Binuclear Ten-Membered Ring Cyclometallated Complexes of Digold(I) and their Reactions with Iodine and Bromine

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The cyclometallated digold(I) complexes $[Au_2(\mu\text{-}2\text{-}C_6H_4CH_2PPh_2)_2]$ (**10**) and $[Au_2(\mu\text{-}2\text{-}CH_2C_6H_4PPh_2)_2]$ (**11**) have been synthesized by the reaction of $Li[2\text{-}C_6H_4CH_2PPh_2]$ and $Li[2\text{-}CH_2C_6H_4PPh_2]$, respectively, with $[AuBr(PEt_3)]$. A single crystal X-ray structure analysis of **10** shows the linearly coordinated gold(I) atoms to be separated by 3.0035(9) Å in a puckered ten-membered ring. Both complexes add one mol equivalent of iodine to form initially gold(I)-gold(III) complexes $[Au(\mu\text{-}2\text{-}C_6H_4CH_2PPh_2)_2AuI_2]$ (**14a**) and $[Au(\mu\text{-}2\text{-}CH_2C_6H_4PPh_2)_2AuI_2]$ (**17**), which isomerize to the corresponding salts $[Au(\kappa^2\text{-}P,C\text{-}C_6H_4CH_2PPh_2)_2][AuI_2]$ (**13a**) and $[Au(\kappa^2\text{-}P,C\text{-}CH_2C_6H_4PPh_2)_2][AuI_2]$ (**16**). In **13a** the gold(III) cation is planar coordinated by a pair of chelate P-C donor ligands, the phosphorus and carbon atoms being, separately, mutually *cis*, as shown by X-ray structural analysis. From the reaction of **10** with 2 mol equivalents of bromine, the neutral chelate complex $[AuBr_2(\kappa^2\text{-}P,C\text{-}C_6H_4CH_2PPh_2)]$ (**15**) has been isolated and structurally characterized.

Key words: Gold(I), Cyclometallated Complexes, Phosphine Complexes