

## Monodentate behaviour of 2,2'-bipyridine and 1,10-phenanthroline in cyclometallated rhodium(III) complexes – $^1\text{H}$ and $^{13}\text{C}$ NMR evidence

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Binuclear cyclometallated complex (I)  $[\text{RhCl}(\text{mCl})(\text{bBzIH}_2\text{bz})]_2$  [ $\text{bBzIH}_2\text{bzH} = 1,3\text{-bis}(\text{benzimidazolyl})\text{benzene}$ ] undergoes dichlorobridge cleavage reaction with monodentate ligands to produce mononuclear and heterocycle bridged binuclear complexes of the types  $\text{RhCl}(\text{bBzIH}_2\text{bz})(\text{OCIO}_3)(\text{L}/\text{N-N})$  ( $\text{L} = \text{AsPh}_3$ ;  $\text{N-N} = 2,2'$ -bipyridine (bipy) or 1,10-phenanthroline (phen)) and  $[\text{RhCl}_2(\text{bBzIH}_2\text{bz})]_2(\text{mN-N})$  ( $\text{N-N} = \text{pyrazine}$  or 4,4'-bipyridine), respectively. In the former complex (II), the bidentate chelating N-heterocycles show a monodentate coordination as evidenced by 2-D  $^1\text{H}$ - $^1\text{H}$  correlated and NOE experiments (DQF-COSY and ROESY),  $^1\text{H}$ - $^{13}\text{C}$  single- and multiple-bond correlated 2-D NMR experiments (PFG-HSQC and PFG-HMBC) and  $^1\text{H}$ ,  $^{13}\text{C}$  spin lattice relaxation time measurements. The non-coordination of the pendant nitrogen of the heterocycle, bipy or phen is evidenced by the observation of two sets of signals together with the presence of interligand NOEs only between the coordinated part of the heterocycle and the *bis*benzimidazole as seen in the corresponding ROESY spectrum. Further, the  $^1\text{H}$  and  $^{13}\text{C}$  spin lattice relaxation times are lower for the nuclei in the coordinated part of the heterocycle, bipy or phen than those for the uncoordinated part supporting the fact that only one of the two nitrogens of the heterocycle is coordinated to the metal.

