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Confinement makes the difference: α - and β -cyclodextrin derivatives bearing introverted P(III) donor atoms readily form monophosphane complexes in which the cyclodextrin cavity tightly wraps around the metal centre. When used as ligands in the rhodium-catalysed hydroformylation of styrene, they lead to *both* high isoselectivity *and* enantioselectivity.

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 both 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.

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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 an efficient control of the reaction outcome. Phosphanes displaying high steric demand further constitute ideal ligands for the protection of reactive metal centres,^[2] the stabilisation 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, multi-phosphane complexes being then 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) centre, 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 centre. Another potential method for forming monoligated complexes consists in using a bowl-shaped phosphane in which the phosphorus atom sits deeply in a cavity that obstructs the binding of a second phosphane after metal complexation.^[1d,f,g,6]

In the rhodium-catalysed hydroformylation of olefins, bulky phosphanes are typically employed for increasing isoselectivity.^[7] Chiral versions thereof^[8], including cyclodextrin-containing phosphines^[9], should thus be highly relevant to enantioselective hydroformylation.^[10] However, it is generally believed that high isoregioselectivity 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 core. We anticipated that these introverted ligands would tightly embrace a metal centre 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 rhodium monophosphane complexes **1** and **2** (Scheme 1). These formed quantitatively by reacting $[\text{Rh}(\text{acac})(\text{CO})_2]$ (acac = acetylacetonate) with one equiv. of the corresponding HUGPHOS ligand. Excess ligand did not lead to a bis-phosphane complex. Both $^{31}\text{P}\{^1\text{H}\}$ NMR spectra consist of a doublet ($\delta =$

34.3 (**1**), 31.5 (**2**) ppm), with a $J(\text{PRh})$ coupling constant of 167 Hz. ROESY experiments (see SI) 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, complex **1**, which features a smaller inner space, has its acac fragment oriented towards the exterior of the cavity, which means that the CO ligand is located inside the CD in this case. Both complexes are remarkably air stable.

Styrene was chosen as 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/H₂ and L/Rh ratios as well as precatalyst loadings.

Scheme 1. Synthesis of rhodium monophosphane complexes **1** and **2**.

The best catalytic results were obtained with complex **1** when operating at room temperature under a pressure of 40 bar (1:1 molar mixture of CO/H₂) (Table 1, entry 7). Under these conditions, the selectivity to 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 achieved only with diphosphorus ligands.^[7g,h,14] 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/H₂ gas pressure of 20 bar led to higher reactions rates, however at the expense of both regioselectivity and enantioselectivity (Table 1, entries 1-4). In stark contrast with classical diphosphane rhodium complexes, an increase of the CO partial pressure led to both higher catalytic activity and enantioselectivity, while adding free ligand was detrimental to the catalyst performance (see

SI).^[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 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 during 3 days for both complexes (See SI).

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

Entry	Complex	$p(\text{CO}/\text{H}_2)^{[b]}$	T	Conv ^[c]	Aldehydes ^[c]		b/l ^[d]	<i>ee</i> ^[c]
		[bar]	[°C]		[%]	l [%] b[%]		
1	1	20	80	86.3	27.2	72.8	2.7	33 (<i>R</i>)
2 ^[e]	1	20	60	100	11.4	88.6	7.8	62 (<i>R</i>)
3 ^[e]	1	20	40	99.8	6.3	93.7	14.9	80 (<i>R</i>)
4 ^[e]	1	20	20	30.6	1.0	99.0	99.0	93 (<i>R</i>)
5 ^[e]	1	5	40	19.8	21.4	78.6	3.7	41 (<i>R</i>)
6 ^[e]	1	40	40	99.2	3.9	96.1	24.6	90 (<i>R</i>)
7 ^[e]	1	40	20	60.7	1.7	98.3	57.8	95 (<i>R</i>)
8 ^[e]	1	40	4	34.0	traces	100	>100 ^[f]	93 (<i>R</i>)
9	2	20	80	96.8	37.1	62.9	1.7	27 (<i>R</i>)
10	2	20	120	31.5	43.0	57.0	1.3	34 (<i>S</i>)
11	2	20	60	43.7	13.9	86.1	6.2	63 (<i>R</i>)
12 ^[e]	2	20	40	79.0	6.8	93.2	13.7	80 (<i>R</i>)
13 ^[e]	2	40	20	66.2	1.7	98.3	57.8	92 (<i>R</i>)

^[a] Styrene (5 mmol), styrene/complex = 2500, *t* = 24 h, toluene/*n*-decane (15mL/0.5mL), incubation overnight at 80°C under *p*(CO/H₂) = 20 bar. ^[b] CO/H₂ 1:1 v/v. ^[c] Determined by GC using decane as internal standard. ^[d] b/l aldehyde ratio. ^[e] Run carried out with a styrene/complex ratio of 250. ^[f] Exact value not determined because of a very low amount of branched aldehydes.

While studying the coordination chemistry of HUGPHOS ligands towards group 9 and 10 metal ions, we discovered that their unique confining properties prevented formation of

bis-phosphane complexes. Thus, when mixing excess HUGPHOS-1 with $[\text{RhCl}(\text{CO})_2]_2$ (Scheme 2), only *cis*- $[\text{RhCl}(\text{HUGPHOS-1})(\text{CO})_2]$ (**3**) formed, rather than the expected complex *trans*- $[\text{RhCl}(\text{HUGPHOS-1})_2(\text{CO})]$. 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] this being a further proof for the presence of two *cis* configured CO ligands.^[17]

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

Furthermore, reaction of $[\text{PdCl}_2(\text{PhCN})_2]$ with HUGPHOS-2 gave quantitatively, after column chromatography, the singly P-ligated aqua complex *trans*- $[\text{PdCl}_2(\text{HUGPHOS-2})(\text{H}_2\text{O})]$ (**4**), the molecular structure of which was confirmed by a single crystal X-ray diffraction study (Scheme 3, top).^[18] Similarly, reaction of $[\text{PtCl}_2(\text{PhCN})_2]$ with HUGPHOS-2 in excess, followed by 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 that showed strong correlations between the pyridinic H-4 atom and the H-5 and H-6 atoms of glucose unit E. Overall, these results prove the high potential of HUGPHOS ligands to stabilise medium-sized metal organic fragments bound to a single phosphane ligand.

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

In order to investigate whether analogous species also formed under the chosen hydroformylation conditions, complex **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 (toluene- d_8) study (SI). Mass spectrometric measurements together with the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR data obtained at high pressure unequivocally proved the formation of the complex *trans*- $[\text{RhH}(\text{CO})_3(\text{HUGPHOS-2})]$ (**6**). 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) corresponding to the $[M + \text{H}]^+$ ion. The ^1H NMR spectrum of **6** (25°C, 40 bar) revealed a hydride signal at -8.8 ppm ($J(\text{RhH}) = 6.2$ Hz) with a large $J(\text{PH})$ coupling constant of 103 Hz, a value which is typical for a linear P-Rh-H arrangement.^[8b,19] In the corresponding $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, the P atom appeared as a doublet at 28.1 ppm ($J(\text{RhP}) = 95$ Hz).^[20] The trigonal bipyramidal complex **6** constitutes the second reported monophosphane $[\text{RhH}(\text{CO})_3\text{L}]$ 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 that minimises steric interactions between the carbonyl ligands and the cavity wall, and which is best fulfilled with a linear PRhH arrangement.

Scheme 4. Selective formation of complex **6** under 40 bar CO/H₂ at 80°C.

In conclusion, the cyclodextrin-derived HUGPHOS ligands readily form square planar and trigonal bipyramidal, *mono-phosphane* complexes in which the CD cavity tightly embraces the metal centre. When used in the Rh-catalysed hydroformylation of styrene, they result *both* in 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)] under optimised catalytic conditions, and to embed the whole metal centre 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.

Keywords: asymmetric hydroformylation • bulky phosphanes • cyclodextrins • styrene • metal confinement

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