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Synthesis of new rhodium complexes with a hemilabile nitrogen-containing bis(phosphinite) or bis(phosphine) ligand. Application to hydroformylation of styrene

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Abstract

Two new cationic rhodium(I) complexes with a hemilabile nitrogen-containing bis(phosphinite) or bis(phosphine) ligand have been prepared. ^{31}P-NMR studies provide evidence that the ligands are coordinated to the metal in *P*,*P*-bidentate mode, whereas for the bis(phoshine)-based ligand, a *P*,*N*,*P*-tridentate mode is also possible to be found at low temperatures. The complexes were applied to the hydroformylation of styrene and displayed a high chemoselectivity for aldehydes with a very good branched/linear ratio.

Keywords: Bisphosphine; Bisphosphinite; *P*,*N*,*P*-Ligand; Hemilabile ligand; Rhodium complex; Hydroformylation

1. Introduction

The importance of ligands possessing both 'soft' phosphorus and 'hard' nitrogen atoms as chelating reagents is well known, and the use of these ligands can be expected to improve the catalytic activity of some complexes [1–13]. This class of compounds includes *P*,*N*,*P*-ligands containing sp^3, sp^2 or sp nitrogen donors, whose coordination behavior towards transition metals has been widely studied [4–11].

In the last few years, interest in bis(phosphinites) as ligands in homogeneously catalytic processes, mostly in hydrogenation, has increased considerably [14–21]. This increase is due to their facile preparation by the reaction of readily available diols with chlorophosphines in the presence of a base. The catalytic activity of bis(phosphinites) versus bis(phosphines) has been studied and, according to a recent report, rhodium complexes of achiral bis(phosphinites) exhibit lower reactivity than bis(phosphines) in the hydrogenation of imines while the situation is reversed for the chiral analogues [20]. In contrast to the significant number of publications concerning bis(phosphinites), nitrogen-containing bis(phosphinites) have been less studied and refer to ligands based on pyridine or pyrrolidine moieties [5,6,19]. The enormous interest in hydroformylation, one of the most important industrial applications of homogeneous catalysis, is well known [22,23]. Up to now, the use of such ligands in hydroformylation has been limited [19]. The application of nitrogen-containing bis(phosphines) (e.g. ligands with aminomethylphosphine moieties) in hydroformylation has also been reported [24–27].

Recently, we reported the synthesis of new *P*,*N*-ligands and their application in rhodium-catalyzed hydroformylation and domino hydroformylation-reductive amination reactions [28,29]. As an extension of the ongoing research, in this paper the synthesis and characterization of new cationic rhodium complexes with the hemilabile nitrogen-substituted bis(phosphinite) $PhN(CH_2CH_2OPPh_2)_2$ (**2**) and the bis(phosphine) $PhN(CH_2CH_2PPh_2)_2$ (**5**), are described. The coordination behavior of the latter ligand towards palladium and rhenium has been reported previously [10,30]. The catalytic activity of the complexes was tested on the hydroformylation of styrene, under varying conditions.

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2. Results and discussion

2.1. Synthesis of the ligands

The synthetic sequence for the preparation of the ligands and their complexes in the present work is outlined in Scheme 1. *N*-Phenyldiethanolamine (**1**) was used as starting material for their synthesis.

Bis(phosphinite) **2** was prepared in 89% yield by hydrogen abstraction of **1**, using two equivalents of *n*-BuLi and subsequent reaction of the resulting bis(alkoxide) with two equivalents of Ph_2PCl. Replacement of the hydroxyl groups in **1** by the diphenylphosphino group for the synthesis of ligand **5** was achieved via its bis(tosylate) [10].

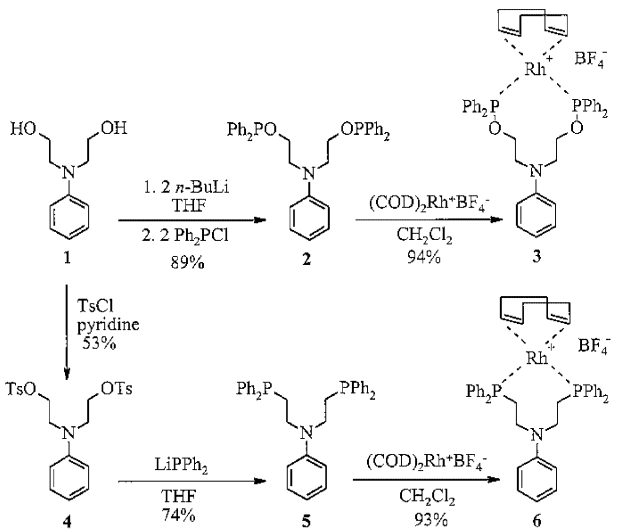
2.2. Synthesis and characterization of the rhodium complexes

Treatment of $(COD)_2Rh^+BF_4^-$ in dichloromethane solution with one equivalent of ligand **2** or **5**, yielded the cationic rhodium complexes **3** or **6,** respectively, in high yield (Scheme 1).

The coordination mode in the complexes was determined by spectroscopic techniques. The observation of the $[LRh(COD)]^+$ ion (L = **2** or **5**) and the absence of higher aggregates in the ESI MS spectra suggests the monomeric nature of the complexes. The ^{31}P-NMR spectra clearly indicate that both phosphorus atoms are bonded to the metal. In CD_2Cl_2 at room temperature, complex **3** shows a doublet at δ 120.00 ($J_{RhP} = 181.8$ Hz) and for complex **6** a doublet at δ 17.33 ($J_{RhP} = 142.6$ Hz). Lack of coupling between the two phosphorus atoms indicates their equivalence. The chemical shift and the Rh–P coupling constant in the ^{31}P-NMR of **3** are in full accordance with the corresponding values of large size chelate rhodium complexes with bis(phosphinites), indicating the absence of Rh–N coordination, which would create a six-membered chelate ring [18]. In the ^{1}H-NMR spectrum of **3**, the NCH_2 resonance is slightly shifted to a high field compared to the free ligand, contrary to that expected for the case of Rh–N coordination. This observation is additional evidence that the NCH_2 protons are situated away from the coordination sphere around the metal. A *P*,*P*-bidentate coordination mode was also observed for complex **6**, at room temperature, according to the ^{31}P-NMR spectrum. In the ^{31}P-NMR spectrum of five-membered chelate rhodium complexes with analogous *P*,*N*-ligands, e.g. $Ph_2PCH_2CH_2NMe_2$, the phosphine resonance is observed at δ ca. 40, with a ^{31}P-coordination chemical shift δ ($\delta_{P(coord)} - \delta_{P(free)}$) of around 60 ppm [12,28]. The resonance at δ 17.33 with a coordination chemical shift = 38.55 ppm in complex **6** is quite different from these values, indicating the absence of a five-membered *P*,*N*-chelate ring, at room temperature. The absence of Rh–N coordination has been reported in the solid state for the similar rhodium complex $[(PhN(CH_2PPh_2)_2)Rh(COD)]BF_4$ [26].

In the variable-temperature ^{31}P-NMR spectra, complexes **3** and **6** show different behavior (Fig. 1). The ^{31}P-NMR spectrum of **3** did not significantly change even at temperatures down to 213 K, indicating that the room temperature conformation and coordination mode is retained at low temperatures. For complex **6** on the other hand, the doublet at δ 17.33, observed at 300 K, on cooling starts to become broader at 233 K and merges to a broad singlet at 213 K. On further cooling to 183 K two broad signals of different intensity are observed at approximately 10 and 22 ppm which at even lower temperature (173 K) become a well-resolved doublet at 10.18 ppm ($J_{RhP} = 137.3$ Hz) and two broad signals at approximately 17.5 and 27.5 ppm. A possible explanation for this behavior is the presence of different coordination modes or conformations of the ligand at low temperature, one of which, corresponding to the signal at 17.5 ppm, is probably the same as that at 300 K. The additional resonances may possibly be due to an alternative *P*,*N*,*P*-coordination mode of the ligand.

Despite the absence or presence of Rh–N coordination in complexes **3** and **6**, the existence of an additional coordination site as a stabilizing group during the course of a metal-mediated reaction could improve the catalytic efficiency of the complexes, as shown below for hydroformylation. Indeed, in complexes of the type $[(R(NCH_2PPh_2)_2)Rh(COD)]BF_4$, where Rh–N coordination is absent, the presence of a nitrogen in the backbone improves considerably the catalytic activities as opposed to analogous ligands with the all-carbon bridge [26].



Scheme 1.

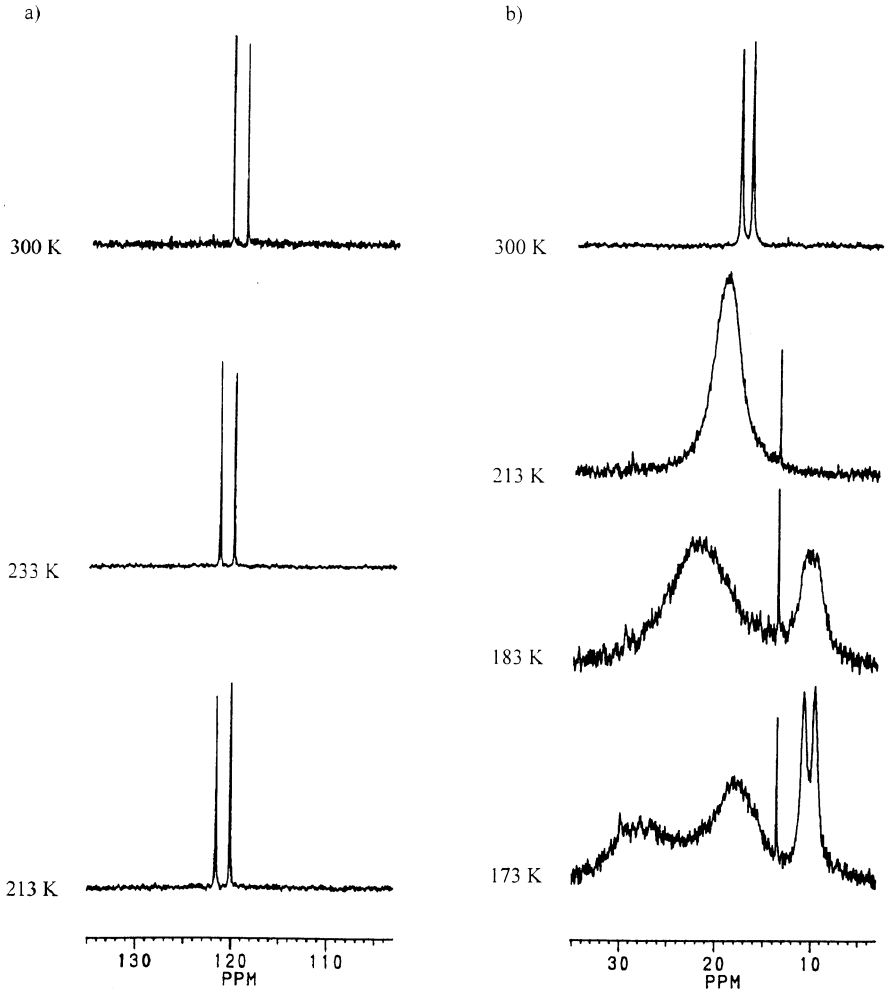
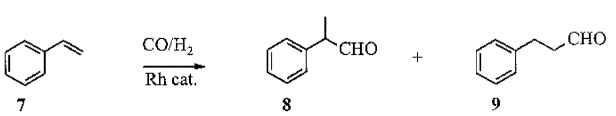


Fig. 1. Variable-temperature $^{31}P\{^{1}H\}$-NMR spectra for the complexes: (a) **3** and (b) **6**. The sharp signal at approximately 13.5 ppm, which although of very small peak area compared to the adjacent peaks, is prominent in the low temperature spectra, is due to a small amount of impurity which is barely observable in the room temperature spectrum.

2.3. Hydroformylation

The catalytic activity of the rhodium complexes **3** and **6** was tested on the hydroformylation of styrene, under variable conditions of pressure and temperature (Scheme 2; Table 1). In general, they display a high chemoselectivity for aldehydes (over 98%) with a very good branched/linear ratio (up to 96%). In all experiments, ethylbenzene as hydrogenation product was present only in traces (0.1–0.7%). For both complexes, at 100 bar total pressure of syngas, the regioselectivity towards 2-phenyl-propanal (**8**) (branched aldehyde) was found to be about 96, 95, and 87% at 30, 40, and 60°C, respectively. Lowering the syngas pressure to 30 or 20 bar, at 40°C, the regioselectivity was decreased to about 88 or 87%, respectively. The increase of the temperature not only yields a lower regioselectivity but dramatically effects the reaction rate. At a pressure of 100 bar, after 1 h at 40°C, the conversion of styrene was 17.6 and 11.9% using the complexes **3** and **6** (entries 7 and 8), respectively, while at 60°C, both complexes yielded an almost complete conversion of styrene after 1 h (entries 11 and 12). At 30°C, the conversion of styrene was not complete even after 22 h (entries 1 and 2).

According to the above mentioned results, the rhodium complexes **3** and **6** are very active and selective catalysts for the hydroformylation of styrene. It is of interest to note that, under identical reaction conditions, their reactivity is higher than five-membered chelate rhodium(I) complexes with *P,N*-ligands previously reported by our group [28]. At a pressure of 100 bar, after 4 h at 40°C, for instance, the TON's using **3** and **6** are 1305 and 1107, respectively, in contrast to the



Scheme 2.

Table 1
Hydroformylation of styrene catalyzed by rhodium complex **3** or **6** [a]

Entry	Catalyst [b]	T (°C)	P [c] (bar)	Time (h)	Conversion (%)	R_c [d] (%)	R_{br} [e] (%)	TON [f]
1	**3**	30	100	22	93.1	99.1	96.1	1342
2	**6**	30	100	22	85.9	98.9	96.0	1236
3	**3**	40	100	22	99.9	98.5	95.3	1432
4	**6**	40	100	22	99.9	98.8	95.1	1436
5	**3**	40	100	4	90.7	98.9	94.9	1305
6	**6**	40	100	4	76.8	99.1	95.0	1107
7	**3**	40	100	1	17.6	98.1	94.8	251
8	**6**	40	100	1	11.9	98.8	94.7	171
9	**3**	60	100	4	99.9	99.4	87.2	1445
10	**6**	60	100	4	99.8	98.2	87.0	1426
11	**3**	60	100	1	99.4	98.1	87.1	1419
12	**6**	60	100	1	98.6	98.6	87.0	1415
13	**3**	40	30	68	99.5	99.2	88.3	1436
14	**6**	40	30	68	98.5	99.7	87.9	1429
15 [g]	**3**	40	20	72	99.9	99.2	87.3	720
16 [g]	**6**	40	20	72	98.8	99.5	87.0	715

[a] Styrene/catalyst = 1455:1.
[b] A 4 mM solution in CH_2Cl_2.
[c] P = initial total pressure of CO/H_2 (1:1).
[d] R_c = chemoselectivity towards aldehydes **8** and **9**.
[e] R_{br} = regioselectivity towards branched aldehyde **8**.
[f] Turnover no. (TON) = aldehydes fraction × substrate/catalyst ratio.
[g] Styrene/catalyst = 727:1.

rhodium(I) complex containing a methoxy amino phosphine, which led to a TON of 821, under the same reaction conditions [28]. The catalytic activity of **3** in the hydroformylation of styrene was also compared to that of the analogue rhodium complex with a nitrogen-containing bis(phosphinite) ligand based on a pyrrolidine moiety [19]. Under similar conditions (styrene/catalyst = 727:1, $P(CO/H_2) = 20$ bar, $T =$ 40°C) complex **3** led to almost quantitative conversion of styrene after 72 h, yielding the desired aldehydes with a regioselectivity of 87% towards the branched aldehyde **8**. In contrast to these experimental results, hydroformylation of styrene by the rhodium complex with the pyrrolidine-based bis(phosphinite) ligand, led to only 10% conversion into aldehydes after 72 h, with a 77% regioselectivity towards the branched aldehyde [19]. The much lower activity and selectivity of this system, in contrast to the bis(phosphinite)-based rhodium complex reported in this paper, could be due to the rigid pyrrolidine moiety in the backbone which restricts the conformational flexibility of the chelate. The improved reactivity of rhodium complexes by increasing the flexibility of the metal chelate is also known for the hydrogenation of imines [20].

3. Conclusions

Two new cationic rhodium complexes with a nitrogen-substituted bis(phosphinite) or bis(phosphine) ligand, respectively, have been synthesized. The bis(phosphinite)-based ligand is bonded to the metal exlucively in a *P*,*P*-bidentate coordination mode, whereas for the bis(phoshine)-based ligand, a *P*,*N*,*P*-tridentate mode is also possible together with the most favorable *P*,*P*-bidentate mode. The complexes were examined as catalysts for the hydroformylation of styrene, providing a very good activity and selectivity.

4. Experimental

4.1. General

N-Phenyldiethanolamine (**1**) was commercially available. $(COD)_2RhBF_4$ was prepared from rhodium trichloride hydrate according to a literature procedure [31–33]. *n*-BuLi was prepared from lithium metal and *n*-BuCl in methylcyclohexane. All preparations and hydroformylations were carried out under argon by using dry and degassed solvents. THF and diethylether were distilled from 9-fluorenylpotassium and Na/benzophenone, respectively. Styrene was distilled from CaH_2 and kept under argon. Hydroformylation studies were performed in a stainless steel autoclave (300 ml) with magnetic stirring. The syngas CO/H_2 (1:1) (CO, 1.8; H_2, 3.0) was purchased from Messer Griesheim GmbH. 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, the ^{31}P-NMR

shifts were referenced to external 85% H_3PO_4 in D_2O. 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.

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

To a solution of **1** (5.2 g, 28.69 mmol) in THF (50 ml) under argon, *n*-butyllithium (1.79 M in methylcyclohexane, 33 ml, 59.07 mmol) was added at −78°C. The reaction mixture was stirred at room temperature for 20 min and subsequently a solution of chlorodiphenylphosphine (10.7 ml, 59.60 mmol) in THF (30 ml) was added dropwise, and the mixture then stirred overnight. The volatile materials were removed by evaporation, the residue was suspended in toluene (100 ml) and filtered to remove the inorganic salts. The solution was then passed through a short column of basic alumina to remove the phosphorus impurities. Evaporation of the solvent under reduced pressure afforded **2** as a viscous oil (14.05 g, 89%), which turned to a white solid upon standing, m.p. 63–66°C. ^{1}H-NMR ($CHCl_3$-*d*, δ ppm): 7.51–7.35 (m, 20H, Ar); 7.23–7.18 (m, 2H, Ar); 6.71 (obscured with the doublet at 6.70 ppm, 1H, Ar); 6.70 (d, $^3J = 7.8$ Hz, 2H, Ar); 3.97 (dt, $^3J_{PH} = 9.0$ Hz, $^3J_{HH} = 6.5$ Hz, 4H, CH_2O); 3.63 (t, $^3J = 6.5$ Hz, 4H, CH_2N). ^{13}C{^{1}H}-NMR ($CHCl_3$-*d*, δ ppm): 147.31–112.00 (Ar); 66.48 (d, $^2J_{PC} = 16.9$ Hz, CH_2O); 52.03 (d, $^3J_{PC} = 7.7$ Hz, CH_2N). ^{31}P{^{1}H}-NMR ($CHCl_3$-*d*, δ ppm): 114.63 (s). ESI MS: *m*/*z* 550 ($[M + H]^+$). Anal. Found: C, 74.35; H, 6.06; N, 2.34. Calc. for $C_{34}H_{33}NO_2P_2$ (549.59): C, 74.31; H, 6.05; N, 2.55%.

4.3. *N,N-bis[2-(p-Tolylsulfonoxy)ethyl]-benzenamine (**4**) [10]*

To a solution of **1** (9.7 g, 53.5 mmol) in pyridine (80 ml), *p*-toluenesulfonyl chloride (20.4 g, 107.0 mmol) was added slowly at 0°C, and the reaction mixture was then stirred at this temperature for 3 h. 1 M HCl (300 ml) was added, and the solution was extracted with CH_2Cl_2 (5 × 100 ml). The combined organic layers were washed with 200 ml of saturated brine, dried over Na_2SO_4, filtered and evaporated to dryness, yielding 24.8 g of the crude product as a brown very viscous oil, which turned to a yellow solid by addition of 20 ml of cold methanol. The resulting solid was washed once more with 20 ml of cold methanol, yielding **4** (13.75 g, 53%) as a white solid, m.p. 89–91°C. The ^{1}H-NMR spectrum has previously been reported [10]. ^{13}C{^{1}H}-NMR ($CHCl_3$-*d*, δ ppm): 145.61, 144.92, 132.48, 129.81, 129.36, 127.72, 117.51 and 111.96 (Ar); 66.53 and 50.07 (OCH_2CH_2N). ESI MS: *m*/*z* 490 ($[M + H]^+$), 318 ($[M - OTs]^+$). Anal. Found: C, 58.46; H, 5.67; N, 2.75. Calc. for $C_{24}H_{27}NO_6S_2$ (489.60): C, 58.88; H, 5.56; N, 2.86%.

4.4. *N,N-bis[2-(Diphenylphosphino)ethyl]-benzenamine (**5**) [10,30]*

A solution of lithium diphenylphosphide, freshly prepared from lithium (0.9 g, 128.6 mmol) and chlodiphenylphosphine (1.85 ml, 10.3 mmol) in THF (100 ml), was added to a solution of **4** (2.45 g, 5.0 mmol) in THF (40 ml) at room temperature and stirred for 1 h. Then methanol (4 ml) was added and the solution was evaporated under vacuum. The residue was suspended in toluene (100 ml) and filtered. The solution was passed through a short column of Celite and alumina and the solvent was evaporated under reduced pressure, yielding 2.12 g of the crude product as a white viscous oil, which was solidified by ether at −20°C. The resulting solid was washed once more with cold ether, yielding **5** (1.91 g, 74%) as a white solid, m.p. 102–104°C, which was identified by ^{1}H-, ^{13}C-, ^{31}P-NMR and MS spectra [10].

4.5. *[Rh(COD)-**2**]BF_4 (**3**)*

A solution of the bis(phosphinite) **2** (0.2830 g, 0.52 mmol) in CH_2Cl_2 (10 ml) was added dropwise to the dark red solution of $(COD)_2Rh^+BF_4^-$ (0.2093 g, 0.52 mmol) in CH_2Cl_2 (10 ml) at −78°C. The reaction mixture was warmed slowly to room temperature within 1 h, and stirred at this temperature for an additional 2 h. The resulting orange solution was evaporated under reduced pressure to 2 ml, and addition of ether (20 ml) caused the precipitation of a dark orange solid. The supernatant solution was decanted, the solid was washed with ether (10 ml) and dried by vacuum, yielding rhodium complex **3** (0.4145 g, 94%). ^{1}H-NMR (CH_2Cl_2-d_2, δ ppm): 7.73–7.33 (m, 20H, Ar); 7.09–7.04 (m, 2H, Ar); 6.63 (t, $^3J = 7.1$ Hz, 1H, Ar); 6.26 (d, $^3J = 8.3$ Hz, 2H, Ar); 4.49 (sl br s, 4H, COD–CH); 4.04–3.98 (m, 4H, CH_2O); 3.18 (t, $^3J = 4.1$ Hz, 4H, CH_2N); 2.25 (sl br s, 8H, COD–CH_2). ^{13}C{^{1}H}-NMR (CH_2Cl_2-d_2, δ ppm): 146.74–111.74 (Ar); 102.77–102.56 (m, COD–CH); 66.64–66.51 (m, CH_2O); 53.96 (s, CH_2N); 30.43 (s, COD–CH_2). ^{31}P{^{1}H}-NMR (CH_2Cl_2-d_2, δ ppm): 120.00 (d, $J_{RhP} = 181.8$ Hz). ESI MS: *m*/*z* 760 ($[M - BF_4]^+$). Anal. Found: C, 58.98; H, 5.39; N, 1.55. Calc. for $C_{42}H_{45}BF_4NO_2P_2Rh$ (847.48): C, 59.52; H, 5.35; N, 1.65%.

4.6. *[Rh(COD)-**5**]BF_4 (**6**)*

According to the procedure described for the synthesis of **3**, rhodium complex **6** was prepared from the bis(phosphine) **5** (0.2476 g, 0.48 mmol) and $(COD)_2Rh^+BF_4^-$ (0.1944 g, 0.48 mmol), as an orange

solid (0.3646 g, 93%). ^{1}H-NMR (CH_2Cl_2-d_2, δ ppm): 7.50–7.34 (m, 20H, Ar); 7.28 (t, $^3J = 7.7$ Hz, 2H, Ar); 6.91 (t, $^3J = 7.0$ Hz, 1H, Ar); 6.70 (m, 2H, Ar); 4.53 (sl br s, 4H, COD–CH); 3.68 (sl br m, 4H, CH_2); 2.60 (sl br s, 4H, CH_2); 2.35 (sl br s, 4H, COD–CH_2); 2.19–2.12 (m, 4H, COD–CH_2). ^{13}C{^{1}H}-NMR (CH_2Cl_2-d_2, δ ppm): 149.03–115.94 (Ar); 99.14–98.59 (m, COD–CH); 50.75–50.68 (m, CH_2); 30.93 (s, COD–CH_2); 28.53–28.46 (m, CH_2). ^{31}P{^{1}H}-NMR (CH_2Cl_2-d_2, δ ppm): 17.33 (d, $J_{RhP} = 142.6$ Hz). ESI MS: m/z 728 ([M − BF_4]$^+$), 620 ([M − COD − BF_4]$^+$). Anal. Found: C, 62.58; H, 6.05; N, 1.44. Calc. for $C_{42}H_{45}BF_4NP_2Rh$ (815.48): C, 61.86; H, 5.56; N, 1.72%.

4.7. Hydroformylation

In a typical experiment, styrene (2 ml, 17.456 mmol) and a 4 mM solution of rhodium complex 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 required 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.

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References

[1] Review of transition metal chemistry of hemilabile ligands: C.S. Slone, D.A. Weinberger, C.A. Mirkin, Prog. Inorg. Chem. 48 (1999) 233.
[2] C. Basoli, C. Botteghi, M.A. Cabras, G. Chelucci, M. Marchetti, J. Organomet. Chem. 488 (1995) C20.
[3] C. Abu-Gnim, I. Amer, J. Organomet. Chem. 516 (1996) 235.
[4] Q. Jiang, D. Van Plew, S. Murtuza, X. Zhang, Tetrahedron Lett. 37 (1996) 797.
[5] R. Sablong, C. Newton, P. Dierkes, J.A. Osborn, Tetrahedron Lett. 37 (1996) 4933.
[6] R. Sablong, J.A. Osborn, Tetrahedron Lett. 37 (1996) 4937.
[7] N. Rahmouni, J.A. Osborn, A. De Cian, J. Fischer, A. Ezzamarty, Organometallics 17 (1998) 2470.
[8] C. Hahn, A. Vitagliano, F. Giordano, R. Taube, Organometallics 17 (1998) 2060.
[9] C. Hahn, J. Sieler, R. Taube, Polyhedron 17 (1998) 1183.
[10] K.K.M. Hii, M. Thornton-Pett, A. Jutand, R.P. Tooze, Organometallics 18 (1999) 1887.
[11] J.L. Bookham, D.M. Smithies, M.T. Pett, J. Chem. Soc. Dalton Trans. (2000) 975.
[12] I. Le Gall, P. Laurent, E. Soulier, J.-Y. Salaün, H. des Abbayes, J. Organomet. Chem. 567 (1998) 13.
[13] J.-X. Gao, X.-D. Yi, P.-P. Xu, C.-L. Tang, H.-L. Wan, T. Ikariya, J. Organomet. Chem. 592 (1999) 290.
[14] K. Yamamoto, S. Momose, M. Funahashi, S. Ebata, H. Ohmura, H. Komatsu, M. Miyazawa, Chem. Lett. (1994) 189.
[15] N. Derrien, C.B. Dousson, S.M. Roberts, U. Berens, M.J. Burk, M. Ohff, Tetrahedron: Asymmetry 10 (1999) 3341.
[16] W. Hu, M. Yan, C.-P. Lau, S.M. Yang, A.S.C. Chan, Y. Jiang, A. Mi, Tetrahedron Lett. 40 (1999) 973.
[17] K. Yonehara, T. Hashizume, K. Mori, K. Ohe, S. Uemura, J. Org. Chem. 64 (1999) 5593.
[18] S. Shin, T.V. RajanBabu, Org. Lett. 1 (1999) 1229.
[19] A. Fuerte, M. Iglesias, F. Sánchez, J. Organomet. Chem. 588 (1999) 186.
[20] V.I. Tararov, R. Kadyrov, T.H. Riermeier, J. Holz, A. Börner, Tetrahedron: Asymmetry 10 (1999) 4009.
[21] V.I. Tararov, R. Kadyrov, T.H. Riermeier, J. Holz, A. Börner, Tetrahedron Lett. 41 (2000) 2351.
[22] Survey of hydroformylation for 1997: F. Ungváry, Coord. Chem. Rev. 170 (1998) 245.
[23] Survey of hydroformylation for 1998: F. Ungváry, Coord. Chem. Rev. 188 (1999) 263.
[24] P.A.T. Hoye, R.D.W. Kemmitt, D.L. Law, Appl. Organomet. Chem. 7 (1993) 513.
[25] M.T. Reetz, S.R. Waldvogel, Angew. Chem. Int. Ed. Engl. 36 (1997) 865.
[26] M.T. Reetz, S.R. Waldvogel, R. Goddard, Tetrahedron Lett. 38 (1997) 5967.
[27] M.T. Reetz, S.R. Waldvogel, R. Goddard, Heterocycles 52 (2000) 935.
[28] I.D. Kostas, C.G. Screttas, J. Organomet. Chem. 585 (1999) 1.
[29] I.D. Kostas, J. Chem. Res. (S) (1999) 630.
[30] D. Michos, X.-L. Luo, R.H. Grabtree, J. Chem. Soc. Dalton Trans. (1992) 1735.
[31] G. Giordano, R.H. Crabtree, Inorg. Synth. 28 (1990) 88.
[32] M.A. Bennett, J.D. Saxby, Inorg. Chem. 7 (1968) 321.
[33] M. Green, T.A. Kuc, S.H. Taylor, J. Chem. Soc. (A) (1971) 2334.