Gold(I) Complexes Bearing P∩N-Ligands: An Unprecedented Twelve-membered Ring Structure Stabilized by Aurophilic Interactions

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\textit{Dedicated to Professor Hubert Schmidbaur on the occasion of his 75\textsuperscript{th} birthday}

The P∩N-ligands Ph\textsubscript{2}Pqn, \textbf{1}, Ph\textsubscript{2}Piqn, \textbf{2}, Ph\textsubscript{2}Ppym, \textbf{3}, and the As∩N-ligands Ph\textsubscript{2}Asqn, \textbf{4}, Ph\textsubscript{2}Asiqn, \textbf{5}, (Ph = phenyl, qn = 8-quinoline, iqn = 1-isoquinoline, pym = 2-pyrimidine) have been synthesized, the ligands \textbf{2} and \textbf{5} for the first time. Their ligand properties were probed by the synthesis of gold(I) complexes. Reaction with (tht)AuCl (tht = tetrahydrothiophene) yielded the chloro-gold complexes Ph\textsubscript{2}RP–Au–Cl (R = qn, \textbf{6}; iqn, \textbf{7}; pym, \textbf{8}) and Ph\textsubscript{2}RAs–Au–Cl (R = qn, \textbf{9}; iqn, \textbf{10}) in high yields. Further treatment of \textbf{7} and \textbf{8} with one equivalent of AgBF\textsubscript{4} provided the complexes [(Ph\textsubscript{2}Piqn)Au]BF\textsubscript{4}, \textbf{11}, [(Ph\textsubscript{2}Ppym)Au]BF\textsubscript{4}, \textbf{12}, and [(Ph\textsubscript{2}Piqn)Au(tht)]BF\textsubscript{4}, \textbf{14}. For comparison, the previously reported complex [(Ph\textsubscript{2}Ppy)Au]BF\textsubscript{4} (py = pyridine), \textbf{13}, was re-investigated. The compounds were characterized by elemental analyses, mass spectrometry and NMR spectroscopy. In addition, the solid-state structures of \textbf{2}, \textbf{3}, \textbf{6}, \textbf{7}–\textbf{14} have been determined by X-ray crystallography.

The chloro-gold compounds crystallize in the common rod-like structure known from R\textsubscript{3}EAuCl (R = aryl, E = P, As) complexes without further aggregation \textit{via} aurophilic interactions. In all cases the phosphine acts as a monodentate ligand. In the solid state compounds \textbf{11}–\textbf{13} feature an unprecedented cyclic trinuclear aggregation pattern, in which the Au(I) atoms are linearly coordinated by the bridging phosphine ligands forming a cyclic (P–Au–N)\textsubscript{3} arrangement. The resulting twelve-membered ring is further stabilized by Au···Au interactions. Due to the presence of these Au···Au contacts, \textbf{11}–\textbf{13} are emissive in the solid state but not in solution.

\textit{Key words:} Gold(I) Complexes, Phosphines, Arsines, P∩N Ligands, Luminescence, Aurophilic Interactions