Abstract

Among several nitrogen donor ligands, pyrazole moiety-containing ligands have attracted tremendous importance owing to the presence of both the nucleophilic nitrogen atom and the hydrogen bonding NH group. As a result, very interestingly, a variety of pyrazole-based ligands have been used to synthesize numerous multinuclear transition and rare earth metal complexes using simple synthetic procedures. Moreover, the electronic and steric properties of pyrazole-derived ligands are readily tuned by the variation of the nature of alkyl and aryl groups attached to the pyrazole ring. Both the neutral pyrazole and anionic pyrazolate ligands are well known for their versatile coordination behaviors. Pyrazole ligands built from pyridine or imidazole rings are enormous, whereas those with a pyrrole ring are rarely reported. This study has focused on the synthesis of new pyrrole-bridged pyrazole ligands bearing group 11 metal complexes and their catalytic applications.

The new ligand 2-(3,5-dimethylpyrazolylmethyl)-5-(phenylthiomethyl)pyrrole **L1** was synthesized in multisteps starting from pyrrole. The oxidation of **L1** gave 2-(3,5-dimethylpyrazolylmethyl)-5-(phenylsulfonylmethyl)pyrrole **L2**. The equimolar reaction of **L1** with copper(I) halides afforded the binuclear complexes: $[\mathrm{Cu}(\mu\text{-X})(\mu\text{-}\mathbf{L1}\text{-}\kappa^2\text{-}S,N)]_2$ (X = Cl, Br and I) in high yields. The analogous reaction of **L2** with copper(I) halides gave the three coordinate complexes: $[\mathrm{Cu}(\mu\text{-Cl})(\mathbf{L2}\text{-}\kappa^1\text{-}N)]_2$ and $[\mathrm{CuX}(\mathbf{L2}\text{-}\kappa^1\text{-}N)_2]$, X = Br and I. An ionic complex $[\mathrm{Cu}(\mathbf{L2}\text{-}\kappa^1\text{-}N)_2]\mathrm{PF_6}^-$ was isolated when the reaction was carried out in the presence of $\mathrm{KPF_6}$. Its $\mathrm{BF_4}^-$ analogue was obtained by the reaction of three coordinate chloro-bridged dimer with $\mathrm{AgBF_4}$. All complexes were structurally characterized.

The 2:1 mole ratio reaction between **L2** and $\mathrm{AgBF_4}$ afforded the mononuclear complex $[\mathrm{Ag}(\mathbf{L2})_2]\mathrm{BF_4}$. Conversely, the equimolar reaction of **L2** with $\mathrm{AgOCOCF_3}$ resulted in the formation of 1D polymeric structure $[\mathrm{Ag}(\mu\text{-}\mathbf{L2})(\mu\text{-CF_3COO})]_n$. The sulfate ion encapsulated three-coordinate complex $[\mathrm{Ag}(\mathbf{L2})_3]_2\mathrm{SO_4}$ was obtained by the 3:1 mole ratio reaction of **L2** with $\mathrm{Ag_2SO_4}$. When $\mathrm{Ag_2SO_4}$ was treated with 3,5-dimethylpyrazole, the metal-metal bonded dimer $[\mathrm{Ag_2(3,5\text{-}dimethylpyrazole)_4}(\mu\text{-SO_4})]$ was obtained. Interestingly, it exhibits a fluxional property in solution and was studied by the VT NMR method.

These copper(I) complexes catalyzed the hydroamination-alkynylation reaction between several secondary amines and alkyl and aryl terminal alkynes. Using 1 mol% of complexes as catalysts, both tri- and tetrasubstituted propargylamines were isolated. Alternatively, phenylacetylene and different secondary amines afforded the corresponding trisubstituted propargylamines as the major products, and alkyl terminal alkynes gave the tetrasubstituted products in excellent yields. In addition, the role of counter anions such as TfO^-, $\mathrm{PF_6}^-$, $\mathrm{BF_4}^-$, $\mathrm{PO_4}^{3-}$ and $\mathrm{Ph_4B}^-$ on the product selectivity was studied. When fluorinated anions such as TfO^-, $\mathrm{PF_6}^-$, and $\mathrm{BF_4}^-$ were present with the copper complexes, the hydroamination-hydrovinylation product 1-aminodiene was observed, which was not formed with $\mathrm{PO_4}^{3-}$, $\mathrm{Ph_4B}^-$ or halide ions. Specifically, the TfO^- and $\mathrm{PF_6}^-$ favored the formation of diene, while $\mathrm{BF_4}^-$ favored the tetrasubstituted product as the major product. This was further supported by the isolated copper(I) complexes containing $\mathrm{PF_6}^-$ and $\mathrm{BF_4}^-$ and by other specific reactions. The peaks for enamines and $[\mathbf{L}\mathrm{Cu}]^+$ species in the HRMS spectra of the reaction mixtures and the isolation of the morpholinium copper(I) salt support the proposed mechanism.