In conclusion, the present study demonstrates that open-framework metal phosphates can be generated under relatively mild conditions by treating amine phosphates with metal ions and that amine phosphates are intermediates in hydrothermal syntheses. The amine phosphates initially give chain or ladder structures that give rise to more complex structures, depending on time and temperature.

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[1] J. M. Thomas, *Angew. Chem.* **1994**, *106*, 963; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 913; J. M. Thomas, *Chem. Eur. J.* **1997**, *3*, 1557.

[2] A. K. Cheetham, G. Ferey, T. Loiseau, *Angew. Chem.* **1999**, *111*, 3466; *Angew. Chem. Int. Ed.* **1999**, *38*, 3268.

[3] S. Oliver, A. Kuperman, G. A. Ozin, *Angew. Chem.* **1998**, *110*, 48; *Angew. Chem. Int. Ed.* **1998**, *37*, 46; S. Oliver, A. Kuperman, A. Lough, G. A. Ozin, *Chem. Mater.* **1996**, *8*, 2391.

[4] S. Ayyappan, X. Bu, A. K. Cheetham, S. Natarajan, C. N. R. Rao, *Chem. Commun.* **1998**, 2181.

[5] G. Ferey, *C. R. Acad. Sci. Paris, Series II*, **1998**, 1.

[6] S. Oliver, A. J. Lough, G. A. Ozin, *Inorg. Chem.* **1998**, *37*, 5021, and references therein.

[7] S. M. Golubev, Y. D. Kondrashev, *Zh. Strukt. Khim.* **1984**, 25, 471; M. T. Averbuch-Pouchot, A. Durif, *Acta Crystallogr. Sect. C* **1984**, *43*, 1894; S. Kamoun, A. Jouini, A. Daoud, *Acta. Crystallogr. Sect. C* **1991**, *47*, 117; S. Kamoun, A. Jouini, A. Daoud, A. Durif, J. C. Guitel, *Acta Crystallogr. Sect. C* **1992**, *48*, 133; D. Riou, T. Loiseau, G. Ferey, *Acta Crystallogr. Sect. C* **1993**, *49*, 1237.

[8] In a typical synthesis, 0.5 mmol of ZnO was stirred in 100 mmol of water, to which 1 mmol of HCl (35%) was added. After stirring the mixture for a few minutes, 2.7 mmol of amine phosphate (e.g., DAPP) was added, and the mixture was stirred for 30 min. The homogenized mixture was sealed in a 23-mL teflon-lined Parr autoclave and heated at the given temperature and for the given duration (see Table 1). The product was collected by filtration, and X-ray analysis of the crystals was carried out on a Siemens SMART X-ray diffractometer with a CCD detector.

[9] W. T. A. Harrison, Z. Bircsak, L. Hannooman, Z. Zhang, *J. Solid State Chem.* **1998**, *136*, 93.

[10] P. Feng, X. Bu, G. D. Stucky, *Angew. Chem.* **1995**, *107*, 1911; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1745.

[11] W. T. A. Harrison, T. E. Martin, T. E. Gier, G. D. Stucky, *J. Mater. Chem.* **1992**, *2*, 175.

[12] M. E. Davis, R. F. Lobo, *Chem. Mater.* **1992**, *4*, 756; R. E. Morris, S. J. Weigel, *Chem. Soc. Rev.* **1997**, *26*, 309; R. J. Francis, D. O'Hare, *J. Chem. Soc. Dalton Trans.* **1998**, 3133.

[13] Reaction of the amine phosphate with Zn^{II} at all temperatures first yields a fine particulate open-framework zinc phosphate with a low-angle XRD line ($d_{hkl} = 11.8$ Å). Time-dependent XRD studies show that the low-angle line due the precursor decreases in intensity when the characteristic reflections of the ladder, layer, and three-dimensional structures start to appear. The aqueous dispersion of the particulate material shows a ^{31}P NMR signal ($\delta = 3.82$) whose intensity first increases with time and then decreases due to the formation of a edge-shared ladder or layer structures. We consider the initial phosphate material formed to be the precursor, since on further reaction or passage of time it gives the more complex ladder, layer, or three-dimensional structures. It seems likely that the precursor is a corner-shared linear ladder phosphate which we have isolated from some reactions of the amine phosphates. Accordingly, the Zn:P ratio in the precursor phosphate is 1:1 (in contrast to the edge-shared ladder phosphates, in which it is 1:2).

[14] R. J. Francis, S. O'Brien, A. M. Fogg, P. S. Halasyamani, D. O'Hare, T. Loiseau, G. Ferey, *J. Am. Chem. Soc.* **1999**, *121*, 1002.

[15] P. Feng, X. Bu, G. D. Stucky, *Nature* **1997**, *388*, 735; X. Bu, P. Feng, G. D. Stucky, *Science* **1997**, *278*, 2080.

Self-Assembly of a Radially Functionalized Hexagonal Molecule: Hexakis(4-hydroxyphenyl)benzene[**]

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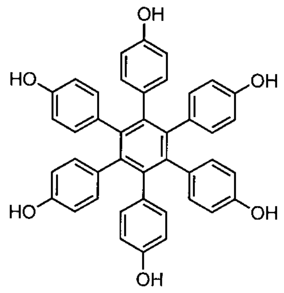
Supramolecular approaches to self-assembly of molecular solids rely in a predictable manner on directional and complementary noncovalent interactions.[1] Particular attention has recently focused on the rational design of microporous solids with specific properties such as selective adsorption[2] and catalytic activity.[3] However, the formation of hydrogen-bonded networks with large cavities often results in self-interpenetration to fill the voids in the initial host structure.[4] The introduction of sterically demanding substituents into trigonal molecules[5, 6] and the use of rigid hexagonal macrocycles[7] with multiple hydrogen-bonding sites are potential methods to prevent interpenetration of networks. Aoyama and ourselves recently prepared porous networks of bis-resorcinol orthogonal aromatic triads for the preorganization of host molecules.[8] Hexaarylbenzene derivatives[9] are highly symmetrical molecules that can bear diverse and multifunctional radial substituents and exhibit an orthogonal arrangement of the interactive groups with respect to the core moiety.[10, 11] Here we report on the porous two-dimensional hydrogen-bonded networks of hexakis(4-hydroxyphenyl)benzene (**1**); the topology of the network structures is flexible and guest-dependent.



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Host **1** was prepared by the $[Co_2(CO)_8]$-catalyzed cyclotrimerization[9] of bis(4-methoxyphenyl)acetylene (81% yield) followed by deprotection of the resulting hexakis(4-methoxyphenyl)benzene (**2**) with BBr_3 (92% yield). Recrystallization of **1** from various solvents afforded inclusion cocrystals, the stoichiometries of which were evaluated by ^{1}H NMR spectroscopy in CD_3OD: $\mathbf{1}\cdot 3\,C_6H_5COOCH_3$ from a

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mixture of methyl benzoate and benzene; $\mathbf{1}\cdot 3\,\mathrm{CH_3COOEt}$ from a mixture of ethyl acetate and hexane; $\mathbf{1}\cdot 4\,\mathrm{Et_2O}$ and $\mathbf{1}\cdot 3\,\mathrm{CH_3COOEt}$ in a 4:1 ratio from a mixture of diethyl ether and ethyl acetate; $\mathbf{1}\cdot 4\,\mathrm{DMF}$ from a mixture of ethyl acetate, diethyl ether, and DMF (*N*,*N*-dimethylformamide). Thus, in the solid state, **1** prefers to include more polar guests. The crystal structures of $\mathbf{1}\cdot 4\,\mathrm{Et_2O}$ (**3**) and $\mathbf{1}\cdot 4\,\mathrm{DMF}$ (**4**) were determined by X-ray diffraction analysis[12] (Figure 1).

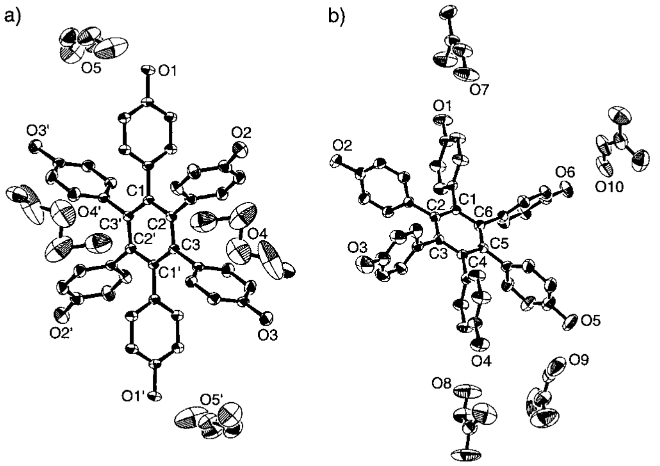

Figure 1. ORTEP plots (30 % probability thermal ellipsoids) of a) **3** and b) **4**. Hydrogen atoms are omitted for clarity.

The molecular structure of **3** has a center of symmetry (Figure 1 a). Two of the four included ether molecules are hydrogen-bonded to the hydroxyl groups HO1 of **1** (O1 ⋯ O5 2.69 Å). The other two ether molecules interact with the aromatic core of **1**, whereby the distance between the methyl group and the face of the core is about 3.6 Å. The dihedral angles between the phenol rings and the aromatic core at C1–C3 are 102.8, 68.2, and 96.7°, respectively.

All hydroxyl groups of **1** participate in the two-dimensional hydrogen-bonded network (molecular sheet) of **3** (Figure 2 a), in which the intermolecular hydrogen-bonding patterns are O2H ⋯ O3H ⋯ O1H with O ⋯ O distances of 2.81 and 2.74 Å, respectively. This network is an antiparallel assembly of one-dimensional ladder-type networks (molecular tapes). Each tape is formed by two-point O2H ⋯ O3H hydrogen bonds between adjacent molecules along the *b* axis, and the tapes are assembled into the molecular sheet in a stairlike fashion by O3H ⋯ O1H hydrogen bonds (Figures 2 a and b). Hence, this molecular sheet has two types of cavities: cavities **A** (ca. 7.6 × 7.6 Å) in the tapes, and cavities **B** (ca. 6.0 × 7.6 Å) between them. One molecule of **1** constitutes one cavity **A** and two cavities **B**.[13] The molecular sheets are layered without translation, so that two types of extended channels **A** and **B** are generated along the *a* axis (Figure 2 c). The sheet–sheet (core center to core center) distance along the *a* axis is 9.87 Å.

The molecular structure of **4** has no symmetry; the dihedral angles between the phenol rings and the aromatic core at C1–C6 are 91.3, 99.6, 77.2, 83.6, 76.3, and 97.7°, respectively (Figure 1 b). All DMF molecules (O7, O8, O9, and O10) are hydrogen-bonded to the hydroxyl groups HO1, HO4, HO5, and HO6 of **1** with O ⋯ O distances of 2.70, 2.69, 2.64, and 2.55 Å, respectively.

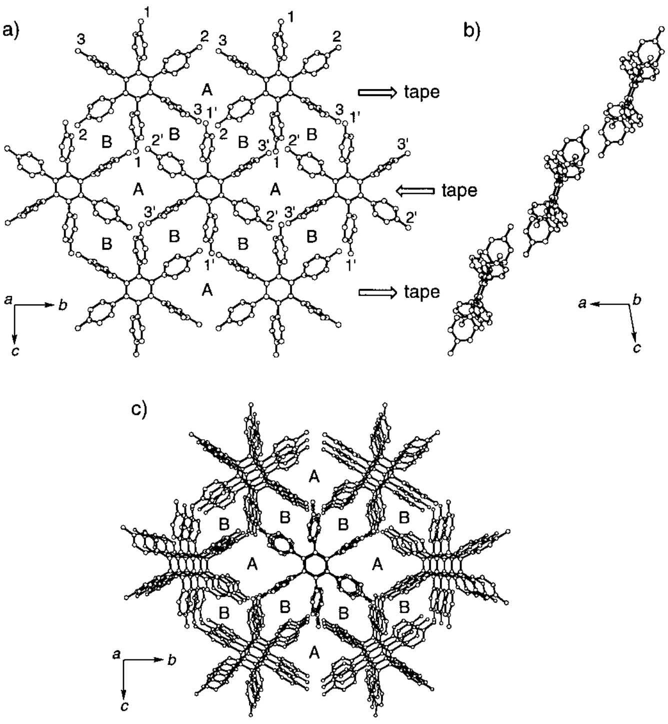

Figure 2. Views of the X-ray crystal structure of **3**: a) the two-dimensional hydrogen-bonded network (one sheet) parallel to the *a* axis, b) one sheet parallel to the *b* axis, and c) three neighboring sheets parallel to the *a* axis (perspective view). Diethyl ether molecules are omitted for clarity.

The two-dimensional hydrogen-bonded network of **4** is considerably different from that of **3**. Four hydroxyl groups of **1** are involved in the network of **4** (Figure 3a), in which the intermolecular hydrogen-bonding patterns are O2H ⋯ O6H (O ⋯ O 2.75 Å) and O3H ⋯ O5H (O ⋯ O 2.74 Å). The molecular sheet is almost flat (Figure 3 b). Although the conformational asymmetry of **1** (Figure 1 b) makes this host chiral, both enantiomers are alternately aligned along the hydrogen-bonded chains to give a racemic crystal of **4**. The network topology of **4** has large cavities (ca. 15.5 × 15.5 Å) which are partitioned by two phenol rings of **1**. In contrast to **3**, the adjacent sheets of **4** are laterally offset in an ABAB sequence by 11.58 Å along the *a* axis. Thus, each cavity in a sheet is sandwiched between two host molecules of adjacent sheets as ceiling and floor to form a chamber instead of a channel (Figure 3 c).[14] The sheet–sheet distance is about 5.9 Å.

The host **1** in single crystals of **3** and **4** occupies 40 and 45 % of the total volume of the unit cell, respectively. The respective ratios of the volume occupied by guests in **3** and **4** are 0.51 and 0.41, which are comparable to those of 4 A and 13 X molecular sieves.[8b] Single crystals of **4** are quite stable because all of the DMF molecules that are hydrogen-bonded to **1** are accommodated in the chamber.[15] Thermogravimetric analysis (10 °C min^{-1}) of **4** showed the loss of three DMF molecules at 143–180 °C and the remaining molecule at 201–228 °C.

In summary, we have demonstrated that hexakis(4-hydroxyphenyl)benzene (**1**) as a radially functionalized hexagonal host assembles into two types of porous two-dimensional

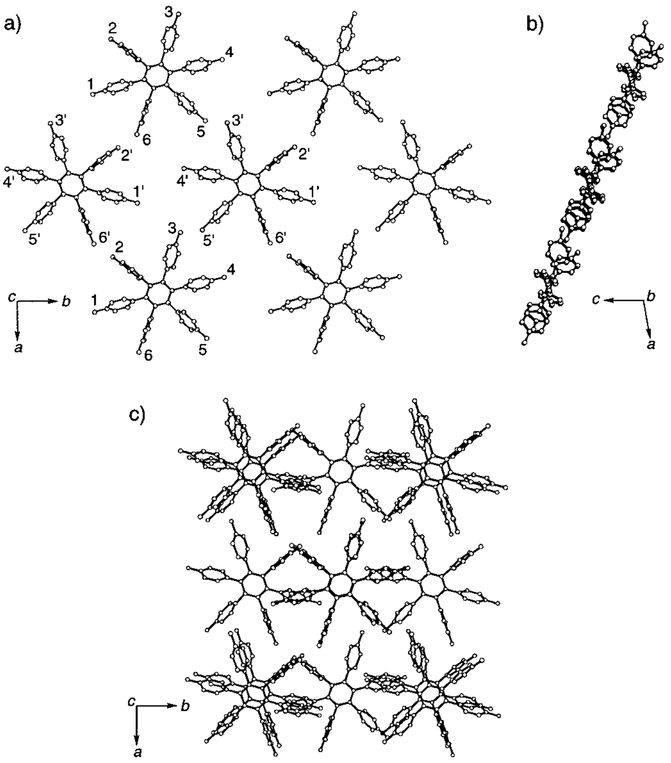

Figure 3. Views of the X-ray crystal structure of **4**: a) the two-dimensional hydrogen-bonded network (one sheet) parallel to the *c* axis, b) one sheet parallel to the *b* axis, and c) three neighboring sheets parallel to the *c* axis (perspective view). DMF molecules are omitted for clarity.

hydrogen-bonded networks without interpenetration. These are layered to form a channel or a chamber structure, depending on the nature of guest molecules. Studies on the functionalization of hexaphenylbenzene with other substituents such as carboxyl and amide groups are underway.

Experimental Section

2: A mixture of bis(4-methoxyphenyl)acetylene (480 mg, 2.01 mmol) and [$Co_2(CO)_8$] (70 mg, 0.20 mmol) in dry 1,4-dioxane (20 mL) under argon was stirred at 100°C for 24 h. After evaporation of solvent, the residue was subjected to column chromatography on silica gel with hexane/diethyl ether (9/1) as eluent. The crude product was recrystallized from CH_2Cl_2/EtOH to give **2** (388 mg, 81%). M.p. 390°C (decomp.); ^1H NMR (270 MHz, $CDCl_3$): $\delta = 3.63$ (s, 18H), 6.43 (d, $J = 8.9$ Hz, 12H), 6.66 (d, $J = 8.9$ Hz, 12H); ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 54.9$, 112.1, 132.4, 133.6, 140.2, 156.7; EI-MS: *m*/*z* (%): 714 (96) [M^+]; elemental analysis calcd for $C_{48}H_{42}O_6 \cdot 0.5\,H_2O$: C 79.65, H 5.99; found: C 79.73, H 6.16.

1: A solution of BBr_3 (0.75 mL, 7.93 mmol) in dry CH_2Cl_2 (10 mL) was added to a suspension of **2** (860 mg, 1.20 mmol) in dry CH_2Cl_2 (80 mL) at −20°C over 10 min. The mixture was allowed to warm to room temperature over 18 h and then poured into 2 M NaOH (30 mL). The aqueous layer was washed with CH_2Cl_2, acidified with 3 M HCl, and extracted with ethyl acetate. After evaporation of the solvent, the white solid was recrystallized from ethyl acetate/diethyl ether and dried in vacuo to give **1** (696 mg, 92%). M.p. 250°C (decomp.); ^1H NMR (270 MHz, CD_3OD): $\delta = 6.29$ (d, $J = 8.6$ Hz, 12H), 6.57 (d, $J = 8.6$ Hz, 12H); ^{13}C NMR (67.5 MHz, CD_3OD): $\delta = 115.3$, 134.5, 135.1, 142.5, 156.5; FAB-MS: *m*/*z* (%): 630 (35) [M^+]; elemental analysis calcd for $C_{42}H_{30}O_6 \cdot 1.5\,H_2O$: C 76.70, H 5.06; found: C 76.68, H 4.79.

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[1] a) G. R. Desiraju, *Crystal Engineering*, Elsevier, Amsterdam, **1989**; b) J. C. MacDonald, G. M. Whitesides, *Chem. Rev.* **1994**, *94*, 2383–2420; c) G. R. Desiraju, *Angew. Chem.* **1995**, *107*, 2541–2558; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2311–2327.

[2] a) C. Janiak, *Angew. Chem.* **1997**, *109*, 1499–1502; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1431–1434; b) P. Brunet, M. Simard, J. D. Wuest, *J. Am. Chem. Soc.* **1997**, *119*, 2737–2738; c) V. A. Russell, C. C. Evans, W. Li, M. D. Ward, *Science* **1997**, *276*, 575–579; d) O. M. Yaghi, H. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474–484; e) T. Dewa, K. Endo, Y. Aoyama, *J. Am. Chem. Soc.* **1998**, *120*, 8933–8940.

[3] a) M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151–1152; b) K. Endo, T. Koike, T. Sawaki, O. Hayashida, H. Masuda, Y. Aoyama, *J. Am. Chem. Soc.* **1997**, *119*, 4117–4122.

[4] a) D. J. Duchamp, R. E. Marsh, *Acta Crystallogr. Sect. B* **1969**, *25*, 5–19; b) O. Ermer, *J. Am. Chem. Soc.* **1988**, *110*, 3747–3754; c) S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558–1595; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494.

[5] S. V. Kolotuchin, E. E. Fenlon, S. R. Wilson, C. J. Loweth, S. C. Zimmerman, *Angew. Chem.* **1995**, *107*, 2873–2876; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2654–2657.

[6] For coordination networks of trigonal molecules, see: a) G. B. Gardner, Y.-H. Kiang, S. Lee, A. Asgaonkar, D. Venkataraman, *J. Am. Chem. Soc.* **1996**, *118*, 6946–6953; b) ref. [2d].

[7] D. Venkataraman, S. Lee, J. Zhang, J. S. Moore, *Nature* **1994**, *371*, 591–593.

[8] a) K. Kobayashi, K. Endo, Y. Aoyama, H. Masuda, *Tetrahedron Lett.* **1993**, *34*, 7929–7932; b) K. Endo, T. Sawaki, M. Koyanagi, K. Kobayashi, H. Masuda, Y. Aoyama, *J. Am. Chem. Soc.* **1995**, *117*, 8341–8352; c) K. Kobayashi, M. Koyanagi, K. Endo, H. Masuda, Y. Aoyama, *Chem. Eur. J.* **1998**, *4*, 417–424.

[9] A. Stabel, P. Herwig, K. Müllen, J. P. Rabe, *Angew. Chem.* **1995**, *107*, 1768–1770; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1609–1611.

[10] For the hexakis-host clathrates which are based on benzene rings hexasubstituted by flexible but bulky side arms such as arylthio groups, see: D. D. MacNicol, G. A. Downing in *Comprehensive Supramolecular Chemistry, Vol. 6* (Eds.: D. D. MacNicol, F. Toda, R. Bishop), Pergamon, Oxford, **1996**, chap. 14, pp. 421–464.

[11] For a coordination network based on the hexakis-host strategy, see: B. F. Hoskins, R. Robson, D. A. Slizys, *Angew. Chem.* **1997**, *109*, 2861–2863; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2752–2755.

[12] Reflection data were collected on a Rigaku AFC-7R four-circle diffractometer ($Mo_{K\alpha}$, $\lambda = 0.71069$ Å) in the $\omega/2\theta$ scan mode at $T = 296$ K. All data were corrected for Lorentzian, polarization, and absorption effects. The teXsan program package (**1992**) was used for structure solution (SIR92) and full-matrix least-squares refinements on *F*. The hydrogen atoms were included in fixed positions but not refined. Crystal data for **3**: $C_{29}H_{35}O_5$, crystal dimensions $0.80 \times 0.50 \times 0.30$ mm, monoclinic, space group $P2_1/c$, $a = 9.873(6)$, $b = 13.72(1)$, $c = 20.408(6)$ Å, $\beta = 102.43(4)°$, $V = 2699(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.141$ g cm^{-3}, $\mu = 0.77$ cm^{-1}, $2\theta_{max} = 55.0°$. Of 6545 observed reflections, 2749 were unique ($I > 3.0\sigma(I)$; min./max. transmission 0.68/1.00) and were used in the final refinement (308 variables), which converged to $R = 0.079$, $R_w = 0.071$, and a maximum residual electron density of 0.58 e Å^{-3}. Crystal data for **4**: $C_{54}H_{58}N_4O_{10}$, crystal dimensions $0.35 \times 0.15 \times 0.15$ mm, monoclinic, space group Pc, $a = 11.579(6)$, $b = 18.550(9)$, $c = 11.685(7)$ Å, $\beta = 96.11(5)°$, $V = 2495(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.228$ g cm^{-3}, $\mu = 0.85$ cm^{-1}, $2\theta_{max} = 60.0°$. Of 8910 unique reflections collected, 5217 ($I > 2.0\sigma(I)$; min./max. transmission 0.63/1.00) were used in the final refinement (613 variables), which converged to $R = 0.069$, $R_w = 0.059$, and a maximum residual electron density of 0.35 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-127431 (**3**) and CCDC-127432 (**4**). Copies of the data can be obtained free of charge on application to

CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[13] In **3**, each cavity **A** accommodates two hydrogen-bonded ether molecules, and each cavity **B** accommodates one non-hydrogen-bonded ether molecule.

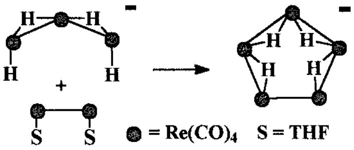
[14] In **4**, each cavity in a sheet is filled with two molecules of DMF (O7, O8) that are hydrogen-bonded in the same sheet and two molecules of DMF (O9, O10) which are hydrogen-bonded to each of the adjacent sheets.

[15] Single crystals of **3** quickly become opaque, probably due to loss of non-hydrogen-bonded diethyl ether.

$[Re_6(\mu\text{-}H)_5(CO)_{24}]^-$: The First Carbonyl Cluster with a Cyclohexane-Like Structure**

Mirka Bergamo, Tiziana Beringhelli, Giuseppe D'Alfonso,* Pierluigi Mercandelli, Massimo Moret,* and Angelo Sironi

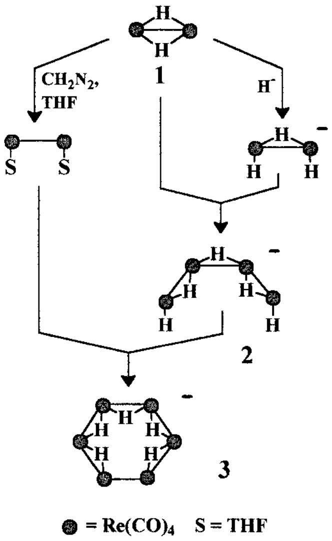
We have recently reported[1] the synthesis of the pentametallic ring cluster $[Re_5(\mu\text{-}H)_4(CO)_{20}]^-$ through the cycloaddition of the $[Re_3H_2(\mu\text{-}H)_2(CO)_{12}]^-$ anion and the $Re_2(CO)_8$ fragment originated from the labile complex $[Re_2(CO)_8(thf)_2]$[2] (Scheme 1). The reaction exploits the well-known σ-donor capability of M–H bonds toward coordinatively unsaturated metal centers[3] and shows that polyhydridic complexes can behave as multidentate "ligands". The Re_5 cluster anion—or, better, its neutral $[Re_5(\mu\text{-}H)_5(CO)_{20}]$ protonation derivative[1]—were the highest members of a series of cyclic $[ReH(CO)_4]_n$ oligomers ($n = 3-5$),[4] which are isolobal analogues of the corresponding $(CH_2)_n$ cycloalkanes owing to the isolobal relationship[5] between (singlet) methylene and the $ReH(CO)_4$ moiety.



Scheme 1. Synthesis of the pentametallic ring cluster $[Re_5(\mu\text{-}H)_4(CO)_{20}]^-$.

If this approach would be used to obtain a six-membered ring cluster, a tetranuclear chain complex would be required containing two terminal hydrides, which should thus act as a bidentate bridging "ligand" toward the $Re_2(CO)_8$ fragment. The unsaturated complex $[Re_2(\mu\text{-}H)_2(CO)_8]$ (**1**) is known to easily add $M\text{–}H^-$ anions, giving L-shaped $[M(\mu\text{-}H)Re(CO)_4(\mu\text{-}H)ReH(CO)_4]^-$ derivatives.[1, 6, 7] We therefore treated **1** with one equivalent of the $[NEt_4]^+$ salt of the dinuclear anion $[Re_2H_2(\mu\text{-}H)(CO)_8]^-$ [4, 8] and obtained rapidly and with satisfactory selectivity the addition derivative $[Re_4H_2(\mu\text{-}H)_3(CO)_{16}]^-$ (**2**).

In Scheme 2 we have depicted one of the possible rotational conformers of **2**, whose fast dynamics accounts for the 2:2:1 pattern of the hydride resonances in the ^1H NMR spectrum. High conformational lability around the Re-H-Re linkages has been observed in all the other Re_4 chain clusters characterized so far.[6, 7]



Scheme 2. Synthesis of the hexametallic ring cluster $[Re_6(\mu\text{-}H)_5(CO)_{24}]^-$.

The reaction of **2** with an equimolar amount of $[Re_2(CO)_8(thf)_2]$ afforded a complex mixture containing several unidentified species. Monitoring by ^1H NMR spectroscopy showed that the resonance of the expected $[Re_6(\mu\text{-}H)_5(CO)_{24}]^-$ anion (**3**, Scheme 2) never exceeded 40% of the total integrated intensity of the hydride region. Crystallization of this mixture led to the isolation of orange crystals of the $[NEt_4]^+$ salt of **3**.

An X-ray diffraction analysis[9] confirmed the nature of anion **3**. Indeed, the metal centers in $[Re_6(\mu\text{-}H)_5(CO)_{24}]^-$ (96 valence electrons) exhibit a cyclohexane-like geometry (Figure 1), which is unprecedented among clusters containing only carbonyl ligands. Some metal complexes containing Ag, Ni, or Pd have metallic cores with hexagonal geometries, but the metals centers are held together by bridging sulfur ligands.[12] The closest structural analogue of **3** is the irregular hexagon made of alternating $Fe(CO)_4$ and Cd(2,2′-bipyridyl) groups, which is present in $[Fe(CO)_4\{\mu\text{-}Cd(bipy)\}]_3$.[13] Therefore anion **3** represents to our knowledge the first example of a hexagonal frame of metal centers built of three-center, two-

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