

Preliminary communication

Divalent ruthenium complexes containing non-planar *hexahapto*-benzene

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Zelonka and Baird¹ have recently re-examined the dehydrogenation of cyclohexa-1,3-diene by ethanolic RuCl_3 to form $\text{C}_6\text{H}_6\text{RuCl}_2$ ². They report that the derivatives of formula $\text{C}_6\text{H}_6\text{RuCl}_2\text{L}$ (L = phosphite, tertiary phosphine or tertiary arsine) are monomeric in chloroform solution, in contrast with the original finding² that $\text{C}_6\text{H}_6\text{RuCl}_2[\text{P}(\text{n-Bu})_3]$ is dimeric in freezing bromoform. We³ have independently made observations which are in general agreement with those of Zelonka and Baird, and have also prepared a series of brown, diamagnetic complexes of general formula $(\pi\text{-arene})\text{RuCl}_2$ (arene = PhMe, *p*- $\text{C}_6\text{H}_4\text{Me}_2$, *p*- $\text{MeC}_6\text{H}_4\text{CHMe}_2$ or PhOMe) from methanolic or ethanolic RuCl_3 and the appropriate cyclohexa-1,3-diene or cyclohexa-1,4-diene. The *p*-cymene complex is dimeric in chloroform, as shown by osmometry (found, 579; calcd. 612), but the other complexes are too insoluble for molecular weight determinations. The coordinated *p*-cymene in the monomeric adducts $(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2\text{L}$ (L = tertiary phosphine) is readily displaced on heating with toluene, mesitylene or hexamethylbenzene.

We report herein single crystal X-ray diffraction studies of $\text{C}_6\text{H}_6\text{RuCl}_2(\text{PMePh}_2)$ and $(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2(\text{PMePh}_2)$ using Picker FACS-1 diffractometer data, which show that these molecules are structurally similar to the well-known $(\pi\text{-arene})\text{Cr}(\text{CO})_3$ complexes, with one important difference; the π -arene rings in the ruthenium(II) complexes are slightly but significantly non-planar.

Experimental details and crystal data are as follows: $\text{C}_6\text{H}_6\text{RuCl}_2(\text{PMePh}_2)$; $M = 451.3$, monoclinic, $a = 10.02$, $b = 10.74$, $c = 17.07\text{\AA}$, $\beta = 100^\circ 26'$, $V_c = 1805.6\text{\AA}^3$, spacegroup $P2_1/c$, $D_m = 1.66$, $D_c = 1.66\text{g}\cdot\text{cm}^{-3}$, $Z = 4$. Crystal monochromated Cu- K_α radiation, $\mu = 107.85\text{cm}^{-1}$. Rejection criteria $I/\sigma(I) \leq 3$, $\Delta B/\sigma(\Delta B) \geq 3$. Block diagonal least squares refinement, heavy atoms (4) anisotropic, carbon atoms isotropic, hydrogen atoms not included, 2423 unique data, 113 parameters, $R = 0.06$.

(*p*-MeC₆H₄CHMe₂)RuCl₂(PMePh₂): $M = 507.5$, monoclinic, $a = 19.08$, $b = 7.25$, $c = 22.31 \text{ \AA}$, $\beta = 133^\circ 1'$, $V_c = 2256.4 \text{ \AA}^3$, spacegroup $P2_1/c$, $D_m = 1.49$, $D_c = 1.49 \text{ g} \cdot \text{cm}^{-3}$, $z = 4$. Other experimental details are as above, except $\mu = 86.97 \text{ cm}^{-1}$, all non-hydrogen atoms isotropic, 2961 unique data, 109 parameters, $R = 0.07$. Correction for specimen absorption effects is in progress, and refinement of both structures is continuing. E.s.d.'s are virtually identical for both structures and average 0.003 \AA (Ru-Cl and Ru-P), 0.01 \AA (Ru-C, P-C and C-C), 0.08° (Cl-Ru-Cl and P-Ru-Cl), 0.35° (Ru-P-C), 0.45° (C-P-C) and 1° (C-C-C).

Salient stereochemical features of each molecule are shown in Figs. 1 and 2.

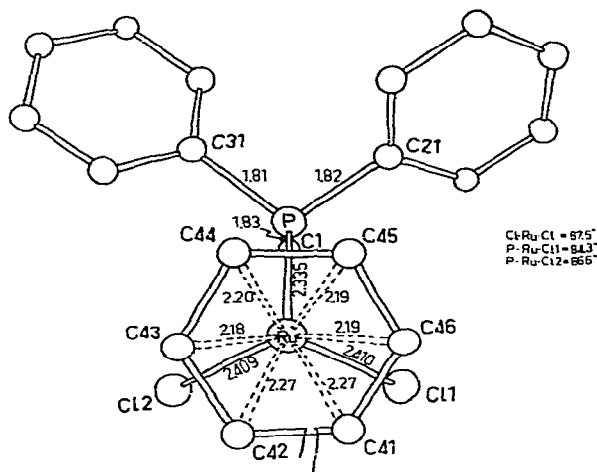


Fig.1. Stereochemistry of $C_6H_6RuCl_2(PMePh_2)$ viewed perpendicular to the arene plane.

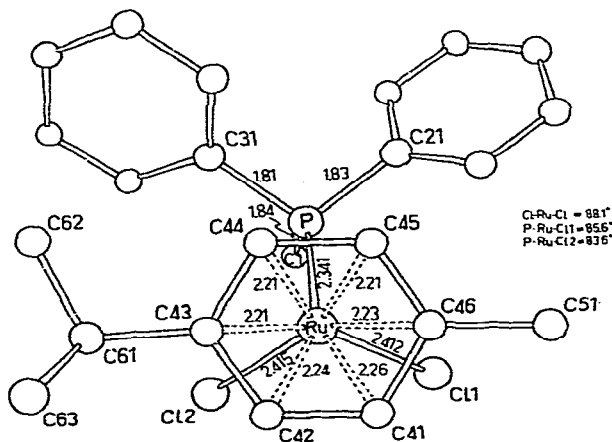


Fig.2. Stereochemistry of (*p*-MeC₆H₄CHMe₂)RuCl₂(PMePh₂) viewed perpendicular to the arene plane.

The molecules have a "piano-stool" structure like that of $C_6H_6Cr(CO)_3$ ⁴, in which the π -arene rings and the three other ligands are mutually staggered. The detailed agreement between stereochemical parameters of the two molecules is particularly satisfactory. Except for small differences in bond angles subtended at the metal atoms and in the dihedral angles defining the axial orientation of the π -arene rings (the angle between C_{36} -ring centre-Ru and ring centre-Ru-P is 31° and 35° in the benzene and *p*-cymene complexes respectively), corresponding bond distances and bond angles are uniformly equal within experimental error. Though small, the angular differences are statistically highly significant and probably reflect the differing steric requirements of the two arenes. The π -arene rings are slightly bent about C(43)-C(46), the associated ring dihedral angles being 5° (benzene) and 2° (*p*-cymene). The ruthenium-carbon distances occur as one set of four equivalent short bonds and one set of two equivalent long bonds (Figs. 1 and 2), the two long bonds in each case being *trans* to the tertiary phosphine. Much larger distortions of coordinated *tetrahapto* arenes have been observed in $h^5-C_5H_5Rh-h^4-C_6(CF_3)_6$ ⁵ and in $h^6-C_6Me_6Ru-h^4-C_6Me_6$ ⁶, but there are only two established examples of significantly distorted *hexahapto* arenes: $[PdAlCl_4C_6H_6]_2$ ⁷ and $Rh[P(OMe)_3]_2(PhBPh_3)$ ⁸. We suggest that the asymmetric metal-ring bonding in our two compounds is a consequence of the *trans* bond-weakening property of the tertiary phosphine *cf.* the asymmetric π -allyl metal bond in $PdCl(h^3-2\text{-methallyl})(PPh_3)$ ⁹. The fact that the rings are bent, and not merely tilted, implies significant localisation of the ring π -electrons. Surprisingly, the PMR spectra of the arene complexes give no indication of ring asymmetry. Thus, $C_6H_6RuCl_2(PMePh_2)$ and $C_6H_6RuCl_2[P(OMe)_3]$ in $CDCl_3$ at 34° show sharp doublets ($J(PH) = 0.8$ Hz) at τ 4.64 and τ 4.26 respectively. Spectra have been measured down to -100° for $C_6H_6RuCl_2[P(n-C_8H_{17})_3]$, and to -125° for $C_6Me_6RuCl_2[P(n-Bu)_3]$ and $1,3,5-C_6H_3Me_3RuCl_2[P(n-Bu)_3]^*$, but no evidence for inequivalence of the ring or methyl protons was observed.

Preliminary X-ray results for the non-stoichiometric complex $C_6H_6RuCl_{0.5}Br_{1.5}[P(n-Bu)_3]$ also indicate asymmetric metal-arene bonding, but in this case the ring and ligands adopt an eclipsed configuration. Owing to complex disordering effects, however, the absolute precision of the analysis is relatively unsatisfactory.

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