

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

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The P $\cap$ N-ligands Ph<sub>2</sub>Pqn, **1**, Ph<sub>2</sub>Piqn, **2**, Ph<sub>2</sub>Ppym, **3**, and the As $\cap$ N-ligands Ph<sub>2</sub>Asqn, **4**, Ph<sub>2</sub>Asiqn, **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 Ph<sub>2</sub>RP–Au–Cl (R = qn, **6**; iqn, **7**; pym, **8**) and Ph<sub>2</sub>RAs–Au–Cl (R = qn, **9**; iqn, **10**) in high yields. Further treatment of **7** and **8** with one equivalent of AgBF<sub>4</sub> provided the complexes [(Ph<sub>2</sub>Piqn)Au]BF<sub>4</sub>, **11**, [(Ph<sub>2</sub>Ppym)Au]BF<sub>4</sub>, **12**, and [(Ph<sub>2</sub>Piqn)Au(tht)]BF<sub>4</sub>, **14**. For comparison, the previously reported complex [(Ph<sub>2</sub>Ppy)Au]BF<sub>4</sub> (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 R<sub>3</sub>EAuCl (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)<sub>3</sub> arrangement. The resulting twelve-membered ring is further stabilized by Au $\cdots$ Au interactions. Due to the presence of these Au $\cdots$ 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