework and two directly bonded rhodium atoms with different electronic environments.

There is considerable interest in the preparation and characterization of polynuclear metal complexes and in their potential use for the study of multicentred catalysis. In this context, intense effort has been directed to the class of compounds with so-called molecular 'A frames'.[1] Among those several dinuclear complexes which each contain a rhodium–rhodium bond bridged by a carbonyl group and by two bis(diphenylphosphino)methane ligands have been reported.[2] Here we describe the preparation and structural characterisation of a tetranuclear rhodium complex that has a number of unusual features and appears to contain the first example of a rhodium–rhodium bond bridged by one carbonyl group and a *single* bidentate nitrogen donor ligand.

As part of a programme aimed at the study of the chemical and co-ordinative behaviour of potentially bidentate nitrogen donor ligands,[3] we have studied the reaction of the complex [RhCl(nbd)(Haz)] [Haz = 7-azaindole (**1**), nbd = norborna-2,5-diene] with $[Rh(acac)(CO)_2]$ (acac = MeCOCHCOMe). From this reaction, or alternatively by treatment of $[RhCl(CO)_2(Haz)]$ with [Rh(acac)(nbd)] in methanol, we have isolated an orange microcrystalline solid (**2**) in 80—85% yield for which analytical and spectroscopic data indicate an unsymmetrical bridged complex of the formula [(nbd)Rh(μ-az)(μ-CO)RhCl(CO)]. The i.r. spectrum of (**2**) in Nujol shows bands for bridging and terminal carbonyl groups at 2060w, 2015s, 1957w and 1840s, 1797w cm^{-1}, respectively.



(**1**)

Electron counting for the above proposed 30-electron

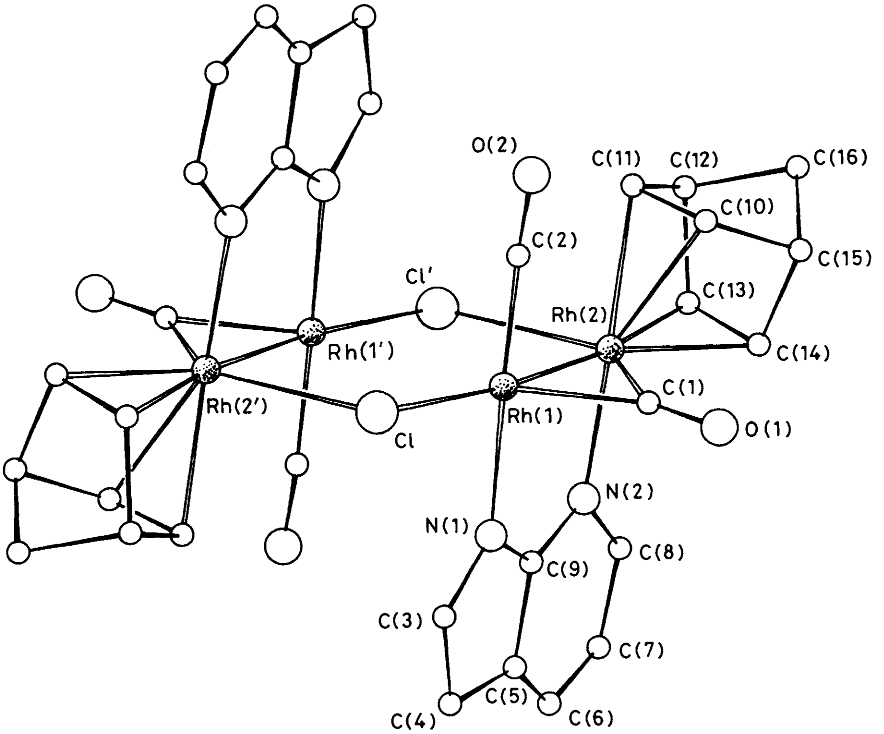


Figure 1. A view of the complex $[Rh_4(\mu\text{-}Cl)_2(\mu\text{-}az)_2(\mu\text{-}CO)_2(CO)_2(nbd)_2]$ (**2**). Selected bond distances (Å) and angles (°) are: Rh(1)–Rh(2) 2.686(2), Rh(1)–Cl, 2.401(5), Rh(2)–Cl' 2.627(5), Rh(1)–C(1) 1.97(2), Rh(2)–C(1) 2.05(2), Rh(1)–C(2) 1.84(2); Rh(2)–Rh(1)–Cl, 167.5(2), Rh(1)–C(1)–Rh(2), 83.9(7), Rh(1)–Cl–Rh(2') 104.1(2), Rh(1)–Rh(2)–Cl' 88.4(2).

bimetallic unit suggests the presence of a single metal–metal bond. Complete characterization of (**2**) was achieved by a single crystal *X*-ray diffraction study.†

The crystal structure of (**2**) (Figure 1) consists of a centrosymmetrical tetranuclear complex in which two chlorine atoms asymmetrically bridge two dinuclear units in such a way as to form a unique planar Rh_4Cl_2 ring.

In each dinuclear unit the rhodium atoms share a bond and have different co-ordination geometries. One rhodium atom [Rh(1)] has a distorted trigonal bipyramidal co-ordination with the carbon atom of the terminal carbonyl group and the N(1) atom of the 7-azaindolate ligand in the apical positions and in the equatorial positions a chlorine atom, the carbon atom of the bridging carbonyl group, and the Rh(2) atom. The co-ordination around the second rhodium atom [Rh(2)] can be described as distorted octahedral involving the olefinic bonds of the norbornadiene ligand, the carbon atom of the bridging carbonyl group, the N(2) atom of the 7-azaindolate ligand, the Cl' atom, and the Rh(1) atom.

The Rh(1)–Rh(2) distance [2.686(2) Å] is in the range expected for a Rh–Rh single bond.[4] The bond between the two metal atoms could be described as a donor bond from Rh(2) (electron rich) to Rh(1) (electron poor), as suggested recently for dinuclear phosphidorhodium complexes.[5] Finally, it is of interest to point out the relatively short distance between Rh(1) and Rh(1') [3.156(2) Å]; weak Rh–Rh interactions have been postulated in dimeric systems in which the Rh–Rh separation is as high as 3.167(1) Å.[6]

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† *Crystal data:* $C_{32}H_{26}Cl_2N_4O_4Rh_4$, $M = 1013.11$, monoclinic, space group $P2_1/n$. $a = 11.091(3)$, $b = 16.615(6)$, $c = 8.531(4)$ Å, $\beta = 91.63(3)°$, $U = 1571(1)$ Å^3, $D_c = 2.14$ g cm^{-3}, $Z = 2$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 22.50$ cm^{-1}. 2184 Independent reflections were collected on a Siemens AED diffractometer ($3<\theta<23°$). The crystal structure was solved by Patterson and Fourier methods. The refinement was carried out by means of full-matrix least-squares with anisotropic thermal factors for the heavier atoms. Hydrogen atoms were found from a difference Fourier map and refined. The current *R* value is 0.041 for 1201 observed reflections [$I \geqslant 2\sigma(I)$].

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.