Structural Variations in Tetrasilver(I) Complexes of Pyrazolate-bridged Compartmental *N*-Heterocyclic Carbene Ligands

Maria Georgiou, Simone Wöckel, Vera Konstanzer, Sebastian Dechert, Michael John, and Franc Meyer

Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstraße 4, 37077 Göttingen, Germany

Reprint requests to Prof. Dr. Franc Meyer. Fax: +49551393063.
E-mail: franc.meyer@chemie.uni-goettingen.de

Z. Naturforsch. **2009**, *64b,* 1542 – 1552; received October 13, 2009

Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

A set of pyrazole-bridged bis(imidazolium) compounds $[H_3\mathbf{L^1}]X_2$ – $[H_3\mathbf{L^4}]X_2$ ($\mathbf{L^1}$ = 3,5-bis[1-(*tert*-butyl)imidazolium-1-ylmethyl]-1*H*-pyrazole; $\mathbf{L^2}$ = 3,5-bis[1-(*tert*-butyl)imidazolium-1-ylmethyl]-4-phenyl-1*H*-pyrazole; $\mathbf{L^3}$ = 3,5-bis[1-(1-adamantyl)imidazolium-1-ylmethyl]-1*H*-pyrazole; $\mathbf{L^4}$ = 3,5-bis[1-(1-adamantyl)imidazolium-1-ylmethyl]-4-phenyl-1*H*-pyrazole; X = Cl^-, BF_4^- or PF_6^-) has been prepared, and three compounds have been characterized by X-ray crystallography. The unique $[H_3\mathbf{L^4}][H_2\mathbf{L^4}](PF_6)_3$ features a dimeric face-to-face arrangement of two molecules due to the involvement of both the pyrazole-NH and the imidazolium C^2H in hydrogen bonding. $[H_3\mathbf{L^1}]X_2$ – $[H_3\mathbf{L^4}]X_2$ serve as precursors for silver(I) complexes with compartmental pyrazolate-bridged bis(NHC) ligands. The complexes have been readily prepared by the Ag_2O route and feature either the known $[(\mathbf{L^{1-4}})_2Ag_4]^{2+}$ or the new $[(H_2\mathbf{L^1})_4Ag_4]^{8+}$ motif, depending on the solvent for the reaction (MeCN or acetone). $[(H_2\mathbf{L^1})_4Ag_4](PF_6)_8$ contains a central $(pzAg)_4$ ring with pendant imidazolium side arms. Upon further reaction with Ag_2O in MeCN it was found to undergo transformation to the corresponding $[(\mathbf{L^1})_2Ag_4](PF_6)_2$. All complexes have been thoroughly studied by NMR spectroscopy in solution, and preliminary luminescence data of $[(H_2\mathbf{L^1})_4Ag_4](PF_6)_8$ have been recorded.

Key words: N-Heterocyclic Carbenes (NHC), Pyrazole, Silver, Oligonuclear Complexes