

Aryldiazenido complexes of ruthenium(II) with tris(pyrazolyl)borate: A DFT study

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Abstract

Aryldiazenido complexes of ruthenium(II) with tris(1-pyrazolyl)borate as ancillary ligand of the kind $[\text{Ru}(\text{N}\equiv\text{NAr})(\text{Tp})\text{P}'\text{P}''](\text{BF}_4)_2$ [Tp = hydrotris(pyrazol-1-yl)borate; $\text{P}'\text{P}'' = (\text{PPh}_3)\{\text{P}(\text{OEt})_3\}$, $(\text{PPh}_3)\{\text{PPh}(\text{OEt})_2\}$, $\{\text{P}(\text{OEt})_3\}_2$; $\text{Ar} = \text{C}_6\text{H}_5$, $4\text{-CH}_3\text{C}_6\text{H}_4$] have recently been reported. The exceptionally high values of $\nu(\text{NN})$ stretching in infrared spectra indicate a near-linear $[\text{Ru}]\text{-N}\equiv\text{N-Ar}$ group. Further support to this hypothesis and information about the structural and electronic properties of these complexes were obtained by DFT B3LYP calculations.

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Interest in the chemistry of “diazo” complexes is due to its relationship with the intermediates of biological dinitrogen fixation and to research regarding new ways of obtaining derivatives of dinitrogen reduction. The chemistry of “diazo” compounds of transition metals has developed extensively in the last 30 years, with π -acceptors such as carbonyl, phosphines and cyclopentadienyl anions as ancillary ligands [1]. The first examples of “diazo” derivatives of the iron triad containing (pyrazolyl)borates as supporting ligands were dicationic aryldiazenido complexes of ruthenium(II) $[\text{Ru}(\text{N}\equiv\text{NAr})(\text{Tp})\text{P}'\text{P}''](\text{BF}_4)_2$ [Tp = hydrotris(pyrazol-1-yl)borate; $\text{P}'\text{P}'' = (\text{PPh}_3)\{\text{P}(\text{OEt})_3\}$, $(\text{PPh}_3)\{\text{PPh}(\text{OEt})_2\}$, $\{\text{P}(\text{OEt})_3\}_2$; $\text{Ar} = \text{C}_6\text{H}_5$, $4\text{-CH}_3\text{C}_6\text{H}_4$] [2]. “Single bent” aryldiazenido complexes usually exhibit an $\text{N}_1\text{-N}_2\text{-Ar}$ angle of about 120° and $\nu(\text{NN})$ stretching of about $1600\text{--}1800\text{ cm}^{-1}$ [3], but the exceptionally high values of $\nu(\text{NN})$ stretching (between 2073 and 2095 cm^{-1}) in the

infrared spectra of $[\text{Ru}(\text{N}\equiv\text{NAr})(\text{Tp})\text{P}'\text{P}''](\text{BF}_4)_2$ derivatives indicate a rare near-linear arrangement of the Ru-bonded ArN_2 ligand [4,5] (see Fig. 1).

This paper reports the results of DFT calculations on these compounds, which strongly support the above hypothesis. Geometrical optimization of the $[\text{Ru}(\text{N}\equiv\text{NPh})(\text{Tp})\text{P}'\text{P}'']^{2+}$ [$\text{P}'\text{P}'' = (\text{PPh}_3)\{\text{P}(\text{OEt})_3\}$ (**a**) and $\{\text{P}(\text{OEt})_3\}_2$ (**b**)] cations was performed applying restricted DFT B3LYP calculations with the SDD basis set. Initial refinement of the geometries was obtained with the restricted semi-empirical PM3 and DFT B3LYP/3-21G* calculations; atomic charges derived from Mulliken population analysis [6]. All calculations were carried out with computers equipped with Intel Pentium 4 Willamette processors operating at 1.8 GHz frequency; software were Gaussian 98 [7] and Spartan 02 [8].

Table 1 shows selected bond lengths and angles for compounds **a** and **b**. Calculated data are in agreement with quite linear $[\text{Ru}]\text{-N}\equiv\text{N-Ph}$ groups for both complexes, with the $\text{Ru-N}_1\text{-N}_2$ (α) angle between 173° and 178° and the $\text{N}_1\text{-N}_2\text{-Ph}$ (β) angle between 168° and 171° . $r(\text{N}_1\text{-N}_2)$ bond lengths fall between 1.1576 and

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Table 1
Selected angles and bond lengths calculated for complexes **a–b**

Complex	α Angle	β Angle	$r(\text{Ru}-\text{N}_1)$ (Å)	$r(\text{N}_1-\text{N}_2)$ (Å)
(a) $[\text{Ru}(\text{N}\equiv\text{NPh})(\text{Tp})(\text{PPh}_3)\{\text{P}(\text{OEt})_3\}]^{2+}$	172.871°	167.740°	1.8498	1.1635
(b) $[\text{Ru}(\text{N}\equiv\text{NPh})(\text{Tp})\{\text{P}(\text{OEt})_3\}_2]^{2+}$	178.212°	171.330°	1.8682	1.1576

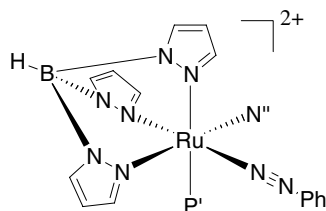


Fig. 1. Aryldiazenido complexes of Ru(II) with tris(pyrazolyl)borate.

1.1635 Å, only slightly longer than that obtained with DFT B3LYP/SDD calculations for the free diazonium cation $[\text{N}\equiv\text{NPh}]^+$ (1.1415 Å) and shorter than that near 1.25 Å observed in the majority of the “single bent” aryldiazenido complexes. $r(\text{Ru}-\text{N}_1)$ lengths indicate the relatively less strong interaction of the N_2Ph ligand with the metal centre [3].

Bond lengths are also similar to those obtained from X-ray structure of the dicationic $[\text{Ru}(\text{N}\equiv\text{NC}_6\text{H}_4\text{OMe})(\text{Cp})(\text{PPh}_3)_2]^{2+}$ compound [4], which has a quite linear $[\text{Ru}]-\text{N}\equiv\text{N}-\text{Ar}$ group ($\alpha = 175.4^\circ$, $\beta = 158.9^\circ$). In this complex, $r(\text{Ru}-\text{N}_1)$ is 1.8561 Å and $r(\text{N}_1-\text{N}_2)$ is 1.1463 Å (see Fig. 2).

The structure of the aryldiazenido fragment in complexes **a** and **b** does not significantly depend on the bulk of the other ligands, since in both complexes the smaller distance between the atoms of the aryldiazenido ligand and of the other ancillary ligands is about 3 Å. Also, the structure of the $[\text{Ru}(\text{N}\equiv\text{NPh})(\text{Tp})(\text{PPh}_3)\{\text{P}(\text{OEt})_3\}]^{2+}$ cation obtained from geometrical optimization with the constraint β angle = 120° does not show any particular interaction of the N_2Ph fragment with other parts of the molecule. As described by Sutton et al. [4], one explanation for the data in Table 1 comes from the π -acidity of aryldiazenido ligands; π back-donation from the metal centre weakens the N_1-N_2 bond and reduces the β angle but, because of the dicat-

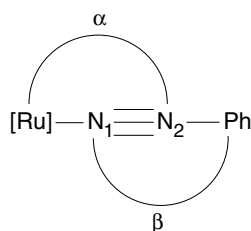


Fig. 2. α and β angles.

ionic charge of complexes like $[\text{Ru}(\text{N}\equiv\text{NPh})(\text{Tp})\text{P}'\text{P}''](\text{BF}_4)_2$ [1], $[\text{Ru}(\text{N}\equiv\text{NC}_6\text{H}_4\text{OMe})(\text{Cp}')(\text{PR}_3)_2](\text{BF}_4)_2$ [4] or $[\text{Ru}(\text{N}\equiv\text{NAr})(\text{Cl})(\text{bpy})_2](\text{PF}_6)_2$ [5], π back-donation from ruthenium to the aryldiazenido ligand is quite low and the $[\text{Ru}]-\text{N}\equiv\text{N}-\text{Ar}$ fragment is near-linear (see Fig. 3).

The dependency of bond lengths and angles on the nature of phosphine shown in Table 1 supports this hypothesis: the $[\text{Ru}]-\text{N}\equiv\text{N}-\text{Ph}$ group in complex **b** is more linear than in complex **a** and the bond lengths show that the interaction between ruthenium and aryldiazenido ligand is stronger for complex **a**, whereas the N_1-N_2 bond is shorter in complex **b**. Substitution of PPh_3 for the more π -acceptor $\text{P}(\text{OEt})_3$ still reduces back-donation to π^* orbitals of the aryldiazenido ligand, weakening the $\text{Ru}-\text{N}_1$ bond and increasing N_1-N_2 bond strength. The greater strength of the bond between the two nitrogen atoms in complex **b** is shown by the experimental $\nu(\text{NN})$ stretching frequency, which is 2079 cm^{-1} for $[\text{Ru}(\text{N}\equiv\text{NPh})(\text{Tp})(\text{PPh}_3)\{\text{P}(\text{OEt})_3\}]^{2+}$ (**a**) and 2087 cm^{-1} for $[\text{Ru}(\text{N}\equiv\text{NPh})(\text{Tp})\{\text{P}(\text{OEt})_3\}_2]^{2+}$ (**b**).

$[\text{Ru}(\text{N}\equiv\text{NAr})(\text{Tp})\text{P}'\text{P}'']^{2+}$ compounds easily react with hydride sources like $\text{Li}[\text{BHET}_3]$, leading to the formation of aryldiazene derivatives $[\text{Ru}(\text{NH}=\text{NAr})(\text{Tp})\text{P}'\text{P}'']^+$. Results show that the lowest unoccupied molecular orbital (LUMO) of aryldiazenido complexes

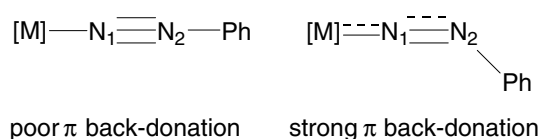


Fig. 3. π back-donation in aryldiazenido complexes.

Table 2
Selected Mulliken charges for complexes **a–b**

Complex	N_1 charge	N_2 charge
(a) $[\text{Ru}(\text{N}\equiv\text{NPh})(\text{Tp})(\text{PPh}_3)\{\text{P}(\text{OEt})_3\}]^{2+}$	-0.018	0.106
(b) $[\text{Ru}(\text{N}\equiv\text{NPh})(\text{Tp})\{\text{P}(\text{OEt})_3\}_2]^{2+}$	0.028	0.109

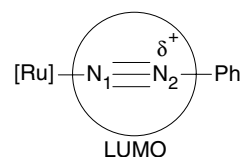


Fig. 4. Location of the LUMO.

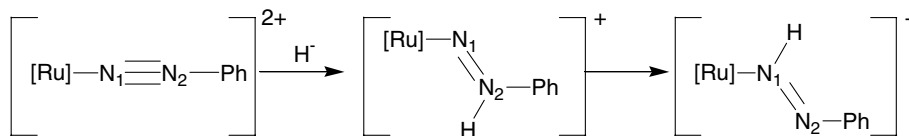


Fig. 5. Formation of aryldiazene derivatives from aryldiazenido complexes.

is concentrated on the nitrogen atoms of the $[\text{Ru}]-\text{N}\equiv\text{N}-\text{Ph}$ fragment, supporting the electrophilic nature of the aryldiazenido group. The dipolar moment vector is oriented approximately along the aryldiazenido group towards the metal centre, with values between about 4.8 and 6.9 Debye, so that electrostatic interaction favours the approach of negative-charged molecules to the aryldiazenido ligand. As shown in Table 2, the Mulliken charge is more positive on N_2 than on N_1 : values for N_1 fall between -0.018 and 0.028 , whereas the N_2 charge falls between 0.106 and 0.109 (see Fig. 4).

One explanation for both charge distribution and reactivity of $[\text{Ru}(\text{N}\equiv\text{NAr})(\text{Tp})\text{P}'\text{P}'']^{2+}$ complexes towards hydride sources is an initial attack of the hydride on the N_2 atom, followed by a proton shift from N_2 to N_1 , which leads to the final aryldiazene derivatives, as shown in Fig. 5. This hypothesis fits low-temperature NMR observations for the reaction between $[\text{Ru}(\text{N}\equiv\text{NC}_6\text{H}_4\text{OMe})(\text{Cp})(\text{PPh}_3)_2](\text{BF}_4)_2$ and NaBH_4 [4].

DFT B3LYP/6-311+G** calculations on $\text{NH}=\text{NPh}$ and $\text{N}=\text{NHPH}$ free molecules show that the former is thermodynamically more stable, its total energy being 22 kcal/mol lower than that of $\text{N}=\text{NHPH}$. This energy difference fits the proton shift shown in Fig. 5.

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