



The formation of dinuclear trichloro-bridged and mononuclear ruthenium complexes from the reactions of dichlorotris(*p*-tolylphosphine)ruthenium(II) with diazabutadiene ligands

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Abstract

Ru(II) complexes with diazabutadiene (R-DAB) ligands have been prepared. The reaction of $\text{RuCl}_2 \cdot n\text{H}_2\text{O}$ with $\text{P}(p\text{-tolyl})_3$ gave a $[\text{RuCl}_2\{\text{P}(p\text{-tolyl})_3\}]$ precursor, whose reactions with R-DAB in toluene gave dinuclear trichloro-bridged Ru(II) complexes $[\text{Ru}_2\text{Cl}_3(\text{P}(p\text{-tolyl})_3)_2(\text{R-DAB})_2](\text{BF}_4)$ which have been characterized by spectroscopic methods. In addition, one of the complexes was characterized using X-ray crystallography. Meanwhile, two mononuclear Ru(II) complexes $[\text{RuCl}_2(\text{P}(p\text{-tolyl})_3)_2(\text{R-DAB})]$ were obtained from the reactions of the $[\text{RuCl}_2\{\text{P}(p\text{-tolyl})_3\}]$ precursor with R-DAB ligands in THF. The two *trans*-mononuclear complexes were characterized by X-ray crystallography and solid-state ^{31}P NMR. A temperature-dependent ^{31}P NMR study was carried out to monitor the formation of dinuclear and mononuclear complexes.

Introduction

A number of derivatives of 1,4-diaza-1,3-butadiene, also known as diazabutadiene (R-DAB), and their complexes have been reported in the past decades [1–6]. Coordination between the R-DAB ligand and metal centre generally occurs through the two nitrogen atoms of the imine groups, giving complexes with five-membered chelate rings [1, 7]. Such five-membered chelate ring ruthenium complexes have drawn significant attention in view of the remarkable photophysical properties of ruthenium bipyridine (bpy) complexes [8–12]. However, compared with ruthenium bpy complexes, the synthesis of ruthenium R-DAB complexes is much less documented. This can in part be attributed to the formation of dinuclear ruthenium complexes instead of the mononuclear analogues. Although several dinuclear ruthenium R-DAB complexes were reported in the 1980s and 1990s,

[4, 13–16], mononuclear ruthenium R-DAB complexes are more rare. In 1980, Chaudret and Poilblanc [13] reported the formation of dinuclear ruthenium R-DAB complexes with three proposed structures; but they could not identify the exact structures of these complexes. In 2014, Ghosh and co-workers reported mononuclear ruthenium R-DAB complexes obtained from the reaction between the precursor complex dichlorotris[tri(*p*-tolyl)phosphine] ruthenium(II), $[\text{RuCl}_2\{\text{P}(p\text{-tolyl})_3\}_3]$ and R-DAB ligands [17]. Surprisingly, although we used similar methodology to that reported by Ghosh et al. in our own subsequent studies, the ruthenium R-DAB complexes obtained were dinuclear analogues rather than the mononuclear molecules. This has drawn our interest to further investigate the formation of dinuclear as well as mononuclear ruthenium R-DAB complexes by using the R-DAB ligands as shown in Scheme 1. In addition, a ^{31}P NMR temperature-dependent study has been carried out in order to gain insight into the formation of dinuclear versus mononuclear complexes. The outcome of these experiments is presented herein.

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