

Preliminary communication

HETEROBINUCLEAR PYRAZOLATE-BRIDGED RUTHENIUM(II)— RHODIUM(I), IRIDIUM(III)—RHODIUM(I), AND RHODIUM(III)— IRIDIUM(I) COMPLEXES. CRYSTAL STRUCTURE OF [(*p*-cymene)Ru(μ -Cl)₂(μ -pz)Rh(tetrafluorobenzo[5.6]bicyclo[2.2.2]octan-2,5,7- triene)]

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Summary

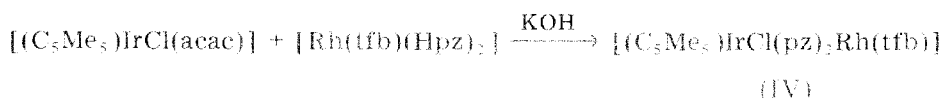
Heterobinuclear complexes of formula [LMCl₂(pz)M'(tfb)] (M = Ru, L = *p*-cymene, M' = Rh; M = Ir, L = C₅Me₅, M' = Rh; M = Rh, L = C₅Me₅, M' = Ir) and [(C₅Me₅)IrCl(pz)₂Rh(tfb)] (tfb = tetrafluorobenzo[5.6]bicyclo[2.2.2]octan-2,5,7-triene) have been prepared. The molecular structure of [(*p*-cymene)Ru(μ -Cl)₂(μ -pz)Rh(tfb)] has been determined by X-ray diffraction. It consists of two moieties, (*p*-cymene)Ru and (tfb)Rh, triply-bridged by a pyrazolate group and two chlorine atoms.

The pyrazolate chemistry of platinum metals (Rh [1], Ir [2], Pd [3], Pt [4], Ru [5]) has attracted considerable interest in recent years, but most of the research has been concentrated on homobimetallic rhodium and iridium complexes [1,2]. In particular, Gray and coworkers [6] have shown that homobinuclear pyrazolate-iridium complexes can be versatile photoreagents for the reductive activation of inert substrates. On the other hand we have recently described [7] the preparation of hetero- and homo-bridged mixed valence complexes of formula [(C₅Me₅)ClRhCl(pz)RhL₂] (L₂ = diolefin, L = CO) and

$[(C_5Me_5)ClRh(pz)_2RhL_2]$. We now report a simple synthetic strategy which permits the preparation of pyrazolate heterobimetallic Ru–Rh and Ir–Rh complexes.

The reaction of mononuclear pyrazole complexes of formula $[LMCl_2(Hpz)]$ ($M = Ru$, $L = \eta^5\text{-}p\text{-cymene}$; $M = Rh$ or Ir , $L = \eta^5\text{-}C_5Me_5$) (prepared by cleavage of the $[LMCl_2]_2$ dimers with pyrazole) with $[M'(acac)(tfb)]$ ($M' = Rh$ or Ir , $tfb = \text{tetrafluorobenzo}[5.6]\text{bicyclo}[2.2.2]\text{octa-2,5,7-triene}$) derivatives leads to new heterobinuclear complexes of formula $[LMCl_2(pz)M'(tfb)]$ ($M = Ru$, $L = p\text{-cymene}$, $M' = Rh$ (I), $M = Ir$, $L = C_5Me_5$, $M' = Rh$ (II); $M = Rh$, $L = C_5Me_5$, $M' = Ir$ (III))* . The latter combination of oxidation states $[Rh^{III}\text{--}Ir^I]$ is unusual because iridium has a greater tendency than rhodium to be in oxidation state III.

Another route for the preparation of heterobimetallic $[Ir^{III}\text{--}Rh^I]$ complexes is exemplified by the following sequence:



In the above-mentioned complexes the pyrazolate group must be acting as *exo*-bidentate ligand. However, the situation of the chlorine atoms is not so obvious. In particular, the X-ray structure of complex I shows a triple-bridged formulation, in contrast with the double-bridged formulation observed for the iso-electronic $[(C_5Me_5)ClRh(\mu\text{-Cl})(\mu\text{-}pz)Rh(tfb)]$ [7].

Crystal data. $C_{25}H_{23}N_2Cl_2F_4RhRu$, $M = 702.345$, triclinic, space group $P\bar{1}$, a 13.0432(5), b 13.1989(5), c 8.2107(3) Å, α 97.982(3), β 101.706(3), γ 61.964(3), U 1220.2(1) Å³, D_{calc} 1.912 g cm⁻³, $Z = 2$, $\rho(Cu\text{-}K\alpha)$ 132.51 cm⁻¹.

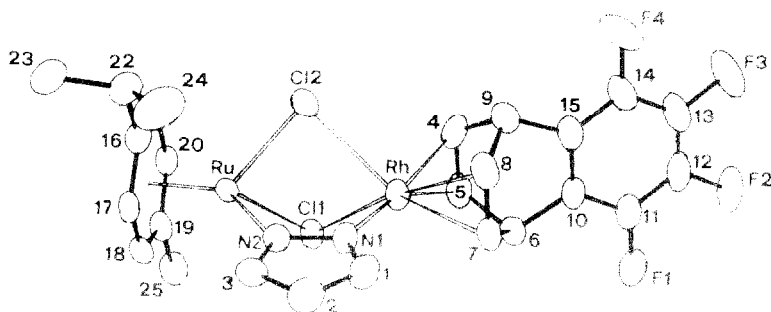


Fig. 1. ORTEP drawing of the compound with 40% probability ellipsoids showing the atomic numbering. Atom C(21) is eclipsed by C(24). Selected bond distances (Å) and angles (°) are: Rh–Cl(1) 2.498(1), Rh–Cl(2) 2.699(2), Rh–N(1) 2.053(5), Rh–C(4) 2.114(6), Rh–C(5) 2.138(6), Rh–C(7) 2.073(6), Rh–C(8) 2.077(6), Ru–Cl(1) 2.434(1), Ru–Cl(2) 2.428(1), Ru–N(2) 2.096(6), Ru–C(16) 2.186(5), Ru–C(17) 2.171(5), Ru–C(18) 2.175(4), Ru–C(19) 2.187(5), Ru–C(20) 2.201(7), Ru–C(21) 2.184(7), Cl(1)–Rh–Cl(2) 77.81(4), Cl(1)–Rh–N(1) 86.04(13), Cl(1)–Rh–C(4,5) 99.40(14), Cl(1)–Rh–C(7,8) 149.59(13), Cl(2)–Rh–N(1) 81.98(13), Cl(2)–Rh–C(4,5) 106.42(15), Cl(2)–Rh–C(7,8) 132.37(13), N(1)–Rh–C(4,5) 171.46(18), N(1)–Rh–C(7,8) 100.71(18), C(4,5)–Rh–C(7,8) 71.29(18), Cl(1)–Ru–Cl(2) 84.44(5), Cl(1)–Ru–N(2) 84.74(2), Cl(2)–Ru–N(2) 83.94(12), Cl(1)–Ru–G 127.14(9), Cl(2)–Ru–G 127.93(9), N(2)–Ru–G 132.30(14). C(4,5) and C(7,8) denote the midpoints of the C(4)–C(5) and C(7)–C(8) bonds, respectively.

*All the complexes reported were fully characterized by analytical and spectroscopic methods (IR and ¹H NMR).

The diffraction data were collected on a Philips PW 1100 four-circle automatic diffractometer, using the $\omega/2\theta$ scan technique and graphite-monochromated Cu- K_{α} radiation (λ 1.54178 Å). The structure was solved by standard Patterson and Fourier methods, and refined by full-matrix least-squares on F_{obs} with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were found from a difference Fourier map and refined isotropically. The refinement converged at $R = 0.037$ and $R_w = 0.039$ for the 3748 reflections ($\theta < 65^\circ$) having $I > 3\sigma(I)^*$.

Figure 1 shows the solid-state molecular structure of $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\mu\text{-Cl})_2(\mu\text{-pz})\text{Rh}(\text{tfb})]$ together with the atom-numbering scheme and some important bond distances and angles. Compound I is a heterobinuclear complex formed by a Rh^{I} and a Ru^{II} atom bridged by a pyrazolate group and two chlorine atoms. The coordination spheres of the metals are completed by a tfb molecule, acting as a 1,4-diolefin ligand on the Rh atom, and by a *p*-cymene ligand on the Ru atom. If the centroid of the *p*-cymene ring (G) is regarded as the center of a three *fac*-octahedral site, an octahedral arrangement can be discerned around this last metal, with the η^6 -arene ring and the three other ligands adopting a ‘‘piano-stool’’ configuration (see Fig. 1).

The intermetallic distance $\text{Rh}\dots\text{Ru}$, 3.514(1) Å, is significantly shorter than that in the related homometallic double bridged $[(\text{C}_5\text{Me}_5)\text{ClRh}(\mu\text{-Cl})(\mu\text{-pz})\text{Rh}(\text{tfb})]$ complex (3.715(2) Å) [7], probably owing to the additional bridging character of the Cl(2) atom. This chlorine is bonded to the Ru atom with an interatomic distance, 2.428(1) Å, in the range of usual $\text{Ru}^{\text{II}}\text{-Cl}$ bond distances (2.40–2.50 Å) [8]. The $\text{Rh}\text{-Cl}(2)$ distance, 2.699(2) Å, is longer than the $\text{Rh}^{\text{I}}\text{-Cl}$ bond distances usually observed in related structures with bridging chlorine atoms (range 2.35–2.60 Å) [9]. Slightly shorter $\text{Rh}^{\text{I}}\text{-Cl}$ bond distances have been reported for terminal chlorine, 2.635(4) Å [10], or for bridging Cl atoms, 2.607(2) Å [9a], in cases in which there was no doubt about the nature of the bond.

The coordination around the Rh atom can be described as distorted square pyramidal with the Cl(2) atom in the apical position. This type of coordination is supported by the dihedral angle between the planes $\text{Cl}(1)\text{-Rh}\text{-N}(1)$ and $\text{C}(4,5)\text{-Rh}\text{-C}(7,8)^{**}$ ($29.5(1)^\circ$, compared with a value of $6(1)^\circ$ in the related double-bridged dirhodium complex [7]), and the marked deviation of the Rh atom (0.3194(4) Å) from the best plane through N(1), Cl(1), C(4,5) and C(7,8) towards the Cl(2) atom.

Also noteworthy is the high asymmetry of the Cl(2) bridge. A similar situation was found in the $[\{\mu\text{-}(\text{Ph}_2\text{P})_2\text{py}\}_2\text{Rh}_4(\mu\text{-CO})(\text{CO})_2(\mu\text{-Cl})_2\text{Cl}_2]$ complex [9c], where the chlorine has been described as ‘‘semi-bridging’’. The *p*-cymene ring makes an angle of $24.8(2)^\circ$ with the plane holding the four atoms of the olefinic bonds. The relative position of these two groups, as viewed along the

*The atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication.

**C(4,5) and C(7,8) denote the mid-points of the C(4)–C(5) and C(7)–C(8) bonds, respectively.

Ru...Rh line, is such that C(20) and C(17) atoms are eclipsed by the double bonds C(4)–C(5) and C(7)–C(8), respectively.

For complex II, $[\text{Rh}^{\text{III}}\text{--Ir}^{\text{I}}]$ the possibility of a triple-bridged formulation can not be excluded, in view of the greater tendency of the Ir-tfb moiety to adopt a pentacoordinate arrangement around the iridium atom [11]. On the other hand, we suspect a double-bridged formulation for complexes III and IV $[\text{Ir}^{\text{III}}\text{--Rh}^{\text{I}}]$, as found for the recently characterized $[(\text{C}_6\text{Me}_6)_3\text{ClRh}(\mu\text{-Cl})(\mu\text{-pz})\text{-Rh}(\text{tfb})]$ [7].

Further work on the synthesis and reactions of related heterobinuclear complexes is in progress.

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