

Abstract

A new type of pyrrole-based NNN-pincer ligand, 2,5-bis(3,5-dimethylpyrazol-1-ylmethyl)pyrrole, **3** was readily synthesized in two steps from pyrrole and structurally characterized. The lithiation reaction of **3** with *n*-BuLi yielded the dimeric Li complex $[\text{Li}\{\mu\text{-C}_4\text{H}_2\text{N-2,5-(CH}_2\text{Me}_2\text{pz)}_2\text{-N,N,N}\}]_2$. The reactions of **3** with Pd(II) precursors afforded the mononuclear Pd(II) complexes, $[\text{PdX}\{\text{C}_4\text{H}_2\text{N-2,5-(CH}_2\text{Me}_2\text{pz)}_2\text{-N,N,N}\}]$ (X = OAc, **4** and Cl, **6**) and the helical binuclear Pd(II) complex, $[\text{Pd}_2\text{Cl}_4\{\mu\text{-C}_4\text{H}_3\text{N-2,5-(CH}_2\text{Me}_2\text{pz)}_2\text{-N,N}\}]_2$. Complexes **4** and **6** exhibit fluxional behaviors and were studied by variable temperature NMR method. Complex **4** was found to be an excellent catalyst for the Suzuki coupling reaction in water yielding products with excellent turnover numbers; TON of 2×10^6 was obtained for 4-bromoacetophenone. This complex also catalyzed the copper-free Sonogashira coupling reactions in water. The DDQ oxidation reaction of the **3** afforded novel compounds- 2,5-bis(3,5-dimethylpyrazolylcarbonyl)pyrrole **8**, 5-{bis-(3,5-dimethylpyrazolyl)methyl}pyrrole-2-carbaldehyde **9**, 2,5-bis[bis-(3,5-dimethylpyrazolyl)methene]pyrrole **12**. Compound **12** is fluorescent and readily reacts with O₂ only under sunlight irradiation to give oxidized compounds **8**, 2-(3,5-dimethylpyrazolylcarbonyl)-5-(3,5-dimethylpyrazolyl)pyrrole **13** and bis-(3,5-dimethylpyrazolyl)methanone **14**. The reaction of **12** with $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$ gave a bis-chelate complex, $[\text{Pd}_2\text{Cl}_4\{\mu\text{-C}_4\text{H}_3\text{N-2,5-(C}(\text{Me}_2\text{pz)}_2\text{-N,N,N,N)\}]$.

A new type of pyrrole-based polydentate ligand 2,3,4,5-tetrakis(3,5-dimethylpyrazol-1-ylmethyl)pyrrole, **17** was synthesized from the double Mannich base of pyrrole. The novel polydentate ligand **17** gave the mononuclear Pd(II) complexes, $[\text{PdX}\{\text{C}_4\text{N-2,3,4,5-(CH}_2\text{Me}_2\text{pz)}_4\text{-N,N,N}\}]$ (X = OAc, and Cl) and the binuclear Pd(II) complex, $[\text{Pd}_2\text{Cl}_4\{\mu\text{-C}_4\text{HN-2,3,4,5-(CH}_2\text{Me}_2\text{pz)}_4\text{-N,N,N,N}\}]$. On the contrary, when CuX was treated with **17**, the ionic binuclear Cu(I) complexes, $[\text{Cu}_2(\mu\text{-X})\{\text{C}_4\text{HN-2,3,4,5-(CH}_2\text{Me}_2\text{pz)}_4\text{-N,N,N,N}\}]^+[\text{CuX}_2]^-$ (X = Cl, and I) were isolated. Further, another ionic binuclear three-coordinate Ag(I) complex, $[\text{Ag}_2\{\mu\text{-C}_4\text{HN-2,3,4,5-(CH}_2\text{Me}_2\text{pz)}_4\text{-N,N,N,N}\}(\text{CH}_3\text{CN})_2]^+[\text{BF}_4^-]_2$, analogous to the Pd(II) complex, was isolated yield from the reaction between **17** and AgBF₄. The treatment of 2,6-bis[(dimethylamino)methyl]-4-methylphenol with $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$ or $[\text{Pd}(\text{OAc})_2]$ gave the mononuclear Pd(II)

complexes, $[\text{PdCl}_2(\text{OC}_6\text{H}_2(\text{CH}_2\text{NMe}_2)\text{-2-Me-4-(CH}_2\text{NHMe}_2)\text{-6-O,N)]$ and
 $[\text{Pd}(\text{OC}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-2,6-Me-4-O,N})_2]$, respectively.