

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

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Z. Naturforsch. **2009**, *64b*, 1513 – 1524; received June 23, 2009

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

The P \cap N-ligands Ph₂Pqn, **1**, Ph₂Piqn, **2**, Ph₂Ppym, **3**, and the As \cap N-ligands Ph₂Asqn, **4**, Ph₂Asiqn, **5**, (Ph = phenyl, qn = 8-quinoline, iqn = 1-isoquinoline, pym = 2-pyrimidine) have been synthesized, the ligands **2** and **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 Ph₂RP–Au–Cl (R = qn, **6**; iqn, **7**; pym, **8**) and Ph₂RAs–Au–Cl (R = qn, **9**; iqn, **10**) in high yields. Further treatment of **7** and **8** with one equivalent of AgBF₄ provided the complexes [(Ph₂Piqn)Au]BF₄, **11**, [(Ph₂Ppym)Au]BF₄, **12**, and [(Ph₂Piqn)Au(tht)]BF₄, **14**. For comparison, the previously reported complex [(Ph₂Ppy)Au]BF₄ (py = pyridine), **13**, was re-investigated. The compounds were characterized by elemental analyses, mass spectrometry and NMR spectroscopy. In addition, the solid-state structures of **2**, **3**, **6**, **7**, **9**–**14** have been determined by X-ray crystallography.

The chloro-gold compounds crystallize in the common rod-like structure known from R₃EAuCl (R = aryl, E = P, As) complexes without further aggregation *via* auophilic interactions. In all cases the phosphine acts as a monodentate ligand. In the solid state compounds **11**–**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)₃ arrangement. The resulting twelve-membered ring is further stabilized by Au ··· Au interactions. Due to the presence of these Au ··· Au contacts, **11**–**13** are emissive in the solid state but not in solution.

Key words: Gold(I) Complexes, Phosphines, Arsines, P \cap N Ligands, Luminescence, Auophilic Interactions