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Synthesis of a tetramethoxy and an amphiphilic tetrahydroxy hemilabile *N*,*P*,*N*-ligand. Coordination behavior towards rhodium(I) and application to hydroformylation of styrene or hydrogenation of *trans*-cinnamaldehyde

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Dedicated to Professor Dr Friedrich Bickelhaupt on the occasion of his 70th birthday and in recognition of his important contributions to organometallic chemistry and their applications to organic synthesis

Abstract

A tetramethoxy hemilabile *N*,*P*,*N*-ligand and the corresponding amphiphilic tetrahydroxy ligand have been synthesized via *ortho*-lithiation of *N*,*N*-bis(2-methoxyethyl)-benzenamine and *N*,*N*-bis[2-(methoxymethoxy)ethyl]-benzenamine, respectively. The coordination behavior of the ligands towards rhodium(I) in solution was investigated and, according to ^{1}H-, ^{13}C- and ^{31}P-NMR data, at room temperature both ligands are coordinated to the metal in a *N*,*P*,*N*-tridentate mode without any Rh–O interaction, whereas at low temperature a P–Rh–N bridged dimeric species was also found together with the most favored tridentate monomer. The rhodium complex of the former ligand was applied to hydroformylation of styrene and the complex of the latter ligand was evaluated in the hydrogenation of *trans*-cinnamaldehyde. © 2001 Published by Elsevier Science B.V.

Keywords: *N*,*P*,*N*-ligand; Hemilabile ligand; Amphiphilic ligand; Cinnamaldehyde; Hydroformylation; Hydrogenation

1. Introduction

Phosphorus–nitrogen based hemilabile ligands have received much attention in recent years due to the improved catalytic activity of their transition metal complexes [1]. This class of compounds includes tridentate ligands which contain mixed donor sets [1,2]. Amongst these, examples have been reported of *N*,*P*,*N*-ligands, which have been the subject of some recent studies in homogeneous catalytic processes, mostly in hydrogenation [3–5]. In addition, phosphine ligands possessing methoxy or hydroxy groups have received particular attention due to their potential properties [1,6–9]. In recent years, a new concept of functionalised phosphines has also emerged, namely that of amphiphilic phosphines, and the benefits offered by their application to homogeneous catalysis have been discussed elsewhere [10–13].

Hydroformylation and hydrogenation are well established as homogeneous catalytic processes and, although numerous of papers have been reported, they are still research areas of great significance [14]. The hydroformylation reaction has been recognized as one of the most important applications of homogeneous catalysis and represents the best technology for the synthesis of aldehydes from olefins [14–16]. The selective hydrogenation of α,β-unsaturated aldehydes is also a topic of high interest, and has been studied as a monophasic or aqueous biphasic homogeneous catalytic process [12,17–19]. In this transformation, rhodium complexes are well-known to effect easily the C=C hydrogenation and the formation of saturated aldehydes, in contrast to ruthenium or iridium complexes which effect the selective C=O hydrogenation, yielding the corresponding unsaturated alcohols which are more valuable products [12,17–19].

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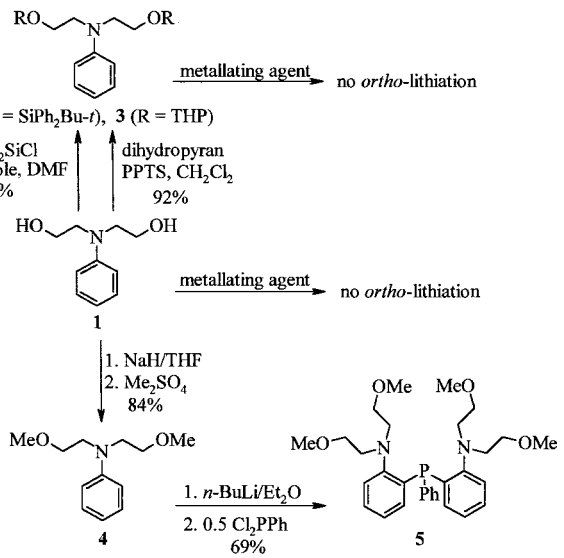
We have previously reported the synthesis of rhodium complexes with *P*,*N*-ligands possessing a hydroxy or a methoxy group, and their application to hydroformylation and hydroaminomethylation reactions [20,21]. According to these results, the rhodium complex possessing the methoxy group gave higher reaction rates towards hydroformylation of styrene than that with the hydroxy group [20]. The influence of the hydroxy groups in phosphorus ligands towards metal-catalyzed transformations has also been reported several times by other authors [9]. A very good activity and selectivity towards hydroformylation of styrene was also exhibited by rhodium complexes with hemilabile nitrogen-containing bis(phosphinite) or bis(phosphine) ligands, recently reported by our group [22]. These ligands were synthesized from *N*-phenyldiethanolamine (**1**) which used as starting material [22].

N-Phenyldiethanolamine (**1**) was also used for the synthesis of the tetramethoxy hemilabile *N*,*P*,*N*-ligand **5** and the corresponding amphiphilic tetrahydroxy ligand **8**, reported in this paper. The solution dynamics of their rhodium(I) complexes were studied by variable-temperature NMR spectroscopy, and the different coordination modes of the ligands are discussed. The complex of the former ligand was evaluated in the hydroformylation of styrene, whereas that of the latter ligand was applied to the hydrogenation of *trans*-cinnamaldehyde.

2. Results and discussion

2.1. Metallation of N-phenyldiethanolamine. Synthesis of the ligands

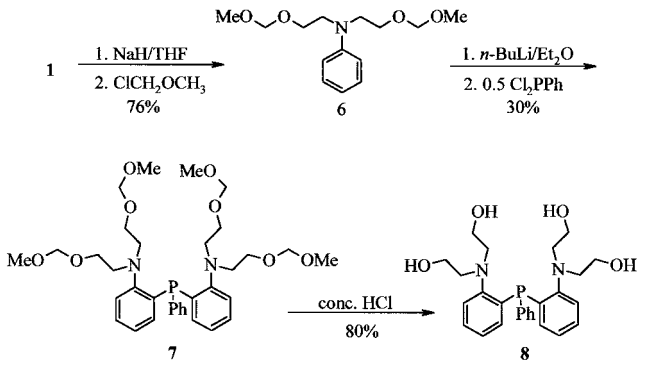
Organolithium compounds are among the most attractive reagents for selective carbon–phosphorus bond formation. It was thus very tempting to try the synthesis of a polyhydroxy phosphorus ligand, containing additional potential coordination sites, via *ortho*-lithiation of *N*-phenyldiethanolamine (**1**). We have reported previously the ability of the ω-lithioxyalkoxy ($-O(CH_2)_nOLi$) or 2-lithioxyethylamino ($-NCH_2CH_2OLi$) group to function as an *ortho*-directing substituent in the lithiation of aromatic compounds, as a result of the complex-induced proximity effect process (CIPE), leading to the ease metallation of ω-phenoxy alcohols and *N*-(2-hydroxyethyl)-*N*-methyl-aniline, respectively [20,23,24]. In contrast to these results, the *ortho*-lithiation of *N*-phenyldiethanolamine (**1**) failed. The metallation reaction was attempted using a variety of metallating reagents (*n*-BuLi, *n*-BuLi/TMEDA, *s*-BuLi, three equivalents) under variable conditions concerning the solvent (ether, THF, methylcyclohexane) and the temperature (−65 to −40 °C, room temperature or in refluxing solvent), and the reaction mixture was then quenched with electrophiles, such as chlorodiphenylphosphine, dichlorophenylphosphine, dimethyl disulfide (Scheme 1). Metallation was also attempted by three equivalents of *n*-BuLi/TMEDA/THF under sonication or by formation of the bis-(sodium or potassium alkoxide) of **1** and subsequent addition of one equivalent of *n*-BuLi. Unfortunately, all attempts led to very discouraging results, as the work-up procedure gave mixtures containing the starting material **1** and/or a variety of identified by-products. A probable explanation for the unsuccessful metallation of **1** could be the precipitation of the bis(alkoxide) which occurred in most cases, thereby effectively inhibiting the subsequent lithiation, as has previously been reported for the unsuccessful direct lithiation of dihydric phenols [25].



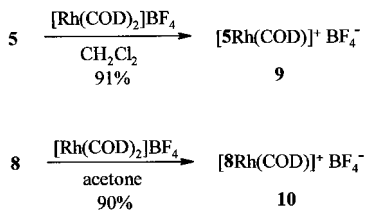
Scheme 1.

The unsuccessful *ortho*-lithiation of **1** led us to protect the hydroxy groups by common protective groups according to known procedures prior to metallation [26] (Scheme 1). Unfortunately, the *t*-butyldiphenylsilyl ether **2** and the tetrahydropyranyl ether **3** were also unreactive towards lithiation reagents, probably due to steric hindrance by the bulky protecting groups. The most effective substrate towards metallation was found to be the methyl ether **4**. Ligand **5** was prepared in a 69% yield via *ortho*-lithiation of **4** in ether with one equivalent of *n*-BuLi and subsequent reaction of the resulting aryllithium with 0.5 equivalents of $PhPCl_2$. The activity of the Me_3SiCl/NaI system towards the cleavage of the methyl groups, however, was too low, with no synthetic value for the preparation of the ligand **8**.

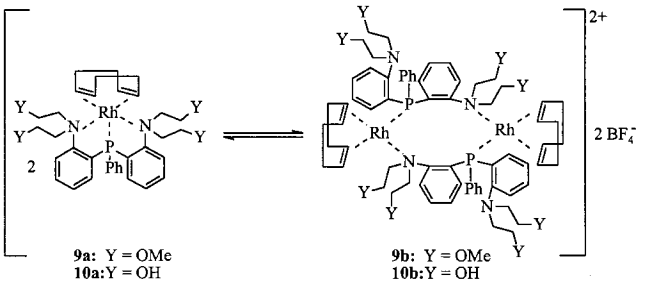
The most effective protection of the hydroxy groups in the synthesis of the tetrahydroxy ligand **8**, was found to be the methoxymethyl ether **6** (Scheme 2). *ortho*-Lithiation of **6** in ether with one equivalent of *n*-BuLi



Scheme 2.



Scheme 3.



Scheme 4.

and subsequent quenching with 0.5 equivalents of $PhPCl_2$, led to a moderately low yield (30%) of phosphine **7**, the protecting methoxymethyl groups of which were removed easily by conc. HCl. Even though ligand **8** possesses four hydrophilic groups (OH), the presence of the hydrophobic aromatic rings results a very low solubility of **8** in water, in contrast to the high solubility in water of an analogous hexahydroxy aminomethylphosphine [27].

2.2. Synthesis and characterization of the rhodium complexes

Treatment of $[Rh(COD)_2]BF_4$ with one equivalent of ligand **5** in dichloromethane or **8** in acetone solution, yielded the cationic rhodium complexes **9** or **10**, respectively, in high yield (Scheme 3). The elemental analyses are in accordance with the molecular formula of the complexes, and the observation of the $[LRh(COD)]^+$ ion (L = **5** or **8**) and the absence of higher aggregates in the ESI MS spectra suggests their monomeric nature.

The solution dynamics of the complexes were studied by variable-temperature ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy. In the ^{31}P-NMR spectrum in CD_2Cl_2 at 300 K, complex **9** shows a doublet at δ 40.39 ($J_{RhP} = 155.7$ Hz), which is characteristic for a rhodium complex with a phosphine which is involved in a N–P five-membered chelate [20,28]. In the ^{13}C-NMR spectrum of **9** at room temperature, the four CH_2N carbons are represented by only one peak at δ 57.29, indicating their equivalence. The same occurs for the four OCH_3 carbons (δ 58.99) and the four CH_2O carbons (δ 70.00). The CH_2N resonance at δ 57.29 has been slightly shifted (3.02 ppm) to low field compared to that of the free ligand **5**, as a result of Rh–N coordination. In the ^{1}H- and ^{13}C-NMR spectra, the OCH_3 resonances, on the other hand, are almost in the same position as those of the free ligand, indicating the absence of Rh–O coordination. According to the above-mentioned data, it can be concluded that, at ambient temperature, the ligand in complex **9** is coordinated to rhodium in a *N*,*P*,*N*-tridentate mode without any Rh–O interaction, indicating that the proposed equilibrium is shifted to the left (mode **9a**, Scheme 4). In the ^{31}P-NMR spectrum of **9**, the decrease of the temperature to 233 K caused a broadening of the signal (Fig. 1). At 188 K, two well-separated doublets at δ 37.57 ($J_{RhP} = 156.3$ Hz) and δ 48.70 ($J_{RhP} = 138.1$ Hz) with a ratio of about 3:2 were observed, indicating a dynamic equilibrium between two distinct species in both of which phosphorus is coordinated to rhodium. The resonance at δ 37.57, with a coupling constant close to that observed at room temperature, has to be assigned to structure **9a**, which is the most favorable mode even at low temperature. In the ^{13}C-NMR spectrum at 188 K, the existence of signals with the above-mentioned chemical shifts corresponding to CH_2N, OCH_3 and CH_2O carbons provide extra evidence for the presence of mode **9a** at low temperature. A dynamic equilibrium between the *N*,*P*,*N*-tridentate coordination mode **9a** and the corresponding monomeric *P*,*N*-bidentate mode is unlikely because the resonance at δ 48.70 with a $J_{RhP} = 138.1$ Hz is not characteristic for a N–P five-membered chelate rhodium complex. The resonance at δ 48.70 corresponds to a mode in which a Rh–O interaction must be excluded for two reasons. The first has to do with the ^{13}C-NMR spectrum at 188 K, in which two signals (δ 58.18 and 58.43) corresponding to OCH_3 carbons, in addition to the signal with chemical shift corresponding to the OCH_3 carbons in mode **9a**, are shifted very close to that of the free ligand **5**. The second reason is that a probable Rh–O coordination would create an O–P eight-membered chelate complex with a resonance in the ^{31}P NMR spectrum shifted to higher field compared to that of the five-membered ring as a result of the decreased ring strain [29]. The resonance at δ 48.70 is in contrast with this consideration,

indicating the absence of Rh–O coordination. In the ^{13}C-NMR spectrum of **9** at 188 K, in addition to the signals with chemical shifts corresponding to the OCH_2CH_2N carbons in mode **9a**, we observed several signals at δ 68.42–50.21 for the methylene carbons, some of which have to be assigned to the NCH_2 carbons. These resonances are shifted slightly to lower or higher field compared with that of the free ligand, indicating the presence of a mode which contains both coordinated and non-coordinated nitrogen(s). The above-mentioned data and analysis indicate that the mode corresponding to the resonance at δ 48.70 in the ^{31}P-NMR spectrum of **9** at 188 K must fill the following conditions: (a) N–P five-membered chelation is ruled out; (b) Rh–O coordination must be excluded; (c) both coordinated and non-coordinated nitrogen(s) are present; and (d) phosphorus is fully coordinated to the metal; in the case of dimeric species, we must postulate a symmetry in the molecule which makes the two phosphorus atoms equivalent. These conditions are fully filled by the proposed mode **9b**. In this structure, it is necessary to consider a P–Rh–N sequence in the coordination sphere around the metal, as the P–Rh–P sequence must be excluded due to the lack of P–P coupling in the ^{31}P-NMR spectrum.

Complex **10** displays analogous behavior. In the ^{31}P-NMR spectrum in acetone-d_6 at 300 K, it exhibits a doublet at δ 41.41 ($J_{RhP} = 150.6$ Hz). At room temperature, in the ^{1}H-NMR spectrum, all the OCH_2CH_2N protons are shifted to δ 3.59–3.38 and, in the ^{13}C-NMR spectrum, the four CH_2N carbons and the four CH_2O carbons are represented by one peak at δ 61.24 and 60.66, respectively. The CH_2N resonance has been slightly shifted (1.45 ppm) downfield compared to that of the free ligand **8**. In the ^{1}H-NMR spectrum at room temperature, the four hydroxy protons have a chemical shift close to that of the free ligand indicating that there is no coordination between rhodium and any hydroxy group [20]. By contrast, the proton resonance of the coordinated hydroxy group is shifted to a considerably lower field compared to that of the free ligand [30]. Following the analysis for the analogous complex **9** as detailed above, these data indicate that the proposed equilibrium is shifted to the left (mode **10a**, Scheme 4). In the variable-temperature ^{31}P-NMR spectra, the coalescence temperature was observed at 213 K (Fig. 1). At 188 K, two broad signals of different intensity were observed at approximately 39 and 54 ppm, which have to be assigned to the modes **10a** and **10b**, respectively. In the ^{1}H-NMR spectrum at low temperature, the resonance corresponding to the four hydroxy protons has a chemical shift very close to that observed at room temperature, indicating that association of the hydroxy group to rhodium does not take place at low temperature.

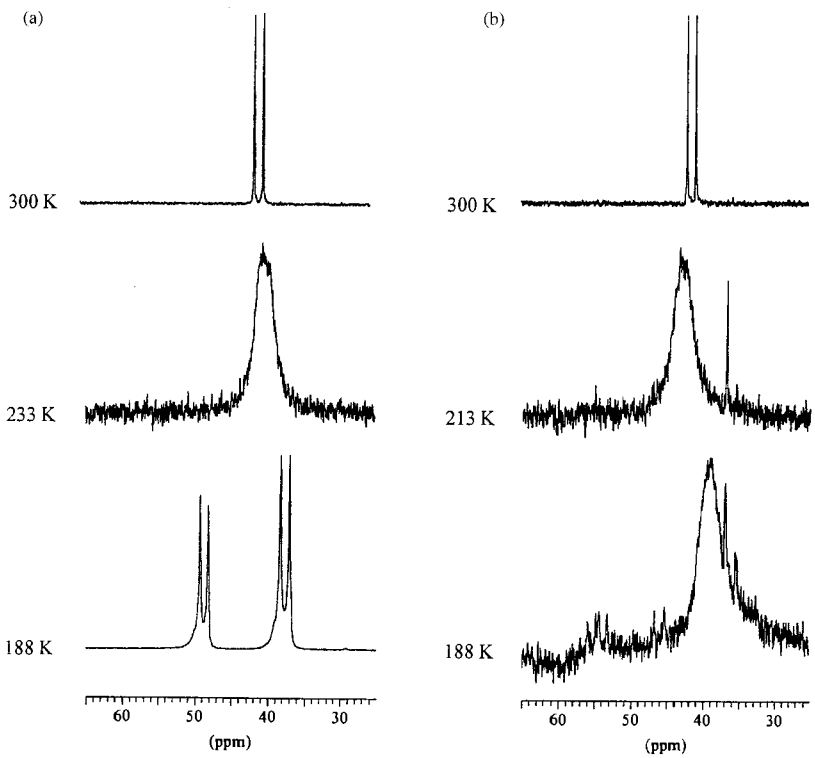
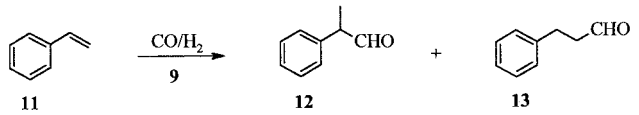
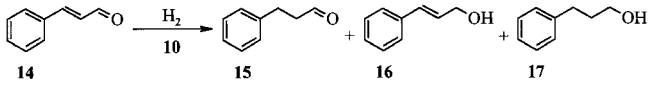


Fig. 1. Variable-temperature ^{31}P{^{1}H}-NMR spectra for the complexes: (a) **9** and (b) **10**. In the spectrum of **10**, the singlets at 36.86 and 35.45 ppm, which, although of very small peak area compared to the adjacent peaks, are prominent in the low temperature spectra, are due to a small amount of impurities which are barely observable in the room temperature spectrum.



Scheme 5.



Scheme 6.

The absence of Rh–O coordination in complexes **9** and **10** has also been reported previously by our group for the analogous rhodium(I) complexes with *P*,*N*-ligands possessing a hydroxy or a methoxy group [20]. In the ^{1}H-NMR spectra of **9** and **10** at room temperature, of the four COD olefinic protons, only two or three protons, respectively, are apparent as a broad signal. This behavior is analogous to that observed for the above-mentioned *P*,*N*-ligands [20]. As explained above, analytical data of the complexes in the solid state indicate their monomeric nature. In contrast, there is evidence for a dynamic equilibrium between two distinct species for both complexes in solution. The existence at low temperature of two coordination modes in the complexes reported in this paper, a monomeric and another bridged dimeric species, is not usual for di- or polydentate ligands. However, this behavior is not unique; it has been reported previously, for example, that it is possible even at room temperature, for a rhodium complex with α,ω-bis(diphenylphosphino)pentane [31].

2.3. Hydroformylation of styrene

The rhodium complex **9** was applied to the hydroformylation of styrene (**11**) with a high styrene:**9** ratio (1455:1), under variable conditions of pressure and temperature (Scheme 5; Table 1). A study of its catalytic activity towards hydroformylation is of interest, since the species present under these conditions are unknown. Complex **9** displays good turnover numbers (up to 1407), a high chemoselectivity for aldehydes (over 97%) with a very good branched:linear ratio (up to 95.2%). The variation observed in this work in the regioselectivities obtained under variable conditions of pressure and temperature is as expected for hydroformylation of styrene using rhodium systems. It is also of interest to note that, under identical reaction conditions, complex **9** has a lower reactivity than an analogous five-membered chelate rhodium(I) complex with a methoxy amino phosphine reported previously by our group, while the regioselectivity towards the branched aldehyde was found to be in the same range [20]. It is possible that the presence of different coordination modes of **9** in solution could play a role in its catalytic activity.

2.4. Hydrogenation of trans-cinnamaldehyde

The catalytic activity of complex **10** was tested in the hydrogenation of cinnamaldehyde (**14**), chosen as a model compound of the α,β-unsaturated aldehydes (Scheme 6; Table 2). The reactions were carried out in a *i*-PrOH/H_2O (95:5) mixture with a substrate:catalyst ratio of 497:1. As shown in Table 2, the catalyst exhibits a good selectivity for C = C hydrogenation, which yields the hydrocinnamaldehyde (**15**), over C=O or both C=C and C=O hydrogenation, yielding the cinnamyl alcohol (**16**) or the hydrocinnamyl alcohol (**17**), respectively. Decarbonylation products were present only in traces or non existent. The reaction rate is temperature and pressure dependent. After 24 h at $P = 30$ bar, the conversion of cinnamaldehyde was found to be 42.3, 55.2 and 92.2% at 30, 50 and 80 °C, repectively (entries 1, 3, 5). Increasing the pressure to 100 bar also increases the reaction rate (entries 6, 7). After 3 h at $P = 30$ bar and $T = 50$ °C, there was only a low conversion of cinnamaldehyde (6.1%) with a quantitative selectivity to hydrocinnamaldehyde **15**, as

Table 1
Hydroformylation of styrene catalyzed by rhodium complex **9**

Entry	T (°C)	P [a] (bar)	Time (h)	Conversion (%)	R_c [b] (%)	R_{br} [c] (%)	TON [d]
1	30	100	22	64.0	98.3	95.2	915
2	40	100	22	97.7	99.0	94.2	1407
3	40	100	4	34.4	99.5	94.7	498
4	60	100	4	98.2	97.0	86.9	1386
5	40	30	22	72.5	97.7	87.6	1031

A 4 mM solution in CH_2Cl_2. Styrene:catalyst = 1455:1.
[a] P, initial total pressure of CO/H_2 (1/1).
[b] R_c, chemoselectivity towards aldehydes **12** and **13**.
[c] R_{br}, regioselectivity towards branched aldehyde **12**.
[d] Turnover no. (TON) = aldehydes fraction × substrate:catalyst ratio.

a result of the favored C=C over C=O hydrogenation (entry 4). When the substrate:catalyst ratio was decreased to 99:1, cinnamaldehyde was converted in high yield (97.8%) after 24 h, under mild reaction conditions ($P = 30$ bar; $T = 30$ °C) (entry 2). Taking into consideration the selectivity of the reaction for conversions over 92%, we can conclude that the increased temperature yields a lower selectivity towards **15**, which at $P = 30$ bar was found to be 87.7 and 71.0% at 30 and 80 °C, respectively (entries 2, 5). The hydrogen pressure on the other hand, does not significantly affect the selectivity of the reaction. At 30 °C, the selectivity for **15** was about 88% for a pressure of 30 or even 100 bar (entries 2, 6).

3. Conclusions

Two cationic rhodium(I) complexes with hemilabile *N*,*P*,*N*-ligands possessing four methoxy or four hydroxy goups, respectively, have been synthesized. The tetramethoxy ligand was prepared via *ortho*-lithiation of *N*,*N*-bis(2-methoxyethyl)-benzenamine. Metallation of *N*-phenyldiethanolamine (**1**) was found to be unsuccessful and, for that reason, the analogous tetrahydroxy ligand was prepared via *ortho*-lithiation of the methoxymethyl ether of **1**. At room temperature both ligands are bound to rhodium in a *N*,*P*,*N*-tridentate coordination mode without any Rh–O interaction, whereas at low temperature a P–Rh–N bridged dimeric species was also found together with the most favored tridentate monomer. The complexes were examined as catalysts for the hydroformylation of styrene or hydrogenation of cinnamaldehyde, providing a good activity and selectivity towards the formation of 2-phenyl-propanal or hydrocinnamaldehyde, respectively.

4. Experimental

4.1. General

n-BuLi was prepared from lithium metal and *n*-BuCl in methylcyclohexane. $[Rh(COD)_2]BF_4$ was prepared according to literature procedure [32–34]. All the other chemicals were commercially available. All preparations and catalysis were carried out under argon by using dry and degassed solvents. THF and diethyl ether were distilled from 9-fluorenylpotassium and Na/benzophenone, respectively. Hydroformylation and hydrogenation studies were performed in a stainless steel autoclave (300 ml) with magnetic stirring. Syngas: CO/H_2 (1/1) (CO, 1.8; H_2, 3.0). NMR: Bruker AC 300 (300.13, 75.47 and 121.50 MHz for ^1H, ^{13}C and ^{31}P, respectively); ^1H- and ^{13}C-NMR shifts were referenced to the solvents and the ^{31}P-NMR shifts were referenced to external 85% H_3PO_4 in D_2O. The distinction of the CH, CH_2 and CH_3 carbons in the ^{13}C-NMR spectra was performed by DEPT-NMR experiments. ESI MS: Finnigan MAT TSQ 7000. GC–MS (EI): Varian Saturn 2000 with a 30 m × 0.25 mm DB5-MS column. GC: Varian Star 3400 CX with a 30 m × 0.53 mm DB5 column. Elemental analyses for C, H, N: Perkin–Elmer PE 2400 II.

4.2. *N*,*N*-bis[2-[(*t*-Butyldiphenylsilyl)oxy]ethyl]-benzenamine (**2**)

To a mixture of **1** (8 g, 44.14 mmol) and imidazole (15.2 g, 223.27 mmol), *N*,*N*-dimethylformamide (160 ml) was added with an ice-water bath cooling. The reaction mixture was stirred at room temperature (r.t.) for 1 h and subsequently *t*-butyldiphenylchlorosilane (27 ml, 103.83 mmol) was added while cooling at 0 °C. After an overnight stirring, DMF was removed by

Table 2
Hydrogenation of cinnamaldehyde catalyzed by rhodium complex **10**

Entry	*T* (°C)	*P* [a] (bar)	Time (h)	Conversion (%)	Selectivity (%) [b]			TON [c]
					15	**16**	**17**	
1	30	30	24	42.3	96.4	–	3.6	210
2[d]	30	30	24	97.8	87.7	3.8	8.5	97
3	50	30	24	55.2	88.9	5.8	5.3	274
4	50	30	3	6.1	100.0	–	–	30
5	80	30	24	92.2	71.0	20.0	9.0	458
6	30	100	24	94.6	87.9	2.7	9.4	470
7	50	100	24	95.0	86.3	2.2	11.5	472

A 2 mM solution in *i*-PrOH/H_2O (95:5). Cinnamaldehyde/catalyst = 497:1.

[a] *P*, initial pressure of H_2 at r.t.

[b] (Product/converted **14**) × 100.

[c] Turnover no. (TON) = fraction of products (**15** + **16** + **17**) × substrate/catalyst ratio.

[d] Cinnamaldehyde/catalyst = 99:1.

evaporation, water was added and the product was extracted with dichloromethane (3 × 150 ml). The combined organic layers were dried over Na_2SO_4, filtered and evaporated to dryness, yielding 37.2 g of a yellow viscous oil, which solidified upon standing. It was recrystallized from ethanol, yielding **2** (26.3 g, 91%) as a white solid, m.p. 103–105 °C. ^{1}H-NMR ($CHCl_3$-*d*, δ ppm): 7.67 (d, $^3J = 6.7$ Hz, 8H, Ar); 7.47–7.35 (m, 12H, Ar); 7.02 (t, $^3J = 7.4$ Hz, 2H, Ar); 6.57 (t, $^3J = 7.1$ Hz, 1H, Ar); 6.31 (d, $^3J = 7.9$ Hz, 2H, Ar); 3.77 (t, $^3J = 6.4$ Hz, 4H, CH_2O); 3.48 (t, $^3J = 6.4$ Hz, 4H, CH_2N); 1.08 (s, 18H, $C(CH_3)_3$). ^{13}C{^{1}H}-NMR ($CHCl_3$-*d*, δ ppm): 147.59, 135.59, 133.49, 129.66, 129.10, 127.68, 115.45 and 111.22 (Ar); 60.80 and 52.93 (OCH_2CH_2N); 26.83 ($C(CH_3)_3$); 19.09 ($C(CH_3)_3$). ESI MS: m/z 658.5 ([M + H]$^+$). Anal. Found: C, 76.36; H, 7.85; N, 2.04. Calc. for $C_{42}H_{51}NO_2Si_2$ (658.04): C, 76.66; H, 7.81; N, 2.13%.

4.3. N,N-bis[2-[(Tetrahydro-2H-pyran-2-yl)oxy]ethyl]-benzenamine (3) [35]

To a solution of **1** (6.5 g, 35.86 mmol) and freshly distilled dihydropyran (30 ml, 331.67 mmol) in dichloromethane (150 ml), piridinium-toluene-4-sulfonate (2.0 g, 7.96 mmol) was added and stirred at r.t. for 6 days. The solution was then diluted by the addition of dichloromethane (100 ml), washed with half-saturated brine and then with water. The organic phase was dried over Na_2SO_4, filtered and evaporated to dryness, yielding 12.65 g of a purple oil. Isolation of pure product was carried out by column chromatography over silica gel using a mixture of hexane/THF (5:1) as eluent, yielding **3** (11.5 g, 92%) as a colorless oil. ^{1}H-NMR ($CHCl_3$-*d*, δ ppm): 7.20 (t, $^3J = 7.8$ Hz, 2H, Ar); 6.74 (d, $^3J = 8.3$ Hz, 2H, Ar); 6.66 (t, $^3J = 7.2$ Hz, 1H, Ar); 4.59 (s, 2H, CH–THP); 3.91–3.80 (m, 4H, CH_2); 3.61–3.56 (m, 6H, CH_2); 3.50–3.46 (m, 2H, CH_2); 1.87–1.43 (m, 12H, CH_2–THP). ^{13}C{^{1}H}-NMR ($CHCl_3$-*d*, δ ppm): 147.58, 129.08, 115.70 and 111.48 (Ar); 98.95 (CH); 64.67, 62.05, 50.89, 30.48, 25.29 and 19.34 (CH_2). GC–MS (EI): m/z (relative intensity) 349 ([M$^+$], 7), 221 (36), 150 (100), 85 (51), 77 (12), 55 (54). Anal. Found: C, 68.70; H, 9.16; N, 3.74. Calc. for $C_{20}H_{31}NO_4$ (349.47): C, 68.74; H, 8.94; N, 4.01%.

4.4. N,N-bis(2-Methoxyethyl)-benzenamine (4) [36]

A solution of **1** (29 g, 160 mmol) in THF (100 ml) was added dropwise to a suspension of NaH (previously washed twice with THF to remove the mineral oil, 13 g, 80% in NaH, 433 mmol) in THF (100 ml) cooled with an ice-water bath, and then stirred at r.t. for 1 h. A solution of dimethyl sulfate (35 ml, 368 mmol) in THF (100 ml) was then added dropwise at 0 °C. After stirring at r.t. overnight, THF was removed by evaporation, water was added, the product was extracted with dichloromethane (3 × 100 ml), dried over Na_2SO_4, filtered and evaporated to dryness. Purification was carried out by distillation, yielding **4** (28.2 g, 84%), b.p. 105 °C (0.1 mmHg). ^{1}H-NMR ($CHCl_3$-*d*, δ ppm): 7.23–7.20 (m, 2H, Ar); 6.74–6.67 (m, 3H, Ar); 3.59–3.54 (m, 8H, OCH_2CH_2N); 3.37 (s, 6H, OCH_3). ^{13}C{^{1}H}-NMR ($CHCl_3$-*d*, δ ppm): 147.75, 129.26, 116.05 and 111.73 (Ar); 70.04 (CH_2O); 58.94 (OCH_3); 50.88 (CH_2N). GC–MS (EI): m/z (relative intensity) 209 ([M$^+$], 23), 164 (100), 132 (16), 106 (12), 91 (6), 77 (15), 59 (25). Anal. Found: C, 68.81; H, 9.24; N, 6.61. Calc. for $C_{12}H_{19}NO_2$ (209.29): C, 68.87; H, 9.13; N, 6.69%.

4.5. 2,2′-(Phenylphosphinidene)-bis[N,N-bis(2-methoxyethyl)-benzenamine] (5)

n-BuLi (1.80 M in methylcyclohexane, 26 ml, 46.80 mmol) was added to a solution of **4** (9 g, 43.06 mmol) in ether (35 ml), under argon. The reaction mixture was subsequently stirred at r.t. for 29 h, and then, a solution of dichlorophenylphosphine (3 ml, 22.12 mmol) in ether (25 ml) was added dropwise with ice-water bath cooling and the mixture stirred at r.t. overnight. The volatile materials were removed by evaporation, water (100 ml) was added, the product was extracted with toluene (3 × 100 ml), the organic phase washed with water, dried over Na_2SO_4, filtered and evaporated to dryness, yielding 13.65 g of an orange oil. Purification was carried out by column chromatography over silica gel. During the elution, the eluent was gradually changed in 10% increments from pure hexane to pure ethyl acetate, yielding **5** (7.8 g, 69%) as a viscous oil. ^{1}H-NMR ($CHCl_3$-*d*, δ ppm): 7.29–7.25 (m, 7H, Ar); 7.21–7.17 (m, 2H, Ar); 7.00–6.96 (m, 2H, Ar); 6.67–6.64 (m, 2H, Ar); 3.27–3.22 (m, 8H, CH_2O); 3.19–3.09 (m, 8H, CH_2N); 3.14 (s, 12H, OCH_3). ^{13}C{^{1}H}-NMR ($CHCl_3$-*d*, δ ppm): 154.93–123.87 (Ar); 70.96 (CH_2O); 58.46 (OCH_3); 54.27 (CH_2N). ^{31}P{^{1}H}-NMR ($CHCl_3$-*d*, δ ppm): −22.63 (s). ESI MS: m/z 525 ([M + H]$^+$). Anal. Found: C, 68.55; H, 7.92; N, 5.24. Calc. for $C_{30}H_{41}N_2O_4P$ (524.64): C, 68.68; H, 7.88; N, 5.34%.

4.6. N,N-bis[2-(Methoxymethoxy)ethyl]-benzenamine (6)

A solution of **1** (12.7 g, 70.07 mmol) in THF (60 ml) was added dropwise to a suspension of NaH (previously washed twice with THF to remove the mineral oil, 5.7 g, 80% in NaH, 190 mmol) in THF (100 ml) and refluxed for 1 h. After cooling at r.t., a solution of chloromethyl methyl ether (13 ml, 174.39 mmol) in

THF (50 ml) was added dropwise and the resulting mixture refluxed for 2 h. THF was removed by evaporation, water was added, the product was extracted with dichloromethane (3 × 100 ml), dried over Na_2SO_4, filtered and evaporated to dryness, yielding 17.1 g of a brown oil. Purification was carried out by distillation, yielding **6** (14.4 g, 76%), b.p. 135–140 °C (0.01 mmHg). ^{1}H-NMR ($CHCl_3$-*d*, δ ppm): 7.22 (t, $^3J = 8.0$ Hz, 2H, Ar); 6.75–6.67 (m, 3H, Ar); 4.63 (s, 4H, OCH_2O); 3.73–3.69 (m, 4H, CH_2O); 3.64–3.60 (m, 4H, NCH_2); 3.36 (s, 6H, OCH_3). ^{13}C{^{1}H}-NMR ($CHCl_3$-*d*, δ ppm): 147.50, 129.25, 116.12 and 111.69 (Ar); 96.60 (OCH_2O); 65.04 (CH_2O); 55.16 (OCH_3); 50.97 (NCH_2). GC–MS (EI): *m*/*z* (relative intensity) 269 ([M$^+$], 24), 238 (7), 207 (17), 194 (100), 134 (72), 91 (11), 77 (26), 45 (52). Anal. Found: C, 62.61; H, 8.73; N, 5.43. Calc. for $C_{14}H_{23}NO_4$ (269.34): C, 62.43; H, 8.61; N, 5.20%.

4.7. 2,2′-(Phenylphosphinidene)-bis[N,N-bis[2-(methoxymethoxy)ethyl]-benzenamine] (7)

n-BuLi (1.80 M in methylcyclohexane, 24 ml, 43.20 mmol) was added dropwise to a solution of **6** (10.6 g, 39.41 mmol) in ether (35 ml), cooled with ice-water bath, and then stirred at r.t. for 25 h and refluxed for 5 h. After cooling with ice-water bath, a solution of dichlorophenylphosphine (2.8 ml, 20.65 mmol) in ether (20 ml) was added dropwise and the mixture stirred at r.t. overnight. The volatile materials were removed by evaporation, water (100 ml) was added, the product was extracted with dichloromethane (3 × 100 ml), the organic phase washed with water, dried over Na_2SO_4, filtered and evaporated to dryness, yielding 12.05 g of an orange viscous oil. Purification was carried out by column chromatography over silica gel. During the elution, the eluent was gradually changed from hexane/ethyl acetate (3:1) to (1:1), yielding **7** (3.8 g, 30%) as a viscous oil. ^{1}H-NMR ($CHCl_3$-*d*, δ ppm): 7.29–7.25 (m, 7H, Ar); 7.20–7.16 (m, 2H, Ar); 7.00–6.96 (m, 2H, Ar); 6.67–6.64 (m, 2H, Ar); 4.42 (s, 8H, OCH_2O); 3.33–3.26 (m, 16H, OCH_2CH_2N); 3.26 (s, 12H, OCH_3). ^{13}C{^{1}H}-NMR ($CHCl_3$-*d*, δ ppm): 154.72–123.83 (Ar); 96.39 (OCH_2O); 66.04 (CH_2O); 55.01 (OCH_3); 54.33 (CH_2N). ^{31}P{^{1}H}-NMR ($CHCl_3$-*d*, δ ppm): –22.53 (s). ESI MS: *m*/*z* 645 ([M + H]$^+$); 613 ([M − OCH_3]$^+$). Anal. Found: C, 63.24; H, 7.93; N, 4.04. Calc. for $C_{34}H_{49}N_2O_8P$ (644.74): C, 63.34; H, 7.66; N, 4.34%.

4.8. 2,2′-(Phenylphosphinidene)-bis[N,N-bis(2-hydroxyethyl)-benzenamine] (8)

Concentrated HCl (2 ml) was added to the solution of **7** (1.54 g, 2.39 mmol) in methanol (30 ml) and refluxed for 1 h. Methanol was evaporated, the residue was alkalinized by a 10% aqueous solution of NaOH, the product was extracted with dichloromethane (3 × 50 ml), the organic phase washed with water, dried over Na_2SO_4, filtered and evaporated to dryness, yielding **8** (0.89 g, 80%, essential pure according to ^{1}H- and ^{31}P-NMR spectroscopy) as a yellow jelly, which solidified upon standing. Recrystallization from dichloromethane at –20 °C yielded a white solid, m.p. 161–165 °C. ^{1}H-NMR (acetone-d_6, δ ppm): 7.41–7.36 (m, 7H, Ar); 7.26–7.21 (m, 2H, Ar); 7.11–7.06 (m, 2H, Ar); 6.76–6.72 (m, 2H, Ar); 3.77 (s, 2H, OH); 3.70 (sl br, 2H, OH); 3.35–3.30 (m, 8H, CH_2O); 3.10 (t, ^3J = 6.1 Hz, 8H, CH_2N). ^{13}C{^{1}H}-NMR (acetone-d_6, δ ppm): 157.74–126.50 (Ar); 61.35 and 59.79 (OCH_2CH_2N). ^{31}P{^{1}H}-NMR (acetone-d_6, δ ppm): –27.50 (s). ESI MS: *m*/*z* 469.2 ([M + H]$^+$, 7). Anal. Found: C, 67.12; H, 7.25; N, 6.02. Calc. for $C_{26}H_{33}N_2O_4P$ (468.53): C, 66.65; H, 7.10; N, 5.98%.

4.9. [5Rh(COD)]BF_4 (9)

A solution of the ligand **5** (0.1727 g, 0.33 mmol) in dichloromethane (15 ml) was added dropwise to the dark red solution of [Rh(COD)$_2$]BF_4 (0.1338 g, 0.33 mmol) in dichloromethane (5 ml) with a dry ice/acetone cooling bath. The reaction mixture was warmed slowly to r.t. within 1 h, and stirred at this temperature for an additional 1 h. The resulting light orange solution was evaporated to dryness, the residue washed with ether and dried, yielding **9** (0.2471 g, 91%) as a yellow solid, m.p. (dec.) 171–174 °C. ^{1}H-NMR (CH_2Cl_2-d_2, δ ppm): 7.94–7.88, 7.61–7.38 and 7.27–7.22 (3 × m, 13H, Ar); 5.43 (br s, 2H, COD–CH); 3.55 and 3.31 (2 × br m, 16H, NCH_2CH_2O); 3.18 (s, 12H, OCH_3); 2.54 (br s, 4H, COD–CH_2); 2.22–2.11 (br m, 4H, COD–CH_2). ^{13}C{^{1}H}-NMR (CH_2Cl_2-d_2, δ ppm): 154.28–124.87 (Ar); 111.76–111.58 (m, COD–CH); 71.67 (d, J_{RhC} = 13.4 Hz, COD–CH); 70.00 (s, CH_2O); 58.99 (s, OCH_3); 57.29 (sl br s, CH_2N); 32.03 and 28.33 (2 × s, COD–CH_2). ^{31}P{^{1}H}-NMR (CH_2Cl_2-d_2, δ ppm): 40.39 (d, J_{RhP} = 155.7 Hz). ESI MS: *m*/*z* 735 ([M − BF_4]$^+$). Anal. Found: C, 55.48; H, 6.49; N, 3.04. Calc. for $C_{38}H_{53}BF_4N_2O_4PRh$ (822.53): C, 55.49; H, 6.49; N, 3.41%.

4.10. [8Rh(COD)]BF_4 (10)

A solution of the ligand **8** (0.1107 g, 0.24 mmol) in acetone (15 ml) was added dropwise to the dark red solution of [Rh(COD)$_2$]BF_4 (0.0960 g, 0.24 mmol) in acetone (5 ml) with a dry ice/acetone cooling bath. The reaction mixture was warmed slowly to r.t. within 1 h, and stirred at this temperature for an additional 1 h. The resulting light orange solution was evaporated under reduced pressure to a minimal volume, and addition of dichloromethane caused the precipitation of a yellow solid. The mixture was evaporated to dryness, yielding **10** (0.1650 g, 90%), m.p. (dec.) 198–203 °C.

^{1}H-NMR (acetone-d_6, δ ppm): 7.86–7.76, 7.66–7.61, 7.50–7.45 and 7.32–7.28 (4 × m, 13H, Ar); 4.12 (br s, 3H, COD–CH); 3.73 (sl br s, 4H, OH, exchangeable with D_2O); 3.59–3.38 (m, 16H, NCH_2CH_2O); 2.59 (m, 4H, COD–CH_2). Four of the COD–CH_2 protons are not observed and are assumed to be obscured by the acetone-d_5 signal. ^{13}C{^{1}H}-NMR (acetone-d_6, δ ppm): 156.59–126.71 (Ar); 69.97 (COD–CH); 61.24 and 60.66 (NCH_2CH_2OH). The COD–CH_2 carbons are not observed and are assumed to be obscured by the acetone-d_6 signal. ^{31}P{^{1}H}-NMR (acetone-d_6, δ ppm): 41.41 (d, $J_{RhP} = 150.6$ Hz). ESI MS: m/z 679 ($[M - BF_4]^+$). Anal. Found: C, 52.63; H, 5.83; N, 3.06. Calc. for $C_{34}H_{45}BF_4N_2O_4PRh$ (766.42): C, 53.28; H, 5.92; N, 3.66%.

4.11. Hydroformylation of styrene catalyzed by rhodium complex **9**

In a typical experiment, styrene (2 ml, 17.456 mmol) and a 4 mM solution of rhodium complex **9** in dichloromethane (3 ml, 0.012 mmol) were placed under argon in an oven-dried autoclave, which was then closed, pressurized with syngas ($CO/H_2 = 1:1$) to 100 bar and brought to the corresponding temperature. After the required reaction time, the autoclave was cooled to room temperature, the pressure was carefully released and the solution was passed through celite and analyzed by GC, GCMS and ^{1}H NMR spectra. Conversions were determined by GC.

4.12. Hydrogenation of trans-cinnamaldehyde catalyzed by rhodium complex **10**

A typical experiment was performed in an autoclave, in which air was evacuated and replaced with argon. A 2 mM solution of rhodium complex **10** in i-PrOH/H_2O (95:5) (4 ml, 0.008 mmol) and cinnamaldehyde (0.5 ml, 3.972 mmol) were placed under argon in the autoclave, which was then closed, pressurized with hydrogen (30 or 100 bar) and brought to the corresponding temperature. After the required reaction time, the work-up and the analysis of the products was performed as described above for hydroformylation.

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