

Preparation and Characterization of Novel Tris- α -di-imino-complexes of Ruthenium(0) and Ruthenium(II). X-Ray Crystal and Molecular Structure of the Electron-rich Complex Tris-[1,2-bis-(*p*-methoxyphenyliminoethane)]ruthenium(0)-Toluene

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Summary The reaction between $[\text{RuH}_2(\text{PPh}_3)_4]$ or $[\text{RuH}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ and the α -di-imine dad [$(p\text{-Me-OC}_6\text{H}_4\text{N}=\text{CH})_2$] produces in high yield the black crystal-

line complex $[\text{Ru}(\text{dad})_3]^0$, a formally 20-electron derivative of ruthenium(0), the structure of which has been confirmed by an X-ray study; the complex is diamagnetic

in the solid state and is rapidly oxidized by molecular oxygen into $[\text{Ru}(\text{dad})_3]^{2+}$.

FOLLOWING our study on ruthenium-diazadiene complexes,¹ we were interested in preparing tris-ligand complexes, which are of current interest. We obtained a neutral tris- α -di-imino complex which can formally be considered as a 20-electron complex of ruthenium(0). Although some complexes of this kind are known {e.g. $[\text{Fe}(\text{bipy})_3]^0$,² $[\text{Co}(\text{bipy})_3]^+$; ⁴ bipy = 2,2'-bipyridyl}, the only ruthenium compound known of this type is the poorly characterized $[\text{Ru}(\text{bipy})_3]^0$.⁵ We report the X-ray crystal structure of $[\text{Ru}(\text{dad})_3]^0$ as well as its oxidation to give the dication $[\text{Ru}(\text{dad})_3]^{2+}$.

The reaction between $[\text{RuH}_2(\text{PPh}_3)_4]$ or $[\text{RuH}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]^6$ and dad [1,2-bis-(*p*-methoxyphenylimino)-ethane] in toluene (overnight; 80 °C) produces in good yield a black crystalline compound analysing satisfactorily for $[\text{Ru}(\text{dad})_3]\cdot\text{toluene}$ {yield from $[\text{RuH}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ 60% after crystallization from toluene-hexane}. Its i.r. spectrum is very similar to that of the free ligand and shows no evidence for hydride. Magnetic susceptibility measurements in the solid state (Faraday balance) or in solution (Evans' method) show that it is diamagnetic. Its ¹H n.m.r. spectrum in C₇D₈ at -80 °C [δ 3.2 (sharp s, OMe) and δ 7-8 (br. m, ArH + NH)] is consistent with these observations. However, at higher temperatures the phenyl resonances shift considerably, and the OMe singlet much less. The resonances due to the solvated toluene are not moved. (For example at room temperature the aromatic and imino peaks are observed at δ 10.3, 7.2, -0.7, and -17.) This paramagnetic behaviour seems to contradict the magnetic measurements. It is noteworthy that the analogous formally 20-electron complex $[\text{Fe}(\text{bipy})_3]^0$ is paramagnetic,³ so it is reasonable to assume for the ruthenium compound, having the same geometry and number of electrons, a temperature-dependent spin-free-spin-paired equilibrium. The population of the paramagnetic state would remain very small.

However, these results could also be explained by major changes in the structure and the mode of co-ordination of the ligand and since no structural data are available on these complexes we undertook an X-ray study at room temperature on a crystal obtained from toluene-light petroleum.

Crystal data: C₄₈H₄₈N₆O₆Ru.C₇H₈, triclinic, space group P $\bar{1}$, $a = 14.269(2)$, $b = 24.999(2)$, $c = 13.967(2)$ Å, $\alpha = 92.04(1)$, $\beta = 95.01(1)$, $\gamma = 104.3(1)^\circ$, $U = 4799.5$ Å³, $D_c = 1.38$ g cm⁻³, $Z = 4$. 7692 Independent reflections were measured with a four-circle diffractometer ($2 < \theta < 19^\circ$), of which 3867 had $I > 3\sigma(I)$ and were used in the refinement, to a current R value of 0.108. The high R value is believed to be due to the large number of parameters and to thermal agitation particularly of the heavy atoms and of the crystallization solvent. A low-temperature study in progress should solve this problem.†

The asymmetric unit is formed by two enantiomeric $[\text{Ru}(\text{dad})_3]$ moieties and two toluene molecules. One of the enantiomers is shown in the Figure. The geometry found resembles that² for $[\text{Ru}(\text{bipy})_3]^{2+}$ and in particular the three

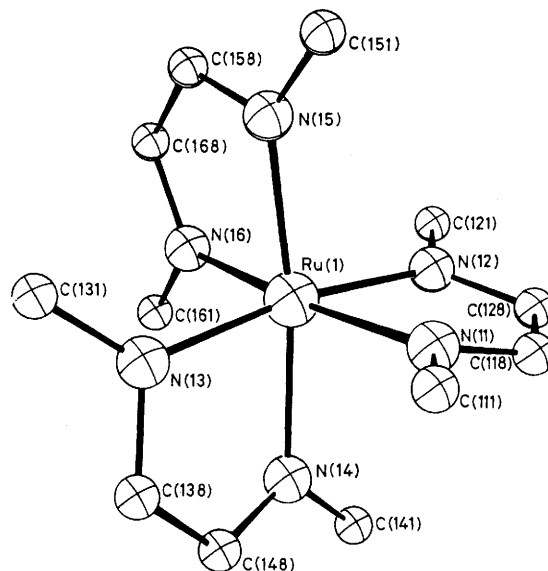


FIGURE. The structure of the central part of the $[\text{Ru}(\text{dad})_3]$ molecule. Only the carbon atoms of the aromatic rings which are directly bonded to the imino-nitrogen atoms are shown [atoms C(111)—C(161)].

ligands are equivalent. The six Ru-N(dad) bond lengths vary from 2.04 to 2.10 Å with an average of 2.06(3) Å. The dad ligand thus seems to be clearly σ -bonded to the ruthenium through the nitrogen atoms since the imino carbon atoms (average Ru-C 2.9 Å) are too far away to allow the C=N double bond to be involved in ligand-metal bonding. The N-Ru-N (dad) angles within each bidentate dad ligand are in the range 74.4—78.7° and can be considered as constant. The first carbon atoms of the aromatic rings and the nitrogen and imino carbon atoms lie in the same plane with a maximum deviation of 0.1 Å. The C=N bond lengths are in the range 1.28—1.38 Å [mean 1.34(5) Å] whereas the imino carbon-carbon bond lengths are in the range 1.33—1.45 Å [mean 1.37(5) Å]. These values do not appear to be significantly different from those for related systems [see, e.g.,⁷ $[\text{Ni}(\text{dad})_2]$].

The complex $[\text{Ru}(\text{dad})_3]^0$ does not react with H₂ or CO but is rapidly oxidized by CHCl₃, I₂, and HCl, as well as by molecular oxygen and even excess of diazadiene. The dication $[\text{Ru}(\text{dad})_3]^{2+}$ is produced quantitatively and is easily isolated as red crystals of the Cl⁻, BPh₄⁻, or PF₆⁻ salts, which have been fully characterized by i.r. and ¹H n.m.r. spectroscopy [δ (CD₂Cl₂) 8.55 (s, =NH), 6.75 (dd, ArH), and 3.85 (s, OMe); all peaks sharp; in the case of the BPh₄⁻ salt correct integration ratio of 3dad to 2BPh₄], conductivity [2:1 conductor in acetone (BPh₄⁻, PF₆⁻) and methanol (Cl⁻)], and microanalysis.

All these data show that $[\text{Ru}(\text{dad})_3]^0$ is a neutral formally 20-electron complex since, as shown by the room-temperature X-ray study, the structure of the ligand is not modified significantly and since it is rapidly oxidized into a well

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

characterized 18-electron ruthenium(II) dication. This is in agreement with the conclusion reached for $[\text{Fe}(\text{bipy})_3]^{0+}$ from e.s.r. results.³

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