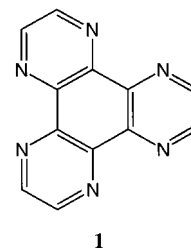


- [3] A. M. LaPointe, F. C. Rix, M. Brookhart, *J. Am. Chem. Soc.* **1997**, *119*, 906–917, and references therein.
- [4] a) H. Saso, W. Ando, *Chem. Lett.* **1988**, 1567–1570; b) H. Sakurai, T. Imai, *Chem. Lett.* **1975**, 891–894.
- [5] N. Chatani, T. Hanafusa, *J. Chem. Soc. Chem. Commun.* **1985**, 838–839.
- [6] A. Ogawa, H. Kuniyasu, M. Takeba, T. Ikeda, N. Sonoda, T. Hirao, *J. Organomet. Chem.*, in press.
- [7] M. Hada, Y. Tanaka, M. Ito, M. Murakami, H. Amii, Y. Ito, H. Nakatsuji, *J. Am. Chem. Soc.* **1994**, *116*, 8754–8765, and references therein.
- [8] a) H. Yamashita, T. Kobayashi, T. Hayashi, M. Tanaka, *Chem. Lett.* **1991**, 761–762; b) N. Chatani, N. Amishiro, S. Murai, *J. Am. Chem. Soc.* **1991**, *113*, 7778–7780; c) N. Chatani, N. Amishiro, T. Morii, T. Yamashita, S. Murai, *J. Org. Chem.* **1995**, *60*, 1834–1840.
- [9] H. Yamashita, M. Tanaka, M. Goto, *Organometallics* **1997**, *16*, 4696–4704, and references therein.
- [10] Recent reviews on the application of zirconocene complexes in syntheses: a) R. F. Jordan, *Adv. Organomet. Chem.* **1991**, *32*, 325–387; b) E. Negishi in *Comprehensive Organic Synthesis Vol. 5*, (Ed.: L. A. Paquette), Pergamon, Oxford, **1991**, pp. 1163–1184; c) E. Negishi, T. Takahashi, *Acc. Chem. Res.* **1994**, *27*, 124–130.
- [11] It has been proposed that $[\text{Cp}_2\text{ZrCl}_2]$ reacts with two equivalents of $n\text{BuMgCl}$ to yield the $[\text{Cp}_2\text{Zr}(\text{butene})]$ complex, which serves as an equivalent of “ Cp_2Zr ”; a) E. Negishi, F. E. Cederbaum, T. Takahashi, *Tetrahedron Lett.* **1986**, *27*, 2829–2832; see also references [10b, c]; for recent studies on the mechanism of $[\text{Cp}_2\text{Zr}(\text{butene})]$ formation, see b) V. K. Dioumaev, J. F. Harrod, *Organometallics* **1997**, *16*, 1452–1464; c) F. Soleil, R. Choukroun, *J. Am. Chem. Soc.* **1997**, *119*, 2938–2939.
- [12] The content and position of deuterium in **9** was determined by ^1H NMR spectroscopy. The deuterium content of **10** was determined by a comparison of the mass spectrum of **10** (EI, 70 eV) with that of octane. Incorporation of a deuterium at the terminal carbon atom of **10** was confirmed by ^{13}C NMR spectroscopy (100 MHz, CDCl_3): A signal for a terminal carbon atom at $\delta = 13.9$ that appears as a triplet due to coupling with D ($J = 1.9$ Hz) is observed in addition to a singlet at $\delta = 14.2$ for the other terminal carbon atom.
- [13] T. Takahashi, M. Hasegawa, N. Suzuki, M. Saburi, C. J. Rousset, P. E. Fanwick, E. Negishi, *J. Am. Chem. Soc.* **1991**, *113*, 8564–8566; M. R. Kesti, M. Abdulrahman, R. M. Waymouth, *J. Organomet. Chem.* **1991**, *417*, C12–C15; J. Y. Corey, X.-H. Zhu, *Organometallics* **1992**, *11*, 672–683; M. R. Kesti, R. M. Waymouth, *Organometallics* **1992**, *11*, 1095–1103.
- [14] $[\text{Cp}_2\text{Zr}(\text{SiMe}_3)\text{Cl}]$ does not react with ethylene (6 atm, Et_2O , 2 d); a) T. D. Tilley, *J. Am. Chem. Soc.* **1985**, *107*, 4084–4085; however, insertion of ethylene into Zr–Si bonds of $[\text{Cp}^*\text{ZrCl}_2\text{Si}(\text{SiMe}_3)_3]$ and $[\text{CpCp}^*\text{ZrCl}[\text{Si}(\text{SiMe}_3)_3]]$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) has been reported; b) J. Arnold, M. P. Engeler, F. H. Elsner, R. H. Heyn, T. D. Tilley, *Organometallics* **1989**, *8*, 2284–2286.
- [15] As the pathway leading to **13** is similar, it has been proposed that zirconate complexes $[\text{Cp}_2\text{ZrEt}(\text{CH}_2=\text{CH}_2)\text{MgBr}]$ and $[\text{Cp}_2\text{ZrPh}(\text{CH}_2=\text{CH}_2)\text{MgBr}]$ are formed by the reaction of $[\text{Cp}_2\text{ZrCl}_2]$ with three equivalents of EtMgBr or by the reaction of $[\text{Cp}_2\text{ZrPh}_2]$ with one equivalent of EtMgBr : T. Takahashi, N. Suzuki, M. Kageyama, Y. Nitto, M. Saburi, E. Negishi, *Chem. Lett.* **1991**, 1579–1582.

A Robust (10,3)-a Network Containing Chiral Micropores in the Ag^{I} Coordination Polymer of a Bridging Ligand that Provides Three Bidentate Metal-Binding Sites**

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A major goal in the crystal engineering of coordination polymers is the design and synthesis of microporous networks that maintain structural integrity upon exchange or loss of channel guest molecules. One strategy to achieve more robust framework structures that we have been developing is to harness the powerful chelate effect by employing bridging ligands that bind metal centers strongly at chelating sites. The planar ligand 1,4,5,8,9,12-hexaazatriphenylene (hat, **1**) provides a pleasingly symmetrical array of three bidentate sites at which metal centers can realistically be expected to be strongly and predictably bound, each site closely resembling those in the classical chelating agents 2,2'-bipyridine and 1,10-phenanthroline. The ligand hat has already been put to use to bind trios of metal ions in discrete molecular species,^[1] but our interest is to generate infinite networks.



A particularly appealing aspect of connecting ligands providing two or more bidentate sites is that when a metal center takes on three of them the metal itself adopts the role of three-connecting node. Ligands such as hat, therefore, in combination with appropriate metal centers provide access, in principle, to a range of intriguing and little known three-connected nets whose topologies have been catalogued by Wells.^[2]

One feature of hat of potentially great interest and usefulness is its delocalized π -electron system which may provide facile electronic communication between attached metal centers; such communication throughout an extended 3D network could lead to unusual properties. Intense interest has been focussed on the photophysical properties associated with the metal-to-ligand charge transfer chromophores in complexes of 2,2'-bipyridine and related ligands and upon binuclear and oligonuclear mixed-valence complexes of bridging ligands containing pyridine and pyrazine residues,^[3] including hat itself.^[4] We believe that mixed-valence 3D coordination polymers of planar bridging ligands with delocalized π -electron systems, of which hat is only one example, may provide unique physical properties; the generation of such systems is one of our long-term objectives. The results reported here are part of an initial exploratory study of the

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potential of hat to generate well-defined coordination polymer networks in the form of single crystals. We start here with the monovalent and relatively “innocent” metal center Ag^I and hope by studies of “simple” systems of this type to build up a foundation of knowledge and experience from which the more ambitious assault on mixed valence structures can be launched. The system described below is the first structurally characterized coordination polymer of hat^[5] or, for that matter, of any bridging ligand that provides three bidentate sites with strong metal-binding properties. It has the (10,3)-a topology^[2] and provides micropores that are chiral. Furthermore, as described below, the retention of framework integrity upon exchange of the solvent housed in its chiral channels indicates an encouraging network resilience.

Slow intermixing of solutions of hat in nitromethane and AgClO_4 in acetonitrile by diffusion gave orange crystals of composition $[\text{Ag}(\text{hat})\text{ClO}_4] \cdot 2\text{CH}_3\text{NO}_2$ which were studied by single-crystal X-ray diffraction. The unit cell is tetragonal but almost equidimensional ($a = 12.652(1)$, $c = 12.362(1)$ Å). Individual crystals are enantiomorphous as indicated by the chiral space group of the one selected for study. Presumably enantiomorphous crystals of both hands are formed. All silver centers are equivalent, being chelated by three hat ligands which provide an N_6 coordination environment intermediate between octahedral and trigonal prismatic. The ligands are also all equivalent, each chelating three metal centers. Some essential features of the structure are shown in Figure 1 which

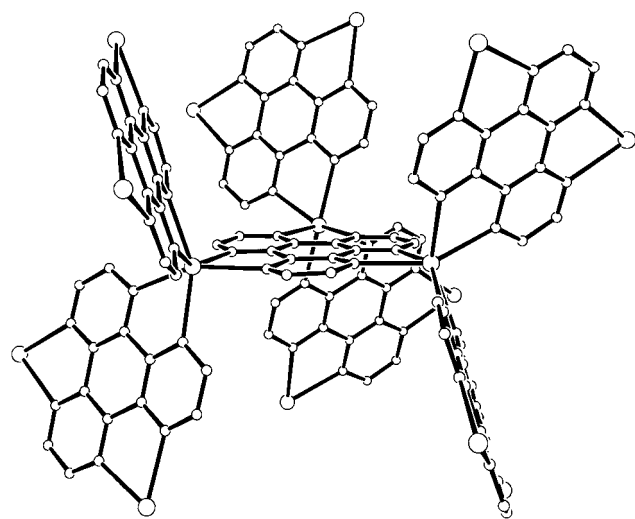


Figure 1. A segment of the Ag/hat framework in $[\text{Ag}(\text{hat})\text{ClO}_4] \cdot 2\text{CH}_3\text{NO}_2$. Larger circles represent the Ag and smaller circles the C/N atoms.

focuses on a central (horizontal) hat ligand bound by three silver atoms each in turn bearing two other hat ligands. The extended 3D network therefore is three-connected with two types of essentially trigonal node, one located at the metal and the other at the midpoint of the ligand. The topology is that of the (10,3)-a net, the most symmetrical of all the three-connected nets, which in its geometrically most regular form is cubic with strictly trigonal planar nodes and exactly 120° angles.^[2] Figure 2 shows two versions of the structure seen from the same angle slightly displaced from the tetragonal axis.

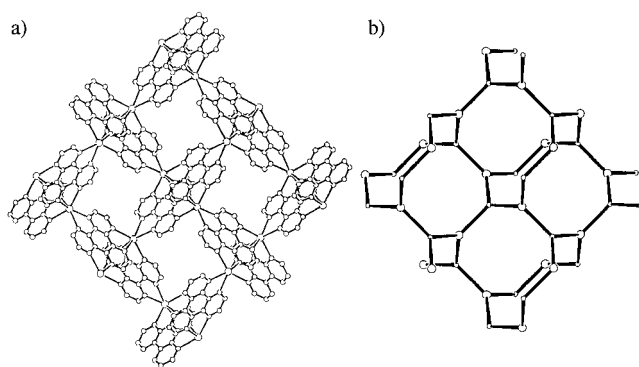


Figure 2. Representation of the Ag/hat framework topology viewed from a direction slightly displaced from the tetragonal axis. In a) Ag atoms (larger circles) and the C/N atoms of hat (smaller circles) are shown, whilst in b) the (10,3)-a connectivity is revealed more clearly by replacing each ligand by a single trigonal node (smaller circles).

The three planar ligands around each silver atom produce three “bays”. The perchlorate ions, which are positionally ordered but orientationally disordered, are found in one of these three bays and it is this positional ordering that reduces the overall symmetry from cubic to tetragonal. The Ag/hat framework nevertheless shows only very minor deviations from the most regular form possible for the (10,3)-a net. The framework was estimated to occupy about 48 % of the crystal volume by using the PLATON program.^[6]

The nitromethane molecules, which are unusually well ordered relative to the solvent molecules in many other solvated coordination polymers, are located in the large micropores clearly apparent in Figure 2. Each nitromethane molecule associates with two neighbors, making very close $\text{N}^{\delta+} \cdots \text{O}^{\delta-}$ contacts of 3.02 Å, and thereby generates fourfold helices (Figure 3). The nitromethane helices have the same left-handed character as the internal surfaces of the chiral framework micropores by which they are surrounded and templated. Similarly short $\text{N} \cdots \text{O}$ contacts (3.00–3.07 Å) are observed in the crystal structure of nitromethane itself.^[7]

After the data collection had been completed the crystal was removed from its Lindemann tube and allowed to equilibrate with the atmosphere. Remarkably, the same crystal still displayed X-ray diffraction, which now revealed a cubic structure with a cell volume of $1935.6(2)$ Å³, significantly smaller than that of the original tetragonal cell of $1978.9(3)$ Å³. A structural determination for the cubic daughter crystal indicated retention of an almost unchanged Ag/hat framework. The solvent molecules however were now unresolved and the perchlorate anions, which were clearly defined, were disordered over three crystallographically equivalent sites. These sites were located within the bays between ligands referred to above at positions similar to that of the ordered perchlorate in the tetragonal nitromethane-containing parent. Infra-red analysis of other crystals obtained from the same reaction mixture indicated replacement of nitromethane by H_2O upon exposure to the atmosphere. Estimation of the nonframework volume and the electron densities in the intraframework regions by using the PLATON program suggested the composition had changed to $[\text{Ag}(\text{hat})\text{ClO}_4] \cdot 4\text{H}_2\text{O}$,^[8] in good agreement with the composition indicated

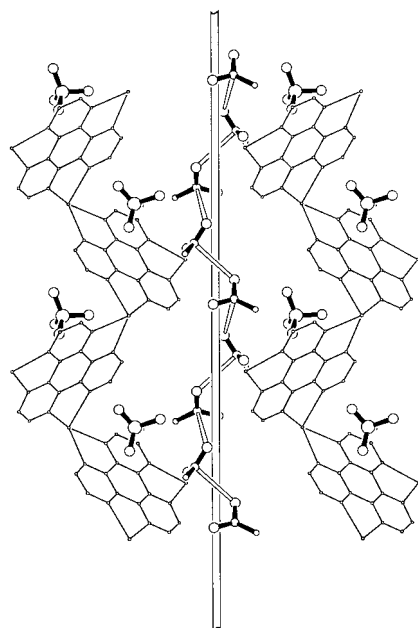


Figure 3. The disposition of the anions and the fourfold helical arrangement of the nitromethane molecules in $[\text{Ag}(\text{hat})\text{ClO}_4] \cdot 2\text{CH}_3\text{NO}_2$. Circles in order of decreasing size represent Cl, O, N, and C, respectively. For ease of visualization the $(\text{CH}_3\text{NO}_2)_n$ helix is shown wrapped around an imaginary central "pole". The "open" connections represent close $\text{N}^{\delta+} \cdots \text{O}^{\delta-}$ intermolecular contacts (3.02 Å). For clarity only part of the Ag/hat helical channel (very small circles) which surrounds the nitromethane helix is shown; those parts behind and in front are omitted as are the perchlorate anions associated with them.

by the elemental analysis of a sample exposed to the atmosphere ($[\text{Ag}(\text{hat})\text{ClO}_4] \cdot 3.5\text{H}_2\text{O}$). Following this second data collection, the *same* crystal was further immersed in nitromethane and resealed in a Lindemann tube. This granddaughter crystal still diffracted and now showed a cubic unit cell of volume of $1987(2) \text{ Å}^3$ —essentially the same as the volume of the tetragonal cell of the original grandparent crystal. It appears that, in the second exchange of solvent, the crystal is unable to regain the grandparent's regular ordering of the anion. Upon reexposure of the *same* crystal to the atmosphere it reverts once again to the smaller cubic cell ($1929.1(8) \text{ Å}^3$). Despite the changes in crystal symmetry and in unit cell volume, it is clear that the Ag/hat framework persists from generation to generation in these successive solvent exchanges.

Treatment of AgBF_4 with hat under identical reaction conditions to those used above for the perchlorate salt gave tetragonal crystals with the essentially identical dimensions $a = 12.647(2)$, $c = 12.347(3) \text{ Å}$.

A number of coordination polymers with the (10,3)-a topology have been discovered in recent times.^[9] We suspect that as the rapidly expanding field of coordination polymers continues to evolve, more and more examples of this net, referred to by Wells as the three-connected analogue of diamond, will emerge and that it may come to dominate three-connected 3D structures in the same way diamond is presently the dominant structure for four-connected 3D coordination polymers.

The preliminary results presented in this report bode well for the future generation of a range of crystalline coordination polymers of hat (and related ligands) with a wide variety of

metal centers, in some cases with chiral channels, with real prospects of unusual properties and robust enough for practical applications.

Experimental Section

A solution of AgClO_4 (23 mg) in CH_3NO_2 (3 mL) was added to a suspension of hat (15 mg) in CH_3NO_2 and the mixture was heated in a sealed vessel on the steam bath for three days. The bright yellow suspended solid was collected by filtration, washed with CH_3NO_2 , then equilibrated with the atmosphere for several days. Yield, 18 mg. IR (KBr): $\tilde{\nu} = 437\text{m}$, 629s, 637s, 1087vs, 1100vs, 1114vs, 1233s, 1343w, 1385vs, 1473s, 1543w cm^{-1} ; elemental analysis calcd. for $\text{C}_{12}\text{H}_{13}\text{AgClN}_6\text{O}_{7.5}$ ($[\text{Ag}(\text{hat})\text{ClO}_4] \cdot 3.5\text{H}_2\text{O}$): C 28.6, H 2.6, N 16.6; found: C 28.9, H 1.3, N 16.5. Powder XRD indicated this material had the same cubic unit cell as the daughter crystal. The best single crystals for crystallographic study were obtained as follows: CH_3NO_2 (8 mL) was added to hat (5 mg) in a long 8 mm diameter tube; not all the hat dissolved. A solution of AgClO_4 (7 mg) in CH_3CN (4 mL) was carefully layered on top of the hat/ CH_3NO_2 mixture followed by benzene (6 mL). The tube was stoppered and light was excluded. After three weeks large, bright orange multifaceted crystals suitable for X-ray crystallography were obtained. A selected crystal was sealed with mother liquor in a Lindemann glass capillary tube for diffraction measurements and then exposed to the atmosphere, after which diffraction experiments on the cubic hydrated form were performed. Crystal data for $[\text{Ag}(\text{hat})\text{ClO}_4] \cdot 2\text{CH}_3\text{NO}_2$ (and for $[\text{Ag}(\text{hat})\text{ClO}_4] \cdot 4\text{H}_2\text{O}$ in parentheses): $M_r = 563.64$ (513.61), tetragonal (cubic), space group $P4_22_1$ ($P2_13$), $a = 12.652(1)$ (12.463(1)), $c = 12.362(1) \text{ Å}$, $V = 1978.9(3)$ (1935.6(3)) Å^3 , $Z = 4$ (4), $\rho_{\text{calcd}} = 1.872$ (1.762) g cm^{-3} , $\mu(\text{MoK}\alpha) = 1.218$ (1.232) mm^{-1} , $F(000) = 1096$ (1024). Intensity data for 4570 (4490) reflections ($2\theta_{\text{max}} = 50$ (50°)), yielding 1739 (1145) independent reflections were measured at 295(2) K with $\text{MoK}\alpha$ radiation (graphite monochromator) using an Enraf-Nonius CAD-4 MachS diffractometer employing ω ($\omega/2\theta$) scans. Data were corrected for Lorentz, polarization and absorption^[10] effects, min./max. transmission factors = 0.7868/0.8502 (0.7835/0.8721). The structures were solved by using the Patterson method^[11] (direct methods^[12]). Full-matrix least-squares refinement^[13] based on F^2 converged with $R1 = 0.0554$ (0.1576), $wR2 = 0.1523$ (0.4499); 125 (22) parameters. Max. residual electron density 0.52 (0.87) e Å^{-3} . Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101558 (CCDC-101559). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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- a) R. Nasielski-Hinkens, M. Benedek-Vamos, D. Maetens, J. Nasielski, *J. Organomet. Chem.* **1981**, *217*, 178; b) A. Masschelein, A. Kirsch-De Mesmaeker, C. Verhoeven, R. Nasielski-Hinkens, *Inorg. Chim. Acta* **1987**, *129*, L13; c) P. Baxter, J.-M. Lehn, A. DeCian, J. Fischer, *Angew. Chem.* **1993**, *105*, 92; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 69.
- A. F. Wells, *Three-Dimensional Nets and Polyhedra*, Wiley, New York, **1977**, chap. 5.
- P. Bonhôte, A. Lécas, E. Amouyal, *Chem. Commun.* **1998**, 885, and references therein; V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, **1991**.
- K. Warnmark, O. Heyke, J. A. Thomas, J.-M. Lehn, *Chem. Commun.* **1996**, 2603; T. J. Rutherford, O. Van Gijte, Kirsch-De Mesmaeker, F. R. Keene, *Inorg. Chem.* **1997**, *36*, 4465; T. J. Rutherford, F. R. Keene, *Inorg. Chem.* **1997**, *36*, 3580.
- Lehn and co-workers^[14] have speculated on the possibility of forming oligomers and polymers with the hexaphenyl derivative of hat.
- Platon Program: A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34.
- I. Y. Bagryanskaya, Y. V. Gatilov, *Zh. Strukt. Khim.* **1983**, *24*, 158.

- [8] The number of nitromethane molecules and perchlorate anions per unit cell in the tetragonal $[\text{Ag}(\text{hat})\text{ClO}_4] \cdot 2\text{CH}_3\text{NO}_2$ crystal indicated by the crystallography showed excellent agreement with the number calculated with the PLATON Program^[6] on the basis of the electron density in the framework voids. This agreement affords confidence in the number of water molecules ($4\text{H}_2\text{O}$ per $[\text{Ag}(\text{hat})\text{ClO}_4]$) present in the cubic hydrated crystal calculated in the same way by using the PLATON program, which in addition accorded well with the $3.5\text{H}_2\text{O}$ indicated by elemental analysis.
- [9] S. Decurtins, H. W. Schmalle, P. Schneuwly, H. R. Oswald, *Inorg. Chem.* **1993**, 32, 1888; S. Decurtins, H. W. Schmalle, P. Schneuwly, J. Ensling, P. Gutlich, *J. Am. Chem. Soc.* **1994**, 116, 9521; S. Decurtins, H. W. Schmalle, R. Pellaux, P. Schneuwly, A. Hauser, *Inorg. Chem.* **1996**, 35, 1451; Carlucci, G. Ciani, D. M. Proserpio, A. Sironi, *J. Am. Chem. Soc.* **1995**, 117, 12861; B. F. Abrahams, S. R. Batten, H. Hamit, B. F. Hoskins, R. Robson, *Chem. Commun.* **1996**, 1313; L. Carlucci, G. Ciani, D. M. Proserpio, A. Sironi, *Chem. Commun.* **1996**, 1393; C. J. Kepert, M. J. Rosseinsky, *Chem. Commun.* **1998**, 31.
- [10] G. M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, U. K., **1976**.
- [11] G. M. Sheldrick, SHELX-86, Program for Crystal Structure Solution, Universität Göttingen, **1986**.
- [12] G. M. Sheldrick, SHELX-97, Program for Crystal Structure Solution, Universität Göttingen, **1997**.
- [13] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, **1997**.

Efficient Palladium-Catalyzed Cyclotrimerization of Arynes: Synthesis of Triphenylenes**

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Over the last 15 years much effort has been devoted to the preparation and characterization of transition metal complexes of arynes.^[1] Parallel studies on the reactivity of these complexes—particularly those of Ti, Zr,^[2] and Ni^[3]—have shown that characteristic reactions involve insertion of molecules containing multiple bonds (e.g. alkenes, alkynes, CO) into the metal–aryne bond, which in a way is reminiscent of the chemistry of alkyne complexes. However, while alkynes participate in a number of synthetically useful metal-catalyzed transformations,^[4] the synthetic applications of metal–aryne complexes are limited owing to the lack of a general and mild method for their generation and the need for stoichiometric amounts of metal in their reactions.

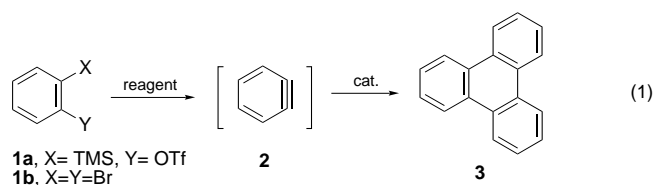
As part of a project aimed at the development of new reactions of arynes promoted by metal complexes, here we report on the metal-mediated cyclotrimerization of arynes.

These preliminary results show that the reaction proceeds in the presence of catalytic amounts of metal and that it has great potential for the preparation of triphenylenes, which are found at the core of many discotic liquid crystals^[5] and have therefore been the target of many synthetic studies.^[6]

There are many precedents of triphenylene formation under conditions that lead to arynes, especially when arynes are generated from an organometallic system.^[7] For example, triphenylene was obtained in 85 % yield from the decomposition of 2-fluorophenylmagnesium bromide in THF.^[8] Closer to our results, triphenylene was isolated in 30 % yield during attempts at obtaining a platinum complex of benzyne (1,2-didehydrobenzene).^[9] An example of the formation of triphenylene as side product of a palladium-catalyzed domino reaction has also been reported.^[10] However, to the best of our knowledge, efficient preparation of triphenylenes by metal-catalyzed reaction of arynes is without precedent.

Development of a catalytic procedure for the trimerization of arynes requires careful selection of the catalyst and the method for generation of the aryne. The catalyst was chosen from among the various metal systems used for trimerization of alkynes; suitable candidates contained metals such as Ni, Co, Pd, and Pt. We decided to carry out the first trials with palladium complexes because they are easy to handle and in general stable. Among the many procedures available for the generation of arynes^[11] we sought one that could be used under mild reaction conditions and did not involve strong bases or oxidants. The method of choice was the fluoride-induced elimination of Me_3Si and TfO groups (Tf = trifluoromethanesulfonyl), which proceeds at room temperature.^[12]

Early in our study we found that when 2-trimethylsilylphenyl trifluoromethanesulfonate (**1a**) was treated with CsF and a catalytic amount (3 mol %) of $[\text{Pd}(\text{PPh}_3)_4]$ in acetonitrile, the only low-polarity product detected was triphenylene (**3**), which was isolated in 52 % yield [Eq. (1)]. To optimize the



reaction conditions, exhaustive experimentation was carried out; some significant results are given in Table 1. The best results were obtained using 10 mol % of $[\text{Pd}(\text{PPh}_3)_4]$ ^[13] and 2 equivalents of anhydrous CsF in acetonitrile at room temperature (entry 1), which afforded triphenylene in 83 % yield. Use of other sources of Pd^0 (entries 2 and 3) or fluoride (entry 4) gave slightly lower yields. Likewise, alternative methods to generate benzyne, such as reaction of 1,2-dibromobenzene (**1b**) with $n\text{BuLi}$, in the presence of $[\text{Pd}(\text{PPh}_3)_4]$ (entry 5) also gave poorer results. It is noteworthy that triphenylene was not detected in the reaction mixture when **1a** was treated with CsF in the absence of a Pd catalyst (entry 6), and that when **1a** was treated with $[\text{Pd}(\text{PPh}_3)_4]$ in the absence of fluoride, the starting material was untouched (entry 7). In our opinion, these two control experiments provide good evidence of the intermediacy of benzyne as the

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