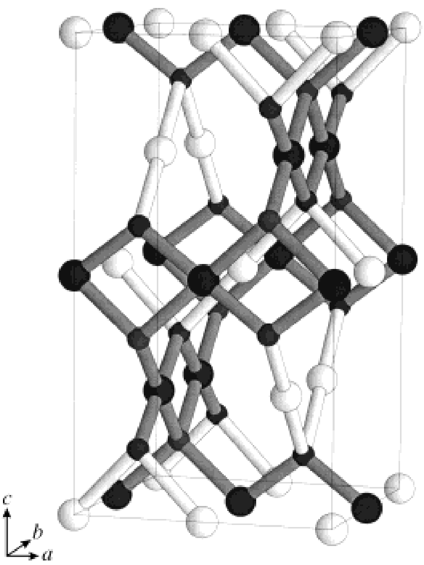

Figure 2. Crystal structure of $Ag_2Cu_2O_3$ (Ag^I: white spheres, Cu^{II}: large black spheres, O: small black spheres). Hexagonal tunnels running parallel to *a* and *b* are interconnected through tetrahedral vacant oxygen sites at (0,3/4,1/8). Bond distances [Å] and angles [°] (O1 is bonded to two Cu and two Ag atoms, and O2 to four Cu atoms): Ag–O1 2.13(1), Cu–O1 1.858(8), Cu–O2 1.9874(1), M···M = M···M′ 2.9429(2), 3.3865(1); O1-Cu-O2 100.1(3), 79.9(6), Ag-O1-Ag 87.5(4), Cu-O1-Cu 104.7(4), Cu-O2-Cu 116.860(8), 95.530(8), Ag-O1-Cu 116.2(4).

coordination (2.02–2.04 Å). The displacement of O1 towards Cu^{II} and away from Ag^I is easy to understand from a simple ionic point of view and explains the thermal stabilization of $Ag_2Cu_2O_3$ mentioned above.

The remarkable structure of $Ag_2Cu_2O_3$ presents a three-dimensional array of tunnels (parallel to *a* and *b*) with a minimum dimension corresponding to the Ag···Cu separation of 2.9429(2) Å (*a*/2). As in $YBa_2Cu_3O_6$, these metal-constrained tunnels could be most adequate for the diffusion of oxygen species. The tunnels lead directly to vacant oxygen sites, which could possibly be occupied with concomitant oxidation of Ag^I (linear) to Ag^{III} (square planar). Similarly, the structure could easily stand the elimination of one oxygen atom (O2) with the simultaneous reduction of Cu^{II} (square planar) to Cu^I (linear). This rich solid-state redox crystal chemistry should lead to a very interesting electroactive phase. Indeed, preliminary cyclic voltammograms of this novel phase confirm this potential.

On the other hand, the efficient low-temperature route to $Ag_2Cu_2O_3$ shows the way for preparing many other silver-containing cuprates of increasing complexity. In combination with the electrochemical control of oxidation states, the low-temperature synthesis and crystallization approach represents a serious alternative to the high-temperature, high-pressure search for silver-based superconductors.

Experimental Section

$Ag_2Cu_2O_3$: $Cu(NO_3)_2 \cdot 3H_2O$ (0.77 g, 3.2 mmol; Merck, p.a. 99.5%) and $AgNO_3$ (0.52 g, 3.1 mmol; Panreac, p.a. 99.98%) were dissolved in deionized water (2 mL). An aqueous solution of 3 M NaOH (4 mL) was added with stirring. The very dark green precipitate formed was isolated by filtration under vacuum and washed with water until the pH value of the filtrate was neutral. This solid precursor of unknown structure was heated in air at 90 °C for 24 hours to yield the black oxide $Ag_2Cu_2O_3$ quantitatively. Collection of powder X-ray data: $10 < 2\theta < 90°$, step 0.02°, $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å). Refined profile parameters: scale factor $1.155(7) \times 10^{-5}$, zero point $-0.185(2)$, $U = 0.87(4)$, $V = -0.20(3)$, $W = 0.037(5)$; η (pseudo-Voigt peak shape parameter) = 0.64(1). Crystal structure analysis of $Ag_2Cu_2O_3$: tetragonal, $a = 5.8857(3)$, $c = 10.6868(7)$ Å, space group $I4_1/amd$, origin choice 2, $Z = 4$; atom (site; fractional coordinates; B_{iso}; occupancy): Ag (*8c*; 0,0,0; 3.01(7); 2), Cu (*8d* ; 0,0,0.5; 2.7(1); 2), O1 (*8e*; 0,0.25,0.144(1); 2.2(6); 2), O2 (*4b*; 0,0.25,0.375; 1.0(8); 1). $R = 0.0391$, $R_{wp} = 0.0561$, $R_{expected} = 0.0267$, $\chi^2 = 4.41$.

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A Self-Assembled Calix[4]arene Dimer Linked through Hydrogen-Bonded 2-Ureidopyrimidin-4(1*H*)-one Groups[**]

Juan J. González, Pilar Prados, and Javier de Mendoza[*]

The self-assembly of simple fragments to form structures with designed cavities and networks mediated by noncovalent, complementary interactions such as hydrogen bonding, hydrophobic interactions, and metal–ligand bonding is a

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[*] Prof. Dr. J. de Mendoza, Dr. J. J. González, Prof. Dr. P. Prados
Departamento de Química Orgánica
Universidad Autónoma de Madrid
Cantoblanco, E-28049 Madrid (Spain)
Fax: (+349) 1-397-3966
E-mail: javier.demendoza@uam.es

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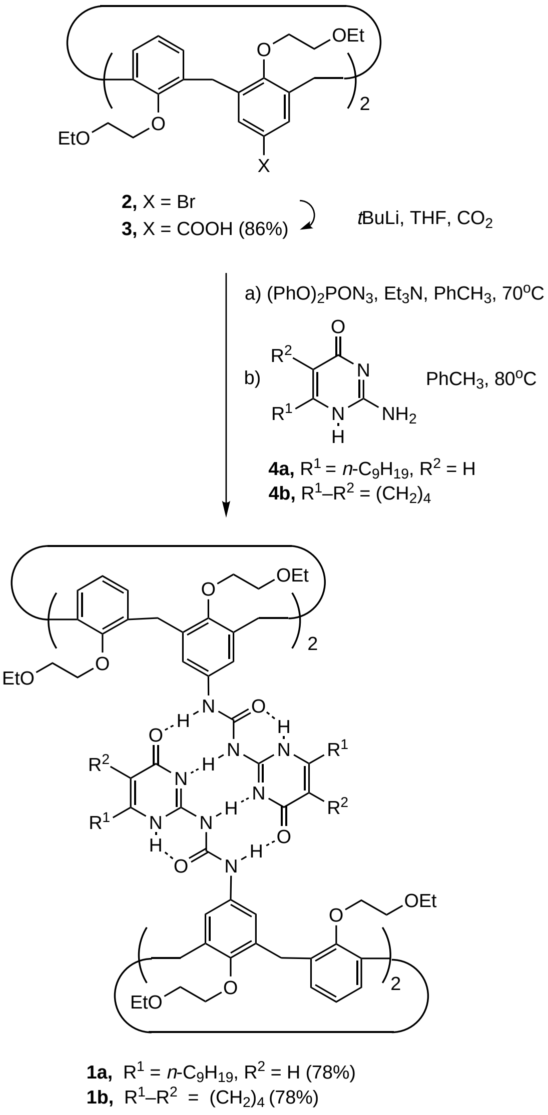
current major goal in supramolecular chemistry.[1, 2] A number of calixarene derivatives have been shown to self-assemble through hydrogen bonding in apolar solvents.[3] The dimerization of calix[4]arenes containing urea substituents at the upper rim has been extensively studied by Rebek et al. and Böhmer et al. independently.[4] Molecules the size of benzene can be encapsulated in these dimers. However, for larger guests, several molecular platforms linked through a more robust network of hydrogen bonds are required to assure the self-assembly of a stable, multicomponent, cavity-containing host. Recently, Meijer et al. have described the dimerization of 6-substituted 2-ureidopyrimidin-4(1*H*)-ones (R^1 = alkyl or aryl, R^2 = H) mediated by a strong linear array of hydrogen bonds in a DDAA arrangement (D = donor, A = acceptor; $K_{ass} > 10^6\,\text{M}^{-1}$).[5] We report here the synthesis of calix[4]arenes dimers **1a** and **1b** in which the calixarenes are in 1,3-*alternate* conformation and linked by eight hydrogen bonds between ureidopyrimidinonyl groups.[6]

The synthesis of compounds **1a** and **1b** was straightforward (Scheme 1). The 1,3-*alternate* calix[4]arene dibromide **2**[6b] was first readily transformed into the corresponding dicarboxylic acid **3** by bromine/lithium exchange. Then, in a single, one-pot reaction **3** underwent a Curtius rearrangement with diphenylphosphoryl azide (DPPA),[7] and the resulting bisisocyanate was allowed to react in situ with the appropriate 2-aminopyrimidinone **4** to yield the corresponding ureidopyrimidinonyl calix[4]arenes as dimers **1a** and **1b** in 78 % overall yield from **3**.



Scheme 1. Synthesis of **1a** and **1b**.

Dimers **1a** and **1b** are soluble in nonpolar solvents such as benzene and toluene but almost insoluble in DMSO and acetone at 30 °C. The ^{1}H NMR spectrum of **1a** ($CDCl_3$) shows large downfield shifts for the urea NH protons at $\delta = 12.02$ and 11.95, consistent with the four DDAA hydrogen bonds present in the dimer. The chelated NH group at position 1 gives rise to a signal at $\delta = 13.37$. None of these signals shift upon dilution (up to 10^{-4} M), a good indication of a strong association ($K_{ass} > 10^6\,\text{M}^{-1}$). Two independent signals are clearly observed for the protons of the substituted arene rings at $\delta = 6.97$ and 7.80 as a consequence of the hindered rotation about the calixarene – urea C–N bond. A similar phenomenon has been described for calix[4]arene tetraurea dimers.[4]

Similar results were obtained for **1b** (signals at $\delta = 13.23$, 12.10, 11.89, 7.84, 7.05). In addition, a heterodimer slowly formed when a 1:1 mixture of **1a** and **1b** in $CDCl_3$ was kept at room temperature; this was supported by a new set of signals in the ^{1}H NMR spectrum ($\delta = 11.97$, 11.84, 7.76, 5.93).[8]

Dimer **1a** was further studied in mixtures of $CDCl_3$ and [D$_6$]DMSO, a strong hydrogen-bond acceptor. Only at $\chi_{DMSO} \geq 0.5$ was the monomer observed by ^{1}H NMR spectroscopy; the NH protons gave rise to broad singlets centered at $\delta = 11.3$, 9.6, and 9.1 ($\chi_{DMSO} = 0.88$). The monomer was the only species observed in pure [D$_6$]DMSO at 373 K. The apparent constant of association (Figure 1 a) was determined

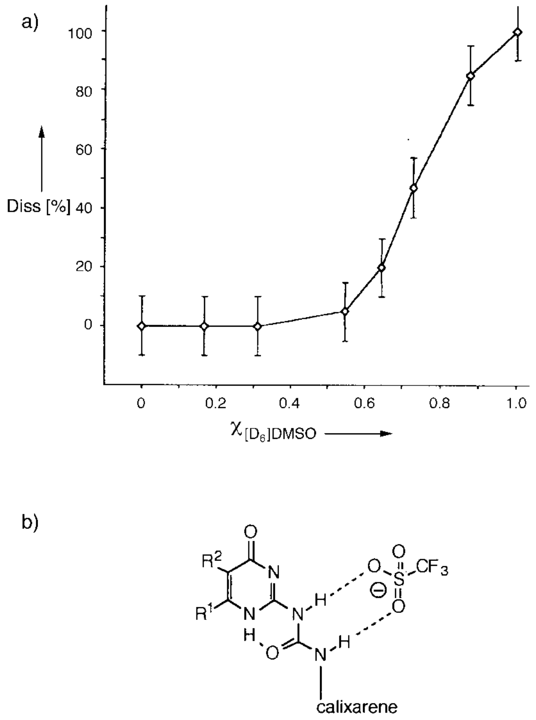


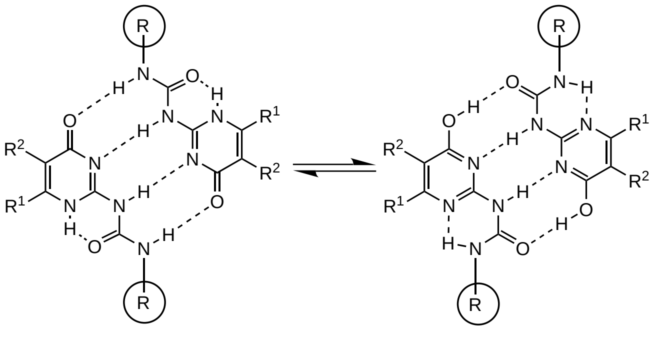
Figure 1. a) Plot of the extent of dissociation versus solvent composition for dimers of **1a** in $CDCl_3$/[D$_6$]DMSO mixtures. The line connecting the data points does not reflect a mathematical function but only serves to guide the eye. b) The complex formed by monomer **1a** and a triflate ion.

by integration at $\chi_{\mathrm{DMSO}} = 0.64$ ($K^{*}_{\mathrm{ass}} = 2500 \pm 20\,\%\ \mathrm{M}^{-1}$) and at $\chi_{\mathrm{DMSO}} = 0.73$ ($K^{*}_{\mathrm{ass}} = 572 \pm 20\,\%\ \mathrm{M}^{-1}$).[9] Another way to break the dimers was the addition of an oxoanion that could act as a strong competitor for the urea hydrogen donors. Thus, in the presence of a trifluoromethanesulfonate (triflate) salt, a less rigid triflate–monomer complex was apparent by NMR spectroscopy (Figure 1b).

Additional evidence for the dimeric structure of **1a** came from mass spectrometry and vapor pressure osmometry (VPO). In addition to a peak at *m/z* 1270 (100% rel. intensity), ascribable to the monomer (calculated mass = 1269), the positive-ion FAB mass spectrum of **1a** shows a sizeable peak at *m/z* 2539 (30%). An average molecular mass of 2535 ± 120 was determined by VPO in chloroform (30 °C, benzil as the standard). These values fully agree with the mass calculated for the proposed dimeric structure ($M_{\mathrm{w}} = 2539$).

Similar results were obtained for the cyclohexane-annelated calix[4]arene dimer **1b**. The positive-ion FAB mass spectrum of **1b** shows a monomer peak at *m/z* 1126 (100%) and another for the dimer at *m/z* 2250 (6%). So far, only dimers from 2-ureidopyrimidinones without substituents at position 5 ($R^2 = H$) have been reported.[5] Our results show that introduction of a substituent in this position (as in **1b**) does not affect the dimerization.

2-Ureidopyrimidin-4(1*H*)-ones are tautomeric structures in solution.[5b] Equilibria are limited to the pyrimidin-4(1*H*)-one and pyrimidin-4-ol forms in the dimers (Scheme 2). The pyrimidinone tautomer in which the terminal R residues attached to the ureas are almost perfectly aligned is highly favored over the pyrimidin-4-ol tautomer when R^1 is alkyl.[5b] For calix[4]arene dimers **1a** and **1b** the pyrimidinone tautomer is also the only one observed by FT-IR spectroscopy (KBr, absence of a 2500 cm^{-1} band) and ROESY NMR experiments.[10] An additional reason for this preference was found in the relative orientation of the terminal R groups attached to the ureas (see Scheme 2, R = calixarene): the residues are almost perfectly aligned in opposite directions in the pyrimidinone case but slightly shifted in the pyrimidin-4-ol tautomer. In the rigid calix[4]arene framework this would likely cause some torsional strain, as can be surmised by simple inspection of space-filling molecular models.



Scheme 2. 2-Ureidopyrimidin-4(1*H*)-one tautomers.

However, as the result of the two relative orientations of the flat hydrogen-bonded 2-ureidopyrimidinone surfaces, each dimer exists in two *syn–anti* isomeric forms. The ^{1}H NMR spectra in $CDCl_3$ indicate roughly a 5:1 ratio of isomers for each dimer (integration of peak areas), which slowly exchange at room temperature on the NMR time scale (Figure 2). Simple inspection of space-filling models shows that the *anti* isomers are twisted and more strained than the corresponding *syn* isomers. Thus, a *syn* arrangement for the major component of these mixtures is likely.

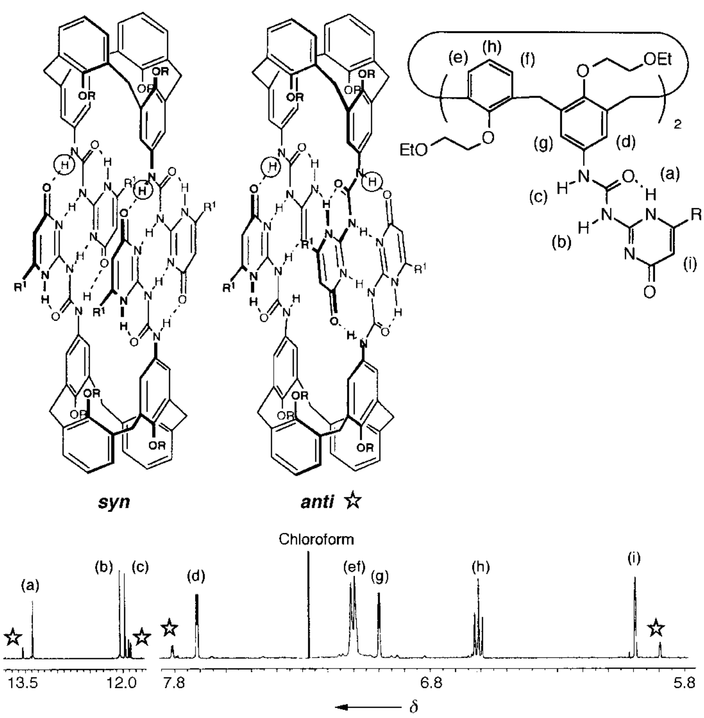


Figure 2. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1a** showing signals arising from the two *syn–anti* isomers. $R = OCH_2CH_2OEt$; $R^1 = n\text{-}C_9H_{19}$.

We have shown that 2-ureido-4-pyrimidinone groups can be easily introduced on calixarene platforms. Bridging positions 5 and 6 with a cyclohexane unit does not perturb the calixarene dimerization. This opens up interesting perspectives in the design of more sophisticated self-assembled supramolecular structures.

Experimental Section

General procedure for the synthesis of **1a** and **1b**: To a suspension of **3** (270 mg, 0.34 mmol) and Et_3N (110 µL, 0.74 mmol) in toluene (5 mL) at 40 °C was added DPPA (160 µL, 0.74 mmol). The solution was stirred for 1 h at 40 °C and for 4 h at 80 °C. Then a suspension of **4** (1.35 mmol) in toluene (3 mL) was added, and the reaction mixture was heated for 16 h at 80 °C. The reaction mixture was concentrated to dryness and triturated with methanol to give **1**.

1a: 78% yield; (5:1 mixture of isomers); m.p. 212–214 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): major isomer: $\delta = 13.37$ (s, 4H; NH), 12.02 (s, 4H; NH), 11.95 (s, 4H; NH), 7.70 (d, ^4J(H,H) = 2.4 Hz, 4H; ArH), 7.09 (d, ^3J(H,H) = 7.6 Hz, 8H; ArH), 6.98 (d, ^4J(H,H) = 2.4 Hz, 4H; ArH), 6.59 (t, ^3J(H,H) = 7.6 Hz, 4H; ArH), 5.96 (s, 4H; pyrimidinonyl (pyrim)), 4.31–4.00 (m, 16H; CH_2), 3.90–3.80 (m, 8H; CH_2), 3.74 (t, ^3J(H,H) = 4.5 Hz, 8H; CH_2), 3.69–3.56 (m, 20H; CH_2, $ArCH_2Ar$), 3.56 (d, ^2J(H,H) = 12.7 Hz, 4H; $ArCH_2Ar$), 3.52 (d, ^2J(H,H) = 12.5 Hz, 4H; $ArCH_2Ar$), 3.41 (d, ^2J(H,H) = 12.5 Hz, 4H; $ArCH_2Ar$), 2.28 (m, 8H; CH_2), 1.60 (m, 8H; CH_2), 1.28 (t, ^3J(H,H) = 7.0 Hz, 12H; CH_3), 1.20 (t, ^3J(H,H) = 7.0 Hz, 12H; CH_3), 1.24–1.16 (m, 48H; CH_2), 0.87 (t, ^3J(H,H) = 6.5 Hz, 12H; CH_3); minor isomer (only signals different from those of the major isomer):

$\delta = 13.52$ (s, 4H; NH), 11.88 (s, 4H; NH), 11.86 (s, 4H; NH), 7.80 (d, ^4J(H,H) = 2.3 Hz, 4H; ArH), 5.87 (s, 4H; pyrim); ^{1}H NMR (300 MHz, [D$_6$]DMSO, 100 °C): $\delta = 10.70-10.00$ (br s, 4H; NH), 9.40 (s, 2H; NH), 7.18 (s, 4H; ArH), 7.04 (d, ^3J(H,H) = 7.5 Hz, 4H; ArH), 6.64 (t, ^3J(H,H) = 7.5 Hz, 2H; ArH), 5.73 (s, 2H; pyrim), 3.80–3.30 (m, 32H; CH$_2$), 2.42 (t, ^3J(H,H) = 7.5 Hz, 4H; CH$_2$), 1.63 (m, 4H; CH$_2$), 1.50–1.20 (m, 24H; CH$_2$), 1.17 (t, ^3J(H,H) = 7.0 Hz, 6H; CH$_3$), 1.09 (t, ^3J(H,H) = 7.0 Hz, 6H; CH$_3$), 0.85 (t, ^3J(H,H) = 7.0 Hz, 6H; CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, Heteronuclear Multiple Quantum Correlation (HMQC)): major isomer: $\delta = 172.2$, 156.0 (CO), 155.1, 154.8, 152.1, 151.2, 133.3, 133.2, 133.1, 131.3 (ArC, pyrimC), 129.6, 129.5, 123.5, 122.6, 121.4 (ArCH), 105.2 (pyrimCH), 72.3, 72.1, 70.0, 69.7(OCH$_2$CH$_2$O), 66.6, 66.1 (OCH$_2$CH$_3$), 34.1, 33.5 (ArCH$_2$Ar), 32.9, 31.8, 29.5, 29.3, 29.2, 29.1, 27.3, 22.6 (CH$_2$), 15.6, 15.3 (OCH$_2$CH$_3$), 14.1 (CH$_3$); IR (KBr): $\tilde{\nu} = 3357$, 1701, 1654, 1587, 1465, 1245 cm^{-1}; positive-ion FAB MS (2-nitrophenyloctyl ether matrix): m/z (%): 2539 (30) [2M+H]$^+$, 1270 (100) [M+H]$^+$; elemental analysis calcd for $C_{72}H_{100}N_8O_{12}$ (%): C 68.11, H 7.94, N 8.83; found: C 67.77, H 8.28, N 8.68.

1b: 78% yield; (mixture of isomers in proportion 3:1): m.p. 264–266 °C; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): major isomer: $\delta = 13.23$ (s, 4H; NH), 12.10 (s, 4H; NH), 11.89 (s, 4H; NH), 7.84 (d, ^4J(H,H) = 2.3 Hz, 4H; ArH), 7.15–7.05 (m, 8H; ArH), 7.05 (d, ^4J(H,H) = 2.3 Hz, 4H; ArH), 6.60 (t, ^3J(H,H) = 7.0 Hz, 4H; ArH), 4.20–3.40 (m, 64H; CH$_2$), 2.62–2.30 (m, 16H; CH$_2$), 1.78 (m, 16H; CH$_2$), 1.34 (t, ^3J(H,H) = 7.0 Hz, 12H; CH$_3$), 1.19 (t, ^3J(H,H) = 7.0 Hz, 12H; CH$_3$); minor isomer (only signals different from those of the major isomer): $\delta = 13.35$ (s, 4H; NH), 12.00 (s, 4H; NH), 11.96 (s, 4H; NH); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): major isomer: $\delta = 171.8$, 156.1 (CO), 155.0, 153.6, 152.0, 143.7, 133.7, 133.0 (multiple peaks), 131.9 (ArC, pyrimC), 129.7, 129.5, 123.1, 122.0, 121.3 (ArCH), 114.9 (pyrimCH), 72.2, 71.5, 70.0, 69.6 (OCH$_2$CH$_2$O), 66.6, 66.3 (OCH$_2$CH$_3$), 34.5, 33.9 (ArCH$_2$Ar), 26.7, 22.3, 21.7 (CH$_2$), 15.4, 15.3 (CH$_3$); minor isomer (only signals different from those of the major isomer): $\delta = 154.7$, 153.8, 143.3, 132.2 (ArC, pyrimC), 129.4, 129.2, 121.8, 121.5 (ArCH), 115.4 (pyrimCH), 72.3, 71.8 (OCH$_2$CH$_2$O), 66.4 (OCH$_2$CH$_3$), 34.1 (ArCH$_2$Ar), 22.0, 21.5 (CH$_2$), 15.7 (CH$_3$); IR (KBr): $\tilde{\nu} = 3337$, 1703, 1653, 1584, 1460, 1245 cm^{-1}; positive-ion FAB-MS (m-nitrobenzyl alcohol matrix): m/z (%): 2250 (6) [2M+H]$^+$, 1126 (100) [M+H]$^+$.

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[8] No heterodimers were observed, however, by addition of 6-*n*-nonyl-2-*n*-octylureidopyrimidin-4(1*H*)-one to **1a**.

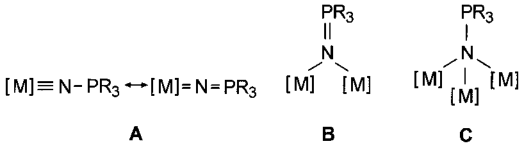
[9] The apparent association constant (K^*_{ass}) was determined from the integrals (I) of the signals of the pyrimidinyl proton in the monomer ($\delta = 5.6$) and dimer ($\delta = 5.9$) using the formula $K^*_{ass} = (1-\alpha_{diss})/4c_0\alpha^2_{diss}$, where $\alpha_{diss} = I_{monomer}/(I_{monomer} + I_{dimer})$ and c_0 is the initial concentration of the dimer. Furthermore, the value of K^*_{ass} determined by integration of one signal of the calixarene unit in the monomer ($\delta = 6.6$, t) and dimer ($\delta = 6.5$, t) was on same order of magnitude.

[10] NH signals were assigned by this experiment.

$[Cu_{12}(NPEt_3)_8]^{4+}$ and $[Ag_{12}(NPEt_3)_8]^{4+}$: Cubane Structures[**]

Ulrike Riese, Naim Faza, Werner Massa, and Kurt Dehnicke[*]

Phosphoraneiminato complexes of transition metals are known in a large variety of forms.[1] The phosphoraneiminato ligands NPR_3^- that are isoelectronic with silanolates $OSiR_3^-$ show great flexibility with regard to coordination chemistry aspects. The terminal bonding mode **A** is preferably realized with electron-deficient transition metals, while increasingly electron-rich transition metals form the μ-bridging type **B** or even the μ_3-type **C**. With divalent transition metals of Mn, Fe, Co, Ni, Zn, and Cd type **C** leads to tetrameric complexes $[XM(NPR_3)]_4$ (X = halogen, organic residue) with M_4N_4 heterocubane structures. With Cu^I, Ag^I, and Au^I such an architecture cannot develop because of their tendency towards sp hybridization. In fact, the build-up of the phosphoraneiminato complexes of Au^I, $[R_3PN\{Au(P'R_3)\}_3]^{2+}$ (R = Ph, NMe$_2$), leads to coordination type **C** with linear axes N-Au-P′.[2]



We have now found that reactions of the silylated phosphaneimine $Me_3SiNPEt_3$ with anhydrous copper(I) trifluoromethanesulfonate (triflate) [Eq. (1)] and of the heterocubane $[BrCo(NPEt_3)]_4$[3] with excess silver triflate [Eq. (2)] provide

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[*] Prof. Dr. K. Dehnicke, Dr. U. Riese, Dr. N. Faza, Prof. Dr. W. Massa
Fachbereich Chemie der Universität
Hans-Meerwein-Strasse, D-35032 Marburg (Germany)
Fax: (+49) 6421-28-8917

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