Homogeneous Catalysis

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Confining Phosphanes Derived from Cyclodextrins for Efficient Regio- and Enantioselective Hydroformylation**

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Abstract: *Two confining phosphane ligands derived from either α- or β-cyclodextrin produce singly P^{III}-ligated metal complexes with unusual coordination spheres. High-pressure NMR studies have revealed that rhodium hydride complexes of the same type are also formed under hydroformylation conditions. This unique feature strongly favors the formation of the branched aldehyde at the expense of the linear one with high enantioselectivity in the rhodium-catalyzed hydroformylation of styrene.*

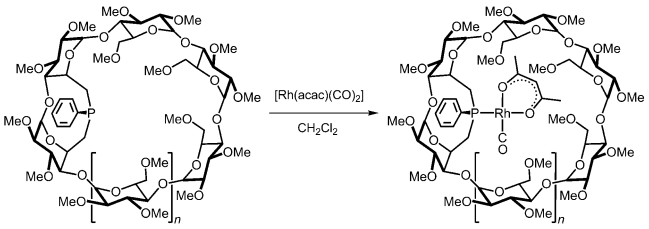
Sterically encumbered phosphanes play an important role in coordination chemistry and catalysis.[1] In many catalytic transformations, such ligands have become *de rigueur*, as they may force the formation of complexes with specific coordination geometries, thereby allowing efficient control of the reaction outcome. Phosphanes displaying high steric demand further constitute ideal ligands for the protection of reactive metal centers,[2] the stabilization of unsaturated species,[3] and sometimes for accelerating a key step of a catalytic cycle.[1e,4]

While in many reactions the formation of catalytic intermediates bearing a single phosphane is highly desirable, such a feature is rarely observed when the phosphane/metal ratio is higher than one, because multiphosphane complexes are most often formed, even if the ligand is bulky. One possible way to achieve exclusive binding of a single PR_3 moiety is by using phosphanes substituted with an additional functional group, which, together with the P^{III} center, may behave as a chelating unit, and consequently prevent coordination of a second phosphane.[5] However, because of their chelating nature, these ligands may considerably alter the expected reactivity of the metal center. Another potential method for forming monoligated complexes consists of using a bowl-shaped phosphane in which the phosphorus atom sits deeply in a cavity which obstructs the binding of a second phosphane after metal complexation.[1d,f,g,6]

In the rhodium-catalyzed hydroformylation of olefins, bulky phosphanes are typically employed for increasing isoselectivity.[7] Chiral versions thereof,[8] including cyclodextrin-containing phosphanes,[9] should thus be highly relevant to enantioselective hydroformylation.[10] However, it is generally believed that high isoselectivity is incompatible with high enantioselectivity and vice versa.[11]

We now describe the high performance of two crowded, chiral phosphanes, namely HUGPHOS-1[12] and HUGPHOS-2,[13] in the asymmetric hydroformylation of styrene. Both ligands, which are respectively derived from α- and β-cyclodextrin, have their phosphorus lone pair directed towards the appended cyclodextrin (CD) core. We anticipated that these introverted ligands would not only tightly embrace a metal center after complexation and thus facilitate chirality transfer, but also restrict phosphane coordination to a single ligand, thus strongly influencing regioselectivity.

The catalytic study was carried out using the rhodium monophosphane complexes **1** and **2** (Scheme 1). These



Scheme 1. Synthesis of the Rh-monophosphane complexes **1** and **2**.

formed quantitatively by reacting $[Rh(acac)(CO)_2]$ (acac = acetylacetonate) with one equivalent of the corresponding HUGPHOS ligand. Excess ligand did not lead to a bis(phosphane) complex. Both $^{31}P\{^1H\}$ NMR spectra consist of a doublet [$\delta = 34.3$ (**1**), 31.5 (**2**) ppm], with a J(PRh) coupling constant of 167 Hz. ROESY experiments (see the Supporting Information) revealed that the acac ligand of **2** is confined in the corresponding β-CD unit. As a result, the CO ligand adopts an *exo* orientation. Conversely, the complex **1**, which features a smaller inner space, has its acac fragment oriented towards the exterior of the cavity.This means that the CO ligand is located inside the CD in this case. Both complexes are remarkably air stable.

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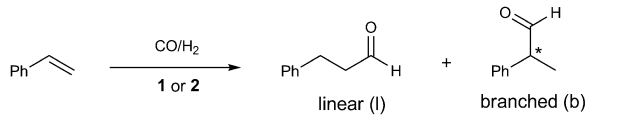
Styrene was chosen as a substrate because it is a source of valuable optically active aldehydes. It is also sterically compatible with the CD inner space. Hydroformylation tests were performed not only at various temperatures and pressures, but also at several CO/H_2 and L/Rh ratios, as well as precatalyst loadings.

The best catalytic results were obtained with **1** when operating at room temperature under a pressure of 40 bar (1:1 molar mixture of CO/H_2; Table 1, entry 7). Under these reaction conditions, the selectivity for the branched aldehyde and the *ee* value reached 98.3% and 95% (*R* enantiomer), respectively. To the best of our knowledge, there is no other example of a monodentate phosphane achieving simultaneously high chiral induction and high isoregioselectivity. So far, comparable performance was only achieved with diphosphorus ligands.[7g,h,14] The complex **2** gave rise to similar selectivities and activities (Table 1, entry 13). Not surprisingly, raising the temperature from 20 to 80 °C at a CO/H_2 gas pressure of 20 bar led to higher reactions rates, but at the expense of both regioselectivity and enantioselectivity (Table 1, entries 1–4 and 9–12). In stark contrast with classical diphosphane rhodium complexes, an increase of the CO partial pressure led to both higher catalytic activity and enantioselectivity, whereas adding free ligand was detrimental to the catalyst performance (see the Supporting Information).[15] Furthermore, a total pressure of at least 40 bar was found necessary to ensure optimal reaction rate and selectivity. For example, by raising the pressure from 5 to 40 bar (at 40 °C) in the presence of **2** the *ee* value increased by 49% and the branched/liner (b/l) ratio from 3.7 to 24.6 (Table 1, entries 5 and 6). Again, these findings are markedly different from observations made for conventional Rh/phosphane systems. It should also be mentioned here that under optimal catalytic conditions (20 °C, 40 bar) no drop of catalytic activity was observed over three days for either complex (see the Supporting Information).

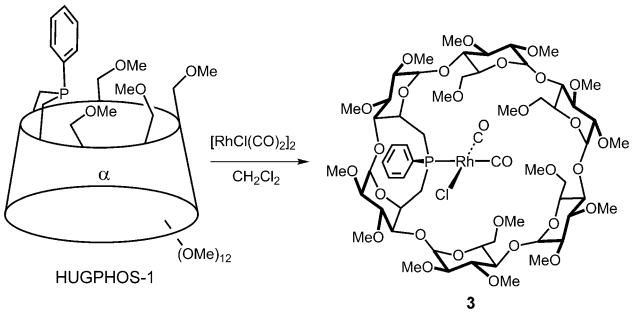
Table 1: Hydroformylation of styrene using the precatalysts **1** and **2**. Variation of pressure and temperature.[a]



Entry	Complex	$p(CO/H_2)$ [bar][b]	T [°C]	Conv. [%][c]	Yield [%][c] l	b	b/l[d]	*ee* [%][g]
1	**1**	20	80	86.3	27.2	72.8	2.7	33 (*R*)
2[e]	**1**	20	60	100	11.4	88.6	7.8	62 (*R*)
3[e]	**1**	20	40	99.8	6.3	93.7	14.9	80 (*R*)
4[e]	**1**	20	20	30.6	1.0	99.0	99.0	93 (*R*)
5[e]	**1**	5	40	19.8	21.4	78.6	3.7	41 (*R*)
6[e]	**1**	40	40	99.2	3.9	96.1	24.6	90 (*R*)
7[e]	**1**	40	20	60.7	1.7	98.3	57.8	95 (*R*)
8[e]	**1**	40	4	34.0	trace	100	>100[f]	93 (*R*)
9	**2**	20	80	96.8	37.1	62.9	1.7	27 (*R*)
10	**2**	20	120	31.5	43.0	57.0	1.3	34 (*S*)
11	**2**	20	60	43.7	13.9	86.1	6.2	63 (*R*)
12[e]	**2**	20	40	79.0	6.8	93.2	13.7	80 (*R*)
13[e]	**2**	40	20	66.2	1.7	98.3	57.8	92 (*R*)

[a] Styrene (5 mmol), styrene/complex = 2500, t = 24 h, toluene/*n*-decane (15 mL/0.5 mL), incubation overnight at 80 °C under $p(CO/H_2)$ = 20 bar. [b] CO/H_2 1:1 v/v. [c] Determined by GC using decane as an internal standard. [d] b/l aldehyde ratio. [e] Run carried out with a styrene/complex ratio of 250. [f] Exact value not determined because the amount of linear aldehyde was too small to be detected. [g] Determined by chiral-phase GC after reduction with $LiAlH_4$.

While studying the coordination chemistry of HUGPHOS ligands towards group 9 and 10 metal ions, we discovered that their unique confining properties prevented the formation of bis(phosphane) complexes. Thus, when mixing excess HUGPHOS-1 with $[\{RhCl(CO)_2\}_2]$ (Scheme 2), only *cis*-

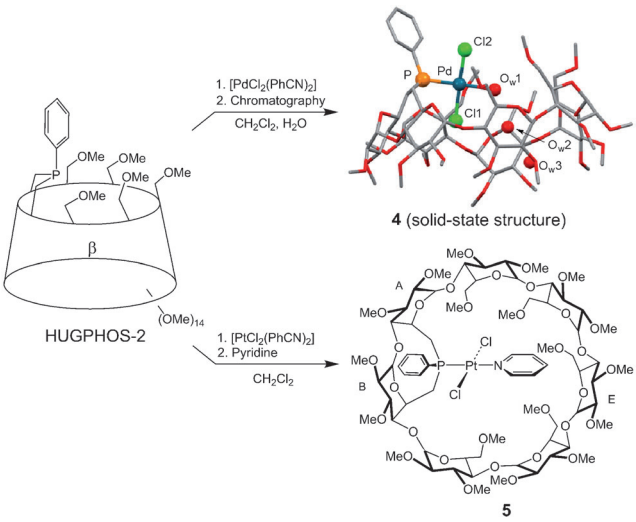


Scheme 2. Synthesis of the complex **3** from HUGPHOS-1.

$[RhCl(HUGPHOS\text{-}1)(CO)_2]$ (**3**) formed, rather than the expected *trans*-$[RhCl(HUGPHOS\text{-}1)_2(CO)]$ complex. The relative *cis* position of the CO ligands of **3** was inferred from the corresponding IR spectrum (strong CO bands at 2009 and 2082 cm^{-1}). The ^1H NMR spectrum of **3** is fully consistent with a CD-encapsulated chlorido ligand,[16] and is further proof for the presence of two *cis*-configured CO ligands.[17]

Furthermore, reaction of $[PdCl_2(PhCN)_2]$ with HUGPHOS-2 gave quantitatively, after column chromatography, the singly P-ligated aqua complex *trans*-$[PdCl_2(HUGPHOS\text{-}2)(H_2O)]$ (**4**), the molecular structure of which was confirmed by a single-crystal X-ray diffraction study (Scheme 3, top).[18] Similarly, reaction of $[PtCl_2(PhCN)_2]$ with HUGPHOS-2 in excess and subsequent addition of pyridine, gave the mixed phosphane-pyridine complex **5** (Scheme 3, bottom). The relative trans-*P,N* arrangement was unambiguously deduced from the ROESY data which showed strong correlations between the pyridinic H4 atom (γ position) and the H3, H5, and OMe-6 atoms of a nonbridged glucose, probably unit E. Overall, these results prove the high potential of HUGPHOS ligands to stabilize medium-sized metal organic fragments bound to a single phosphane ligand.

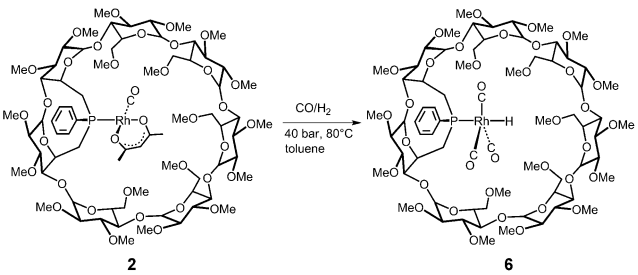
To investigate whether analogous species also formed under the chosen hydroformylation conditions, **2** was activated in toluene at 80 °C with a CO/H_2 mixture (1:1) at 40 bar. Under these conditions, a single hydrido carbonyl species formed, as revealed by a high-pressure NMR ($[D_8]$toluene) study (see the Supporting Information). Mass spectrometric measurements together with the ^1H and $^{31}P\{^1H\}$ NMR data obtained at high pressure unequivocally proved the formation



Scheme 3. Synthesis of the monophosphane complexes **4** and **5** (from HUGPHOS-2). In the solid state the aquo complex **4** crystallized with two additional water molecules embedded in the cavity.

of the complex *trans*-[RhH(CO)$_3$(HUGPHOS-2)] (**6**; Scheme 4). Thus, the mass spectrum recorded from a toluene solution of **6** after CO/H_2 removal displayed a peak at 1663.53 (1%, exact isotopic profile), which corresponds to the $[M+H]^+$ ion. The ^{1}H NMR spectrum of **6** (25 °C, 40 bar) revealed a hydride signal at $\delta = -8.8$ ppm [J(RhH) = 6.2 Hz] with a large J(PH) coupling constant of 103 Hz, a value which is typical for a linear P-Rh-H arrangement.[8b,19] In the corresponding ^{31}P{^{1}H} NMR spectrum, the P atom appeared as a doublet at $\delta = 28.1$ ppm [J(RhP) = 95 Hz].[20] The trigonal bipyramidal complex **6** constitutes the second reported monophosphane [RhH(CO)$_3$L] complex in which the phosphorus lies *trans* to the hydride. The reason for the selective apical binding of the phosphorus atom seemingly arises from the embracing character of the phosphane. This feature forces the resulting trigonal bipyramidal complex to adopt a configuration which minimizes steric interactions between the carbonyl ligands and the cavity wall, and which is best fulfilled with a linear PRhH arrangement.

In conclusion, the cyclodextrin-derived HUGPHOS ligands readily form square-planar and trigonal bipyramidal, monophosphane complexes in which the CD cavity tightly embraces the metal center. When used in the rhodium-catalyzed hydroformylation of styrene, they gave rise to both high regioselectivity and enantioselectivity. Obviously, these two features, which are generally regarded as contradictory, rely on the ligand ability to exclusively form the complex *trans*-[RhH(CO)$_3$(HUGPHOS)] (**6**) under optimized catalytic conditions, and to embed the whole metal center, thereby ensuring unprecedented chirality transfer for a CD-based catalyst in organic media.[21] Clearly, these results constitute a new illustration of the high potential of confining ligand systems in homogeneous catalysis.



Scheme 4. Selective formation of complex **6** under 40 bar CO/H_2 at 80 °C.

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[1] a) C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348; b) A. F. Littke, G. C. Fu, *J. Org. Chem.* **1999**, *64*, 10–11; c) A. F. Littke, G. C. Fu, *J. Am. Chem. Soc.* **2001**, *123*, 6989–7000; d) T. Iwasawa, T. Komano, A. Tajima, M. Tokunaga, Y. Obora, T. Fujihara, Y. Tsuji, *Organometallics* **2006**, *25*, 4665–4669; e) U. Christmann, R. Vilar, *Angew. Chem.* **2005**, *117*, 370–378; *Angew. Chem. Int. Ed.* **2005**, *44*, 366–374; f) H. Ohta, M. Tokunaga, Y. Obora, T. Iwai, T. Iwasawa, T. Fujihara, Y. Tsuji, *Org. Lett.* **2007**, *9*, 89–92; g) T. Fujihara, S. Yoshida, H. Ohta, Y. Tsuji, *Angew. Chem.* **2008**, *120*, 8434–8438; *Angew. Chem. Int. Ed.* **2008**, *47*, 8310–8314; h) D. J. M. Snelders, G. van Koten, R. J. M. K. Gebbink, *J. Am. Chem. Soc.* **2009**, *131*, 11407–11416; i) D. L. Dodds, M. D. K. Boele, G. P. F. van Strijdonck, J. G. de Vries, P. W. N. M. van Leeuwen, P. C. J. Kamer, *Eur. J. Inorg. Chem.* **2012**, 1660–1671; j) *Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis* (Eds.: P. C. J. Kamer, P. W. N. M. van Leeuwen), Wiley, Chichester, **2013**.

[2] L. Poorters, D. Armspach, D. Matt, L. Toupet, S. Choua, P. Turek, *Chem. Eur. J.* **2007**, *13*, 9448–9461.

[3] S. Otsuka, T. Yoshida, M. Matsumoto, K. Nakatsu, *J. Am. Chem. Soc.* **1976**, *98*, 5850–5858.

[4] a) L. Monnereau, D. Semeril, D. Matt, L. Toupet, *Chem. Eur. J.* **2010**, *16*, 9237–9247; b) L. Monnereau, D. Semeril, D. Matt, *Chem. Commun.* **2011**, *47*, 6626–6628.

[5] a) J. P. Wolfe, R. A. Singer, B. H. Yang, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 9550–9561; b) F. Y. Kwong, A. S. C. Chan, *Synlett* **2008**, 1440–1448; c) D. S. Surry, S. L. Buchwald, *Angew. Chem.* **2008**, *120*, 6438–6461; *Angew. Chem. Int. Ed.* **2008**, *47*, 6338–6361; d) N. C. Bruno, S. L. Buchwald, *Org. Lett.* **2013**, *15*, 2876–2879.

[6] a) Y. Ohzu, K. Goto, T. Kawashima, *Angew. Chem.* **2003**, *115*, 5892–5895; *Angew. Chem. Int. Ed.* **2003**, *42*, 5714–5717; b) Y. Ohzu, K. Goto, H. Sato, T. Kawashima, *J. Organomet. Chem.* **2005**, *690*, 4175–4183; c) O. Niyomura, T. Iwasawa, N. Sawada, M. Tokunaga, Y. Obora, Y. Tsuji, *Organometallics* **2005**, *24*, 3468–3475.

[7] a) R. L. Pruett, J. A. Smith, *J. Org. Chem.* **1969**, *34*, 327–330; b) P. W. N. M. van Leeuwen, C. F. Roobeek, *J. Organomet. Chem.* **1983**, *258*, 343–350; c) T. Jongsma, G. Challa, P. W. N. M. Van Leeuwen, *J. Organomet. Chem.* **1991**, *421*, 121–128; d) B. Breit, R. Winde, T. Mackewitz, R. Paciello, K. Harms, *Chem. Eur. J.* **2001**, *7*, 3106–3121; e) V. F. Slagt, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *J. Am. Chem. Soc.* **2004**, *126*, 1526–1536; f) R. A. Baber, M. L. Clarke, K. M. Heslop, A. C. Marr, A. G. Orpen, P. G. Pringle, A. Ward, D. E. Zambrano-Williams, *Dalton Trans.* **2005**, 1079–1085; g) M. L. Clarke, *Curr. Org. Chem.* **2005**, *9*, 701–718; h) M. Kuil, T.

Soltner, P. W. N. M. van Leeuwen, J. N. H. Reek, *J. Am. Chem. Soc.* **2006**, *128*, 11344 – 11345; i) A. A. Dabbawala, R. V. Jasra, H. C. Bajaj, *Catal. Commun.* **2011**, *12*, 403 – 407; j) A. A. Dabbawala, H. C. Bajaj, G. V. S. Rao, S. H. R. Abdi, *Appl. Catal. A* **2012**, *419 – 420*, 185 – 193; k) V. Bocokic, A. Kalkan, M. Lutz, A. L. Spek, D. T. Gryko, J. N. H. Reek, *Nat. Commun.* **2013**, *4*, 3670; l) H. Tricas, O. Diebolt, P. W. N. M. van Leeuwen, *J. Catal.* **2013**, *298*, 198 – 205.

[8] a) R. Bellini, S. H. Chikkali, G. Berthon-Gelloz, J. N. H. Reek, *Angew. Chem.* **2011**, *123*, 7480 – 7483; *Angew. Chem. Int. Ed.* **2011**, *50*, 7342 – 7345; b) R. Bellini, J. N. Reek, *Chem. Eur. J.* **2012**, *18*, 7091 – 7099.

[9] a) R. M. Deshpande, A. Fukuoka, M. Ichikawa, *Chem. Lett.* **1999**, 13 – 14; b) C. Machut-Binkowski, F. X. Legrand, N. Azaroual, S. Tilloy, E. Monflier, *Chem. Eur. J.* **2010**, *16*, 10195 – 10201; c) F. X. Legrand, N. Six, C. Slomianny, H. Bricout, S. Tilloy, E. Monflier, *Adv. Synth. Catal.* **2011**, *353*, 1325 – 1334; d) D. N. Tran, F. X. Legrand, S. Menuel, H. Bricout, S. Tilloy, E. Monflier, *Chem. Commun.* **2012**, *48*, 753 – 755.

[10] a) F. Agbossou, J. F. Carpentier, A. Mortreux, *Chem. Rev.* **1995**, *95*, 2485 – 2506; b) C. Claver, M. Diéguez, O. Pàmies, S. Castillón, *Top. Organomet. Chem.* **2006**, *18*, 35 – 64; c) J. Klosin, C. R. Landis, *Acc. Chem. Res.* **2007**, *40*, 1251 – 1259; d) A. Gual, C. Godard, S. Castillón, C. Claver, *Tetrahedron: Asymmetry* **2010**, *21*, 1135 – 1146.

[11] R. Franke, D. Selent, A. Börner, *Chem. Rev.* **2012**, *112*, 5675 – 5732.

[12] E. Engeldinger, L. Poorters, D. Armspach, D. Matt, L. Toupet, *Chem. Commun.* **2004**, 634 – 635.

[13] R. Gramage-Doria, D. Rodriguez-Lucena, D. Armspach, C. Egloff, M. Jouffroy, D. Matt, L. Toupet, *Chem. Eur. J.* **2011**, *17*, 3911 – 3921.

[14] a) N. Sakai, S. Mano, K. Nozaki, H. Takaya, *J. Am. Chem. Soc.* **1993**, *115*, 7033 – 7034; b) N. Sakai, K. Nozaki, H. Takaya, *J. Chem. Soc. Chem. Commun.* **1994**, 395 – 396; c) J. E. Babin, G. T. Whiteker, *Vol. 5360938*, Union carbide Chemicals & Plastics Technology Corporation, USA, **1994**; d) S. Breeden, D. J. Cole-Hamilton, D. F. Foster, G. J. Schwarz, M. Wills, *Angew. Chem.* **2000**, *112*, 4272 – 4274; *Angew. Chem. Int. Ed.* **2000**, *39*, 4106 – 4108; e) R. Ewalds, E. B. Eggeling, A. C. Hewat, P. C. J. Kamer, P. W. N. M. van Leeuwen, D. Vogt, *Chem. Eur. J.* **2000**, *6*, 1496 – 1504; f) M. Diéguez, O. Pamies, A. Ruiz, S. Castillon, C. Claver, *Chem. Eur. J.* **2001**, *7*, 3086 – 3094; g) C. J. Cobley, J. Klosin, C. Qin, G. T. Whiteker, *Org. Lett.* **2004**, *6*, 3277 – 3280; h) A. T. Axtell, C. J. Cobley, J. Klosin, G. T. Whiteker, A. Zanotti-Gerosa, K. A. Abboud, *Angew. Chem.* **2005**, *117*, 5984 – 5988; *Angew. Chem. Int. Ed.* **2005**, *44*, 5834 – 5838; i) T. P. Clark, C. R. Landis, S. L. Freed, J. Klosin, K. A. Abboud, *J. Am. Chem. Soc.* **2005**, *127*, 5040 – 5042; j) A. T. Axtell, J. Klosin, G. T. Whiteker, C. J. Cobley, M. E. Fox, M. Jackson, K. A. Abboud, *Organometallics* **2009**, *28*, 2993 – 2999; k) T. T. Adint, G. W. Wong, C. R. Landis, *J. Org. Chem.* **2013**, *78*, 4231 – 4238; l) G. M. Noonan, C. J. Cobley, T. Mahoney, M. L. Clarke, *Chem. Commun.* **2014**, *50*, 1475 – 1477.

[15] *Rhodium-Catalyzed Hydroformylation* (Eds.: P. W. N. M. van Leeuwen, C. Claver), Kluwer, Dordrecht, **2000**.

[16] E. Engeldinger, D. Armspach, D. Matt, P. G. Jones, *Chem. Eur. J.* **2003**, *9*, 3091 – 3105.

[17] Some CD H5 protons belonging to nonbridged glucose units are strongly upfield shifted upon metal complexation ($\Delta\delta$ up to 0.7 ppm). Such chemical shifts differences are typical of chlorido encapsulation.

[18] The most striking feature of this structure is the presence of a unique intracavity hydrogen-bonding network which literally fills the cavity with water molecules. The coordinated water molecule (O_w1) is not only hydrogen bonded to the OMe-6 group of glucose unit F, but also to an additional water molecule (O_w2), itself weakly bonded to the Cl1 chlorine atom and a third water molecule (O_w3). The latter is connected to the CD secondary rim through a hydrogen bond with the OMe-2 group of glucose unit G.

[19] a) H. Lehner, D. Matt, A. Togni, R. Thouvenot, L. M. Venanzi, A. Albinati, *Inorg. Chem.* **1984**, *23*, 4254 – 4261; b) S. H. Chikkali, R. Bellini, B. de Bruin, J. I. van der Vlugt, J. N. H. Reek, *J. Am. Chem. Soc.* **2012**, *134*, 6607 – 6616.

[20] The IR spectrum of **6** measured at 40 bar of CO/H_2 displays three strong carbonyl bands at 1981, 1987, and 1991 cm^{-1}. Obviously, this spectrum reflects a local symmetry lower than D_{3h}.

[21] a) Y. T. Wong, C. Yang, K. C. Ying, G. C. Jia, *Organometallics* **2002**, *21*, 1782 – 1787; b) M. Guitet, P. Zhang, F. Marcelo, C. Tugny, J. Jimenez-Barbero, O. Buriez, C. Amatore, V. Mouries-Mansuy, J. P. Goddard, L. Fensterbank, Y. Zhang, S. Roland, M. Menand, M. Sollogoub, *Angew. Chem.* **2013**, *125*, 7354 – 7359; *Angew. Chem. Int. Ed.* **2013**, *52*, 7213 – 7218.

