

Metallocyclo- and polyphosphazenes containing gold or silver: Thermolytic transformation into nanostructured materials

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A cyclotriphosphazene bearing two 4-oxypyridine groups on the same phosphorus atom, gem-[N₃P₃(O₂C₁₂H₈)₂(OC₅H₄N-4)₂] (I), and its analogous polymer [[NP-(O₂C₁₂H₈)UNP(OC₅H₄NM)₂]_{0.3}]_n (II), have been used to prepare gold or silver, cyclic and polymeric, metallo-phosphazenes. The following complexes, gem-[N₃P₃(O₂C₁₂H₈)₂(OC₅H₄N₄(ML))₂] (ML = Au(C₆F₅) (1) or Au(C₆F₅)₃ (2)), [N₃P₃(O₂C₁₂H₈)₂(OC₅H₄N₄[AuPPh₃))]₂] [NO₃], (3), and [N₃P₃-(O₂C₁₂H₈)₂(OC₃H₄N-4{AgPPh₂R})₂][SO₃CF₃]₂ (R = Ph (4) or Me (5)) have been obtained. Complexes 1 and 4 are excellent models for the preparation of the analogous polymers [(NP(O₂C₁₂H₈))_{0.7}{NP(OC₅H₄N-4{ML})₂]_{0.3}]_n (ML = Au(C₆F₅) (P1), Ag(OSO₂CF₃)PPh₃ (P2)). All complexes have been characterized by elemental analysis, various spectroscopic methods, and mass spectrometry. The polymers were further investigated by thermochemical methods (thermogravimetric analysis) and differential scanning calorimetry. For compounds 1-5 and for the starting phosphazene I,