Journal of Organometallic Chemistry 696 (2011) 3050–3057

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

# Synthesis, complexation behavior and application of a new diphosphite ligand in rhodium-catalyzed hydroformylation

Igor S. Mikhel [a], Natalia V. Dubrovina [a], Ivan A. Shuklov [a], Wolfgang Baumann [a], Detlef Selent [a,**], Haijun Jiao [a], Andrea Christiansen [b], Robert Franke [b], Armin Börner [a,c,*]

[a] Leibniz-Institut für Katalyse an der Universität Rostock e.V., Albert-Einstein-St. 29a, 18059 Rostock, Germany
[b] Evonik Oxeno GmbH, Paul-Baumann-Str. 1, 45 772 Marl, Germany
[c] Institut für Chemie der Universität Rostock, Albert-Einstein-St. 3a, 18059 Rostock, Germany

ARTICLE INFO

*Article history:*
Received 16 March 2011
Received in revised form
29 April 2011
Accepted 5 May 2011

*Keywords:*
Homogeneous catalysis
Diphosphite
Rhodium
Palladium
Platinum
Hydroformylation

ABSTRACT

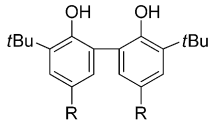
Oxidative coupling of 3-(3-tert-butyl-4-hydroxyphenyl)propionic acid methyl ester (**2**) gave dimethyl 3,3′-(5,5′-di-tert-butyl-6,6′-dihydroxybiphenyl-3,3′-diyl)-dipropionate (**1c**), which upon phosphorylation/transesterification with a phosphochloridite derived from (*R*)-binaphthol, formed the new unsymmetrical binaphthol-bridged diphosphite **4**. A rhodium catalyst based on **4** as ligand gave predominantly iso-selectivity in the hydroformylation of selected styrenes but opposite regioselectivity with 2,6-disubstituted derivatives. New chelate metal complexes (acac)RhL, $PdCl_2L$ and $PtCl_2L$ have been synthesized by reacting **4** with $(acac)Rh(CO)_2$, $PdCl_2(MeCN)_2$ and $PtCl_2(COD)$, respectively. The structure of obtained compounds is determined based on $^{1}H$, $^{13}C$, $^{31}P$ and $^{195}Pt$ NMR spectroscopy and mass spectrometry data.



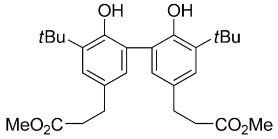
## 1. Introduction

Hydroformylation of olefins is a fundamental transformation in organic synthesis and one of the most powerful tools for the formation of carbon–carbon bonds [1]. Large amounts of commodity oxo products are produced per year by the use of homogeneous rhodium catalysts. Some of these catalysts show high chemo- and regioselectivity towards the formation of commercially preferred linear aldehydes and are very active under less severe conditions, compared to cobalt catalysis.

Particularly useful for fine tuning of Rh-catalysts are trivalent P-ligands, such as phosphites. A frequently used motif for the construction of industrially relevant diphosphites is the biphenol subunit [2,3]. The required biphenols e.g. **1a**,**b** serving as starting material are commercially available. They can be purchased in large quantities, because they are primarily employed for the ton-scale production of phosphate based flame retardants [4]. Unfortunately, the other substituents on the phenols are not suitable for further chemical transformations desired in catalysis, such as anchoring of the ligand to a solid surface or incorporation of more polar groups.




**1a** R = *t*Bu
**1b** R = OMe,



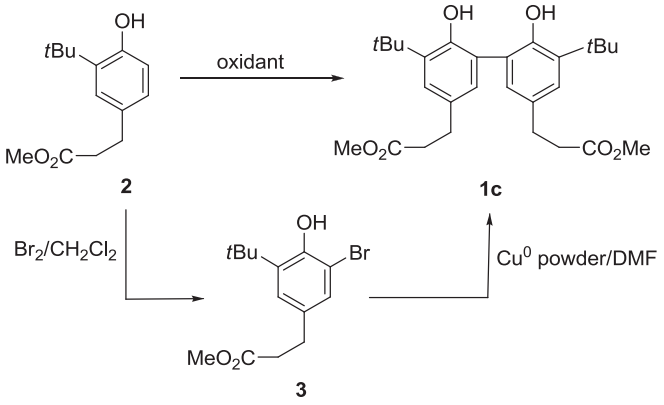

**1c**

As a part of our ongoing search for industrially relevant catalytic systems [2f,i,5], we looked for a biphenol which is more susceptible for chemical alteration. Compound **1c**, bearing two methyl propionate groups in *para*-position to the hydroxyl group revealed therefore an interesting candidate. This biphenol should be available by aryl–aryl coupling of the relevant mono-phenol. The latter is commercially available in a large scale [6].

Herein we will report our results on the synthesis of **1c**. Subsequently trials on the transformation of this diol in a chiral diphosphite ligand will be reported. Finally some complexation studies and results in the hydroformylation of styrenes as model substrates will be likewise detailed.

* Corresponding author. Leibniz-Institut für Katalyse an der Universität Rostock e.V., Albert-Einstein-St. 29a, 18059 Rostock, Germany. Tel.: +49 381 1281 202; fax: +49 381 1281 51202.
** Corresponding author.
*E-mail addresses:* detlef.selent@catalysis.de (D. Selent), armin.boerner@catalysis.de (A. Börner).

0022-328X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2011.05.004




**Scheme 1.** Methods for aryl–aryl couplings.

## 2. Results and discussion

### 2.1. Phenol coupling

For the coupling of phenols several methods have been suggested in the literature. Thus, Waldvogel and co-workers used the anodic oxidation [7] for the selective synthesis of 2,2′-biphenols under solvent-free conditions and in fluorinated alcohols [8]. Also enzyme catalyzed oxidations of related phenols by air gave desired coupling products [9]. 2,2′-Biphenols could be synthesized as well as by Ullmann-type coupling of corresponding arylbromides catalyzed by Cu or Ni [10].

We investigated two routes (Scheme 1) for the synthesis of biphenol **1c** from 3-(3-*tert*-butyl-4-hydroxyphenyl)propionic acid methyl ester (**2**) as a starting material, an Ullmann-type coupling and the direct oxidative C–C bond coupling.

As starting material for the Cu-catalyzed coupling bromo compound, **3** was synthesized via *ortho*-bromination of **2** in 87% yield. Unfortunately, the subsequent Ullmann-coupling of **3** afforded the desired product **1c** in only 11% yield. Mainly, dehalogenation of **3** was observed as a side reaction.

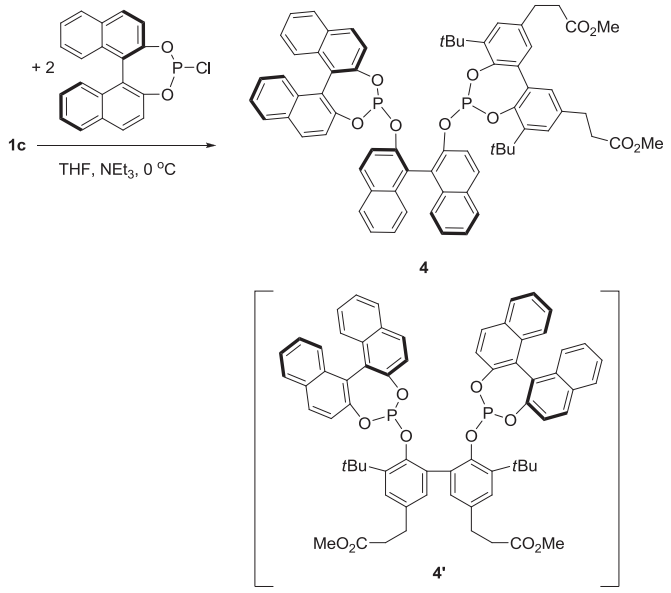
Alternatively the direct oxidative *ortho*-phenol coupling was investigated in detail. In the literature several heterogeneous oxidants such as (*tert*-BuO)$_2$ [11], $FeCl_3/H_2O/O_2$ [12], $H_2O_2$/Cu-complexes [13], Fe-salts [14], $FeSO_4/Na_2S_2O_8$ [15] or $K_2S_2O_8$ [16] are recommended. As oxidants for the homogeneous phenol coupling Fe- or Cu-salts/$O_2$, *m*-chloroperbenzoic acid/$FeCl_3$ [17], $K_3[Fe(CN)_6]$ [18] and the strong oxidant $K_2Cr_2O_7/H_2SO_4$ [19] are reported.

Some typical results of the homogeneously oxidative *ortho*-phenol coupling are listed in Table 1. $K_3[Fe(CN)_6]$, $H_2O_2$, $FeSO_4/H_2O_2$, $CuCl_2/O_2$, $FeSO_4/Na_2S_2O_8$ or $K_2S_2O_8$ did not work. Also the use of sodium phenolates did not enhance the poor yields by application of $H_2O_2$ and $K_3[Fe(CN)_6]$.

Highest yield was achieved by employment of a modified procedure of Wang and co-workers [17] using benzoyl peroxide as oxidants (Run 2) or *m*-chloroperbenzoic acid (=MCPBA)/$FeCl_3$ (Run 3), which hitherto was used only for the *para*-coupling of phenols. MCPBA alone did not work. Compound **1c** was obtained in the best case with 32% isolated yield. The product was purified by column chromatography, followed by bulb-to-bulb distillation.

**Table 1**
Oxidative *ortho*-phenol coupling of **2**.

| Run | Reagent | Method | GC yield (%) | Isolated yield (%) |
|---|---|---|---|---|
| 1 | $K_2Cr_2O_7/H_2SO_4$ | A | 30 | 22 |
| 2 | Benzoyl peroxide | B | 34 | 28 |
| 3 | MCPBA/$FeCl_3$ | C | 36 | 32 |




**Scheme 2.** Synthesis of the diphosphite.

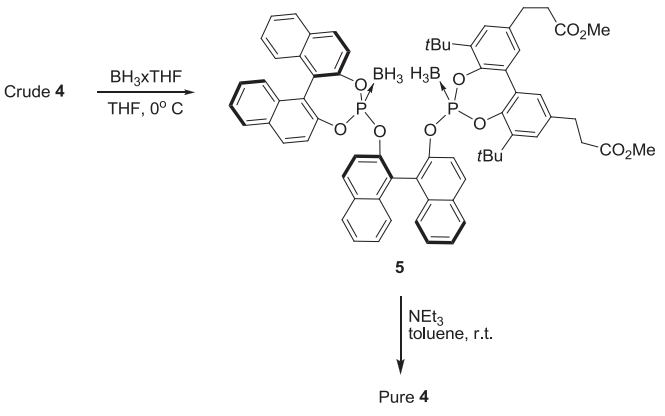
Unfortunately, prolongation of the reaction time or an increase of the temperature did not enhance the yield, but led to over-oxidation.

### 2.2. Synthesis of the diphosphite

Phosphorylation of diol **1c** was accomplished with the phosphochloridite of (*R*)-binaphthol in THF in the presence of triethylamine (Scheme 2). Surprisingly, not the intended symmetrical diphosphite **4′** was obtained, but the unsymmetrical structure **4**.

The structure of **4** was evidenced by NMR spectroscopy. Thus, the $^{31}P$ NMR of the reaction solution in THF was dominated by two doublets centered at $\delta_P$ 145.1 and 137.4 with a $J_{PP}$ coupling of ~3.7 Hz covering about 75% of the overall integral intensity together with a singlet at $\delta_P$ 137.1 (15%) and some other resonances in the range of $\delta_P$ 14–0 corresponding to products of degradation. At first it was attempted to obtain pure ligand by column chromatography of the corresponding borane adduct [**4**$(BH_3)_2$] (**5**), which was expected to be more stable towards air in comparison with **4**, and should be deprotected easily by treatment with amine (Scheme 3).

This concept worked, however, **5** was found to be in equilibrium in $CD_2Cl_2$ solution with a small amount of **4** and additionally, two




**Scheme 3.** Purification of the diphosphite.

monoborane adducts which sum up to a 20% fraction. Monoborane adducts have also been detected by mass spectrometry (see experimental part for all details). This mobile solution equilibrium complicated flash-chromatography and reduced the overall yield down to 28%.

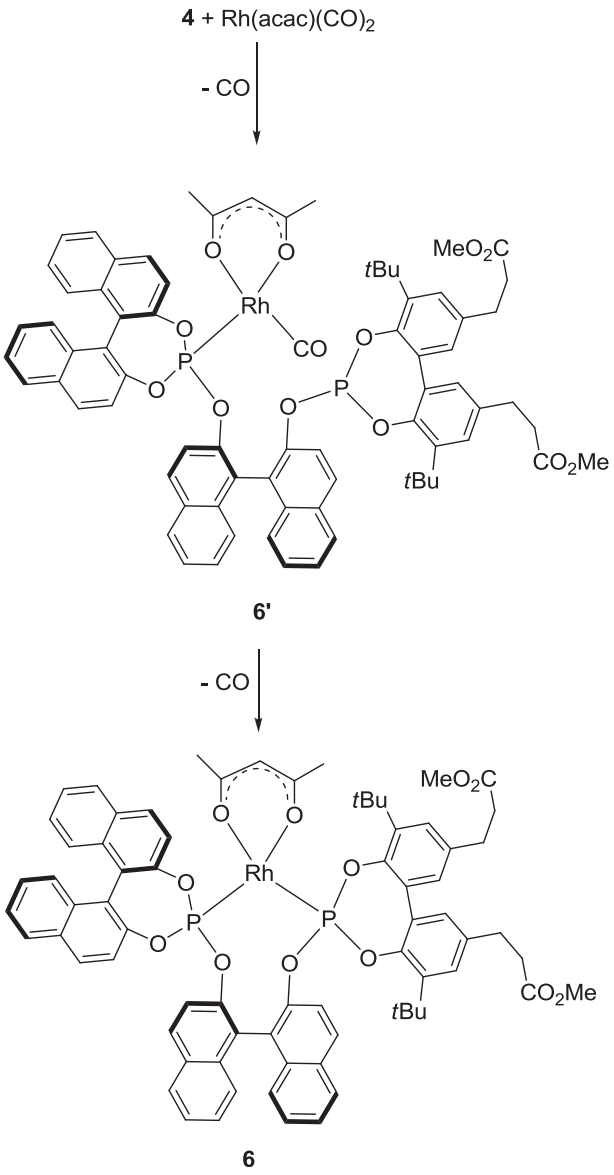
Finally, crude **4** was directly purified chromatographically with 71% yield. The $^{31}P$ spectrum of the pure compound in $CD_2Cl_2$ exhibits two doublets with parameters $\delta_P$ 144.7 and 137.2 and $J_{PP}$ = 3.7 Hz $^{31}P$-$^{31}P$ COSY NMR spectroscopy proved the intramolecular "through space" coupling constant [20] between the different phosphorus atoms. The low field chemical shift could be easily assigned to the binaphthol phosphorus center [5g]. Thus it can be unambiguously concluded that diol **1c** reacts under our conditions with binaphtholchlorophosphite under ring interconversion to give the unsymmetrical diphosphite **4**. Such processes are rarely described in ligand synthesis, only Beller and co-workers reported recently on a related transformation [21].

It is interesting to note, that there is only one set of resonances in the $^{31}P$ NMR spectrum of **4**, consistent with either formation of a single diastereoisomer or two diastereoisomers undergoing rapid interconversion. To clarify this question we measured $^{31}P$ and $^{1}H$ NMR spectra of **4** in $d_8$-toluene in the range of −86 to +100 °C. Upon cooling to −67 °C, the $^{31}P$ NMR spectrum of **4** measured in toluene-$D_8$ showed four singlets of almost equal intensity resonating at $\delta_P$ 147.6, 146.0, 137.7 and 137.4 which is in accordance with a 1:1 mixture of (*R*,*R*,*R*) and (*R*,*R*,*S*) rotamers of **4**, differing in the configuration of the biphenol moiety. It should be also pointed out that the $J_{PP}$ coupling is much smaller in $d_8$-toluene compared to $CD_2Cl_2$ even at room temperature, but could be registered by $^{31}P$–$^{31}P$ COSY NMR. At low temperature, P–P coupling is not longer observed.

### 2.3. Complexation studies

As a first precursor to study the coordination behavior of **4** (acac)Rh(CO)$_2$ was selected. $^{31}P$ NMR spectroscopy proved that the reaction in $d_8$-toluene (or in $CD_2Cl_2$) at room temperature spontaneously affords the complex **6′** with mono-coordinated ligand **4** as the main product, characterized by two broad resonances at $\delta_P$ 145.8 (d, $^{1}J_{PRh}$ = 289.7 Hz) and 139.1 (s, br) (Scheme 4). The broad singlet observed clearly corresponds to the uncoordinated biphenol phosphorus atom because the chemical shift of the non-coordinating phosphorus has changed only slightly compared to the free ligand. Furthermore, 17% of overall signal intensity can be assigned to the dinuclear complex (acac)(CO)RhP∩PRh(acac)(CO) which shows absorptions at $\delta_P$ 145.6 (d, $^{1}J_{PRh}$ = 293.3 Hz) and 132.8 (d, $^{1}J_{PRh}$ = 295.3 Hz), revealing the interesting bridging ability of the diphosphite.

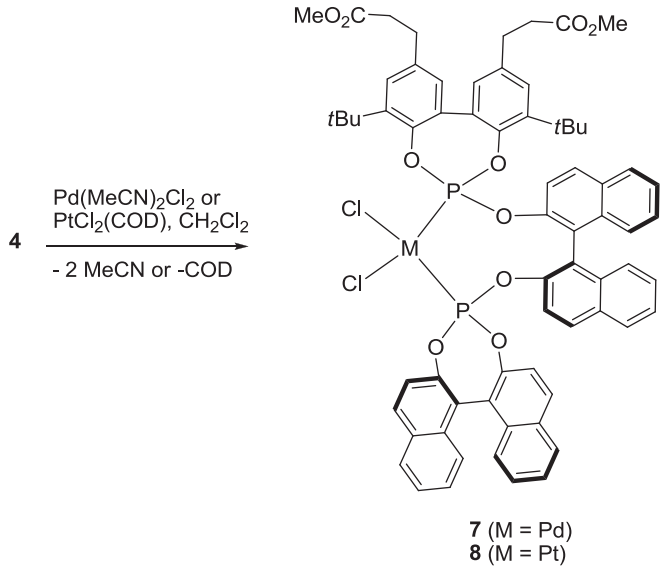
After a few minutes the final complex **6** evolves in the reaction solution. Storage of the reaction mixture at r.t. for several days, or for 10 h in toluene at 80 °C, led to the substitution of the second CO. Finally, we have found an alternative method. The slow addition of ligand **4** under strongly diluted conditions in $CH_2Cl_2$ to the rhodium dicarbonyl complex followed by the evaporation of the solution to dryness under reduced pressure allowed the desired complex **6** to be prepared directly in nearly quantitative yield and high purity. The $^{31}P$ NMR spectrum of **6** after redissolution in $CD_2Cl_2$ shows two doublets of doublets placed at $\delta_P$ 139.3 ($^{1}J_{PRh}$ = 307.3 Hz) and 129.6 ($^{1}J_{PRh}$ = 304.8 Hz) with a large $^{2}J_{PP}$ coupling of 113.2 Hz. The measured $^{1}J_{PRh}$ as well as $^{2}J_{PP}$ coupling constants are characteristic of coordinated diphosphites with a *cis*-configuration for the phosphorus atoms [22]. The proposed solution structure of complex **6** is also consistent with the results of $^{13}C$ and $^{1}H$ NMR studies. Noteworthy is the pronounced asymmetric arrangement of the acac ligand, which is manifested in the fact that each carbon atom exhibits its own signal (see Experimental Part). This seems to be due to the influence of the bulky ligand with two unequivalent phosphorus atoms, which causes a distortion of the geometry of the metal complex.




**Scheme 4.** Synthesis of Rh-complexes.

A *cis*-complexation of ligand **4** was achieved also with other $d^8$ metal fragments. In contrast to the carbonyl rhodium complex, Pd(MeCN)$_2$Cl$_2$ and Pt(COD)Cl$_2$ reacted smoothly already at room temperature with full substitution of acetonitrile or cyclooctadiene, respectively, and the formation of Pd(**4**)Cl$_2$ (**7**) and Pt(**4**)Cl$_2$ (**8**) (Scheme 5).

For **7**, the $^{31}P$ NMR spectrum in $CD_2Cl_2$ solutions contains two doublets at $\delta_P$ 115.2 ($^{2}J_{PP}$ = 65.9 Hz) and 81.8 ($^{2}J_{PP}$ = 66.5 Hz) and two doublets of pseudotriplets for **8** at $\delta_P$ 88.8 ($^{1}J_{PPt}$ = 5989.1 Hz, $^{2}J_{PP}$ = 16.2 Hz) and 57.6 ($^{1}J_{PPt}$ = 5973.6 Hz, $^{2}J_{PP}$ = 19.3 Hz). Interestingly, the resonances which correspond to the binaphthol phosphorus center are reasonably broadened in both complexes. This is probably due to the steric repulsion between two parts of the bulky ligand, which prevents them from stable occupying two adjacent coordination sites. The magnitude of the $^{1}J_{PPt}$ is typical of a phosphite phosphorus atom bonded to the $PtCl_2$ fragment with




**Scheme 5.** Synthesis of metal complexes.

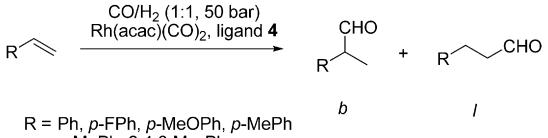
*cis*-configuration of the Cl atoms [23]. This fact is supported by the $^{195}$Pt NMR spectroscopy of **8** in $CD_2Cl_2$; the spectrum displayed a broad triplet with $\delta_{Pt}$ −4215 ($^1J_{PtP}$ = ca. 5980 Hz). The $^{13}$C and $^1$H NMR spectroscopic data are also in good agreement with structures of complexes **7** and **8** (see Experimental Part).

FAB mass spectrometric examination of compounds **6**, **7** and **8** revealed the mononuclear nature of the complexes with the detection of molecular ions (*m*/*z* (I, %)): 1302(38) $[M + H]^+$ and 1203(54) $[M - acac + H]^+$; 1242(85) $[M - Cl + H]^+$ and 1206(21) $[M - 2Cl + H]^+$; 1294(14) $[M - 2Cl + H]^+$, respectively. Intense peaks for the $[M - Cl]^+$ and $[M - 2Cl + H]^+$ ions are typical of many chloride complexes of palladium and platinum [24]. HR ESI mass spectrometry additionally confirmed the elemental composition of all complexes. Unfortunately, numerous attempts to grow single crystals of the new complexes suitable for an X-ray diffraction study failed.

### 2.4. Hydroformylation studies

In order to assess the catalytic properties of ligand **4** it was used in the Rh-catalyzed hydroformylation of styrenes. Results are listed in Table 2. As known from the literature selectivity and yield in the hydroformylation of styrenes can be dominated by the electronic and steric effects of the substrate [25]. In the hydroformylation with the catalyst based on ligand **4** the formation of the branched aldehyde is predominantly observed (Runs 1–5). Obviously the steric bulk of the ligand is not sufficient to compensate the substrate-directed formation of the branched (*iso*)aldehyde. Only two *ortho*-substituents in the substrate force the formation of linear aldehydes and decrease the reaction rates (Runs 14,15). Substituents with different electronic properties on the aromatic ring affect the regioselectivity slightly (Runs 6–11). The reaction temperature influences the regioselectivity as well. Linear products are favorably formed at higher temperatures. For example the amount of the branched aldehyde drops from 2.5:1 at 60 °C to 1.6 at 80 °C with *p*-methylstyrene (Runs 10,11). The same behavior can be observed with 2,4,6-trimethylstyrene as substrate. Here the ratio of *b*:*l* increases from 1.1:1 at 60 °C to 1:1.7 at 80 °C (Runs 14,15). The load of ligand has an impact on the observed regioselectivity (compare runs 2, 4, 5). Increased amount of ligand improved the formation of the linear product. Noteworthy, although an enantiopure ligand was used, no stereoselection was observed.

**Table 2**
Rhodium-catalyzed hydroformylation of styrenes.[a]




| Run | Substrate | *T* (°C) | Conversion (%)[b] | Selectivity for the formation of aldehyde (%) | *b*:*l*[b] |
|---|---|---|---|---|---|
| 1[c] | Styrene | 60 | 90 | 99 | 4:1 |
| 2 | Styrene | 80 | 98 | 99 | 2:1 |
| 3 | Styrene | 100 | 100 | 99 | 1.2:1 |
| 4[d] | Styrene | 80 | 99 | 99 | 2.2:1 |
| 5[e] | Styrene | 80 | 99 | 99 | 1.2:1 |
| 6[c] | *p*-Fluorostyrene | 60 | 99 | 99 | 2.9:1 |
| 7 | *p*-Fluorostyrene | 80 | 98 | 99 | 1.6:1 |
| 8[c] | *p*-Methoxystyrene | 60 | 96 | 99 | 2.3:1 |
| 9 | *p*-Methoxystyrene | 80 | 100 | 99 | 1.6:1 |
| 10[c] | *p*-Methylstyrene | 60 | 98 | 99 | 2.5:1 |
| 11 | *p*-Methylstyrene | 80 | 97 | 99 | 1.6:1 |
| 12[c] | *o*-Methylstyrene | 60 | 90 | 99 | 2.5:1 |
| 13 | *o*-Methylstyrene | 80 | 95 | 98 | 1.3:1 |
| 14 | 2,4,6-Trimethylstyrene | 80 | 3 | 99 | 1.1:1 |
| 15 | 2,4,6-Trimethylstyrene. | 100 | 10 | 99 | 1:1.7 |

[a] Reaction conditions: substrate/Rh(acac)(CO)$_2$/ligand 2800:1:2.2; 50 bar CO/H$_2$ (ratio 1:1), in 5 mL of toluene, 3 h.
[b] Determined by GC, HP 5 (Agilent).
[c] 18 h.
[d] L/Rh = 1.
[e] L/Rh = 6.

## 3. Conclusion

In summary, a new P,P-bidentate diphosphite ligand has been synthesized within two steps starting from a commercially available and functionalized phenol based on an intramolecular transesterification. This approach gives a new access to the straightforward synthesis of unsymmetrical diphosphites bearing different phosphorus atoms.

Some metal complexes were synthesized and characterized as well. In a study of the Rh-catalyzed hydroformylation of styrenes steric effects of the aromatic olefins dominate the regioselectivity as well as the rate of the conversion, more than the properties of the ligand [2e,25b]. Further investigations concerned to the synthesis of related P,P′-bidentate diphosphites and their use in hydroformylation are currently in progress.

## 4. Experimental part

### 4.1. General

Unless otherwise stated, all reactions were carried out under a dry argon atmosphere using standard Schlenk-line techniques. All reagents, unless otherwise mentioned, were purchased from commercial sources and used without additional purification. Solvents were dried and freshly distilled under argon before use. Thin-layer chromatography was performed on pre-coated TLC plates (silica gel 60 F254, Merck). Flash-chromatography was carried out with silica gel 60 (230–400 mesh ASTM). $PCl_3$ and $NEt_3$ were distilled immediately before use. $Pd(MeCN)_2Cl_2$ and $Pt(COD)Cl_2$ were purchased from Aldrich and $Rh(acac)(CO)_2$ was obtained from Umicore. All other reagents were used as received from Aldrich and Acros. NMR $^1$H (250.1, 300.1 and 400.1 MHz), $^{31}$P (101.3 and 162.0 MHz), $^{13}$C (62.9 and 75.5 MHz) and $^{195}$Pt (64.2 MHz)

spectra were recorded on a Bruker Avance 250, Bruker Avance 300 and Bruker Avance 400, respectively. Chemical shifts $\delta$ are quoted in parts per million (ppm) downfield of tetramethylsilane. $^{31}P$ NMR chemical shifts were referenced externally to 85% $H_3PO_4$ ($\delta$ 0.0). Coupling constants *J* are given in Hz. CI and FAB mass spectra were measured on a Finnigan MAT 95-XP mass spectrometer (Thermo Electron Corporation). HRMS was performed on MAT 95-XP (EI) and Agilent 6210 Time-of-Flight LC/MS (ESI). GC–MS was performed on Agilent 5973 chromatograph mass selective detector. GC was performed on Agilent 6890 chromatograph with a 30 m HP5 column.

### 4.2. Phenol coupling

#### 4.2.1. Synthesis of 3-(3-bromo-5-tert-butyl-4-hydroxyphenyl) propionic acid methyl ester (**3**) [26]

A solution of bromine (1.6 g, 0.512 mL, 0.01 mol) in $CH_2Cl_2$ (2 mL) was added dropwise to a solution of phenol 3-(3-*tert*-butyl-4-hydroxyphenyl)propionic acid methyl ester (**2**) (2.2 g, 0.01 mol) in $CH_2Cl_2$ (10 mL) over 10 min at 0 °C, then poured into water (50 mL). The organic layer was diluted with $CH_2Cl_2$ (50 mL), separated and washed with water (6 × 50 mL), dried with $MgSO_4$. The solvent was removed in vacuo to give crude **3**. The product was purified by flash column chromatography (silica gel, *n*-hexane/AcOEt 5:1, $R_f$ = 0.55). Yield 2.740 g (87%). HRMS (EI): Calcd for $C_{10}H_{12}{}^{81}BrO_3$ 316.0491, found 316.0490 $[M]^+$; Calcd for $C_{10}H_{12}{}^{79}BrO_3$ 314.0512, found 314.0509 $[M]^+$. MS (CI, *m*/*z* (I, %)): 316(44) $[M]^+$, 314(44) $[M]^+$, 302(96), 299(98), 243(22), 242(30), 227(100), 225(97). $^1H$ NMR (300.1 MHz, $CDCl_3$): 1.38 (s, 9H, *t*-Bu), 2.58 (t, *J* = 7.8, 2H, $CH_2$), 2.85 (t, *J* = 7.7, 2H, $CH_2$), 3.68 (s, 3H, $OCH_3$), 5.69 (s, 1H, OH), 7.03 (d, *J* = 2.0, 2H, ArH), 7.17 (d, *J* = 2.0, 2H, ArH). $^{13}C$ NMR (75.5 MHz, $CDCl_3$): 29.3 ($C(CH_3)_3$), 30.2 ($CH_2$), 35.5 ($C(CH_3)_3$, 35.9 ($CH_2$), 51.7 ($OCH_3$), 112.0, 126.7, 128.9, 133.0, 137.5, 148.8 (C–O), 173.2 (C=O).

#### 4.2.2. Synthesis of (dimethyl 3,3′-(5,5′-di-tert-butyl-6,6′-dihydroxybiphenyl-3,3′-diyl)-dipropionate) (**1c**)

*4.2.2.1. Method A.* To the solution of **2** (9.450 g, 0.04 mol) in $CH_3COOH$ (34 mL) a solution of $K_2Cr_2O_7$ (4.000 g, 0.0136 mol) in $H_2O$ (24 mL) and $H_2SO_4$ (8 mL) was added dropwise during 40 min at 55 °C. The reactions mixture was stirred for 60 min at 55 °C and then overnight at room temperature (GC-control). The resulting mixture was poured into ice (100 mL) and extracted with $CHCl_3$ (3 × 100 mL). The combined organic layers were neutralized with aqueous $NaHCO_3$, and then dried with $Na_2SO_4$ and the solvents were removed in vacuo. The crude product was purified by chromatography (silica gel, *n*-hexane/AcOEt 5:1, $R_f$ = 0.4) and bulb-to-bulb distillation at 160 °C, 4–6 × $10^{-3}$ bar to give pure **1c**. Yield: 2.050 g (21.8%). HRMS (ESI): Calcd for $C_{28}H_{39}O_6$ 471.2741, found 471.2745 $[M + H]^+$. MS (CI, *m*/*z* (I, %)): 470(100) $[M]^+$, 399(35), 335(53), 293(30). $^1H$ NMR (300.1 MHz, $CDCl_3$): 1.42 (s, 18H, *t*-Bu), 2.63 (t, *J* = 7.9, 2H, $CH_2$), 2.90 (t, *J* = 7.9, 2H, $CH_2$), 3.67 (s, 3H, $OCH_3$), 5.24 (s, 2H, OH), 6.90 (d, *J* = 2.0, 2H, ArH), 7.16 (d, *J* = 2.0, 2H, ArH). $^{13}C$ NMR (62.9 MHz, $CDCl_3$): 29.6 ($C(CH_3)_3$), 30.5 ($CH_2$), 35.0 ($C(CH_3)_3$, 36.1 ($CH_2$), 51.7 ($OCH_3$), 122.6, 127.8, 128.0, 132.4, 137.4, 150.4 (C–O), 173.5 (C=O).

*4.2.2.2. Method B.* To a solution of **2** (0.221 g, 0.001 mol) in toluene (5 mL) was added benzoyl peroxide (0.242 g, 0.001 mol) at 0 °C. The reaction mixture was stirred for 18 h at room temperature (GC-control), and then poured into water (50 mL). The mixture was extracted with diethyl ether (3 × 30 mL). The combined organic layers were washed with aqueous $NaHCO_3$, dried with $Na_2SO_4$ and the solvents were removed in vacuo. The crude **1c** was purified as described above. Yield 0.066 g (28%).

*4.2.2.3. Method C.* To a solution of **2** (4.720 g, 0.02 mol) in $CH_2Cl_2$ (100 mL) was added anhydrous $FeCl_3$ (6.5 mg, 0.04 mmol) and MCPBA (*meta*-chloroperoxybenzoic acid) (3.440 g, 0.02 mol) at 0 °C. The reactions mixture was stirred for 1 h at room temperature (GC-control), and then poured into water (200 mL). The mixture was extracted with $CH_2Cl_2$ (3 × 75 mL). The combined organic layers were neutralized with aqueous $NaHCO_3$, dried with $Na_2SO_4$ and the solvents were removed in vacuo. The crude **1c** was purified by the same method. Yield 1.48 g (31.5%).

*4.2.2.4. Ullmann-coupling.* To a solution of **3** (0.5 g, 0.016 mol) in DMF (20 mL) was added $Cu^0$ powder (0.32 g, 0.05 mol). The mixture was vigorously stirred at 170 °C (GC-control), and then diluted with diethyl ether (30 mL) and filtered. The filter cake was washed with diethyl ether. The combined organic layers were washed with water (5 × 50 mL), and then dried with $Na_2SO_4$ and the solvents were removed in vacuo to give a mixture of product **1c** and **2**. The crude **1c** was purified as described above. Yield 0.041 g (11%).

### 4.3. Synthesis of dimethyl 3,3′-(4,8-di-tert-butyl-6-((1R)-2′-((11bR)-dinaphtho[2,1-d:1′,2′-f] [1,3,2]-dioxaphosphepin-4-yloxy)-1,1′-binaphthyl-2 yloxy)dibenzo[d,f] [1,3,2]dioxaphosphepine-2,10-diyl)dipropionate (**4**)

#### 4.3.1. Synthesis without intermediate P-protection

1-Methylpyrrolidin-2-one (0.01 g, 0.1 mmol) was added to a stirred mixture of (*R*)-binaphthol (1 g, 3.492 mmol) and $PCl_3$ (5 mL). The mixture was refluxed for 10 min until it became completely homogeneous. All volatiles were then removed under vacuum (0.1 Torr). Toluene (20 mL) was added and the solvent was evaporated on a vacuum line to remove traces of $PCl_3$. The obtained product was dried on vacuum (0.05 Torr) for 1 h.

To a stirred solution of the whole of the synthesized binaphtholchlorophosphite in THF (20 mL) was slowly added dropwise a solution of **1c** (0.756 g, 1.606 mmol) and $NEt_3$ (1 mL, 0.726 g, 7.17 mmol) in THF (25 mL) at 0 °C and the resulting mixture was stirred for 2 h. The reaction mixture was allowed to warm to r.t. and stored overnight. The reaction solution was filtered, the filter cake was washed with THF (2 × 15 mL) and the solution was evaporated. The product was dried in vacuum for 2 h (0.05 Torr). The crude ligand thus obtained was purified by flash-chromatography: $R_f$ = 0.3 ($CH_2Cl_2$). Yield: 1.250 g (71%).

White powder. HRMS (ESI): Calcd for $C_{68}H_{60}NaO_{10}P_2$ 1121.3554, found 1121.3551 $[M + Na]^+$; Calcd for $C_{68}H_{61}O_{10}P_2$ 1099.3734, found 1099.3730 $[M + H]^+$. $^{31}P$ NMR (101.3 MHz, $CD_2Cl_2$): 144.7 (d, $J_{PP}$ = 3.7 Hz), 137.2 (d, $J_{PP}$ = 3.7 Hz). $^{13}C$ NMR (62.9 MHz, $CD_2Cl_2$): 173.4 (s, $\underline{C}O_2Me$), 148.5 (d, $J_{CP}$ = 3.7, POC), 148.4 (d, $J_{CP}$ = 7.8, POC), 147.9 (d, $J_{CP}$ = 4.6, POC), 147.4 (d, $J_{CP}$ = 2.3, POC), 146.3 (d, $J_{CP}$ = 19.2, POC), 146.2 (d, $J_{CP}$ = 17.4, POC), 141.7 (d, $J_{CP}$ = 1.8, $C_{arom}$), 141.6 (d, $J_{CP}$ = 1.4, $C_{arom}$), 136.9 (s, $C_{arom}$), 136.8 (s, $C_{arom}$), 134.6 (s, $C_{arom}$), 134.3 (s, $C_{arom}$), 133.2 (s, $C_{arom}$), 133.15 (s, $C_{arom}$), 133.1 (d, $J_{CP}$ = 1.4, $C_{arom}$), 132.9 (d, $J_{CP}$ = 3.7, $C_{arom}$), 132.7 (d, $J_{CP}$ = 1.4, $C_{arom}$), 131.9 (s, $C_{arom}$), 131.5 (s, $C_{arom}$), 131.3 (s, $C_{arom}$), 131.2 (s, $C_{arom}$), 130.6 (s, $C_{arom}$), 130.3 (s, $C_{arom}$), 130.1 (s, $C_{arom}$), 129.9 (s, $C_{arom}$), 129.3 (d, $J_{CP}$ = 3.7, $C_{arom}$), 128.6 (d, $J_{CP}$ = 2.7, $C_{arom}$), 128.5 (s, $C_{arom}$), 128.3 (s, $C_{arom}$), 127.7 (d, $J_{CP}$ = 3.2, $C_{arom}$), 127.3 (s, $C_{arom}$), 127.1 (s, $C_{arom}$), 127.0 (s, $C_{arom}$), 126.6 (s, $C_{arom}$), 126.4 (s, $C_{arom}$), 126.3 (s, $C_{arom}$), 125.6 (s, $C_{arom}$), 125.4 (s, $C_{arom}$), 125.3 (s, $C_{arom}$), 125.1 (s, $C_{arom}$), 124.6 (d, $J_{CP}$ = 5.5, $C_{arom}$), 123.0 (s, $C_{arom}$), 122.9 (s, $C_{arom}$), 122.71 (d, $J_{CP}$ = 1.4, $C_{arom}$), 122.67 (s, $C_{arom}$), 122.0 (d, $J_{CP}$ = 1.4, $C_{arom}$), 121.97 (s, $C_{arom}$), 121.9 (s, $C_{arom}$), 121.8 (s, $C_{arom}$), 121.1 (s, $C_{arom}$), 120.9 (s, $C_{arom}$), 51.8 (s, $OCH_3$), 36.0 (s, $CH_2$), 35.98 (s, $CH_2$), 35.09 (s, $\underline{C}(CH_3)_3$), 35.07 (s, $\underline{C}(CH_3)_3$), 30.87 (s, $CH_2$), 30.82 (s, $C(\underline{C}H_3)_3$), 30.79 (s, $C(\underline{C}H_3)_3$). $^1H$ NMR (400.1 MHz, $CD_2Cl_2$): 8.11 (1H, d, $J_{HH}$ = 9.0, ArH), 8.04 (1H, d, $J_{HH}$ = 8.1, ArH), 7.95–7.88 (4H, m, ArH), 7.85 (1H, d, $J_{HH}$ = 8.0, ArH), 7.63 (1H, d, $J_{HH}$ = 9.0, ArH), 7.58

(1H, d, $J_{HH}$ = 8.8, ArH), 7.49–7.15 (14H, m, ArH), 7.06 (2H, d, $J_{HH}$ = 2.0, ArH), 6.87 (2H, d, $J_{HH}$ = 2.0, ArH), 6.07 (1H, d, $J_{HH}$ = 8.8, ArH), 3.65 (3H, s, $CH_3$), 3.64 (3H, s, $CH_3$), 2.91–2.86 (4H, m, $CH_2$), 2.62–2.55 (4H, m, $CH_2$), 1.00 (9H, s, *t*-Bu), 0.98 (9H, s, *t*-Bu).

*4.3.2. Purification via diborane adduct **5***

*4.3.2.1. Synthesis of diborane adduct [4-($BH_3$)$_2$] (**5**).* To a solution of the whole of synthesized diphosphite **4** in THF (30 mL) $BH_3$ × THF (9 mL, 1 M in THF) was added dropwise at 0 °C. The resulting solution was stirred at r.t. for 24 h. Then the reaction solution was evaporated up to ~1 mL and the product was precipitated with pentane. The obtained solid was washed twice with pentane (2 × 10 mL) and dried in vacuum. The product was purified by flash-chromatography. $R_f$ = 0.45 ($CH_2Cl_2$, silica gel). Yield: 0.645 g (36%).

White powder. HRMS (ESI): Calcd for $C_{68}H_{66}B_2NaO_{10}P_2$ 1149.4230, found 1149.4222 $[M + Na]^+$; Calcd for $C_{68}H_{64}BO_{10}P_2$ 1113.4073, found 1113.4072 $[M - BH_3 + H]^+$; $C_{68}H_{63}BNaO_{10}P_2$ 1135.3893, found 1135.3888 $[M - BH_3 + Na]^+$; Calcd for $C_{68}H_{60}NaO_{10}P_2$ 1121.3554, found 1121.3556 $[M + Na]^+$; Calcd for $C_{68}H_{61}O_{10}P_2$ 1099.3734, found 1099.3711 $[M + H]^+$. $^{31}$P NMR (101.3 MHz, $CD_2Cl_2$): 144.7 (d, $J_{PP}$ = 3.7 Hz, 0.5%), 144.5 (s, 4%), 137.6 (s, 6%), 137.2 (d, $J_{PP}$ = 3.7 Hz, 0.5%), 126.5 (br. s, 45%), 116.8 (br. s, 44%). $^{13}$C NMR (62.9 MHz, $CD_2Cl_2$): 173.4 (s, $\underline{C}O_2Me$), 173.3 (s, $\underline{C}O_2Me$), 146.9 (d, $J_{CP}$ = 6.4, POC), 146.8 (d, $J_{CP}$ = 8.2, P$\underline{O}$C), 146.7 (d, $J_{CP}$ = 10.5, POC), 146.5 (d, $J_{CP}$ = 1.8, POC), 145.05 (d, $J_{CP}$ = 14.2, POC), 145.0 (d, $J_{CP}$ = 11.0, POC), 141.2 (d, $J_{CP}$ = 3.7, $C_{arom}$), 141.0 (d, $J_{CP}$ = 3.7 $C_{arom}$), 138.1 (d, $J_{CP}$ = 0.9, $C_{arom}$), 137.8 (d, $J_{CP}$ = 0.9, $C_{arom}$), 134.0 (s, $C_{arom}$), 133.7 (s, $C_{arom}$), 132.7 (d, $J_{CP}$ = 1.4, $C_{arom}$), 132.3 (s, $C_{arom}$), 132.2 (d, $J_{CP}$ = 1.4, $C_{arom}$), 131.4 (s, $C_{arom}$), 131.2 (s, $C_{arom}$), 130.9 (d, $J_{CP}$ = 2.3, $C_{arom}$), 130.5 (s, $C_{arom}$), 130.4 (s, $C_{arom}$), 130.1 (s, $C_{arom}$), 129.8 (s, $C_{arom}$), 129.0 (s, $C_{arom}$), 128.8 (s, $C_{arom}$), 128.7 (s, $C_{arom}$), 128.4 (s, $C_{arom}$), 128.3 (s, $C_{arom}$), 128.2 (s, $C_{arom}$), 127.6 (s, $C_{arom}$), 127.3 (s, $C_{arom}$), 127.1 (s, $C_{arom}$), 127.05 (s, $C_{arom}$), 127.0 (s, $C_{arom}$), 126.8 (s, $C_{arom}$), 126.4 (s, $C_{arom}$), 126.2 (s, $C_{arom}$), 126.1 (s, $C_{arom}$), 125.8 (s, $C_{arom}$), 122.33 (s, $C_{arom}$), 122.3 (s, $C_{arom}$), 122.1 (s, $C_{arom}$), 121.8 (d, $J_{CP}$ = 2.7, $C_{arom}$), 121.3 (s, $C_{arom}$), 121.26 (s, $C_{arom}$), 120.5 (d, $J_{CP}$ = 1.4, $C_{arom}$), 120.2 (d, $J_{CP}$ = 2.3, $C_{arom}$), 120.1 (d, $J_{CP}$ = 2.3, $C_{arom}$), 51.9 (s, $OCH_3$), 51.87 (s, $OCH_3$), 36.0 (s, $CH_2$), 35.9 (s, $CH_2$), 35.2 (s, $\underline{C}(CH_3)_3$), 35.0 (s, $\underline{C}(CH_3)_3$), 31.0 (s, C($\underline{C}H_3)_3$), 30.9 (s, $CH_2$), 30.84 (s, C($\underline{C}H_3)_3$), 30.8 (s, $\underline{C}H_2$). $^1$H NMR (250.1 MHz, $CD_2Cl_2$): 8.12–7.65 (9H, m, ArH), 7.58–7.22 (11H, m, ArH), 7.14–7.00 (5H, m, ArH), 6.68 (1H, d, $J_{HH}$ = 2.1, ArH), 6.54 (1H, d, $J_{HH}$ = 2.1 ArH), 6.15 (1H, dd, $J_{HH}$ = 8.8, $J_{HH}$ 1.0, ArH), 3.69 (3H, s, $CH_3$), 3.67 (3H, s, $CH_3$), 2.97–2.85 (4H, m, $CH_2$), 2.69–2.58 (4H, m, $CH_2$), 1.05 (9H, s, *t*-Bu), 0.89 (9H, s, *t*-Bu), 1.20–0.00 (6H, v. br., $BH_3$).

*4.3.2.2. Deprotection of diborane adduct **5**.* To a solution of **5** (0.483 g, 0.428 mmol) in toluene (15 mL) $NEt_3$ (0.26 g, 0.36 mL, 2.57 mmol) was added and the resulting mixture was stirred for 72 h. Then the reaction mixture was evaporated and the obtained solid was dried in vacuum. The product **4** was then purified by flash-chromatography ($CH_2Cl_2$, silica gel). Yield: 0.370 g (79%).

*4.4. Synthesis of metal complexes*

*4.4.1. Synthesis of Rh(acac)(**4**) complex (**6**)*

To a stirred solution of Rh(acac)$(CO)_2$ (25.8 mg, 0.1 mmol) in $CH_2Cl_2$ (10 mL) a solution of the ligand (0.1099 g, 0.1 mmol) in $CH_2Cl_2$ (10 mL) was added dropwise in 10 min and the reaction mixture was stirred for 2 h. Then the solvent was evaporated on a vacuum pump and the obtained solid was dried in vacuum. Yield was nearly quantitative.

Yellow–brown powder. HRMS (ESI): Calcd for $C_{73}H_{67}NaO_{12}P_2Rh$ 1323.3055, found 1323.3072 $[M + Na]^+$; Calcd for $C_{73}H_{68}O_{12}P_2Rh$ 1301.3236, found 1301.3237 $[M + H]^+$. MS (FAB, *m*/*z* (I, %)): 1302(38) $[M + H]^+$, 1203(54) $[M - acac + H]^+$. $^{31}$P NMR (101.3 MHz, $CD_2Cl_2$): 139.3 (dd, $^1J_{PRh}$ = 307.3 Hz, $^2J_{PP}$ = 113.2 Hz), 129.6 (dd, $^1J_{PRh}$ = 304.8 Hz, $^2J_{PP}$ = 113.2 Hz). $^{13}$C NMR (62.9 MHz, $CD_2Cl_2$): 185.5 (s, $CO_{acac}$), 185.0 (s, $CO_{acac}$), 173.4 (s, $\underline{C}O_2Me$), 173.3 (s, $\underline{C}O_2Me$), 148.5 (d, $J_{CP}$ = 14.2, POC), 147.8 (d, $J_{CP}$ = 2.7, POC), 147.7 (d, $J_{CP}$ = 8.7, POC), 147.4 (s, POC), 147.0 (d, $J_{CP}$ = 4.1, POC), 146.7 (d, $J_{CP}$ = 14.6, POC), 141.0 (d, $J_{CP}$ = 3.2, $C_{arom}$), 140.8 (d, $J_{CP}$ = 4.6, $C_{arom}$), 136.9 (d, $J_{CP}$ = 0.9, $C_{arom}$), 136.7 (s, $C_{arom}$), 134.2 (s, $C_{arom}$), 133.4 (s, $C_{arom}$), 133.12 (d, $J_{CP}$ = 1.8, $C_{arom}$), 133.1 (d, $J_{CP}$ = 1.4, $C_{arom}$),132.2 (s, $C_{arom}$), 132.14 (s, $C_{arom}$), 132.1 (s, $C_{arom}$), 131.7 (d, $J_{CP}$ = 1.8, $C_{arom}$), 131.5 (s, $C_{arom}$), 131.0 (s, $C_{arom}$), 130.9 (s, $C_{arom}$), 130.7 (s, $C_{arom}$), 130.4 (s, $C_{arom}$), 129.8 (s, $C_{arom}$), 129.3 (s, $C_{arom}$), 128.7 (s, $C_{arom}$), 128.5 (d, $J_{CP}$ = 3.2, $C_{arom}$), 128.3 (s, $C_{arom}$), 128.2 (s, $C_{arom}$), 127.2 (s, $C_{arom}$), 127.2 (s, $C_{arom}$), 126.9 (s, $C_{arom}$), 126.6 (s, $C_{arom}$), 126.4 (s, $C_{arom}$), 126.36 (s, $C_{arom}$), 126.3 (s, $C_{arom}$), 125.5 (s, $C_{arom}$), 125.4 (s, $C_{arom}$), 125.39 (d, $J_{CP}$ = 1.4, $C_{arom}$), 124.3 (d, $J_{CP}$ = 1.8, $C_{arom}$), 124.1 (d, $J_{CP}$ = 2.7, $C_{arom}$), 123.1 (d, $J_{CP}$ = 2.3, $C_{arom}$), 122.9 (d, $J_{CP}$ = 2.7, $C_{arom}$), 123.0 (d, $J_{CP}$ = 6.0, $C_{arom}$), 122.6 (d, $J_{CP}$ = 6.0, $C_{arom}$), 120.9 (s, $C_{arom}$), 120.2 (s, $C_{arom}$), 120.1 (s, $C_{arom}$), 119.9 (s, $C_{arom}$), 99.9 (s, $CH_{acac}$), 51.9 (s, $OCH_3$), 51.7 (s, $OCH_3$), 36.5 (s, $\underline{C}(CH_3)_3$), 36.0 (s, $CH_2$), 35.96 (s, $CH_2$), 34.9 (s, $\underline{C}(CH_3)_3$), 32.8 (s, $\underline{C}(CH_3)_3$), 31.0 (s, C($\underline{C}H_3)_3$), 30.8 (s, $CH_2$), 30.7 (s, $CH_2$), 26.8 (d, $J_{CP}$ = 9.2, $CH_{3acac}$), 25.7 (d, $J_{CP}$ = 9.2, $CH_{3acac}$). $^1$H NMR (250.1 MHz, $CD_2Cl_2$): 8.50 (1H, d, $J_{HH}$ 9.0, ArH), 8.25 (1H, d, $J_{HH}$ = 9.0, ArH), 8.08–7.80 (9H, m, ArH), 7.63 (1H, d, $J_{HH}$ = 8.6, ArH), 7.53–7.14 (12H, m, ArH), 7.06 (1H, d, $J_{HH}$ = 2.2, ArH), 7.02 (1H, d, $J_{HH}$ = 2.2, ArH), 6.93 (1H, d, $J_{HH}$ = 8.5, ArH), 6.90 (1H, d, $J_{HH}$ = 2.2, ArH), 5.05 (1H, s, CH(acac)), 3.71 (3H, s, $CH_3$), 3.53 (3H, s, $CH_3$), 3.02 (2H, t, $J_{HH}$ = 7.6, $CH_2$), 2.84 (2H, t, $J_{HH}$ = 7.6, $CH_2$), 2.71 (2H, t, $J_{HH}$ = 7.6, $CH_2$), 2.55 (1H, t, $J_{HH}$ = 7.9, $CH_2$), 2.53 (1H, t, $J_{HH}$ = 7.9, $CH_2$), 1.92 (9H, s, *t*-Bu), 1.36 (3H, s, $CH_3$(acac)), 0.68 (3H, s, $CH_3$(acac)), 0.67 (9H, s, *t*-Bu).

*4.4.2. Synthesis of Pd(**4**)$Cl_2$ complex (**7**)*

To a stirred solution of Pd$(MeCN)_2Cl_2$ (25.9 mg, 0.1 mmol) in $CH_2Cl_2$ (1 mL) a solution of the ligand **4** (109.9 mg, 0.1 mmol) in $CH_2Cl_2$ (2 mL) was added dropwise and the reaction mixture was stirred for 2 h. Then the solvent was evaporated and the obtained solid was dried in vacuum. Yield was nearly quantitative.

Yellow powder. HRMS (ESI): Calcd for $C_{68}H_{61}Cl_2O_{10}P_2Pd$ 1275.2163, found 1275.2443 $[M + H]^+$. MS (FAB, *m*/*z* (I, %)): 1242(85) $[M - Cl + H]^+$, 1206(21) $[M - 2Cl + H]^+$. $^{31}$P NMR (101.3 MHz, $CD_2Cl_2$): 115.2 (br. d, $^2J_{PP}$ = 65.9 Hz) and 81.8 (d, $^2J_{PP}$ = 66.5 Hz). $^{13}$C NMR (62.9 MHz, $CD_2Cl_2$): 173.1 (s, $\underline{C}O_2Me$), 147.5 (d, $J_{CP}$ = 13.7, POC), 147.3 (d, $J_{CP}$ = 3.7, POC), 147.2 (d, $J_{CP}$ = 11.9, POC), 146.9 (d, $J_{CP}$ = 3.7, POC), 146.89 (d, $J_{CP}$ = 16.5, POC), 146.2 (d, $J_{CP}$ = 6.4, POC), 145.9 (br. s, $C_{arom}$), 140.8 (d, $J_{CP}$ = 4.1, $C_{arom}$), 140.7 (d, $J_{CP}$ = 4.1, $C_{arom}$), 139.6 (d, $J_{CP}$ = 1.4, $C_{arom}$), 138.6 (d, $J_{CP}$ = 0.9, $C_{arom}$), 134.5 (s, $C_{arom}$), 133.8 (s, $C_{arom}$), 133.0 (s, $C_{arom}$), 132.9 (s, $C_{arom}$), 132.64 (s, $C_{arom}$), 132.6 (s, $C_{arom}$), 132.58 (s, $C_{arom}$), 132.2 (d, $J_{CP}$ = 0.9, $C_{arom}$), 132.1 (d, $J_{CP}$ = 3.2, $C_{arom}$), 131.8 (s, $C_{arom}$), 131.5 (s, $C_{arom}$), 131.3 (s, $C_{arom}$), 131.1 (s, $C_{arom}$), 131.0 (s, $C_{arom}$), 130.4 (s, $C_{arom}$), 130.1 (s, $C_{arom}$), 129.5 (s, $C_{arom}$), 129.2 (s, $C_{arom}$), 129.1 (s, $C_{arom}$), 128.7 (s, $C_{arom}$), 128.2 (s, $C_{arom}$), 127.9 (s, $C_{arom}$), 127.8 (s, $C_{arom}$), 127.5 (s, $C_{arom}$), 127.4 (s, $C_{arom}$), 127.2 (s, $C_{arom}$), 127.1 (s, $C_{arom}$), 126.8 (s, $C_{arom}$), 126.6 (s, $C_{arom}$), 126.4 (s, $C_{arom}$), 126.2 (s, $C_{arom}$), 123.1 (d, $J_{CP}$ = 1.8, $C_{arom}$), 122.9 (d, $J_{CP}$ = 2.7, $C_{arom}$), 121.7 (d, $J_{CP}$ = 7.8, $C_{arom}$), 121.5 (d, $J_{CP}$ = 2.3, $C_{arom}$), 121.1 (d, $J_{CP}$ = 6.0, $C_{arom}$), 120.1 (s, $C_{arom}$), 120.0 (s, $C_{arom}$), 119.0 (s, $C_{arom}$), 51.9 (s, $OCH_3$), 51.8 (s, $OCH_3$), 36.1 (s, $\underline{C}(CH_3)_3$), 36.0 (s, $CH_2$), 35.7 (s, $CH_2$), 35.4 (s, $\underline{C}(CH_3)_3$), 31.4 (s, C($\underline{C}H_3)_3$), 30.9 (s, $CH_2$), 30.6 (s, $CH_2$). $^1$H NMR (250.1 MHz, $CD_2Cl_2$): 8.44 (1H, d, $J_{HH}$ = 9.5, ArH), 8.40 (1H, d, $J_{HH}$ = 9.4, ArH), 8.27 (1H, d, $J_{HH}$ = 9.1, ArH), 8.20 (1H, d, $J_{HH}$ = 9.2, ArH), 8.07 (2H, t, $J_{HH}$ = 8.0, ArH), 7.98 (1H, d, $J_{HH}$ = 9.0, ArH), 7.89–7.84 (2H, m, ArH), 7.78 (1H, d, $J_{HH}$ = 8.2, ArH), 7.71 (1H, d, $J_{HH}$ = 9.2, ArH), 7.64 (1H, d, $J_{HH}$ = 1.7, ArH), 7.60–7.23 (8H, m, ArH), 7.17–7.02 (5H, m, ArH), 6.93 (1H, d, $J_{HH}$ = 2.2, ArH), 6.86 (1H, d, $J_{HH}$ = 8.7, ArH), 6.37 (1H, d, $J_{H,H}$ = 9.0, ArH), 3.73 (3H, s, $CH_3$), 3.60 (3H, s, $CH_3$), 3.13 (2H, t, $J_{HH}$ = 7.6, $CH_2$), 2.89 (2H, t, $J_{HH}$ = 7.7, $CH_2$), 2.79 (2H, t, $J_{HH}$ = 7.6, $CH_2$), 2.59 (2H, t, $J_{HH}$ = 7.9, $CH_2$), 1.90 (9H, s, *t*-Bu), 0.58 (9H, s, *t*-Bu).

#### 4.4.3. Synthesis of Pt(**4**)$Cl_2$ complex (**8**)

To a stirred suspension of Pt(COD)$Cl_2$ (37.4 mg, 0.1 mmol) in $CH_2Cl_2$ (1 mL) a solution of ligand **4** (109.9 mg, 0.1 mmol) in $CH_2Cl_2$ (2 mL) was added dropwise and the reaction mixture was stirred for 2 h. The reaction solution was reduced up to ~1 mL and the complex was precipitated by pentane. The obtained solid was washed carefully three times with a small amount of ether and pentane and dried in air and then in vacuum. Yield: 0.128 g (94%).

White powder. HRMS (ESI): Calcd for $C_{68}H_{60}Cl_2NaO_{10}P_2Pt$ 1386.2584, found 1386.2584 $[M + Na]^+$. MS (FAB, *m/z* (I, %)): 1294(14) $[M - 2Cl + H]^+$. $^{31}P$ NMR (101.3 MHz, $CD_2Cl_2$): 88.8 (br. d, $^1J_{PPt}$ = 5989.1 Hz, $^2J_{PP}$ = 16.2 Hz) and 57.6 (d, $^1J_{PPt}$ = 5973.6 Hz, $^2J_{PP}$ = 19.3 Hz). $^{195}Pt$ NMR (64.2 MHz, $CD_2Cl_2$): −4215 (br. t, $^1J_{PtP}$ = ca. 5971 Hz). $^{13}C$ NMR (62.9 MHz, $CD_2Cl_2$): 173.2 (s, $\underline{C}O_2Me$), 147.4 (d, $J_{CP}$ = 13.3, POC), 147.2 (d, $J_{CP}$ = 2.3, POC), 146.9 (d, $J_{CP}$ = 11.4, POC), 146.8 (d, $J_{CP}$ = 2.3, POC), 146.4 (d, $J_{CP}$ = 14.2, POC), 146.3 (br. s, $C_{arom}$), 146.0 (d, $J_{CP}$ = 6.7, POC), 140.9 (d, $J_{CP}$ = 3.2, $C_{arom}$), 140.8 (d, $J_{CP}$ = 2.8, $C_{arom}$), 139.5 (d, $J_{CP}$ = 1.4, $C_{arom}$), 138.4 (d, $J_{CP}$ = 1.4, $C_{arom}$), 134.5 (s, $C_{arom}$), 133.8 (s, $C_{arom}$), 132.8 (s, $C_{arom}$), 132.6 (d, $J_{CP}$ = 1.4, $C_{arom}$), 132.1 (d, $J_{CP}$ = 0.9, $C_{arom}$), 132.0 (d, $J_{CP}$ = 2.7, $C_{arom}$), 131.6 (s, $C_{arom}$), 131.5 (s, $C_{arom}$), 131.3 (s, $C_{arom}$), 131.1 (s, $C_{arom}$), 131.0 (s, $C_{arom}$), 130.4 (s, $C_{arom}$), 130.0 (d, $J_{CP}$ = 0.9, $C_{arom}$), 129.4 (s, $C_{arom}$), 129.14 (s, $C_{arom}$), 129.1 (s, $C_{arom}$), 129.0 (s, $C_{arom}$), 128.7 (s, $C_{arom}$), 128.2 (s, $C_{arom}$), 127.8 (s, $C_{arom}$), 127.6 (s, $C_{arom}$), 127.5 (s, $C_{arom}$), 127.3 (s, $C_{arom}$), 127.2 (s, $C_{arom}$), 127.15 (s, $C_{arom}$), 127.1 (s, $C_{arom}$), 126.7 (s, $C_{arom}$), 126.6 (s, $C_{arom}$), 126.3 (s, $C_{arom}$), 126.1 (s, $C_{arom}$), 123.3 (d, $J_{CP}$ = 2.3, $C_{arom}$), 122.8 (d, $J_{CP}$ = 2.7, $C_{arom}$), 121.7 (d, $J_{CP}$ = 2.3, $C_{arom}$), 121.5 (d, $J_{CP}$ = 7.3, $C_{arom}$), 121.0 (d, $J_{CP}$ = 5.5, $C_{arom}$), 120.3 (s, $C_{arom}$), 120.2 (s, $C_{arom}$), 120.1 (s, $C_{arom}$), 119.1 (s, $C_{arom}$), 51.9 (s, $OCH_3$), 51.7 (s, $OCH_3$), 36.1 (s, $\underline{C}(CH_3)_3$), 36.0 (s, $CH_2$), 35.7 (s, $CH_2$), 35.4 (s, $\underline{C}(CH_3)_3$), 31.5 (s, $C(\underline{C}H_3)_3$), 31.4 (s, $C(\underline{C}H_3)_3$), 30.9 (s, $CH_2$), 30.6 (s, $CH_2$). $^1H$ NMR (250.1 MHz, $CD_2Cl_2$): 8.45 (1H, d, $J_{HH}$ = 9.2, ArH), 8.38 (1H, d, $J_{HH}$ = 9.1, ArH), 8.26 (1H, d, $J_{HH}$ = 9.2, ArH), 8.21 (1H, d, $J_{HH}$ = 9.3, ArH), 8.10–7.96 (3H, m, ArH), 7.87 (2H, d, $J_{HH}$ = 8.5, ArH), 7.78 (1H, d, $J_{HH}$ = 8.2, ArH), 7.70 (1H, d, $J_{HH}$ = 9.2, ArH), 7.64 (1H, d, $J_{HH}$ = 1.6, ArH), 7.60–7.22 (8H, m, ArH), 7.16–7.01 (5H, m, ArH), 6.92 (1H, d, $J_{HH}$ = 2.2, ArH), 6.84 (1H, d, $J_{HH}$ = 8.7, ArH), 6.36 (1H, d, $J_{H,H}$ = 9.0, ArH), 3.73 (3H, s, $CH_3$), 3.59 (3H, s, $CH_3$), 3.13 (2H, t, $J_{HH}$ = 7.6, $CH_2$), 2.88 (2H, t, $J_{HH}$ = 7.6, $CH_2$), 2.78 (2H, t, $J_{HH}$ = 7.6, $CH_2$), 2.57 (2H, t, $J_{HH}$ = 7.9, $CH_2$), 1.91 (9H, s, *t*-Bu), 0.56 (9H, s, *t*-Bu).

### 4.5. General procedure for hydroformylation

A 25-mL Schlenk flask with a magnetic stirring bar was charged with ligand **4** (0.011 g, 0.01 mmol), Rh(acac)$(CO)_2$ (1 mg, 0.0038 mmol) and toluene (5 mL). The mixture was stirred for 60 min then the olefinic substrate (10.8 mmol) was added. The yellow reaction mixture was transferred in a 25 mL Parr autoclave under argon. The autoclave was purged with syngas three times and subsequently charged with syngas ($CO/H_2$ = 1:1, 50 atm). The autoclave was warmed up to 80 °C and the reaction was started by stirring. After 3 h, the autoclave was cooled and the gases were carefully released in a well-ventilated hood. The reaction mixture was analyzed by GC to determine conversion and regioselectivity.

## Acknowledgments

We would like to thank Dr. Christine Fisher for mass spectrometry measurements.

## References

[1] (a) P.W.N.M. van Leeuwen, G. van Koten, in: J.A. Moulijn, P.W.N.M. van Leeuwen, R.A. van Santen (Eds.), Catalysis: An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis, Elsevier, Amsterdam, 1993, pp. 201–222;
(b) M. Beller, B. Cornils, C.D. Frohning, C.W. Kohlpaintner, J. Mol. Cat. A Chem. 104 (1995) 17–85;
(c) C.D. Frohning, C.W. Kohlpaintner, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Two Volumes, vol. 1, VCH Verlagsgesellschaft, Weinheim, 1996, pp. 27–104;
(d) P.W.N.M. van Leeuwen, C. Claver (Eds.), Rhodium Catalyzed Hydroformylation, Kluwer, Dordrecht, 2000;
(e) G. Protzmann, K.-D. Wiese, Erdöl, Erdgas, Kohle 117 (2001) 235–240;
(f) K.-D. Wiese, D. Obst, Top. Organomet. Chem. 18 (2006) 1–33.
[2] (a) E. Billig, A.G. Abatjoglou, D.R. Bryant, (UCC), EP 213639 (1987), EP 214622(1987), US 4769498 (1988).
(b) S. Keiichi, Y. Kawaragi, M. Takai, T. Ookoshi (Mitsubishi Kasei), EP 518241 (1992). (c) G.D. Cuny, S.L. Buchwald, J. Am. Chem. Soc. 115 (1993) 2066–2068;
(d) B. Moasser, W.L. Gladfelter, D.C. Roe, Organometallics 14 (1995) 3832–3838;
(e) A. van Rooy, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Organomet. Chem. 535 (1997) 201–207;
(f) D. Röttger, A. Börner, D. Selent, D. Hess (Oxeno), DE 10031493 (2002).
(g) M.A. Brammer, W.-J. Peng, J.M. Maher (Dow Chemica), WO 2008124468 (2008).
(h) T.C. Eisenschmid, R.R. Peterson, G.A. Miller, A. G. Abatjoglou (UCC), WO 2008115740 (2008).
(i) Selent, A. Börner, B. Kreidler, D. Hess, K.-D. Wiese (Oxeno), WO 2008071508 (2008).
(j) W.-J. Peng, C.L. Rand (Dow Chemical), WO 2008134326 (2008).
[3] For related ligands, which have been used widely in asymmetric hydroformylation, see the following review A. Gual, C. Godard, S. Castillon, C. Claver, Tetrahedron: Asymmetry 21 (2010) 1135–1146 and ref. cited therein.
[4] K.H. Pawlowski, B. Schartel, Polym. Int. 56 (2007) 1404–1414.
[5] For some typical results, see: (a) D. Selent, D. Röttger, K.-D. Wiese, A. Börner, Angew. Chem. Int. Ed. 39 (2000) 1639–1641;
(b) D. Selent, D. Hess, K.-D. Wiese, D. Röttger, C. Kunze, A. Börner, Angew. Chem. Int. Ed. 40 (2001) 1696–1698;
(c) C. Kunze, D. Selent, R. Schmutzler, I. Neda, A. Spannenberg, A. Börner, Heteroatom Chem. 12 (2001) 577–585;
(d) C. Kunze, D. Selent, I. Neda, R. Schmutzler, W. Baumann, A. Börner, Z. Allgem. Anorg. Chem. 628 (2002) 779–787;
(e) D. Selent, W. Baumann, R. Kempe, A. Spannenberg, D. Röttger, K.D. Wiese, A. Börner, Organometallics 22 (2003) 4265–4271;
(f) D. Selent, K.D. Wiese, A. Börner, O-Acylphosphites: new and promising ligands for isomerising hydroformylation. in: J.R. SowaJr (Ed.), Cat. Org. React.. Taylor & Francis, Boca Raton, 2005, pp. 459–469;
(g) D. Selent, W. Baumann, K.-D. Wiese, A. Börner, Chem. Commun. (2008) 6203–6205;
(h) I.A. Shuklov, N.V. Dubrovina, H. Jiao, A. Spannenberg, A. Börner, Eur. J. Org. Chem. (2010) 1669–1680.
[6] Delivered by UFC Corporation, Taiwan.
[7] (a) I.M. Malkowsky, C.E. Rommel, K. Wedeking, R. Fröhlich, K. Bergander, M. Nieger, C. Quaiser, U. Griesbach, H. Pütter, S.R. Waldvogel, Eur. J. Org. Chem. (2006) 241–245;
(b) A. Kirste, M. Nieger, I.M. Malkowsky, F. Stecker, A. Fischer, S.R. Waldvogel, Chem. Eur. J. 15 (2009) 2273–2277.
[8] For a review, compare I.A. Shuklov, N.V. Dubrovina, A. Börner, Synthesis (2007) 2925–2943.
[9] (a) I. Malnar, C.J. Sih, Tetrahedron Lett. 41 (2000) 1907–1911;
(b) S. Ciecholewski, E. Hammer, K. Manda, G. Bose, V.T.H. Nguyen, P. Langer, F. Schauer, Tetrahedron 61 (2005) 4615–4619;
(c) A. Gesell, M. Rolf, J. Ziegler, M.L. Díaz Chávez, F.-C. Huang, T.M. Kutchan, J. Biol. Chem. 284 (2009) 24432–24442.
[10] (a) M.F. Semmelhack, P.M. Helquist, L.D. Jones, J. Am. Chem. Soc. 93 (1971) 5908–5910;
(b) M.F. Semmelhack, P. Helquist, L.D. Jones, L. Keller, L. Mendelson, L. Speltz Ryono, J. Gorzynski Smith, R.D. Stauffer, J. Am. Chem. Soc. 103 (1981) 6460–6471;
(c) M. Lourak, R. Vanderesse, Y. Fort, P. Caubére, J. Organomet. Chem. 54 (1989) 4840–4844;
(d) J. Ishida, M. Kozuka, H. Tokuda, H. Nishino, S. Nagumo, K.-H. Lee, M. Nagai, Bioorg. Med. Chem. 10 (2002) 3361–3365.
[11] D.R. Armstrong, C. Cameron, D.C. Nonhebel, P.G. Perkins, J. Chem. Soc. Perkin Trans. 2 (1983) 563–568.
[12] (a) K. Ding, Y. Wang, L. Zhang, Y. Wu, Tetrahedron 52 (1996) 1005–1010;
(b) P.J. Wallis, K.J. Booth, A.F. Patti, J.L. Scott, Green Chem. 8 (2006) 333–337.
[13] A.M. Guidote, K.-I. Ando, K. Terada, Y. Kurusu, H. Nagao, Y. Masuyama, Inorg. Chim. Acta 324 (2001) 203–211.
[14] M. Ogata, K. Shin-Ya, S. Urano, T. Endo, Chem. Pharm. Bull. 53 (2005) 344–346.
[15] A. Alexakis, D. Polet, S. Rosset, S. March, J. Org. Chem. 69 (2004) 5660–5667.
[16] G. Delogu, M.A. Dettori, A. Patti, S. Pedotti, A. Forni, G. Casalone, Tetrahedron: Asymmetry 14 (2003) 2467–2474.
[17] K. Wang, M. Lü, A. Yu, X. Zhu, Q. Wang, J. Org. Chem. 74 (2009) 935–938.
[18] (a) J.I. van der Vlugt, A.C. Hewat, S. Neto, R. Sablong, A.M. Mills, M. Lutz, A.L. Spek, C. Müller, D. Vogt, Adv. Synth. Catal. 346 (2004) 993–1003;
(b) L. Panella, J. Bross, J. Jin, M.W. Fraaije, D.B. Janssen, M. Jeronimus-Stratingh, B.L. Feringa, A.J. Minnaard, J.G. De Vries, Chem. Commun. (2005) 5656–5658;
(c) R. Jana, J.A. Tunge, Org. Lett. 11 (2009) 971–974.

[19] H.A. Albert, J. Am. Chem. Soc. 76 (1954) 4983–4985.
[20] (a) S.D. Pastor, S.P. Shum, A.D. DeBellis, L.P. Burke, R.K. Rodebaugh, F.H. Clarke, G. Riehs, Inorg. Chem. 35 (1996) 949–958;
(b) G.J.H. Buisman, L.A. van der Veen, A. Klootwihk, W.G.J. de Lange, P.C.J. Kamer, P.W.N.M. van Leeuwen, D. Vogt, Organometallics 16 (1997) 2929–2939;
(c) J.-C. Hierso, A. Fihri, V.V. Ivanov, B. Hanquet, N. Pirio, B. Donnadieu, B. Rebière, R. Amardeil, P. Meunier, J. Am. Chem. Soc. 126 (2004) 11077–11087;
(d) J.-C. Hierso, D. Armspach, D. Matt, Compt. Rendus Chimie 12 (2009) 1002–1013.
[21] I. Piras, R. Jennerjahn, R. Jackstell, W. Baumann, A. Spannenberg, R. Franke, K.-D. Wiese, M. Beller, J. Organomet. Chem. 695 (2010) 479–486.
[22] (a) A. van Rooy, P.C.J. Kamer, P.W.N.M. van Leeuwen, K. Goubitz, J. Fraanje, N. Veldman, A.L. Spek, Organometallics 15 (1996) 835–847;
(b) E.K. van den Beuken, W.G.J. de Lange, P.W.N.M. van Leeuwen, N. Veldman, A.L. Spek, B.L. Feringa, J. Chem. Soc. Dalton Trans. (1996) 3561–3569;
(c) C.J. Cobley, R.D.J. Froese, J. Klosin, C. Qin, G.T. Whiteker, Organometallics 26 (2007) 2986–2999;
(d) L. Pignataro, B. Lynikaite, R. Colombo, S. Carboni, M. Krupicka, U. Piarulli, C. Gennari, Chem. Commun. (2009) 3539–3541.
[23] (a) N. Ahmad, E.W. Ainscough, T.A. James, S.D. Robinson, J. Chem. Soc. Dalton Trans. (1973) 1148;
(b) C.J. Cobley, P.G. Pringle, Inorg. Chim. Acta 265 (1997) 107–115;
(c) R. Kadyrov, D. Heller, R. Selke, Tetrahedron: Asymmetry 9 (1998) 329–340;
(d) S. Cserepi-Szucs, G. Huttner, L. Zsolnai, J. Bakos, J. Organomet. Chem 586 (1999) 70–78;
(e) P. Maji, S.S. Krishnamurthy, M. Nethaji, Polyhedron 27 (2008) 3519–3527.
[24] (a) A. Albinati, F. Lianza, H. Berger, P.S. Pregosin, H. Rüegger, R.W. Kunz, Inorg. Chem. 32 (1993) 478–486;
(b) I.S. Mikhel, K.N. Gavrilov, A.I. Polosukhin, A.I. Rebrov, Russ. Chem. Bull. (Engl. Transl.) 47 (1998) 1585;
(c) I.S. Mikhel, K.N. Gavrilov, A.I. Rebrov, Russ. J. Inorg. Chem. (Engl. Transl.) 44 (1999) 1551;
(d) I.S. Mikhel, O.G. Bondarev, V.N. Tsarev, G.V. Grinselev-Knyazev, K.A. Lyssenko, V.A. Davankov, K.N. Gavrilov, Organometallics 22 (2003) 925–930.
[25] For some recent results, compare: (a) B. El Ali, J. Tijani, M. Fettouhi, A. Al-Arfaj, M. El-Faer, Appl. Organomet. Chem. 19 (2005) 329–338;
(b) S. Yu, Y. Chie, Z. Guan, Y. Zou, W. Li, X. Zhang, Org. Lett. 11 (2009) 241–244;
(c) A.G. Panda, M.D. Bhor, S.S. Ekbote, B.M. Bhanage, Cat. Lett. 131 (2009) 649–655.
[26] S. Akai, T. Ikawa, S. Takayanagi, Y. Morikawa, S. Mohri, M. Tsubakiyama, M. Egi, Y. Wada, Y. Kita, Angew. Chem. Int. Ed. 47 (2008) 7673–7676.