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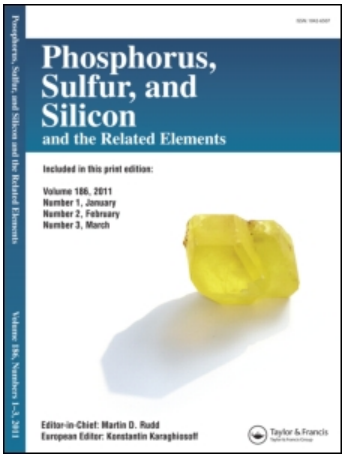

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Formation of Spherical Giant Molecules and Dynamic Behaviour of Supramolecular Assemblies Based on P_{n}-Ligand Complexes

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Formation of Spherical Giant Molecules and Dynamic Behaviour of Supramolecular Assemblies Based on P_n-Ligand Complexes

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We report herein on our concept of using E_n-ligand complexes ($E = P$, As) as linking units for the creation of novel supramolecular ensembles. The reaction of these complexes with Group 11 metal salts of coordinating anions leads to the formation of insoluble oligomers, 1D and 2D polymers as well as soluble spherical nanoscaled clusters. In contrast, the reaction of E_n-ligand complexes with Group 11 metal salts of weakly coordinating anions yields soluble oligomers and polymers, which display monomer-oligomer equilibria in solution.

Keywords Arsenic; group 11 metals; iron; molybdenum; phosphorus; supramolecular chemistry

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INTRODUCTION

In contrast to common approaches in supramolecular chemistry, which make almost exclusive use of N-, O- and/or S-containing organic linkers to connect different metal centres, we employ organometallic E_n-ligand complexes (E = P, As) as connecting moieties. We have already succeeded in isolating several oligomers,[1,2] one-dimensional (1D)[1,3]and two-dimensional (2D) polymers,[3a] and even soluble spherical fullerene-like aggregates[4] by using the complexes **I–IV** (Scheme 1) as starting materials.

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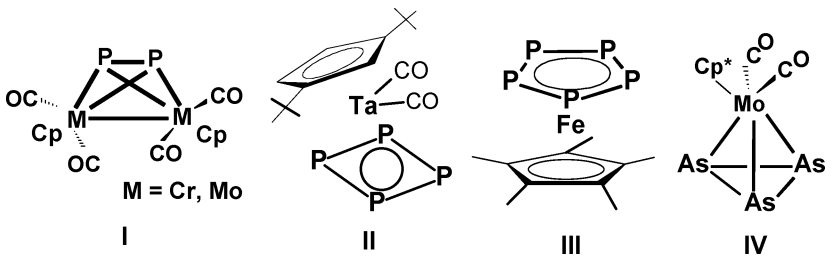

SCHEME 1

RESULTS AND DISCUSSION

Based on the results obtained so far in our group regarding the properties of the isolated supramolecular compounds, this field may be subdivided into two categories:

1) The reaction of E_n-ligand complexes with transition metal compounds possessing a coordinating terminal ligand, such as halogenides or nitrate. Here, insoluble 1D- or 2D-coordination polymers are obtained. Under specific stoichiometric and dilution conditions, the formation of soluble nanoscaled clusters is observed.
   Examples of the mentioned 1D-polymers are the complexes $[Cu(\mu\text{-}X)\{Cp_2Mo_2(CO)_4(\mu,\eta^2{:}\eta^1{:}\eta^1\text{-}P_2)\}]_n$ (X = Cl (**1a**), Br (**1b**), **I** (**1c**)), which are formed quantitatively by the reaction of I (M = Mo) with copper(I) halides.[1] This series of polymers has been characterized by X-ray crystallography (Figure 1) and shows unique ^{31}P MAS NMR spectroscopic features.[3b]

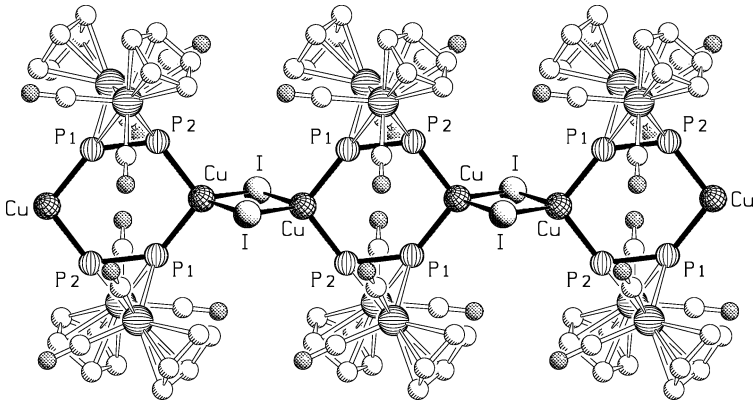

FIGURE 1 Section of the 1D polymeric structure of **1c**.

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By carefully controlling reactant stoichiometry and dilution, the soluble spherical fullerene-like nano-clusters $[\{Cp^xFe(\eta^5{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}P_5)\}_{12}\{CuX\}_{10}\{Cu_2X_3\}_5\{Cu(CH_3CN)_2\}_5]$ ($X = Cl$, $Cp^x = Cp^*$ (**2a**); $X = Br$, $Cp^x = \eta^5\text{-}C_5Me_5$ (**2b**), $\eta^5\text{-}C_5Me_4Et$ (**2c**)[4a,b] are formed from **III** and CuX. In a similar manner **II** reacts with CuCl to form the large spherical cluster $[\{Cp''Ta(CO)_2(\eta^4{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}P_4)\}_6\{CuCl\}_8]$ **3**.[4c]

2) The reaction of E_n-ligand complexes with metal cations, possessing weakly coordinating anions (WCAs) like BF_4^- or PF_6^- as counterions leads to polycationic species displaying moderate solubility. By using super WCAs like $[Al(OR)_4]^-$ ($R = C(CF_3)_3$ a high solubility of the products is achieved, and thus comprehensive investigations on the dynamic depolymerisation processes in solution can be performed. Thus, the reaction of **I** with $Ag(CF_3SO_3)$ yields the oligomeric compound $[Ag_2\langle\{Cp_2Mo_2(CO)_4(\mu,\eta^2\text{-}P_2)\}_2\rangle\langle\{Cp_2Mo_2(CO)_4(\mu,\eta^1{:}\eta^1\text{-}P_2)\}_2\rangle][(CF_3SO_3)_2]$ **4a**. The two silver ions in this compound are bridged by two units of **I** thereby forming a nearly planar Ag_2P_4 six-membered ring.[1] If $[Al(OR)_4]^-$ ($R = C(CF_3)_3$ is used as the counterion in this reaction, the structurally similar, but remarkably more soluble product **4b** is obtained. Hence, comprehensive spectroscopic studies could be performed, whose results led to the proposition of the monomer-dimer equilibrium illustrated in Figure 2.

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The *cyclo*-As_3 ligand complex **IV** reacts with the silver salt of the WCA $[Al\{OC(CF_3)_3\}_4]^-$ to give the dimer **5** (Figure 3).[2] In this so far unprecedented homoleptic arsenic complex of silver the *cyclo*-As_3-ligands connect the two silver cations in an unusual face-bridging mode. ESI-MS investigations reveal the existence of a monocation in solution, whereas VPO investigations reveal the existence of a monomer-dimer equilibrium at ambient temperatures, as corroborated by DFT calculations.[2]

The reaction of **III** with silver salts of WCAs like $CF_3SO_3^-$ or PF_6^- leads to the formation of insoluble precipitates. However if the WCA used is $[Al\{OC(CF_3)_3\}_4]^-$, the soluble polycationic complex **6** can be isolated in excellent yields.[3c] Here a novel 1,2,3-coordination mode of the

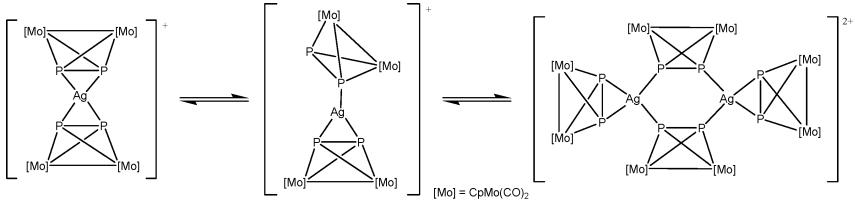

FIGURE 2 Proposed cation equilibria in solutions of **4b**.

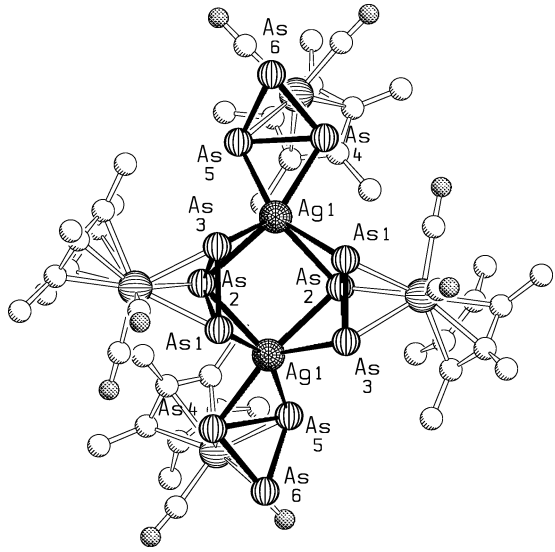

FIGURE 3 Molecular structure of the dication of **5**.

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cyclo-P_5 ring is observed, yielding a 1D polymer (Figure 4). Due to the high solubility of this compound in CH_2Cl_2, ESI-MS and VPO investigations could be carried out and the exclusive existence of a monocation in solution at ambient temperature was revealed. Variable temperature $^{31}P\{^1H\}$ NMR measurements show a complex dynamic behaviour of **6**

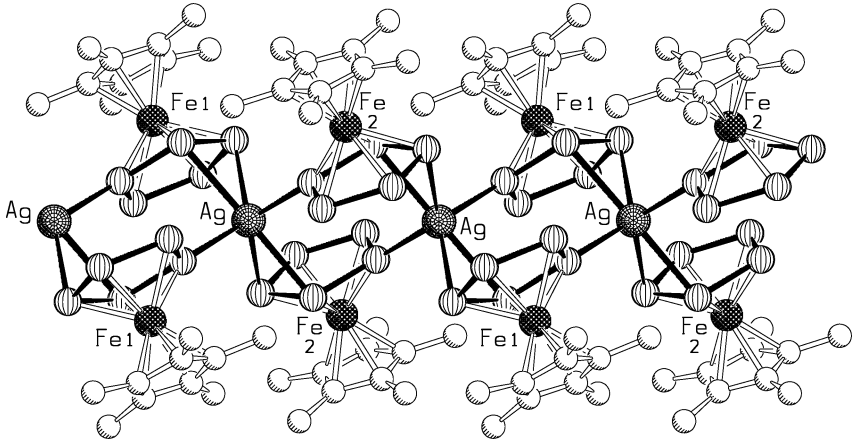

FIGURE 4 Part of the structure of the polycation in **6**.

in solution, which, with the help of DFT calculations, was interpreted as a monomer-dimer-oligomer equilibrium.[3c]

In summary, the use of silver salts of large super WCAs greatly facilitates the investigation of the behaviour of supramolecular compounds in solution and therefore the elucidation of dynamic monomer-oligomer equilibria. This opens up a novel chapter in the study of supramolecular aggregates based on E_n-ligand complexes.

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