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Phosphine-Based Coordination Cages and Nanoporous Coordination Polymers

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Summary: Recent findings in the use of multidentate phosphines to synthesise porous coordination polymers (metal-organic frameworks) and their possible precursor cages are reviewed. Additional recent investigations into using large adamantoid Ag_6 cages as polymer vertices in giant diamandoid structures are also presented. The results are discussed in terms of possible strategies for the controled synthesis of porous coordination polymers.

Keywords: cage; coordination; phosphine; polymer; porous; silver

Introduction

The field of coordination polymers and metal-organic frameworks has advanced very rapidly over the past decade.[1] Examples of highly porous and intricate interpenetrated structures not found in other types of solid have been characterised and initial investigations made of sorption behaviours with regard to eventual applications as chemical separation and storage media. However, virtually all the work reported has been based on N- or O-donor ligands in particular oligopyridines and carboxylates such as those in Figure 1. The rigidity of these ligands tends to place the metals in well-defined positions. This is advantageous since it gives some control over the polymer structure. A related field which has grown greatly in recent years is that of discrete multimetallic ring or cage structures based on bridging organic ligands.[2] Again, almost all work here has been based on N- or O-donor bridging ligands.

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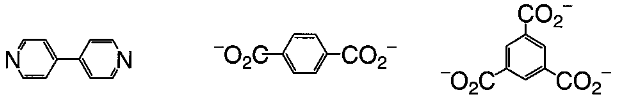

Figure 1. Some important examples of typical N- and O-donor bridging ligands used in coordination polymers and metal-organic frameworks. Note how the 180° mutual orientations of the lone pairs in 4,4'-bipyridine (left) are fixed by the rigidity of the ligand framework.

Against this background, our approach has been to investigate bridging multidentate phosphines, such as those shown in Figure 2, to generate unusual structures, behaviours and mechanistic insights in coordination rings, cages and polymers (at the outset very little work had been published on this[3]).

The key differences between these ligands and those in Figure 1 which have emerged are:

1. Soft donor character, leading to stable structures based on soft late d-block metals.
2. Rotational freedom of lone pairs due to pyramidal geometry of the phosphorus centres. Even where rigid-backboned diphosphines such as dppa or dppet, are used, rotation about P-C(backbone) bonds allows *syn* or *anti* disposition of the lone pairs, which can lead respectively to discrete or extended structures (Figure 2, bottom).
3. Presence of bulky aromatic substituents. Normally, for sufficient stability to air-oxidation (and possibly because they can increase the crystallinity of products), phenyl groups are the chosen substituents at phosphorus. The steric bulk of these groups can determine the structures (nulcearities) of coordination cages, and may also help to generate large pores within metal-organic polymers. The ability of multiple interaromatic contacts to stabilise structure may also be significant, but this has not yet been quantified.
4. Ability to monitor the donor atom directly by NMR spectroscopy. Especially in combination with spin-active metal nuclei, ^{31}P NMR spectroscopy gives valuable information on solution-state speciation and on the local structure of amorphous polymeric products.

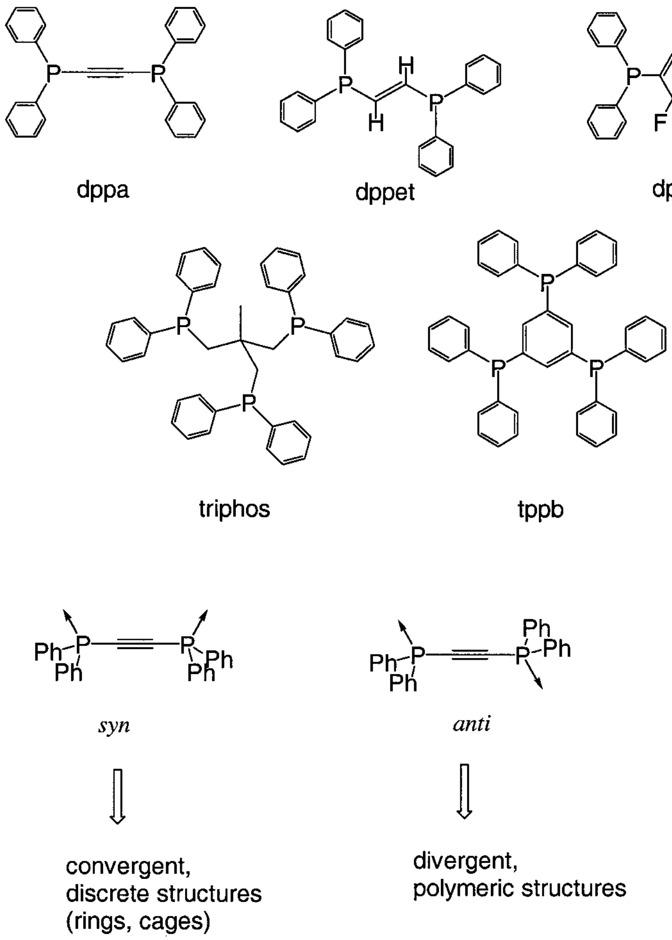

Figure 2. Phosphine P-donor bridging ligands which have been used in our studies, and the *syn* and *anti* conformations of 'rigid' connecting ligands such as dppa, which can give rise respectively to discrete or polymeric structures.

Taking tertiary phosphine ligands out of their familiar environments of organometallic chemistry and homogeneous catalysis, into the areas of coordination cages and polymers can therefore lead to new and interesting aspects in these fields. In this article are reviewed our findings in this research, as well as some previously unpublished results.

Review, Results and Discussion

The starting point for our work was the observation that flexible diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 3-6) give rise to large dinuclear ring structures on reaction with equivalent amounts of silver salts (Figure 3).[4]

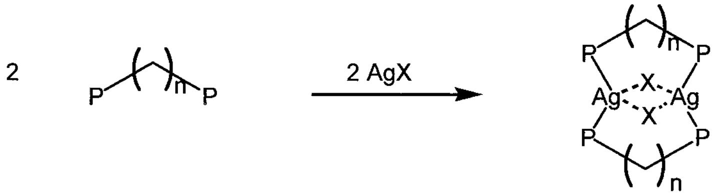

Figure 3. Disilver rings based on flexible bridging diphosphines (P = PPh_2).

Several such complexes have been characterised in the solid state by X-ray crystallography, and in some cases ^{31}P NMR spectroscopy was also consistent with the formation of such structures in solution. Possibly important to this behaviour is the ability of these flexible ligands to allow their lone pairs to point inward, and so set up two metal ions for anion bridging. In this way, anion bridges would be able to stabilise the large-ring dinuclear structure. We therefore examined the effect of changing to rigid-backboned ligands such as dppa and dppet (Figure 2), which disallowed the lone pairs from pointing inward. Accordingly, strikingly different solution-state speciation occurs for dppa in comparison to dppp (Figure 4).[5]

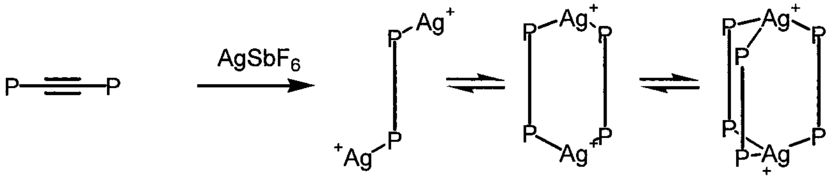

Figure 4. Reaction between the rigid bridging diphos dppa and $AgSbF_6$ at an equimolar ratio, to give a dynamic mixture of Ag_2L, Ag_2L_2 and Ag_2L_3 complexes (P = PPh_2).

In particular, one-two and three-coordinate complexes were observed consistent with the structures shown in Figure 4. At room temperature the complexes were dynamically interconverting on the NMR timescale, although at –60°C the interconversion was slow on the NMR timescale. However, altering the metal-to-ligand ratio to 2:3 revealed that for dppa, triply-bridged species would form then selectively (Figure 5).

Figure 5. Selective formation of $[Ag_2(dppa)_3]^{2+}$ complexes at the appropriate metal to ligand ratio.

The structures of these simple cages were supported by a solution state molecular weight determination and by single crystal X-ray crystallography. This also revealed that the use of anions with different nucleophilicities lead to structures which varied in the bending strain present in the –C≡C– backbones of the bridging ligands (the less nucleophilic anions such as SbF_6 and BF_4 gave more strained structures than the more nucleophilic NO_3 or OTf anions). Interestingly, when crystals of the triflate complex were left in their supernatant for several weeks, they redissolved and a new compound crystallised, which was found to be the polymeric structure shown in Figure 6.[6]

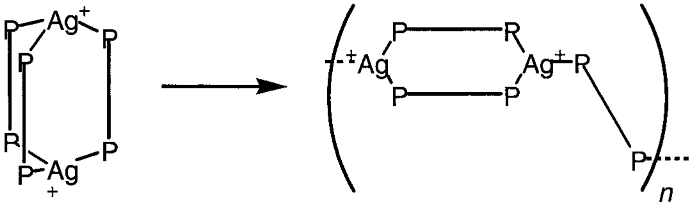

Figure 6. Triply bridged $[Ag_2(dppa)_3(OTf)_2]$cages and their formal ring-opening polymerisation to give $[Ag_2(dppa)_3(OTf)_2]_n$ polymers, P = PPh_2.

Of key interest is the fact that the precursor cage and polymer are formally related to each other by ring-opening polymerization (ROP). Despite the important role played by ROP methodology in main-group polymerizations, we were unaware of any instances where the ROP relationship had been pointed out for coordination cages and polymers (although other examples were pointed out simultaneously and later[7]). Given the difficulties in predicting and controlling the structures of metal-organic polymers, ROP methodology is potentially useful, particularly so if coordination cages can be formed in solution and rational ways then found for their controlled ring-opening. The question of whether coordination polymers represent thermodynamic or kinetic products is also raised by the observation of the ROP relationship. Coordination polymers have most often been assumed to be thermodynamic products because the metal-ligand bonds are normally highly labile, allowing, in principle, kinetic products to rearrange to more stable products. However, the relatively low solubility of coordination polymers could enable them to be trapped as kinetic products, which is in accord with the ROP relationship observed here.

A coordination cage or ring (a potential polymer precursor) might be deliberately destabilised (ring-opened) in a number of ways. Firstly, inter-ligand steric repulsion could be increased through use of bulky groups on the ligands, or potentially nucleophilic solvents, coligands or counterions might encourage P-M dissociation (the first step in ROP). We found that the *trans*-alkene-backboned ligand dppet, appeared to give less stable cages in solution than did dppa.[5] The qualitative evidence for this came from ^{31}P NMR spectroscopy, which at room temperature gave broad peaks most likely due to reversible P-Ag bond formation on the NMR timescale. At low temperatures, however, sharp spectra consistent with the triply-bridged cages were seen, suggesting the ligand-metal dissociation was less significant at lower temperatures. Consistent with the apparent lower stability of cages based on dppet was the fact that, under similar crystallisation conditions as those employed for the dppa cages, only the formal ring-opened polymers were obtained (Figure 7).

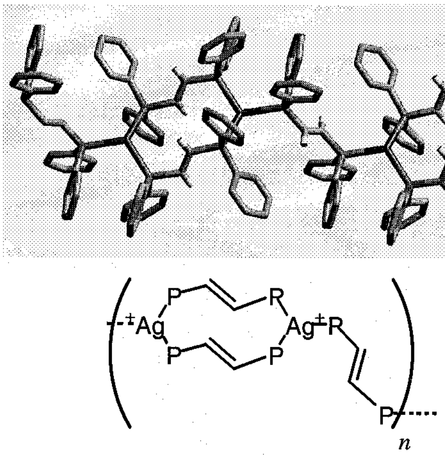

Figure 7. X-ray Crystal structure of the apparently ring-opened polymer $[Ag_2(dppet)_3(SbF_6)_2]_n$, P = PPh_2.

We have also investigated triphosphine ligands, such as those shown in Figure 2. The flexible tripodal neopentane-backboned triphosphine $CH_3C(CH_2PPh_2)_3$ (triphos, Figure 2) was expected to give Ag_3(triphos)$_2$-stoichiometry cages as shown in Figure 8. However, surprisingly, Ag_6(triphos)$_4$ structures with adamantanoid connectivity were obtained exclusively.[8] This initially surprising result seems most likely to be due to the bulky phenyl groups of the triphos ligands, since models suggest that interligand steric crowding would occur in the trinuclear complexes.

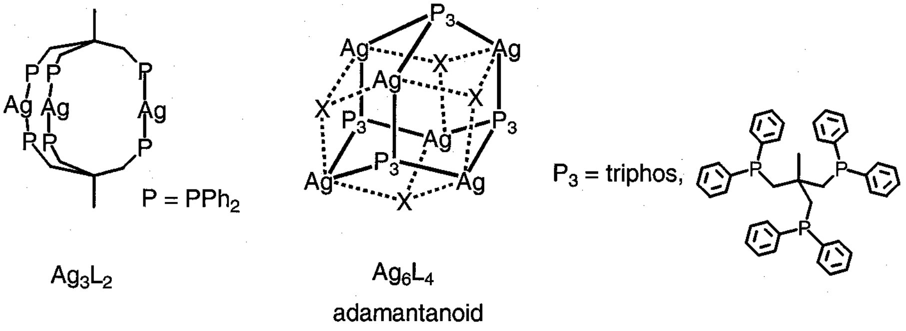

Figure 8. Postulated Ag_3L_2 cages based on tripodal triphosphines, and the actually observed adamantanoid Ag_6L_4 cages formed by $CH_3C(CH_2PPh_2)_3$ (X = $CF_3SO_3^-$, NO_3^-, ClO_4^-, but not BF_4^- or SbF_6^-).

These hexanuclear tetrahedral 2nm cages could potentially be connected into a diamandoid 3-D polymer by the use of bridging anions as shown in Figure 9. The large size of these cages made them of particular interest for generating porous structures, according to the strategy advanced by Yaghi *et al.,* which relies on the fact that large vertices make interpenetration of networks more difficult for steric reasons.[9] Interpenetration frequently mitigates against the generation of porosity coordination polymers. The potentially bridging dianion in Figure 9 has two tripodal sulfonate groups which were expected to template the adamantanoid cages and link them together (previous studies with monoanions showed that tripodal oxoanions such as nitrate, perchlorate and triflate are essential to template the hexanuclear cages $[Ag_6(triphos)_4(anion)_4]^{2+}$, and the use of fluoroanions such as SbF_6^- gave rise instead to dynamic mixtures, presumably due to their lower nucleophilicity and inability to stabilise the cages by bridging between metal ions[8]). Reaction between triphos, $AgSbF_6$ and the bridging dianion rapidly gave insoluble precipitates which XRPD showed to be amorphous. It was not possible to obtain single crystals by slowing down the mixing of the components. However, solid-state ^{31}P NMR spectroscopy (see Figure 10) did reveal that the phosphorus centres were, as hoped, all in very similar chemical environments with chemical shift and $^{109/107}Ag$-^{31}P coupling similar to those seen in the discrete cage in solution ($\delta = -9.32$ ppm, $J = 527$ Hz, assuming the latter to be J coupling rather than dipolar coupling, and that it would therefore be a weighted average of coupling due to ^{107}Ag (48%) and ^{109}Ag (52%), and given that $\gamma^{107}Ag/\gamma^{109}Ag = 1.149$, this corresponds to $^{1}J_{31P\text{-}109Ag} = 566$ Hz, which compares with 561 Hz for $[Ag_6(triphos)_4(O_3SCF_3)_4][O_3SCF_3]_2$[8]). Whilst it seems likely that the desired diamandoid structure was formed, to some degree, the lack of definitive structural determination hampered further progress in the study of these materials.

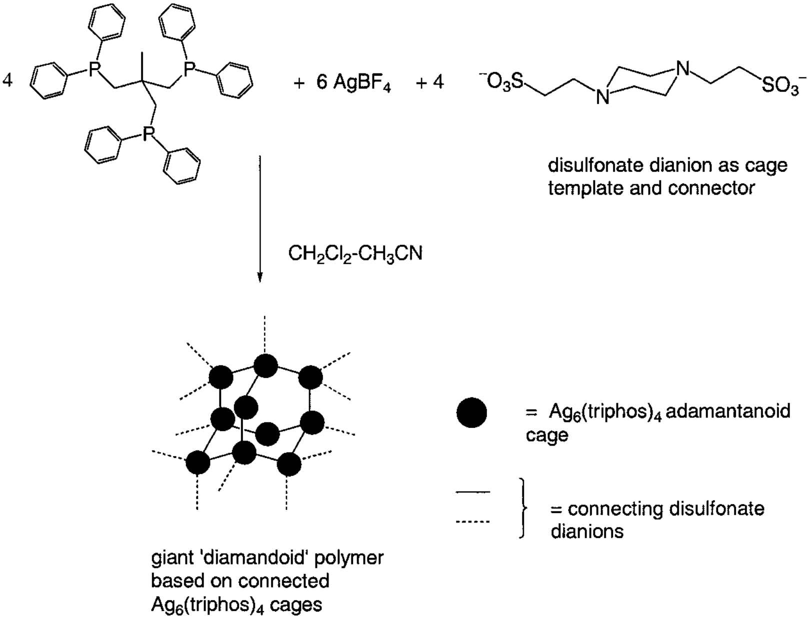

Figure 9. Attempted formation of a porous diamandoid material (**5**) by self-assembly of interconnected adamantanoid Ag_6(triphos)$_4$ cages.

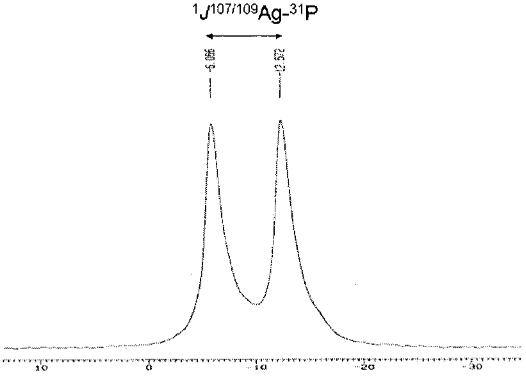

Figure 10. Solid state MAS ^{31}P NMR spectrum of the insoluble product from the reaction shown in Figure 9, showing the suspected J coupling between silver and phosphorus, similar to that seen in discrete cages in solution.

Use of the rigid triphosphine 1,3,5-*tris*(diphenylphosphino)benzene, tppb, did however, give rise to a crystalline large pore open polymer.[10] Reaction between this ligand and AgOTf, in dichloromethane-nitromethane followed by crystallisation by diffusion of diethyl ether vapour into this solution gave hexagonal crystals in *ca.* 10% yield, along with powdery material which was found to be amorphous by XRPD. The X-ray crystal structure of the hexagonal crystals was determined to be that shown in Figure 11.

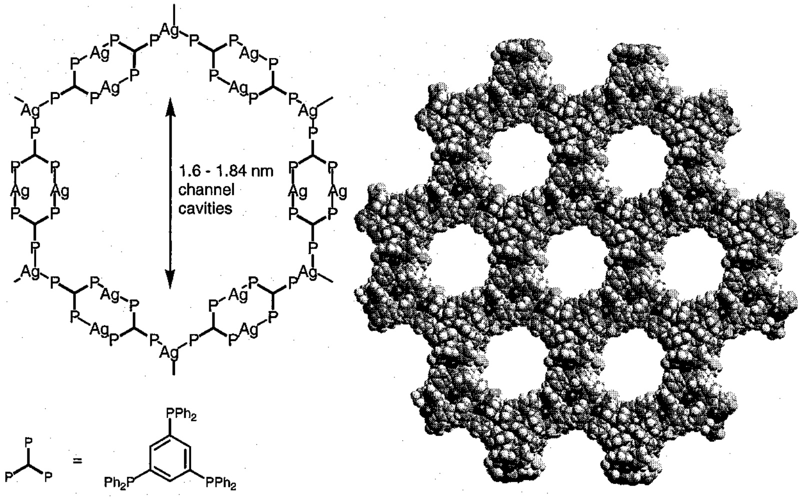

Figure 11. Diagramatic structure of the large fused hexagonal rings in the chickenwire polymer polymer $Ag_4(tppb)_3(OTf)_4$ (left), and the crystal structure of this material (right).

It consists of a fused hexagonal (chickenwire) layers, in which the nodes are trigonal planar AgP_3 centres, and the connectors are $Ag_2(tppb)_2$ units, which contain 12-membered rings. The large hexagonal rings are 72-membered. There are two types of triflate anions – those associated with the trigonal silver nodes, and those associated with the dinuclear rings in the $Ag_2(tppb)_2$ connectors. The latter triflates have their F atoms pointing towards the centres of the large rings. Despite this there remains an very large cavity with a transannular F..F distance of 1.901(3) nm, which corresponds to 1.6 nm when the F van der Waals radius is taken into account. The diameter of the rings is slightly larger between the triflates with an H...H distance of 2.08 nm, corresponding to 1.84 nm when the H van der Waals radius is taken into account. Crucially, the chickenwire layers pack in an eclipsed manner. Therefore the holes line up to form channels through the crystal structure (Figure 11, right). The 1.6-1.84 nm width of the channels is unusually large for a stable crystalline material. The compound was insoluble in chlorinated and aromtaic solvents, but was redissolved by the strongly metal-coordinating acetonitrile. The X-ray crystal structure showed no evidence of guests, however small residual electron density peaks were ascribed to disordered solvent molecules within the channels. The presence of solvent was confirmed with a sample which was washed with ethanol, then dissolved in d_3-acetonitrile for ^{1}H NMR spectroscopy. Signals for the previously included ethanol corresponding to *ca.* 75% of the available channel volume (using the molar volume of pure ethanol) were observed. It was also possible to exchange the included solvent for diethylether by immersion of the ethanol-loaded material in that solvent. A material which was apparently free of included solvent was obtained by immersion in dichloromethane for 24 hours, followed by heating to 170°C at 0.1 mmHg, although it did apparantly contain some residual water, however the ^{1}H NMR signal of the latter corresponded to only *ca.* 4% of the channel volume. Very importantly, the XRPD pattern of this material confirmed that the structure was intact, despite the lack of solvent.

In attempting to understand the formation of this particular structure the nature of the solution-state precursors was investigated. ^{31}P NMR spectroscopy revealed that several species were present in the solution, depending on the concentration, each being apparently highly symmetrical and having AgP_2 coordination. The structures were therefore most likely cage complexes of general formula $\{Ag_3L_2\}_n$ ($n = 1,2$ etc), *i.e.* corresponding to the Ag_3L_2 and Ag_6L_4 structures discussed above for the flexible triphos ligand together, possibly, with higher nuclearity structures. However, puzzlingly, none of these symmetrical cages could have given rise to the hexagonal polymer directly by ROP since the stoichiometries of the polymer $\{Ag_4(tppb)_3\}$ and these symmetrical precursors $\{Ag_3(tppb)_2\}_n$ are different. However, intriguingly, mass spectrometry did show, in addition to peaks corresponding to the $n = 1$ and $n = 2$ structures, a peak corresponding to the $Ag_4(tppb)_3(OTf)_2^{2+}$ cation, which is a potential precursor to the porous network polymer.

Conclusions

The use of multidentate phosphines to generate coordination cages and polymers has lead to some unusual cage and polymeric structures and pointed to a novel formation mechanism for coordination polymers (ROP of coordination cages). The isolation of a stable nanoporous polymer indicates that there is great potential in this field for novel structural chemistry, particularly if it proves possible to control the polymerisation reactions. Current and future aims in our group are to further clarify and exploit the relationship between coordination polymers and their solution-based precursors, as well as to investigate the characteristics of porous coordination polymers with regard to their inclusion behaviour and related chemistry. Funding from EPSRC, McClay Trust and The Leverhulme Trust for the work described here as well as the Questor Centre, Belfast, for funding other projects on porous coordination polymers for environmental remediation and gas storage applications is gratefully acknowledged.

Experimental

The MAS NMR study was conducted on ^{31}P nuclei at resonance frequency of 80 MHz (4.7 T), using a NMR spectrometer (Avance-200 Bruker, Germany). The powder was packed into a zirconia rotor with 4mm of outer diameter and 20mm long and sealed with a Kel-F endcap. Spinning rates of the sample at the magic angle (54.74°) were 5.0 kHz. The spectra were acquired with single pulse excitation and the recycle time between pulses was 5.0 s for ^{31}P. Reference material for ^{31}P chemical shift (in ppm) was relative to 85%H_3PO_4 at zero ppm.

Preparation of $[Ag_6(triphos)_4(O_3SCH_2CH_2NC_4H_8NCH_2CH_2SO_3)_2][BF_4]_2$

$AgBF_4$ (350mg, 1.80 mmol) and triphos (749 mg, 1.20 mmol) were dissolved in a mixture of acetonitrile (1 ml) and dichloromethane (5 ml). To this solution was added a solution of $[NBu_4]_2[O_3SCH_2CH_2NC_4H_8NCH_2CH_2SO_3]$ (468 mg, 0.60 mmol) in acetonitrile (5 ml) dropwise with stirring over 5 minutes. The mixture was allowed to stand for 24 hours, and a white precipitate was collected by filtration and dried in air for 24 hours. Yield 1.08g (86%, based on $[Ag_6(triphos)_4(O_3SCH_2CH_2NC_4H_8NCH_2CH_2SO_3)_2][BF_4]_2$). Elemental analysis % for $[Ag_6(triphos)_4(O_3SCH_2CH_2NC_4H_8NCH_2CH_2SO_3)_2][BF_4]_2.2CH_2Cl_2$ calc. C 53.98, H 4.74, N 1.38; found C 53.76, H 4.92, N 1.90.

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