

Bis-phosphonio-isophosphindolide Copper Complexes

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Bis-triphenylphosphonio-isophosphindolide salts **1**[X] react with Cu(I)-halides CuX to give isolable products of composition [(**1**)Cu₂X₃]. X-ray crystal structure analyses confirmed that for X = Br, Cl dinuclear complexes [(μ -**1**)(μ -X)Cu₂X₂] with $\mu_2, \eta^1(\text{P})$ -bridging cations **1** are formed, while for X = I a solid phase containing a salt (**1**)₂[Cu₄I₆] and a complex [(**1**)₂Cu₄I₆] with a terminal $\eta^1(\text{P})$ -coordinated ligand **1** was obtained. The bonding parameters in the two types of complexes suggest that **1** is a hybrid between a phosphonium cation and a phospholide anion whose π -system is less nucleophilic than the phosphorus lone-pair. ³¹P NMR studies revealed that in solution in all cases binuclear complexes [(**1**)Cu₂X₃] are in dynamic equilibrium with small amounts of mononuclear species and free **1**. The same equilibria were detected in the system **1**[OTf]/CuOTf. NMR studies of ligand exchange reactions indicated that the stability of complexes [(**1**)Cu₂X₃] increases in the order X = OTf < I < Br, Cl, and titration of [(**1**)Cu₂Br₃] with Et₄NBr allowed to determine the equilibrium constant of the complex formation reaction.