Benzimidazolium- and Benzimidazolilydene-Capped Cyclodextrins: New Perspectives in Anion Encapsulation and Gold-Catalyzed Cycloisomerization of 1,6-Enynes.

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Abstract: A new way of introducing a NHC-cap onto cyclodextrins (CDs) has been devised. The benzimidazolium intermediates were found to behave as receptors towards cavity matching anions. The resulting C₁- and C₂-symmetrical regioisomeric NHC gold(I) complexes have been tested in a benchmark asymmetric cycloisomerization of 1,6-enynes. Up to 50% ee was achieved for the enantioselective cycloisomerization of *N*-allyl-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide.

Confining cavity-shaped ligands are increasingly popular in catalysis because of their capacity to control the first coordination sphere of metals and in doing so produce unusual selectivities during metal-catalyzed reactions.^[1] However, their use in asymmetric catalysis remains scarce due to the lack of suitable chiral macrocyclic receptors.^[2] Amongst them, the naturally-occurring CDs^[3] occupy a place of choice as they are cheap, enantiopure, available in different sizes and can be easily derivatized at specific locations. So far most effort has concentrated on asymmetric catalytic reactions taking place in water to take advantage of the host-guest properties of CDs in this medium.^[4] It is only recently with the advent of new ways of functionalizing CDs^[5] that ligands with rigidified donor atoms

have been able to force a metal center to reside inside the CD cavity in organic media, resulting in very promising selectivities, in particular stereoselectivity, for several metal-catalyzed reactions.^[6] Achieving such a desirable outcome in gold(I) catalysis^[7] still constitutes to date a highly challenging target in particular for mononuclear complexes since the gold catalytic center needs to be as close as possible to the selectivity-inducing steric environment as for example in helicene-based systems.^[8] Such a feature can also be achieved by confining *N*-heterocyclic ligands derived from *perbenzylated* CDs, as recently shown by Sollogoub and coll.^[6a, 6e] The corresponding mono-gold complexes gave rise to promising enantio- and ring-size selectivities in two different enyne cycloisomerization reactions. So far, neither their *permethylated* counterparts, nor C₁-symmetrical AC-capped derivatives have been tested. Having a rather accessible cavity compared with their benzylated analogues, such confining NHC ligands should be suitable for sterically more demanding enyne substrates. Moreover, following our previous studies on anion encapsulation in metalloCDs,^[9] we wondered whether we could achieve the same properties with metal-free imidazolium-capped CDs. Herein, we present a new way of introducing a NHC-cap onto CDs, the capacity of benzimidazolium-capped, methylated CDs to behave as middle-sized anion receptors, and the catalytic properties of gold complexes derived from both C₁- and C₂-symmetrical NHC-capped, methylated CDs in the asymmetric cycloisomerization of 1,6-enynes.

Contrary to their *perbenzylated* analogs, *permethylated* CDs could not be capped with an imidazolium or benzimidazolium unit in a straightforward manner.^[10] Thus, reaction of dimesylates **1–4** with either imidazole or benzimidazole resulted in poor yields (< 30%) of capped products or no capping at all in the case of the AC regioisomers. To overcome this hurdle, we devised an indirect strategy for preparing benzimidazole-capped methylated α -CDs (Scheme 1). Thus, dialdehydes **7** and **8**, which were respectively obtained by Swern oxidation of known diols **5** and **6**, were reacted with 1,2-diphenylene diamine under reductive amination conditions to give secondary diamines **9** and **10** in respectively 68% and 61% yields.^[11] Compounds **9** and **10** were then reacted with triethyl orthoformate under acidic

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conditions to give **11** and **12** in high yields (> 90%). Surprisingly, the benzimidazolium N-CH=N protons of these chloride salts resonate in CDCl₃ at markedly different chemical shifts. While the δ value for **12** is typical of a CH $\cdots$ Cl hydrogen bond (δ = 11.98 ppm) involving the chloride counteranion,^[12] that of **11** lies at a much higher field (δ = 9.95 ppm), this being consistent with a weaker hydrogen-bonded proton. However in both salts, inner-cavity H-5 CD protons belonging to bridged glucose units, respectively A and C for **11** and A and D for **12**, are also downfield shifted (δ up to 5.02 ppm and 5.13 ppm for respectively **11** and **12**). This is most likely a result of the inclusion of the chloride anion in the CD cavity, a feature that was confirmed by an X-ray crystal structure in the case of **12** (*vide infra*). The fact that in **11** the benzimidazolium N-CH=N proton is strongly upfield shifted compared to that of **12**, is likely the result of an unfavorable geometry for benzimidazolium-centered CH $\cdots$ Cl hydrogen bond formation within the cavity of the unsymmetrical AC regioisomer **11**. Indeed, when the chloride was exchanged for an anion too large to penetrate the CD cavity such as tetraphenylborate as in both benzimidazolium salts **13** and **14**, δ values (δ = 9.32 and 8.89 ppm respectively) for a non-hydrogen-bonded benzimidazolium N-CH=N proton as well as H-5 protons with unremarkable upfield δ values (δ H-5^{A,C} = 4.63 and 4.71 ppm for **13** and δ H-5^{A,D} = 4.41 ppm for **14**) were observed.

The molecular structure of **12** (Figure 1) shows the inclusion of the chloride counter-anion in the cavity with a bridging benzimidazolium unit almost perfectly parallel to the CD axis.^[13] Surprisingly, the chloride anion is located sideways and disordered over two positions, so that the whole structure is not C₂-symmetrical. This contrasts with the apparent C₂-symmetry inferred from the NMR spectra. The shortest CH $\cdots$ Cl distances are those involving the benzimidazolium H-2 proton (2.32 Å) and the H-5 proton of CD unit A (2.76 Å). These values are well within the range usually observed for CH $\cdots$ Cl hydrogen bonds. Moreover, the chloride anion is also hydrogen bonded to a water molecule lying further down the cavity. We believe that the particular orientation of the handle with respect to the CD framework is highly dependent of these weak interactions since the bridging unit in all analogous structures is always tilted (*vide infra*).

Other medium-sized counteranions can be included in the cavity, notably PF₆[−] as in benzimidazolium salts **15**. Again strongly upfield shifted H-5 protons (δ H-5^{A,D} = 5.06 ppm for **15**) revealed anion encapsulation. Here the δ value for the N-CH=N proton (δ = 9.68 ppm) lies between that of **12** and **14**, which is indicative of some degree of hydrogen bonding between at least one fluorine atom of the PF₆[−] anion and the benzimidazolium N-CH=N proton. This interaction was confirmed by the presence of cross peaks arising from through-space correlations between fluorine atoms and the NHC H-2 proton in the ¹H-¹⁹F HOESY spectra of **15**.^[14] Moreover, the only other protons that correlate with the PF₆[−] fluorine atoms are inner-cavity ones (some of the H-3 and H-5 protons of the CD unit). All these CH $\cdots$ F interactions may contribute to anion stabilization within the CD cavity as already observed with metallocyclodextrins.^[9] Anion encapsulation also takes place in the solid state as confirmed by an X-ray crystal structure of **15** (Figure 1), which clearly shows four fluorine atoms of the PF₆[−] anion in close contact (CH $\cdots$ F < 3 Å) with the H-2 benzimidazolium proton (CH $\cdots$ F : 2.23 and 2.32 Å) as well as some H-3 and H-5 CD protons (5 CH $\cdots$ F H-bonds

Scheme 1. Synthesis of benzimidazolium salts **11–16**. a) Oxalyl chloride (10 equiv.), DMSO (20 equiv.), CH₂Cl₂, −78 °C, 2 h, then NEt₃ (21 equiv.), 30 min; b) 1,2-phenylenediamine, NaBH₃CN, MeOH/AcOH (2:1), 15 h; c) HCl 37%, triethyl orthoformate, 80 °C, 2 h; d) aqueous NaBPh₄; e) aqueous KPF₆.

ranging from 2.59 Å to 2.95 Å). Moreover, the benzimidazolium unit in **15** is slightly tilted unlike that of **12** (tilt angle of about 6.5° with respect to the CD axis). All in all, these observations reflect once again the affinity of methylated cyclodextrins for anions.^[9] The situation is quite different with the AC regioisomer **16**, the

Figure 1. Molecular structures of benzimidazolium salts **12** (only one of the chloride locations is displayed) and **15** showing the encapsulation of respectively the chloride and hexafluorophosphate anions (halide atoms are represented in green).

cavity of which is not suited for accommodating the PF_6^- anion. In this case, the N-CH=N proton resonates at much higher field ($\delta = 9.15$ ppm) in keeping with a weaker $\text{CH}\cdots\text{F}$ H-bond and the inner-cavity protons are not downfield shifted ($\delta \text{H-5}^{\text{A,C}} = 4.70$ and 4.78 ppm). This was confirmed by a ^1H - ^{19}F HOESY experiment, which clearly revealed a weak correlation between fluorine atoms and the benzimidazolium H-2 proton, but strong correlations between the same fluorine atoms and CD outward-oriented protons (6-OMe, H-6 $^{\text{A or C}}$) together with other benzimidazolium protons. Clearly, in this case the PF_6^- anion is located outside the cavity just above the CD primary face.^[15]

Reaction of **11** with $[\text{AuCl}(\text{tth})]$ (tth = tetrahydrothiophene) in CH_2Cl_2 in the presence of K_2CO_3 ^[16] resulted in the formation after 12 h of complex **17** in 87% yield. Surprisingly, under the same reaction conditions, benzimidazolium salt **12** gave a large amount of benzimidazol-2-one **18** (52% yield) together with the expected gold complex **19** (46% yield). The presence of the carbonyl group in **18** was inferred from its IR (ν_{CO} 1699 cm^{-1}) and $^{13}\text{C}\{^1\text{H}\}$ NMR ($\delta = 153.9$ ppm) spectra.^[6a, 17] Using Cs_2CO_3 instead of K_2CO_3 and performing the reaction under strict anhydrous conditions increased the reaction rate significantly (100% conversion after 2 h) and raised the yield of **19** to 80% with no benzimidazol-2-one being detected in the reaction mixture. The formation of imidazol-2-ones has already been observed by Cazin^[18] upon treatment of alkyl N,N' -substituted imidazolium salts with Cu_2O . Although the mechanism of formation of **18** remains unclear, it is likely to be metal-mediated as the reaction does not occur without gold. Furthermore, it most probably involves a hydrolysis step followed by dehydrogenation^[19] rather than direct oxidation as carbenes are not known to be easily oxidized neither with oxygen nor with other oxidizing agents.^[20] Clearly, the heavily encapsulated AD carbene intermediate is less easily metallated than its AC counterpart so that metallation competes with carbene oxidation in the case of the former. As for their perbenzylated counterparts, both complexes **17** and **19** display strongly deshielded inner-

Figure 2. Molecular structures of NHC gold(I) complexes **17** (top) and **19** (bottom; two views) showing the tilt of the benzimidazolidene unit with respect to the CD cavity (left) and the groove that runs through the secondary face (right).

cavity H-5 $^{\text{AD/AC}}$ and H-3 protons ($\delta \text{H-3}^{\text{E}} = 4.15$ ppm and $\delta \text{H-3}^{\text{F}} = 4.00$ ppm for **17**, and $\delta \text{H-3}^{\text{B,E}} = 4.18$ ppm for **19**) as a result of $\text{CH}\cdots\text{Au}$ interactions of the anagostic type and $\text{CH}\cdots\text{Cl}$ H-bonds respectively.^[6e] While the chemical shift of the H-5 inner-cavity protons lies in the expected range for C_2 -symmetrical **19** ($\delta (\text{H-5}^{\text{A,D}}) = 6.44$ ppm), those of bridged units A and C are strongly differentiated in C_1 -symmetric **17**, one of them (H-5 $^{\text{A}}$) having an unprecedented δ value of 7.30 ppm, which corresponds to a $\Delta\delta$ of $+2.63$ ppm when comparing the ^1H NMR spectrum of **17** with that of the corresponding benzimidazolium salt **11**. On the contrary, the H-5 $^{\text{C}}$ proton is hardly affected by metal complexation ($\Delta\delta = +0.14$ ppm). Clearly, the H-5 $^{\text{A}}$ proton interacts more strongly with the metal center in **17** than in its C_2 symmetrical counterpart. The fact that H-5 $^{\text{A}}$ and H-5 $^{\text{C}}$ have very different values is indicative of a large variation of $\text{M}\cdots\text{H-5}$ separations in **17**. Single crystals of both **17** and **19** suitable for X-ray diffraction studies could be grown by slow diffusion of pentane into a CH_2Cl_2 solution of either gold complex. The molecular structure of **19** (Figure 2, bottom) shows that the benzimidazolidene unit is not parallel to the CD axis but is tilted by an angle of about 10.7° , a value that is larger than in both imidazolium salts **12** and **15**.^[21] Since the complex has average C_2 symmetry in solution, a rapid fan-like motion of the benzimidazolium ring above the CD must take place. The H-5 $^{\text{A,D}}$ inner-cavity protons are clearly in close contact with the gold atom, but with two noticeably different $\text{Au}\cdots\text{H}$ separations ($\text{CH}\cdots\text{Au}$: $2.39\text{ \AA}$ for unit A vs. $2.79\text{ \AA}$ for unit D). The marked tilt of the benzimidazolidene unit in **19** is, at least in part, a result of a single anagostic $\text{CH}\cdots\text{Au}$ interaction involving the H-5 proton of glucose unit A. Moreover, the included chloride is weakly hydrogen bonded to a CH_2Cl_2 molecule ($\text{CH}\cdots\text{Cl}$: $2.57\text{ \AA}$), and to a lesser extent to the inner-cavity H-3 proton of glucose unit E ($\text{CH}\cdots\text{Cl}$: $3.08\text{ \AA}$), which is consistent with the solution NMR studies (*vide supra*). As for **17**, its molecular structure (Figure 2, top) shows a NHC-Au-Cl rod slightly deviating from linearity (C-Au-Cl 176.4°) and a more pronounced tilt of the benzimidazolidene unit (42.5°), forcing the chlorido ligand to be

Table 1. Enantioselective cycloisomerization of *N*-tethered 1,6-enynes^[a]

Entry	[Au*]	R	T [°C]	t [h]	Conv. [%]	ee ^[b] [%]
1	17	H	25	48	96	30
2	17	Me	25	48	100	21
3	19	H	25	48	78	50
4	19	Me	25	48	95	36

[a] Ts: toluene-4-sulfonyl.^[b] The configuration of the bicyclic derivatives **22** and **23** was assigned by comparison with authentic samples.^[23] [b] Both catalysts gave rise predominantly to stereoisomers with positive optical rotation values ($c = 1$, CH₂Cl₂). They correspond to the (1*R*,6*R*)-configured bicycles (depicted above), respectively for **22** and **23**.

positioned right in the middle of the molecular groove formed upon capping at the bottom of the cavity. Again the very short M–H distance involving the H-5 proton of unit A (2.41 Å) is commensurate with a single anagostic CH...Au interaction. A CH...Cl hydrogen bond (CH...Cl : 2.89 Å) involving the inner-cavity H-3^E proton was also revealed. Not surprisingly, the NHC ligand of complex **19** displays one of the highest buried volumes reported to date (%V_{Bur}: 81.4 vs. 70.6 for the NHC ligand in **17**).^[22] Unlike the observations made for **19**, there is no indication for **17** to display dynamic behavior in solution.

NHC complexes **17** and **19** were tested in a benchmark asymmetric cycloisomerization reaction, which was already used in conjunction with many gold asymmetric catalysts^[7, 24] including CD-based ones. Given the rather good accessibility of the cavity of methylated CDs, we opted for *N*-tethered 1,6-enynes **20** and **21** as substrates, which are sterically highly demanding at the alkyne end, and yet more common than the ones used by Sollogoub and coll. for asymmetric cycloisomerization.^[8, 23b, 25] Very sluggish reactions were observed when using silver salts other than AgSbF₆ such as Ag(NTf₂) and AgBF₄ for chloride abstraction. The best solvent was found to be toluene, reactions in CH₂Cl₂ proving to be rather slow. Therefore, AgSbF₆ with his weakly coordinating anion combined with toluene were chosen for carrying out all the catalytic studies. The cycloisomerization of the ubiquitous *N*-tethered enyne **20** reaction could be performed at room temperature for both **17** and **19** with activities comparing well with those of classical NHC systems,^[26] the most active one being A,C-capped **17** (Table 1). Classically, C₂-symmetric **19** proved to be the best performing one in terms of enantioselectivity (50% ee vs 29% ee for C₁ symmetric **17**). Given the fact that enantiodiscrimination may result from steric interactions between the *N*-allyl unit and the CD wall,^[6e] we decided to subject to cycloisomerization a *N*-tethered enyne with enhanced steric bulk at the alkene end (**21**). Surprisingly, lower enantioselectivities than those observed for **20** were obtained with all catalysts. As for the *N*-allyl substrate **20**, the highest ee value was obtained with C₂ symmetric **19** (37% ee). In comparison, the perbenzylated analog of **19** only achieved 26% ee with an *N*-tethered 1,6-enyne having a *N*-(2-methyl)allyl substituent. It seems therefore that the alkyne and alkene ends of *N*-tethered 1,6-enynes must be differentiated in terms of size for achieving significant enantiodiscrimination.

Figure 3. Symmetry-unconstrained optimized geometries computed for gas-phase singlet ground state models of 1,6-enyne **20** coordinated to the (CD_{AD})NHC-Au⁺ cation. Two possible conformations are shown: a) CD_{AD}-adduct1 in which the alkene end of **20** is located in the small sub-pocket, and b) CD_{AD}-adduct2 in which the same alkene unit is located in the large sub-pocket (the CD part is depicted in the spacefilling style, while Au-bound **20** is depicted in the ball and sticks style).

The cycloisomerization of *N*-tethered enyne **20** with precatalyst **19** was then investigated by density functional theory (DFT) calculations. In this study, the solid state structure of complex **19** was used as a starting point. As previously postulated by Sollogoub and coll., these calculations revealed that the coordinated alkyne in the corresponding quasi isoenergetic cationic Au(I) complexes CD_{AD}-adduct1/2 (Figure 3) is located in the groove that runs almost parallel to the benzimidazole NHC cap, a feature that is common to all capped CDs herein described, in particular **12**, **15**, **17** and **19** (*vide supra*). Evidence for a significant tilt of the benzimidazole NHC plane with respect to the CD axis and some bending in the C–Au-alkyne unit was also found, the latter distortion being reminiscent of some NHC gold complexes reported by Matt and Brenner^[27] in which the NHC ligand is strongly congested. This means that when complexed to the alkyne end, the metalloCD is no longer C₂ symmetrical as postulated by Sollogoub and coll. but displays two pockets of unequal size. Furthermore, an NCI analysis^[28] (Figure SI-1) carried out on CD_{AD}-adduct2 confirmed the presence of a single attractive CH...Au interaction involving the inner-cavity H-5^A proton, which is also present in complexes **17** and **19** and could be partly responsible for the observed tilt.

Such features have profound implications on the way the enyne can fold to give rise to effective but dissymmetric binding to the Au centre and eventually form the end product. Although predictions are difficult to make given the small energy difference at stake between the two optimized adducts CD_{AD}-adduct1/2, it is likely that the cycloisomerization reaction will take place predominantly in the larger sub-pocket favoring the formation of the (1*R*,6*R*)-configured bicycle. A possible explanation for the drop of ee in the case of the AC catalyst is that the substrate must paradoxically adopt a more central position within the groove similar to the position of the chlorido ligand in **17**. This means that enantiodiscrimination cannot be as effective as in the AD case.

In summary, we have shown, for the first time, that methylated CDs capped with a benzimidazolium unit can entrap anions that fit in the cavity *via* multiple weak hydrogen bonds. When thoroughly dried, these salts can be directly converted into neutral NHC gold(I) complexes under mild conditions without having to synthesize silver salts as intermediates. Although a less active cycloisomerization precatalyst, the sterically congested AD metalloCD **19** outperformed its AC regioisomer **17** in terms of enantioselectivity.

Experimental Section

Experimental details including NMR spectra and X-ray structural data are given in the Supporting Information. CCDC 1863327 (**12**), 1853979 (**15**), 1863324 (**17**) and 1851144 (**19**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- [1] a) R. Gramage-Doria, D. Armspach, D. Matt, *Coord. Chem. Rev.* **2013**, 257, 776-816; b) S. H. A. M. Leenders, R. Gramage-Doria, B. de Bruin, J. N. H. Reek, *Chem. Soc. Rev.* **2015**, 44, 433-448; c) M. Otte, *ACS Catal.* **2016**, 6, 6491-6510; d) N. Natarajan, E. Brenner, D. Sémeril, D. Matt, J. Harrowfield, *Eur. J. Org. Chem.* **2017**, 6100-6113; e) T. Iwasawa, *Tetrahedron Lett.* **2017**, 58, 4217-4226; f) S. Roland, J. M. Suarez, M. Sollogoub, *Chem. Eur. J.* **2018**, 24, 12464-12473.
- [2] T. Gadzikwa, R. Bellini, H. L. Dekker, J. N. H. Reek, *J. Am. Chem. Soc.* **2012**, 134, 2860-2863.
- [3] G. Crini, *Chem. Rev.* **2014**, 114, 10940-10975.
- [4] a) W. D. Woggon, *Curr. Org. Chem.* **2010**, 14, 1362-1379; b) F. Macaev, V. Boldescu, *Symmetry* **2015**, 7, 1699-1720.
- [5] a) D. Armspach, D. Matt, *Carbohydr. Res.* **1998**, 310, 129-133; b) D. Armspach, L. Poorters, D. Matt, B. Benmerad, F. Balegronne, L. Toupet, *Org. Biomol. Chem.* **2005**, 3, 2588-2592; c) M. Sollogoub, *Eur. J. Org. Chem.* **2009**, 1295-1303; d) R. Gramage-Doria, D. Rodriguez-Lucena, D. Armspach, C. Egloff, M. Jouffroy, D. Matt, L. Toupet, *Chem. Eur. J.* **2011**, 17, 3911-3921; e) M. Sollogoub, *Synlett* **2013**, 24, 2629-2640.
- [6] a) M. Guitet, P. L. Zhang, F. Marcelo, C. Tugny, J. Jiménez-Barbero, O. Buriez, C. Amatore, V. Mouries-Mansuy, J. P. Goddard, L. Fensterbank, Y. M. Zhang, S. Roland, M. Ménand, M. Sollogoub, *Angew. Chem. Int. Ed.* **2013**, 52, 7213-7218; b) M. Jouffroy, R. Gramage-Doria, D. Armspach, D. Sémeril, W. Oberhauser, D. Matt, L. Toupet, *Angew. Chem. Int. Ed.* **2014**, 53, 3937-3940; c) M. Jouffroy, R. Gramage-Doria, D. Sémeril, D. Armspach, D. Matt, W. Oberhauser, L. Toupet, *Beilstein J. Org. Chem.* **2014**, 10, 2388-2405; d) M. Jouffroy, D. Armspach, D. Matt, K. Osakada, D. Takeuchi, *Angew. Chem. Int. Ed.* **2016**, 55, 8367-8370; e) P. L. Zhang, C. Tugny, J. M. Suárez, M. Guitet, E. Derat, N. Vanthuyne, Y. M. Zhang, O. Bistri, V. Mouries-Mansuy, M. Ménand, S. Roland, L. Fensterbank, M. Sollogoub, *Chem* **2017**, 3, 174-191.
- [7] a) A. Pradal, P. Y. Toullec, V. Michelet, *Synthesis* **2011**, 1501-1514; b) Y. M. Wang, A. D. Lackner, F. D. Toste, *Acc. Chem. Res.* **2014**, 47, 889-901; c) W. W. Zi, F. D. Toste, *Chem. Soc. Rev.* **2016**, 45, 4567-4589.
- [8] P. Aillard, A. Voituriez, D. Dova, S. Cauteruccio, E. Licandro, A. Marinetti, *Chem. Eur. J.* **2014**, 20, 12373-12376.
- [9] L. Poorters, D. Armspach, D. Matt, L. Toupet, P. G. Jones, *Angew. Chem. Int. Ed.* **2007**, 46, 2663-2665.
- [10] a) F.-X. Legrand, M. Ménand, M. Sollogoub, S. Tilloy, E. Monflier, *New J. Chem.* **2011**, 35, 2061-2065; b) M. Guitet, F. Marcelo, S. A. de Beaumais, Y. M. Zhang, J. Jimenez-Barbero, S. Tilloy, E. Monflier, M. Ménand, M. Sollogoub, *Eur. J. Org. Chem.* **2013**, 3691-3699.
- [11] The same capping procedure with β -CD analogs of **7** and **8** resulted in only very small amounts of capped products.
- [12] a) P. K. Thallapally, A. Nangia, *CrystEngComm* **2001**, 27, 1-6; b) W. W. Zuo, P. Braunstein, *Organometallics* **2010**, 29, 5535-5543.
- [13] The CD axis corresponds to the straight line perpendicular to the mean plane defined by the six O-4 atoms.
- [14] D. Armspach, D. Matt, L. Poorters, R. Gramage-Doria, P. Jones, L. Toupet, *Polyhedron* **2011**, 30, 573-578.
- [15] A very small peak at $\delta = 9.66$ ppm corresponding to the N-CH=N proton of a minor isomer (< 1%) in which the PF_6^- anion is most likely encapsulated was also detected. In the HOESY spectrum, together with a proton resonating at 5.02 ppm, most probably an inner-cavity CD H-5 proton, it gives rise to strong correlations with the PF_6^- fluorine atoms.
- [16] a) R. Visbal, A. Laguna, M. C. Gimeno, *Chem. Commun.* **2013**, 49, 5642-5644; b) A. Collado, A. Gómez-Suárez, A. R. Martin, A. M. Slawin, S. P. Nolan, *Chem. Commun.* **2013**, 49, 5541-5543.
- [17] E. Engeldinger, D. Armspach, D. Matt, P. G. Jones, R. Welter, *Angew. Chem. Int. Ed.* **2002**, 41, 2593-2596.
- [18] C. A. Citadelle, E. Le Nouy, F. Bisaro, A. M. Slawin, C. S. Cazin, *Dalton Trans.* **2010**, 39, 4489-4491.
- [19] J. Ruiz, A. F. Mesa, *Chem. Eur. J.* **2014**, 20, 102-105.
- [20] M. K. Denk, J. M. Rodezno, S. Gupta, A. J. Lough, *J. Organomet. Chem.* **2001**, 617, 242-253.
- [21] E. Engeldinger, D. Armspach, D. Matt, L. Toupet, M. Wesolek, *C. R. Chim.* **2002**, 5, 359-372.
- [22] L. Falivene, R. Credendino, A. Poater, A. Petta, L. Serra, R. Oliva, V. Scarano, L. Cavallo, *Organometallics* **2016**, 35, 2286-2293.
- [23] a) H. Teller, M. Corbet, L. Mantilli, G. Gopakumar, R. Goddard, W. Thiel, A. Fürstner, *J. Am. Chem. Soc.* **2012**, 134, 15331-15342; b) K. Yavari, P. Aillard, Y. Zhang, F. Nuter, P. Retailleau, A. Voituriez, A. Marinetti, *Angew. Chem. Int. Ed.* **2014**, 53, 861-865.
- [24] a) S. Sengupta, X. D. Shi, *ChemCatChem* **2010**, 2, 609-619; b) A. Marinetti, H. Jullien, A. Voituriez, *Chem. Soc. Rev.* **2012**, 41, 4884-4908; c) F. Lopez, J. L. Mascarenas, *Beilstein J. Org. Chem.* **2013**, 9, 2250-2264; d) G. Cera, M. Bandini, *Isr. J. Chem.* **2013**, 53, 848-855.
- [25] a) J. Dubarle-Offner, M. Barbazanges, M. Auge, C. Desmarets, J. Moussa, M. R. Axet, C. Ollivier, C. Aubert, L. Fensterbank, V. Gandon, M. Malacria, G. Gontard, H. Amouri, *Organometallics* **2013**, 32, 1665-1673; b) Z. Y. Wu, K. Isaac, P. Retailleau, J. F. Betzer, A. Voituriez, A. Marinetti, *Chem. Eur. J.* **2016**, 22, 3278-3281.
- [26] F. Sirindil, S. P. Nolan, S. Dagorne, P. Pale, A. Blanc, P. de Frémont, *Chem. Eur. J.* **2018**, 24, 12630-12637.
- [27] M. Teci, E. Brenner, D. Matt, C. Gourlaouen, L. Toupet, *Chem. Eur. J.* **2015**, 21, 10997-11000.
- [28] a) E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen, W. T. Yang, *J. Am. Chem. Soc.* **2010**, 132, 6498-6506; b) J. Contreras-García, E. R. Johnson, S. Keinan, R. Chaudret, J.-P. Piquemal, D. N. Beratan, W. T. Yang, *J. Chem. Theory Comput.* **2011**, 7, 625-632.

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COMMUNICATION

Permethylated cyclodextrins equipped with a benzimidazolium handle behave as receptors towards medium-sized anions. They could be directly converted to gold(I) complexes that act as precatalysts for the asymmetric cycloisomerization of 1,6-enynes.

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