Xantphite: A New Family of Ligands for Catalysis. Applications in the Hydroformylation of Alkenes

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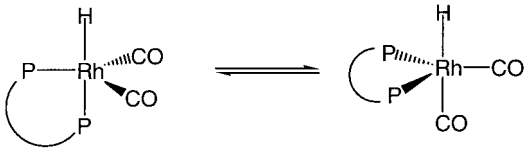
Dedicated to the memory of Professor *Luigi M. Venanzi*

The novel bulky diphosphite (P∩P) ligands (**3** and **4**) based on the 2,7,9,9-tetramethyl-9*H*-xanthene-4,5-diol (**2**) backbone were investigated in the Rh-catalyzed hydroformylation of oct-1-ene, styrene, and (*E*)-oct-2-ene. These diphosphites gave rise to very active and selective catalysts for the hydroformylation of oct-1-ene to nonanal with average rates > 10000 (mol aldehyde)(mol Rh)$^{-1}$h^{-1} ($P(CO/H_2) = 20$ bar, $T = 80°$, [Rh] = 1 mM) and maximum selectivities of 79% for the linear product. Relatively high selectivities towards the linear aldehyde (up to 70%, linear/branched up to 2.3) but very high activities (up to 39000 (mol aldehyde)(mol Rh)$^{-1}$h^{-1}) were observed for the hydroformylation of styrene in the presence of these bidentate ligands ($P(CO/H_2) = 2-10$ bar, $T = 120°$, [Rh] = 0.2 mM). Remarkable activities (up to 980 (mol aldehyde)(mol Rh)$^{-1}$h^{-1}) were achieved with these diphosphites for the hydroformylation of (*E*)-oct-2-ene with selectivities for the linear product of 74% (l/b up to 2.8, $P(CO/H_2) = 2$ bar, $T = 120°$, [Rh] = 1 mM). A detailed study of the solution structure of the catalyst under catalytic conditions was performed by NMR and high-pressure FT-IR. The spectroscopic data revealed that under hydroformylation conditions, the bidentate ligands rapidly formed stable, well-defined catalysts with the structure [RhH(CO)$_2$(P∩P)]. All the ligands showed a preference for an equatorial-apical (**ea**) coordination mode in the trigonal bipyramidal Rh-complexes, indicating that a bis-equatorial (**ee**) coordination is not a prerequisite for highly selective catalysts.

1. Introduction. – Rh-catalyzed hydroformylation of olefins in the presence of P-ligands is among the most important industrial applications of homogeneous catalysis [1–5]. Since the first publications concerning the beneficial effects of P-ligands in catalysis [6–9], the field of ligand design has attracted much attention both from academia and industry. As early as the seventies, research has focused on tuning electronic and steric properties of P-based ligands to control the regio- and chemoselectivities of the overall catalytic reaction. It became clear from these studies that the electronic and steric properties of the ligands have a large influence on the performance of the catalysts. To rationalize the effects of P-ligands in transition metal catalyzed reactions, *Tolman* [10] developed the concept of the cone angle θ and the electronic parameter χ to classify P-ligands with respect to their steric bulk and phosphine basicity. These parameters have been extensively used as a measure of ligand properties in hydroformylation studies [11][12]. Since the eighties, the use of bidentate phosphine and phosphite ligands has been extensively investigated by academia and industry. Recently, *Casey* and *Whiteker* [13] developed the concept of the natural bite angle (β_n) for diphosphine ligands to explain the correlation found between the regioselectivity and the coordination mode of bidentate ligands possessing large P–Rh–P angles. Although it was first believed that bis-equatorial coordination (see **ee**) of the diphosphine [14–17] was a key factor in controlling the regioselectivity of the

hydroformylation reaction, *Van Leeuwen* and co-workers [18] showed that the coordination mode (**ee** or **ea**) of the bidentate ligand is not the sole factor determining the outcome of the catalytic reaction.



ea **ee**

In our group, we have developed a series of diphosphine ligands based on the 9*H*-xanthene backbone to study the effect of ligand structure on the selectivity in the hydroformylation reaction. In particular, the xantphos-type ligands (*Fig. 1*) first developed by *Kranenburg et al.* [16] and later by *Van der Veen et al.* [19–21] have shown a pronounced effect of the natural bite angle on the selectivity for the linear product. Until now, the ligands based on 9*H*-xanthene published by us or other groups are concerned with phosphines [18][20–22], phosphinites [23][24], P-oxo-acid-derived diamides [25], diamines [26] and diarsines [26][27].

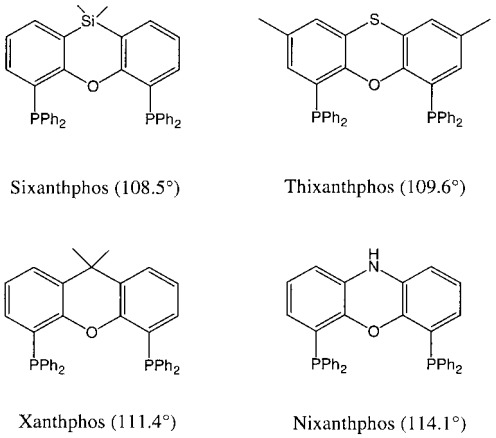


Fig. 1. *Xantphos-type ligands and their calculated β_n values*

Over the last decades, the synthesis and application of bulky monophosphites [12][28][29] in the Rh-catalyzed hydroformylation reaction has gained considerable interest owing to their higher χ [30] and θ values compared to those for phosphines. High rates and selectivities for formation of the linear aldehydes starting from oct-1-ene and styrene were obtained with bulky diphosphites containing bulky [1,1′-biphenyl]-2,2′-diyl linkers developed by *Bryant* and co-workers at *Union Carbide Co.* [31][32] (*Fig. 2*). The activity and regioselectivity of these ligands was shown to be highly sensitive to the exact ligand structure since the steric bulk, introduced at the *ortho* position of the linker, is effectively experienced by the P-atom and, therefore, by the catalytic center [17][31][32]. Interestingly, bulky diphosphites were also shown to

be highly active in the hydroformylation of otherwise less-reactive internal and substituted alkenes [17][31][32]. Encouraged by the promising results obtained by changing the nature of the P-atoms from σ-donor to more π-acceptor, *i.e.*, rate enhancement and higher linearity [33–36], we decided to exploit the 9*H*-xanthene skeleton further as a backbone for the construction of novel diphosphite ligands. We report here on the catalytic performance in the hydroformylation of terminal and internal alkenes in the presence of these ligands.

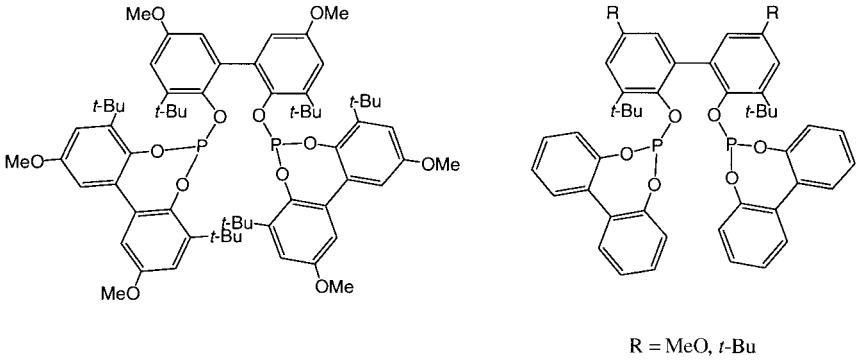
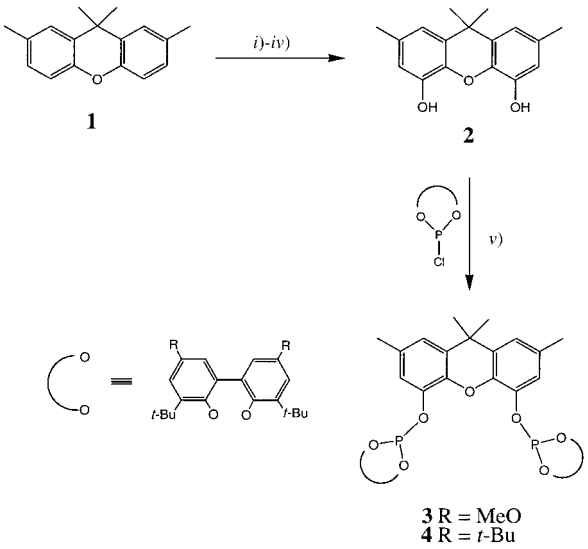


Fig. 2. *Bulky diphosphites based on the [1,1′-biphenyl]-2,2′-diyl linker developed by* Bryant *and co-workers* [31][32]

2. Results and Discussion. – 2.1. *Ligand Synthesis.* The reaction of 2,7,9,9-tetramethyl-9*H*-xanthene-4,5-diol (**2**) with the appropriate phosphorochloridite precursor (see *Scheme*) afforded the ligands **3** and **4** in good yields. In the first step, 2,7,9,9-

Scheme



i) BuLi, tmeda, THF, –78°. *ii*) B[O(i-Pr)]$_3$. *iii*) NaOH/H_2O. *iv*) H_2O_2. *v*) Et_3N, toluene.

tetramethyl-9*H*-xanthene (**1**) was converted to the corresponding xanthenediol **2** by a method similar to that described by *Hopf* and co-workers [37] for the monohydroxylation of [2.2]paracyclophane. This synthetic route to the diphosphite ligands enabled us to influence the steric and electronic properties of the P-atoms by a careful choice of the [1,1′-biphenyl]-2,2′-diyl linker in the phosphorochloridite precursor. Since phosphites generally introduce less steric hindrance close to the Rh-center, bulky substituants (*t*-Bu) were introduced at the *ortho* position of the [1,1′-biphenyl]-2,2′-diyl linker to increase the bulkiness of ligands **3** and **4** (as used in previous studies by *Van Rooy et al.* [17] and *Bryant* and co-workers [31][32]). The introduction of a MeO group at the *para* position in diphosphite **3** should result in a less π-acidic P-ligand compared to **4**. The diphosphite ligands were obtained as white powders showing remarkable stability towards solvolysis and oxidation. The ^{31}P-NMR resonance of ligands **3** and **4** appeared as a singlet in the phosphite region, indicating fast interconversion of the [1,1′-biphenyl]-2,2′-diyl moieties.

An estimation of the flexibility range for ligands **3** and **4** was carried out since calculations of the natural bite angle [13] for phosphites is known to be rather troublesome. It was found during the calculations of the natural bite angle that phosphites **3** and **4** exhibit several minima owing to the various conformations induced by the P–O–C bonds. We found that the ligands have both a smaller flexibility range and lower values as compared to the xantphos-ligand series (95–120° for **3**, 92–118° for **4** *vs.* 99–141° for nixantphos). The latter forms mixtures of **ee** and **ea**, the ratio of which was shown to be dependant on the natural bite angle of the diphosphines. These results suggest that the bulky diphosphite ligands presented here should behave as bidentate ligands that possess a small bite angle, *i.e.,* an **ea** coordination mode in the Rh-complex is expected.

2.2. *Catalyst Studies by NMR and by High-Pressure FT-IR Spectroscopy.* Bidentate phosphite ligands (P∩P) are known to form very stable rhodium hydride species, [RhH(CO)$_2$(P∩P)] having a trigonal-bipyramidal structure under typical hydroformylation conditions [17][38][39]. The catalyst precursors were prepared *in situ* by reacting 1.1 equiv. of the diphosphite with [Rh(CO)$_2$(acac)] (acac = acetylacetonate) at 80° under 20 bar of synthesis gas (CO/H$_2$ 1:1). High-pressure NMR studies of both ligands showed that a short incubation time (1 h) was needed for the preparation of the catalyst precursor. This was evidenced by the presence of one sharp *doublet* in the ^{31}P-NMR spectra and one *triplet* of *doublets* for the hydride signal in the ^{1}H-NMR spectra. After release of the pressure from the high-pressure NMR tube, the solution was transferred to a 5-mm NMR tube for further investigation. Selected spectroscopic data of the hydride complexes [RhH(CO)$_2$(P∩P)] are presented in *Table 1*. The ^{1}H-decoupled ^{31}P-NMR spectra of [RhH(CO)$_2$(P∩P)] displayed typical (Rh,P) coupling constants (206 Hz for **3** and 211 Hz for **4**) for rhodium hydride complexes having a

Table 1. *NMR Data for [RhH(CO)$_2$(P∩P)] Complexes* (P∩P = **3** or **4**)

P∩P	δ (P) [ppm][a]	J(Rh,P) [Hz]	δ (H) [ppm][a]	J(P,H) [Hz]	J(Rh,H) [Hz]
3	150.1 (*d*)	206	– 10.08 (*dt*)	100	8
4	152.5 (*d*)	211	– 6.73 (*dt*)	99	8

[a]) Measured at r.t. under Ar in (D$_6$)acetone/THF 1:1.

trigonal-bipyramidal structure. Generally, a *trans* relationship between the hydride ligand and the P-atom in such a structure is responsible for a large (P,H) coupling constant (160–200 Hz) [17][39][40]. Small *cis* J(P,H) values < 3 Hz are reported for hydridocarbonyl complexes containing bis-equatorially coordinating diphosphite ligands [17][39][41]. In the complexes $[RhH(CO)_2(\mathbf{3})]$ and $[RhH(CO)_2(\mathbf{4})]$, (P,H) coupling constants of 100 and 99 Hz, respectively, were found in the ^{1}H-NMR spectra. These intermediate J(P,H) values suggested a fluxional process on the NMR time scale, which is responsible for the observed average coupling constants [39].

Brown and *Kent* [42] reported that the rhodium hydride complex $[RhH(CO)_2(PPh_3)_2]$ exists as an 85:15 mixture of two isomers, the **ee** (bis-equatorial) and **ea** (equatorial-apical) isomers. At room temperature, the **ee** and **ea** isomers are in rapid equilibrium leading to averaged signals in the NMR spectra and characterized by the presence of four absorption bands for the carbonyl ligands in the high-pressure IR spectra. Only two absorption bands were observed for terminal carbonyl ligands around 1990 and 2029 cm^{-1} in the IR spectra of $[RhH(CO)_2(\mathbf{3})]$ and $[RhH(CO)_2(\mathbf{4})]$. Similar values were reported by *Buisman et al.* [38][39] for bulky diphosphites in trigonal-bipyramidal Rh-complexes. No bridging carbonyl ligands or Rh–H vibration were observed. To assign the bands observed to the **ee** or **ea** isomer, an exchange was performed and the $[RhD(CO)_2(P\cap P)]$ complexes were measured for comparison. Upon H/D exchange, the absorption bands at 1990 and 2029 cm^{-1} did not shift to lower wavenumbers as would be expected for a *trans* hydro-CO relationship [43]. These data were in full agreement with those reported by *Buisman et al.* [39] for diphosphite ligands enforcing an **ea** coordination mode. It is noteworthy that there was a significant effect of the electron-donating MeO group in ligand **3** neither on the carbonyl frequencies nor on the isomer composition. A variable-temperature NMR study was conducted on the $[RhH(CO)_2(P\cap P)]$ complexes to reveal the existence of an exchange process *via* pseudorotations. Such an *intramolecular* ligand interchange of diphosphite ligands resulting in averaged coupling constants has also been reported by *Casey et al.* [14] and *Buisman et al.* [39].

The fluxional behavior of these complexes was evidenced in the ^{31}P- and ^{1}H-NMR experiments by substantial line broadening followed by sharpening and finally almost freezing out of the fluxional process at low temperature. Selected NMR data are given for the low-limit spectra of complexes $[RhH(CO)_2(\mathbf{3})]$ and $[RhH(CO)_2(\mathbf{4})]$ in *Table 2*. At low temperature ($T = 183$ K) in (D_6)acetone/THF 1:1, the ^{31}P-NMR spectrum of the Rh-coordinated ligand **4** displayed two inequivalent P-atoms at δ 151.6 and 155.3 with different J(Rh,P) values (241 and 160 Hz, resp.). The observed and calculated ^{1}H-decoupled ^{31}P-NMR spectra at 183 K are shown in *Fig. 3,a*. Typically, coupling constants for an equatorially coordinated phosphite in a trigonal-bipyramidal structure

Table 2. *NMR Data for [RhH(CO)$_2$(P∩P)] Complexes* (P∩P = **3** or **4**) *at Low Temperature*

P∩P	$\delta(P_{eq})$ [a][b]	$\delta(P_{ax})$ [a][b]	$J(Rh,P_{eq})$ [c]	$J(Rh,P_{ax})$ [c]	$^2J(P_{eq},P_{ax})$ [c]	$\delta(H)$ [a][b]	$^2J(P_{eq},H)$ [c]	$^2J(P_{ax},H)$ [c]	$J(Rh,H)$ [c]
3	149.7[d]	153.2[d]	241[d]	158[d]	58[d]	−10.07[e]	−16[e]	233[e]	8
4	151.6[f]	155.3[f]	241[f]	160[f]	59[f]	−6.75[d]	−15[d]	235[d]	8

[a]) Measured under Ar in (D_6)acetone/THF 1:1. [b]) Chemical shifts δ in ppm. [c]) Coupling constants J in Hz. [d]) $T = 173$ K. [e]) $T = 163$ K. [f]) $T = 183$ K.

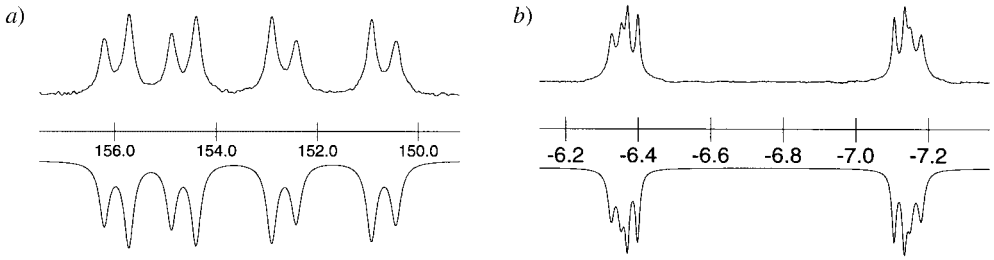


Fig. 3. a) *$^{31}P\{^1H\}$-NMR Spectrum of [RhH(CO)$_2$(**4**)] at 183 K* (observed, upper trace), *and* b) *Hydro-ligand region of the ^{1}H-NMR spectrum of [RhH(CO)$_2$(**4**)] at 173 K* (observed, upper trace)

are in the range 220–246 Hz [44][45]. Therefore, we concluded that the (Rh,P) coupling constant of 241 Hz corresponded to an equatorially coordinated P-atom ($\delta(P_{eq}) = 151.6$). The two nonequivalent P-atoms displayed a coupling constant $^2J(P_{eq},P_{ax})$ of 59 Hz with each other, as already observed by *Van Leeuwen et al.* [46]. The ^{1}H NMR spectrum at 173 K of [RhH(CO)$_2$(**4**)] (see *Fig. 3,b*; observed, upper trace; simulated, lower trace) showed that the fluxional process was almost halted as evidenced by the *doublet-doublet-doublet* structure displayed for the hydride resonance.

The expected large (P_{ax},H) coupling constant of 235 Hz was indicative of a *trans* relationship between the hydride ligand and the axially coordinated P-atom in a trigonal bipyramidal structure. In contrast, the rather large *cis* $|^2J(P_{eq},H)|$ values of 15 Hz indicated **ea** coordination in a distorted trigonal bipyramid. Similarly, we assigned the equatorially and axially coordinated P-atoms in [RhH(CO)$_2$(**3**)] based on the comparison with the results obtained with **4** and reported values. Coordinated ligand **3** displayed similar coupling-constant values in the low-limit ^{31}P- and ^{1}H-NMR spectra indicating also an **ea** coordination mode in a distorted trigonal bipyramidal rhodium hydride complex. Most likely, the distortion observed can be attributed to the bulkiness of the ligand.

2.3. *Hydroformylation results.* 2.3.1. *Oct-1-ene.* The hydroformylation catalysts were prepared *in situ* from 1 mM [Rh(CO)$_2$(acac)] in toluene and 5, 10, or 20 equiv. of the bidentate phosphites at 80° under 20 bar of synthesis gas (CO/H$_2$ 1:1). The production of octene isomers, nonanal, and 2-methyloctanal was monitored by gas chromatography. The averaged turnover frequencies (t.o.f.) were determined at 20–30% conversion.

The hydroformylation results for oct-1-ene as substrate are presented in *Table 3*. As expected for phosphite ligands, high activities were achieved (t.o.f. up to 16900 (mol aldehyde)(mol Rh)$^{-1}$h^{-1}), but, surprisingly, only moderate amounts of internal octene isomers were formed (*ca.* 12%). The reaction rates observed for the diphosphite ligands were comparable to those obtained by *Bryant* and co-workers [31][32] with the bulky diphosphites developed at *Union Carbide Co.*, but lower than their monodentate phosphite analogues [29][44]. The regioselectivity for the linear aldehyde reached 79% (l/b of 7.2) with ligand **4** and was dependant on the (P∩P)/Rh ratio. Such a dependency is indicative of partial ligand dissociation resulting in less selective rhodium monophosphite and/or ligand-free complexes [36]. For oct-1-ene under the catalytic

conditions used in this study ($P(CO/H_2) = 20$ bar, $T = 80°$, [Rh] = 1 mM), the optimum (P∩P)/Rh ratio was found to be 10. An effect of the decreasing π-acceptor capabilities of ligand **3** compared to **4** on the reactivity of the catalyst cannot be deduced from the data in *Table 3*. *Van Rooy et al.* [17] reported similar ambiguous effects of the variation of the electronic properties of diphosphites bearing electron-donating or electron-withdrawing substituents since, in both cases, a positive effect on the selectivity and regioselectivity was reported. Most likely the beneficial effect on the reactivity and the selectivity observed for ligand **4** could arise from the introduction of bulky groups (*t*-Bu) both at the *ortho* and *para* position of the [1,1′-biphenyl]-2,2′-diyl linker. This particular substitution pattern at the bridging [1,1′-biphenyl]-2,2′-diyl results in an efficient transfer of the steric bulk from the P-center to the Rh-center. Such a dependency of the selectivity on the exact ligand structure of the [1,1′-biphenyl]-2,2′-diyl linker has been observed before [17].

Table 3. *Hydroformylation Results of Oct-1-ene at 80°* [a])

P∩P	(P∩P)/Rh	l/b [b])	Linear aldehyde [%] [b])	t.o.f. [b])[c])	Octene isomers [%] [b])
3	5	5.0	73	11700	13
	10	5.6	74	13800	12
	20	5.5	74	12300	13
4	5	6.6	75	16900	13
	10	7.2	79	14800	11
	20	7.2	78	16400	12

[a]) Conditions: CO/H_2 1:1, $P(CO/H_2) = 20$ bar, [Rh] = 1 mM in toluene, substrate/Rh = 1281; in none of the experiments hydrogenation was observed; number of experiments, 3. [b]) l/b Ratio, percent linear aldehyde, percent isomerization to octenes and turnover frequencies (t.o.f.) were determined at 20–30% conversion. [c]) In (mol aldehyde) (mol Rh)$^{-1}$ h^{-1}.

2.3.2. *Styrene.* Styrene has a preference for the formation of branched aldehyde, under standard catalytic conditions due to the stability of the benzylic Rh-species, induced by the formation of a stable η^3-complex [3]. However, the use of phosphites and especially diphosphite ligands for the Rh-catalyzed hydroformylation of styrene has revealed that these bidentate ligands show a different selectivity, *i.e.*, preferential formation of the linear aldehyde. By applying catalytic conditions that promote β-H elimination of the branched alkylrhodium complex, preferential formation of the linear aldehyde was observed [47][48]. Therefore, we performed our catalytic tests at low CO pressure and high temperature ($P(CO/H_2) = 2-10$ bar, $T = 120°$, [Rh] = 0.2 mM). The averaged turnover frequencies were determined at 20–30% conversion. The results obtained with ligands **3** and **4** are shown in *Table 4*. Remarkably high activities for the hydroformylation of styrene with high selectivities towards the linear product were observed when diphosphites **3** and **4** were used. Under 10 bar of synthesis gas, reaction rates as high as 39900 (mol aldehyde)(mol Rh)$^{-1}$h^{-1} were observed for ligand **4**. The reaction rates obtained with ligand **3** were lower by a factor of 2. The selectivity towards the linear aldehyde could be increased to 70% (l/b of 2.3) with ligand **3** by applying a synthesis-gas pressure of 2 bar, albeit with a much lower reaction rate. Surprisingly, we could not detect the formation of the hydrogenation product of styrene, ethylbenzene. The higher rates found for diphosphite **4** could be explained by

electronic factors. Since the P-atom in **4** is a better π-acceptor compared to **3**, replacement of the more labile carbonyl ligand by the alkene should be favored. The overall higher selectivity for the linear aldehyde found with ligand **3** cannot be rationalized in terms of an electronic effect; a more π-acidic P-ligand gives a more electropositive Rh-atom enhancing β-H elimination, and an increase of the l/b ratio might be expected.

Table 4. *Hydroformylation Results of Styrene at 120°* [a])

P∩P	$P(CO/H_2)$ [bar]	l/b [b])	Linear aldehyde [%] [b])	t.o.f. [b])[c])
3	10	2.1	67	23500
	2	2.3	70	6700
4	10	1.9	65	39900
	2	2.1	67	8000

[a]) Conditions: CO/H_2 1:1, (P∩P)/Rh = 10, [Rh] = 0.2 mM in toluene, substrate/Rh = 4364; in none of the experiments hydrogenation was observed; number of experiments, 3. [b]) l/b Ratio, percent linear aldehyde, and turnover frequencies (t.o.f.) were determined at 20–30% conversion. [c]) In (mol aldehyde)(mol Rh)$^{-1}$ h^{-1}.

2.3.3. *(*E*)-Oct-2-ene.* Owing to their high activities, usually combined with high rates of isomerization of terminal alkenes, phosphite ligands have proven to be efficient catalyst for the hydroformylation of the less-reactive internal alkenes. Encouraged by the high activities and selectivities observed for the hydroformylation of oct-1-ene with these novel bulky diphosphites, we decided to test our ligands as catalysts with (*E*)-oct-2-ene as substrate. *Van Leeuwen* and co-workers [20] reported on the hydroformylation of internal alkenes in the presence of new phosphacyclic diphosphines based on the 9*H*-xanthene backbone. The high selectivity (l/b up to 9.5, 90% linearity) and activity (t.o.f. values up to 112 (mol aldehyde)(mol Rh)$^{-1}$ h^{-1}) observed were explained by the decreased phosphine basicity and the wider natural bite angles (>120°) of the ligands. Recently, *Börner* and co-workers [49] have reported on the use of π-acidic bidentate ligands based on a *O*-acylphosphite moiety for the Rh-catalyzed hydroformylation of internal octenes. High activities (t.o.f. up to 4600 (mol aldehyde)(mol Rh)$^{-1}$ h^{-1} at 140°) were observed with this new class of ligands. The reported selectivities were *ca.* 70%. Unfortunately, no studies were done on the solution structure of the active catalyst present under the hydroformylation conditions.

Results for the hydroformylation of (*E*)-oct-2-ene are given in *Table 5*. In a first set of experiments, a ten-fold excess of ligands was used based on the results found for oct-1-ene (*vide supra*). We decided to follow conversion and selectivity over 1 h by stopping the reaction at preset times (8 min, 22 min, and 1 h). The data collected for both ligands showed a severe drop of the activity and selectivity over the reaction time, especially for ligand **4** (l/b varied from 2.4 after 8 min to 1.8 after 22 min reaction time). This suggested that either ligand dissociation or decomposition occurred during the catalytic reactions leading to less-selective rhodium monophosphite and/or ligand-free complexes. A second set of experiments was performed with a 25-fold excess of diphosphites to suppress ligand dissociation. A constant l/b ratio was observed over the reaction time for both ligands with the higher ligand/Rh ratio. With ligand **4**, very high activities were observed (980 (mol aldehyde)(mol Rh)$^{-1}$ h^{-1}) for the hydroformylation

of (*E*)-oct-2-ene with relatively high l/b ratio of 2.8 (74% linearity). It is very likely that the diphosphites **3** and **4** display high isomerization rates necessary to maintain a small concentration of oct-1-ene prior to fast hydroformylation of oct-1-ene as was postulated by *Börner* and co-workers [40]. Prediction of the ideal catalyst properties required for a selective and fast hydroformylation of internal alkenes has proven to be very difficult based only on the catalytic results of terminal alkenes. Although a combination of high isomerization rates and selectivity is probably a prerequisite to form the linear aldehyde, more detailed studies need to be conducted to understand the factors controlling the regioselectivity.

Table 5. *Hydroformylation Results of Oct-2-ene at 120°*[a])

P∩P	(P∩P)/Rh	l/b[b])[c])	Linear aldehyde [%][b])[d])	t.o.f.[b])[e])
3	10	2.2	69	760
	25	2.2	69	880
4	10	2.4	74	760
	25	2.8	74	980

[a]) Conditions: CO/H_2 1:1, $P(CO/H_2) = 2$ bar maintained constant, [Rh] = 1 mM in toluene, substrate/Rh = 640; reaction stopped after 8 min; number of experiments, 2. [b]) l/b Ratio, percent linear aldehyde, and turnover frequencies (t.o.f.) were determined at 20–30% conversion. [c]) l/b Ratio includes all branched aldehydes. [d]) Percentage of linear aldehyde of all products other than octenes. [e]) In (mol aldehyde)(mol Rh)$^{-1}$ h^{-1}.

3. Conclusions. – Rh^I complexes of xantphite, a new class of bulky diphosphite ligands, have been shown to be very selective and active catalysts for the hydroformylation of both terminal and internal alkenes. The combination of a rigid versatile skeleton such as the 9*H*-xanthene backbone, together with the use of bulky phosphites based on [1,1′-biphenyl]-2,2′-diyl linkers, open the way to new, highly robust, and efficient catalysts. The bidentate ligands (P∩P) form exclusively catalysts with the structure $[RhH(CO)_2(P \cap P)]$ in which one of the phosphite donor atoms occupies the apical position and the other one the axial position (= **ea** isomer), as shown by NMR and high-pressure FT-IR spectroscopy. The smaller natural bite angles calculated for these ligands compared to the xantphos derivatives accounts for the **ea** coordination mode found in the trigonal-bipyramidal Rh-complexes. These findings are in contradiction to the assumption that bisequatorial coordination in the active rhodium catalyst is a key factor in controlling the regioselectivity of the overall catalytic reaction. Finally, since chiral analogues of the diphosphites can be easily prepared from the appropriate chiral binaphthols, we believe that our new family of ligands have high potential in the asymmetric hydroformylation of olefins.

Experimental Part

General Procedure. All preparations were carried out under Ar by means of standard *Schlenk* techniques. Toluene and tmeda (*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine) were distilled from Na, and THF and Et_2O from Na/benzophenone. The 2,7,9,9-tetramethyl-9*H*-xanthene [50] and 3,3′,5,5′-tetra(*tert*-butyl)[1,1′-biphenyl]-2,2′-diyl phosphorochloridite [51] were prepared according to literature procedures and 3,3′-di(*tert*-butyl)-5,5′-dimethoxy[1,1′-biphenyl]-2,2′-diyl phosphorochloridite was obtained by the same synthetic procedure as for 3,3′,5,5′-tetra(*tert*-butyl)[1,1′-biphenyl]-2,2′-diyl phosphorochloridite [51]. All glassware was dried by heating under vacuum. Flash column chromatography (FC): silica gel *60* (230–400 mesh) from *Merck*. Gas

chromatography: *Interscience HR-GC-Mega-2* apparatus (split/splitless injector, *J&W Scientific*, *DB1* 30-m column, film thickness 3.0 mm, carrier gas 70 kPa He, FID detector) equipped with a *Hewlett-Packard* data system (*Chrom-Card*). M.p.: *Gallenkamp MFB-595* melting apparatus, in open capillaries; uncorrected. High-pressure (HP) IR spectra: *Nicolet 510* FT-IR spectrometer. NMR spectra: *Bruker AMX-300* spectrometer (^{1}H, ^{31}P) for Rh-complexes, *Varian Innova-500* spectrometer (^{1}H, ^{13}C) for routine spectra; chemical shifts δ in ppm referenced to $SiMe_4$ or H_3PO_4 (external), J in Hz; for the spectra simulation and the chemical-exchange calculations, an NMR simulation program was applied (geNMR version 4.1, 1999, *Ivorysoft*, Dr. *P.H.M. Budzelaar*). MS: *m/z* (rel. %).

Computational Details. The molecular-mechanics calculations were performed by means of the CAChe WorkSystem version 4.1. Calculations were carried out similarly to the method described by *Casey* and *Whiteker* [13], with a Rh–P bond length of 2.315 Å. Minimizations were done by the block-diagonal *Newton-Raphson* method, with the structures allowed to converge with a termination criterion of a rms factor of 0.0001 kcal mol^{-1} $Å^{-1}$ or less.

Catalysis. Hydroformylation experiments were performed in a stainless steel autoclave (196 ml). The alkene was filtered over neutral alumina to remove peroxides. In the case of oct-1-ene and oct-2-ene a soln. of $P(OBu)_3$ (1 ml) in toluene (5 ml) was added to the reaction mixture by overpressure to form a hydroformylation inactive Rh-species. The samples were analyzed by GC with decane as internal standard.

Preparation of [RhH(CO)$_2$(P∩P)]. The complex syntheses under pressure were performed in a sapphire NMR tube of ∅ = 10 mm. In a typical experiment, 5 mg (0.019 mmol) of $[Rh(acac)(CO)_2]$ and 1.1 equiv. of ligand (P∩P) were dissolved in (D_6)acetone/THF 1:1 (1 mL). The soln. was brought into the Ar-flushed tube. After closing, the tube was flushed 5 times with 4 bar of synthesis gas (CO/H_2 1:1) and put under a pressure of 20 bar. The tube was heated to 80° in an oil bath for 2 h. After cooling, the NMR tube was depressurized and the soln. was transferred under Ar in a NMR tube of ∅ = 5 mm.

HP-FT-IR Experiments. High-pressure IR experiments were performed in an *SS-316* 50-ml autoclave equipped with IRTRAN windows (ZnS, transparent up to 700 cm^{-1}, ∅ = 10 mm, optical path length = 0.4 mm), a mechanical stirrer, a temp. controller, and a pressure device. In a typical experiment, 5 mg of $[Rh(acac)(CO)_2]$ and 1.2 equiv. of ligand were dissolved in 15 ml of cyclohexane under Ar. The soln. was brought into the CO/H_2 1:1 flushed autoclave, and, after flushing, pressurizing, and heating of the mixture, the autoclave was placed in the IR spectrometer. While the samples were stirred, the IR spectra were recorded.

*2,7,9,9-Tetramethyl-9*H*-xanthene-4,5-diol* (**2**). To a cold (−78°) soln. of 2,7,9,9-tetramethyl-9*H*-xanthene (7.85 g, 33 mmol) and tmeda (12.5 ml, 82 mmol) in Et_2O (150 ml) was added dropwise a hexane soln. of BuLi (35.8 ml, 82 mmol). After 5 h, neat $B[O(i\text{-}Pr)]_3$ (31 ml, 133 mmol) was added to the yellow soln., resulting in the formation of a white suspension. After 0.5 h, a soln. of NaOH (7.90 g, 197 mmol) in H_2O (50 ml) was added. After 20 min stirring, followed by careful addition of an aq. 34% H_2O_2 soln. (*w*/*w*; 20 ml, 200 mmol), the mixture was left to stir vigorously for 5 h. The aq. phase was washed twice with Et_2O (50 ml) to remove org. impurities. The diol **2** was isolated from the aq. layer by acidification with 10% HCl soln. until complete precipitation of the product was observed. After filtration of the solid and several washings with EtOH, a white powder was obtained: 5.80 g (65%) of **2**. M.p. 250°. ^{1}H-NMR ((D_6)acetone): 8.22 (*s*, 2 H, OH); 6.81 (*s*, H–C(1), H–C(8)), 6.62 (*s*, H–C(3), H–C(6)), 2.26 (*s*, Me–C(2), Me–C(7)), 1.59 (*s*, 2 Me–C(9)). ^{13}C{^{1}H}-NMR ((D_6)acetone): 149.9 (C(4), C(5)); 141.2 (C(4a), C(10a)); 137.8, 135.6 (2*s*, C); 122.2, 119.7 (2*s*, CH(1), CH(3), CH(6), CH(8)); 39.4 (*s*, C(9)); 37.1 (*s*, 2 *Me*–C(9)); 25.6 (*s*, *Me*–C(2), *Me*–C(7)). GC-MS: 270 (20, M^+), 255 (100). Anal. calc. for $C_{17}H_{18}O_3$ (270.32): C 75.53, H 6.71; found: C 75.32, H 6.59.

*General Procedure for the Preparation of 9*H*-Xanthene-Based Diphosphites.* To an ice-cooled soln. of **2** (1.00 g, 4 mmol) and Et_3N (1.2 ml, 8 mmol) in toluene (50 ml) was added dropwise a toluene soln. (40 ml) of the appropriate phosphorochloridite (9 mmol) and Et_3N (1.2 ml, 8 mmol). Immediately, a precipitate was formed, and the mixture was heated to 80° for 4 h. The white precipitate was removed by filtration. Evaporation of the filtrate gave a white foam, which was purified by FL (SiO_2, CH_2Cl_2).

*Bis[3,3′-di(*tert*-butyl)-5,5′-dimethoxy[1,1′-biphenyl]-2,2′-diyl] 2,7,9,9-Tetramethyl-9*H*-xanthene-4,5-diyl Diphosphite* (**3**): 3.84 g (92%). White powder. M.p. 250°, ^{1}H-NMR (CD_2Cl_2): 7.02 (br. *s*, 4 arom. H); 6.80 (br. *s*, H–C(1), H–C(8)); 6.69 (*d*, *J*(H,H) = 2, 4 arom. H); 5.71 (br. *s*, H–C(3), H–C(6)); 3.82 (*s*, 4 MeO); 2.05 (*s*, Me–C(2), Me–C(7)); 1.47 (s, 2 Me–C(9)); 1.40 (*s*, 4 *t*-Bu). ^{13}C{^{1}H}-NMR (CD_2Cl_2): 156.5, 143.3, 142.4, 140.2, 138.9, 134.3, 132.1, 130.2 (8*s*, C); 122.3, 121.7, 114.8, 113.4 (4*s*, CH); 56.1 (*s*, MeO); 35.8 (*s*, Me_3C); 34.5 (*s*, C(9)); 33.9 (*s*, 2 *Me*–C(9)); 31.1 (*s*, Me_3C); 21.1 (*s*, *Me*–C(2), *Me*–C(7)). ^{31}P{^{1}H}-NMR (CD_2Cl_2): 136.3 (*s*). Anal. calc. for $C_{61}H_{72}O_{11}P_2$ (1043.17): C 70.23, H 6.96; found: C 69.99, H 7.08.

*Bis[3,3′,5,5′-tetra(*tert*-butyl)[1,1′-biphenyl]-2,2′-diyl) 2,7,9,9-Tetramethyl-9*H*-xanthene-4,5-diyl Diphosphite* (**4**): 4.00 g (88%). White powder. M.p. 305°. ^{1}H-NMR ($CDCl_3$): 7.45 (br. *s*, 4 arom. H); 7.14 (*d*, *J*(H,H) = 2, 4

arom. H); 6.64 (br. *s*, H–C(1), H–C(8)); 5.59 (br. *s*, H–C(3), H–C(6)); 1.97 (*s*, Me–C(2), Me–C(7)); 1.41 (*s*, 2 Me–C(9)); 1.39 (*s*, 4 *t*-Bu (*ortho*)); 1.36 (*s*, 4 *t*-Bu (*para*)). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 146.5, 146.3, 140.6, 140.2, 138.5, 133.2, 131.3, 129.4 (8*s*, C); 126.8, 124.3, 121.8, 121.3 (4*s*, CH); 35.5, 34.9 (2*s*, Me_3C); 33.9 (*s*, C(9)); 33.8 (*s*, 2 *Me*–C(9)); 31.8, 31.1 (2s, Me_3C); 21.4 (*s*, *Me*–C(2), *Me*–C(7)). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 139.8 (*s*). Anal. calc. for $C_{73}H_{96}O_7P_2$ (1147.49): C 76.41, H 8.43; found: C 76.65, H 8.54.

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