

The bite angle makes the catalyst*

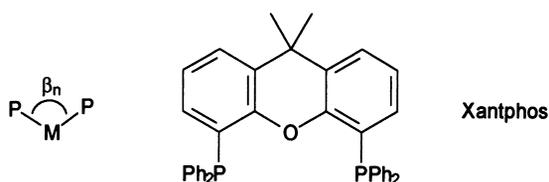
Piet W. N. M. van Leeuwen,† Paul C. J. Kamer and Joost N. H. Reek

*Institute of Molecular Chemistry, Homogeneous Catalysis, Faculty of Chemistry,
University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV, Amsterdam,
the Netherlands*

Abstract: Catalytic reactions are described for metal complexes containing bidentate phosphine ligands that enforce wide bite angles in the complexes. The calculated natural bite angles are in the range 100–120°. Three applications will be discussed: (i) nickel catalysed hydrocyanation, for which the first active phosphine catalyst was found, (ii) palladium catalysed allylic alkylation, for which the selectivity also strongly depends on the bite angle, and (iii) rhodium catalysed hydroformylation, which leads to highly linear products.

INTRODUCTION

Homogeneous catalysis with organotransition metal complexes has become increasingly important in the process industry [1]. The development of organotransition metal chemistry has largely contributed to the enormous growth of homogeneous catalysis [2]. Knowledge about bonding and reactivity in organometallic chemistry has been of great support to catalysis [3]. The reactivity of organotransition metal complexes is dependent on the ligand environment of the metal. In transition metal catalysis extensive research has been devoted to fine-tune the selectivity and activity of catalysts by means of ligand modification, just simply by looking at electronic and steric effects. The Tolman parameters χ and θ [4] have often been used to express ligand-property vs. catalyst-activity relationships. The increased understanding of organotransition metal chemistry has evolved catalyst development from trial and error into rational design (Scheme 1).



Scheme 1

Recently, emphasis has been put on the influence of specific geometries of ligands around the catalytic center on the rate and selectivity of the reaction [5–14]. Bidentate ligands can have a preference for a specific geometry, since the Donor Atom–Metal–Donor Atom angle (the bite angle β_n) is strongly dependent on the bridge between the two ligands. Metal complexes with chelating ligands preferring a bite angle of 90° for instance, stabilise square planar geometries. Furthermore, ligands that enforce a well-defined bite angle can be used to induce distortions of certain geometries and as a result destabilise them. In this way a reaction can be steered by influencing the initial state, transition state or final state of the metal complex involved. Not only will this have impact on activity and selectivity of a catalytic reaction

* Lecture presented at the 10th IUPAC Symposium on Organo-Metallic Chemistry Directed Towards Organic Synthesis (OMCOS 10), Versailles, France, 18–22 July 1999, pp. 1381–1547.

† Corresponding author: E-mail: pwnm@anorg.chem.uva.nl

but even alternative reaction pathways can become accessible. Already in the late 1970s Hoffmann calculated that in the transition state of an insertion reaction of a palladium-bis(phosphine) complexes the bite angle P-Pd-P is larger than that in the starting complex [15].

Recently we prepared a series of ligands that enforce bite angles in the range of 100–120° which enable systematic studies of the effect of large bite angles on catalytic reactions [5–11]. It has been shown that diphosphine ligands favouring bite angles around 110° can be used to stabilise a bisequatorial coordination mode in trigonal bipyramidal Rh(I) complexes. Also, these ligands tend to stabilise a tetrahedral over a square planar geometry. So far, however, the bidentate ligands that were used to study the influence of the different preferred bite angles on the catalytic activity also differed in electronic and steric properties. Therefore we designed bidentate phosphine ligands based on xanthene-type backbones (xantphos, **5**), which allowed a systematic study of bite-angle effects in transition metal catalysis. Changing the bite angle, however, also effects the steric hindrance on the metal or the accessible molecular surface (AMS) of the metal centre [16]. It depends on the reaction studied if the bite angle effect operates via metal valence angles, which leads to certain geometric preferences, or via its influence on steric hindrance. Here we present three examples of such effects in catalytic reactions that are optimised rationally by changing the bite angle of metal diphosphine complexes.

LIGAND DESIGN

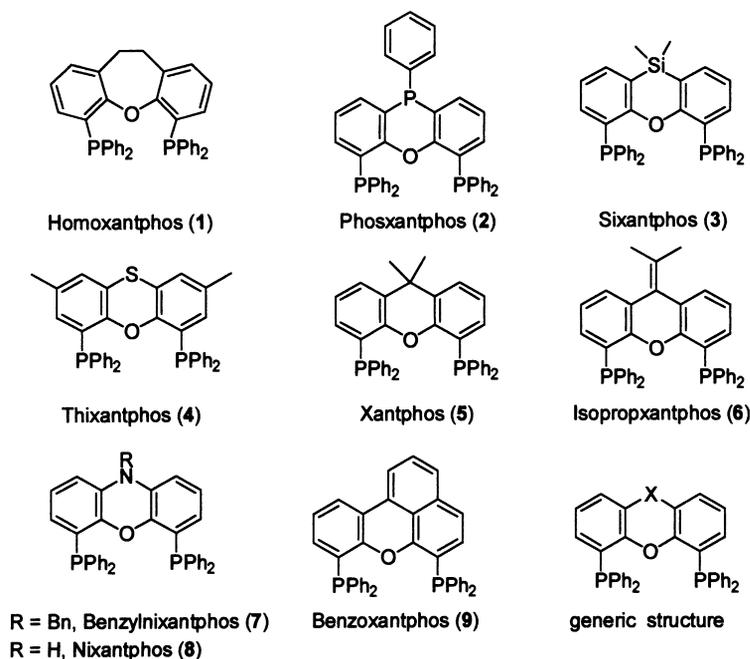
Molecular mechanics has proven to be a useful tool in the development of new bidentate diphosphines. The natural bite angle (β_n) and flexibility range of a bidentate ligand, introduced by Casey & Whiteker [12], are useful parameters, which can be calculated using molecular modelling. The natural bite angle is defined as the preferred chelation angle determined only by ligand backbone and not by metal valence angles. The flexibility range is defined as the bite angles that can be reached within an energy barrier of 3 kcal/mol. In the actual calculation a ‘dummy’-type atom is used for the metal atom with no defined geometry and a typical M-P bond length known from X-ray structures of similar complexes. The force constant for P-M-P bending is defined to be zero and consequently the structure of the complex is determined by the organic ligand only. The outcome of the calculations is dependent on the defined M-P distance, which is influenced by the metal of choice. In this way the natural bite angle can be calculated easily, since the parameters for the metal are not needed in the actual calculations. The flexibility range is calculated by forcing the P-M-P angle to deviate from the natural bite angle. All known complexes proved to have bite angles (in the solid state) within the calculated flexibility range, which suggests that these calculations can be a valuable tool, in spite of the applied simplifications [17].

We applied this method to our newly developed series of Xantphos ligands. By varying the bridge at the 10 position we were able to induce small variations in the bite angle. According our Molecular Mechanics calculations (Table 1), these ligands have natural bite angles ranging from 102° to 121° and a flexibility range of $\approx 35^\circ$. It should be noted that the absolute values of the calculations will be dependent on the force field used, but the relative results and therefore the observed trends will be the same. The

Table 1 The natural bite angles (β) and the flexibility range calculated for the xantphos ligands

X	Ligand	β_n	Flexibility range
H,H;	DPEphos	102	86–120
C ₂ H ₄	1	102	92–120
PhP	2	108	96–127
Si(CH ₃) ₂	3	109	96–130
S	4	110	96–133
C(CH ₃) ₂	5	111	97–133
C=C(CH ₃) ₂	6	113	98–139
NBz	7	114	99–139
NH	8	114	99–141
‘benz’	9	121	102–146

X-ray crystal structure of the free Xantphos ligand shows that only very little adjustment of the structure is necessary to form a chelate; the orientation of the diphenyl-phosphine-moieties is nearly ideal. The observed P...P distance in the free ligand is 4.080 Å, while MM studies indicate that a decrease of the P...P distance to 3.84 Å is necessary for chelation with a P-Rh-P angle of 111.7°, a decrease of only 0.24 Å. The P atoms are brought together by means of a slight decrease of the angle between the two phenyl planes in the backbone of the ligand from $\approx 166^\circ$ to 158° . As a consequence, these Xantphos type ligands do not form bimetallic species, whereas the oxygen atom in the backbone prevents metallation of the ligand (Scheme 2).

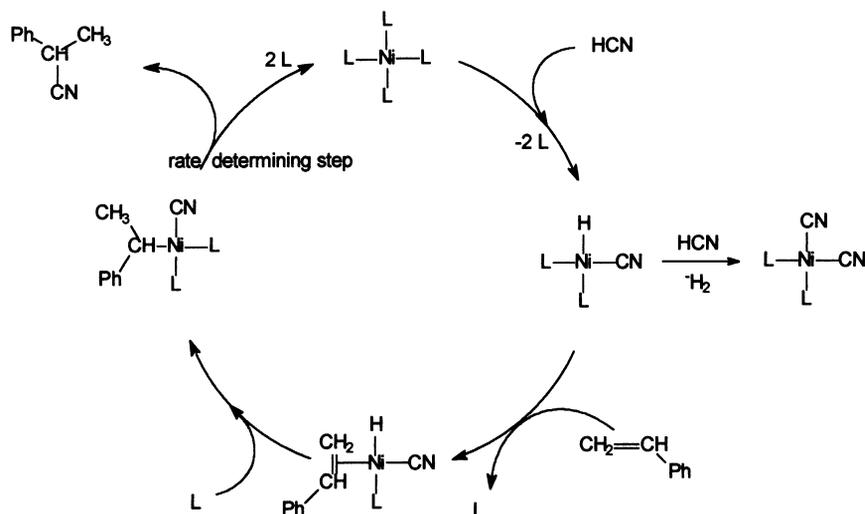


Scheme 2

HYDROCYANATION OF ALKENES

The addition of HCN to alkenes (Scheme 3) is a very useful reaction for the functionalisation of organic substrates. Industrially it has a tremendous impact mainly because of the adiponitrile production by Du Pont via hydrocyanation of butadiene using aryl phosphite modified nickel catalysts [1].

An oxidative addition of HCN to the tetrahedral Ni(0) species takes place, after which the alkene coordinates resulting in a square planar Ni(II) π -olefin complex. The σ -alkyl complex is formed via insertion of the olefin into the metal-hydride, and subsequent reductive elimination of RCN yields the alkyl nitrile and the tetrahedral Ni(0) species. Whereas phosphites have proven to be versatile ligands in the hydrocyanation reaction, phosphine ligands, however, lead to catalysts with hardly any activity [18–21]. The explanation is straightforward; the mechanism involves a rate-determining reductive elimination of the alkylcyanide [22–25] and thus the reaction proceeds faster when more electron withdrawing phosphites or phosphinites are employed. Secondly, a derailment of the catalytic reaction occurs via a side-reaction with HCN leading to a completely inactive $\text{LnNi}(\text{CN})_2$ species (see Scheme 3). In order to suppress this side-reaction the concentration of HCN is kept low in the catalytic process and high excesses of ligand are necessary, even when phosphites or phosphinites are used [26]. The crucial reductive elimination step involves the transformation of a square planar Ni(II) compound into a tetrahedral Ni(0) compound. It occurred to us that ligands favouring bite angles of $\approx 110^\circ$, like the xantphos-type compounds **1**, would (a) destabilise the square planar Ni(II) species, and (b) stabilise the tetrahedral Ni(0) complexes, thus enhancing the reductive elimination and the overall catalysis.



Scheme 3 Simplified mechanism for the hydrocyanation of styrene.

We showed that indeed the hydrocyanation of styrene using nickel-catalysts containing these ligands as catalyst components resulted in remarkable yields and selectivity, especially when compared to common diphosphines (Table 2) [7]. The use of DPEphos, the ligand in our series with the smallest β_n of 101° induced a yield (based on HCN) of 35–41%, which is modest but still a significant enhancement when compared to PPh_3 or $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n=2,3$). When the bite angle is increased further to 105 – 106° using **3** or **4**, the yields increased up to 95%. When **5**, with a calculated bite angle of 109° was applied the yield was slightly lower, 75%. Application of DBF [18] (dibenzofurandiphos, X = bond in generic structure), β_n of 138° resulted in virtually no yield. The common diphosphines dppe and dppp, and monophosphine PPh_3 gave very low yields of nitriles, 0–11% (based on HCN) under identical conditions. Large amounts of a precipitate were observed using these ligands, presumably nickel dicyanides.

Table 2 Nickel-catalysed hydrocyanation of styrene, using diphosphine ligands

Ligand	β_n^*	%yield †	% branched
DPEphos	100.9	35–41	88–91
3	104.9	94–95	97–98
4	105.7	69–92	96–98
5	109.0	27–75	96–99
DBF	138.4	0.7	83
PPh_3	–	0	–
dppe	78.5	<1	≈ 40
dppp	87.3	4–11	≈ 90

Reaction conditions: Styrene/Ni = 28.5, HCN/Ni = 17.5, $[\text{Ni}] = 73.3 \text{ mM}$, $T = 60^\circ\text{C}$, $t = 18 \text{ h}$.

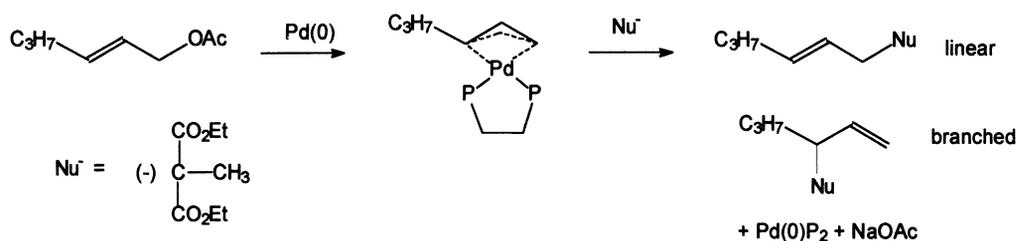
* Natural bite angle ($^\circ$) calculated for nickel complexes.

† Yields are based on HCN. Maximum yields based on styrene are 61%.

These results indicate clearly that effective nickel-phosphine catalysed hydrocyanation can be achieved when the phosphines enhance the reductive elimination step by supporting a tetrahedral geometry. Diphosphine ligands with calculated natural bite angles near 106° allow very high conversion and selectivity in the hydrocyanation of styrene. The optimal bite angle is 105 – 106° while either a slight increase to 109° or decrease to 101° already results in a significant drop in activity.

ALLYLIC ALKYLATION USING PALLADIUM

After the initial discovery of the alkylation by Tsuji [27], extensive research by Trost has led to many applications of this reaction in organic synthesis [28]. An X-ray structure of a highly enantioselective palladium diphosphine catalyst showed that the phosphine has a large bite angle of 110.5° [29]. This indicates that the bite angle can also be of importance in this reaction. Åkermark and co-workers investigated the influence of the steric bulk of bidentate ligands (phenanthrolines) on the regioselectivity [30]. Most studies on allylic alkylation, however, have ignored the effect of the bite angle of the ligands. Trost reported that enlarging the bridge of chelating chiral diphosphines led to a higher asymmetric induction [31]. We performed a study on the effect of the bite angle of diphosphines on catalyst activity and selectivity [10]. The catalyst system we employed was prepared *in situ* using $\text{Pd}(\text{DBA})_2$ and diphosphine in DMF. As substrates we used 2-hexenylacetate and sodium diethyl methylmalonate. Only two products were observed: the linear product, diethyl 2-(2-hexen-1-yl)-2-methylmalonate, and the branched product, diethyl 2-(1-hexen-2-yl)-2-methylmalonate (Scheme 4).



Scheme 4 The palladium catalysed alkylation of 2-hexenylacetate with sodium diethyl methylmalonate.

In order to get an insight in the bite angle effect in this reaction various bidentate ligands with a broad range of bite angles were studied. The diphosphine ligands studied as catalyst components were dppe, dppp, dppb (1,4-bis(diphenylphosphino)-butane), dppf, DPEphos, **3** and **5**.

The selectivity of the reaction towards the linear product is dependent on the bite angle of the ligand used and increases with an increasing bite angle (see Table 3). Using dppe, a ligand with a small bite angle (78.1°), 96.2% of linear product is obtained, while dppf (with a bite angle of 99.1°) leads to 99%. All the Xantphos-type ligands with bite angles $> 100^\circ$ resulted in selectivities of 99% or higher. It is noteworthy that when **5** is employed 100% of linear product is observed, without even a trace of the branched one, which means that the usage of this ligand can prevent laborious purification of the desired product. The selectivities reported were obtained at maximal conversion, which is nearly quantitative.

Table 3 Alkylation of 2-hexenylacetate with sodium diethyl methylmalonate in DMF

Ligand	β_n ($^\circ$)	t.o.f.*	time (h)	conversion (%) [†]	% linear	% branched
dppe	78.1	82	5	98.5	96.2	3.8
dppp	86.2	111	5	97.9	96.6	3.4
dppb	98.6	393	1	98.0	97.7	2.3
dppf	99.07 [‡]	118	5	97.6	99.0	1.0
DPEphos	102.7	114	5	98.4	99.7	0.3
3	106.5	91	20	97.5	99.6	0.4
5	110.0	22	20	92.1	100.0	0.0

Conditions: 0.01 mmol $\text{Pd}(\text{DBA})_2$, 0.02 mmol ligand, 1.0 mmol of **2**, 2.0 mmol of **3** in 3.0 ml DMF, $T = 20^\circ\text{C}$. The 95% confidence interval of the mean measured values is $\pm 0.1\%$.

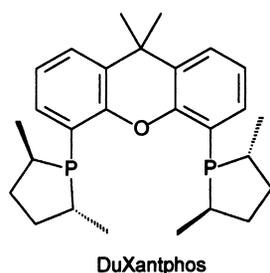
* Initial turn-over frequency, mol/mol Pd/hr, determined after 5 min reaction time.

[†] Based on **2**.

[‡] P-Pd-P angle in X-ray of (dppf) PdCl_2 [32].

The formation of linear product is the result of a nucleophilic attack on the unsubstituted carbon atom of the allyl moiety. In the transition state, the hybridisation of this carbon atom changes from sp^2 to sp^3 , which results in a bending of the propyl group towards the phosphine. This causes steric interference of the propyl group with the diphosphine ligand. The positive effect of large bite angles on the selectivity is a result of increased steric interaction of the phenyl substituents of the ligand with the substrate. Recent work has shown that replacing the propyl group by a methyl group leads indeed to lower linearities (60–80%) [33]. The increasing embracement of the allyl fragment at large bite angles not only dictates the regioselectivity, but it increasingly hampers the reaction. It is therefore not surprising, that the initial turnover frequencies decrease when the natural bite angle of the diphosphine used becomes 100° or larger.

Recently, chiral variants of Xantphos ligands were reported [35] containing phospholane groups as introduced by Burk in DUPHOS ligands [36]. The new DuXantphos ligands turned out to be very versatile, giving high enantiomeric excesses in many reactions including kinetic resolution of O-acetylcyclohex-2 enol (Scheme 5). A late transition state was proposed with restricted rotation of the alkene in the palladium-ligand adduct, to which the enantioselectivity was ascribed.



Scheme 5

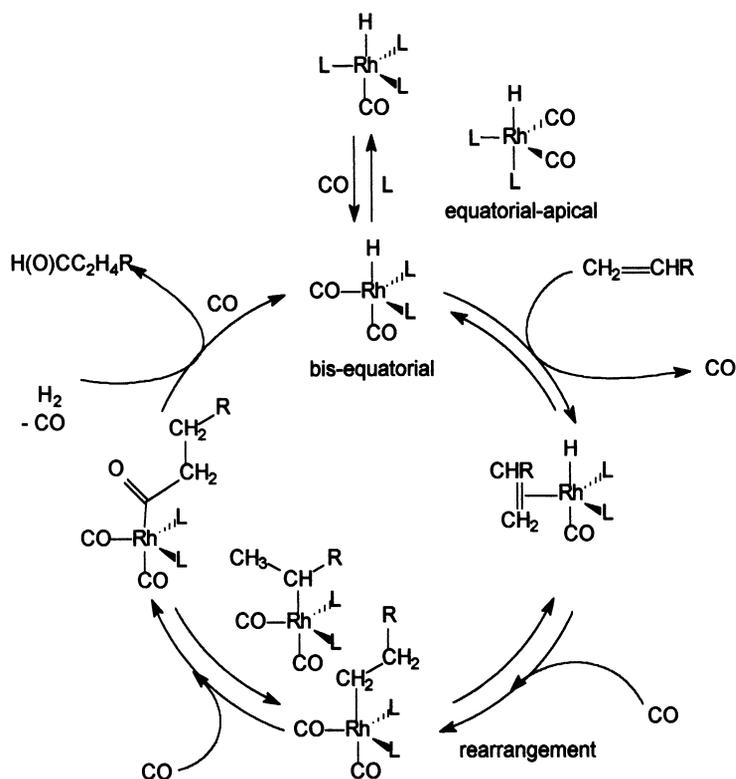
HYDROFORMYLATION

Rhodium catalysed hydroformylation of alkenes is a mild and clean method for the functionalization of hydrocarbons. The atom economy of the reaction is 100% and the selectivity for the desired aldehyde can be very high. Hydroformylation of alkenes is one of the most important homogeneously catalysed reactions in industry [1].

The generally accepted mechanism for the rhodium triphenylphosphine catalysed reaction as originally proposed by Heck & Breslow is shown in Scheme 6. The active catalyst is a trigonal bipyramidal hydrido-rhodium complex, which usually contains two phosphorus donor ligands. Under actual reaction conditions the rate limiting step is often the displacement of a carbonyl ligand by the incoming alkene, which explains the observed negative order in CO pressure and the positive order in alkene concentration.

Mechanistic studies have shown that the triphenylphosphine based catalyst has two isomeric structures in which the phosphine ligands coordinate in a bis-equatorial (e-e) fashion and an equatorial-apical (e-a) fashion. Bidentate ligands can give rise to these two types of bipyramidal complexes, Scheme 6, depending on their natural bite angle. The majority of diphosphines known in literature contain a bridge between the two phosphorus atoms consisting of 2, 3 or 4 carbon atoms. The preferred valence angle of these ligands is around 90° and as a result an equatorial-apical coordination mode predominates in these complexes. Studies of rhodium diphosphite catalysts have shown that often the highest selectivities for the linear aldehyde in the hydroformylation of 1-alkenes are obtained using bisequatorial coordinating ligands [34].

It was emphasised that diphosphine ligands that enforce bite angles around 120° would stabilise the bisequatorial coordination mode in the trigonal bipyramidal Rh(I) complexes. Casey and co-workers were the first to report that the bite angle of bidentate diphosphines can have a dramatic influence on the regioselectivity of the rhodium catalysed hydroformylation of 1-alkenes [12,13]. They studied in detail a ligand developed by workers at Eastman, 2,2'-bis((diphenylphosphino)methyl)-1,1'-biphenyl (BISBI, 8)



Scheme 6 Hydroformylation of alkenes.

and found that the bite angle of this ligand is $\approx 120^\circ$ and that the preferential mode of co-ordination is bisequatorial. For the bis-equatorially coordinated BISBI, a linear to branched aldehyde ratio as high as 66:1 was reported, while equatorially apically coordinating dppe gave a linear to branched ratio of only 2:1. Most likely the bite angles of the ligands are responsible for the observed selectivities, but no detailed study had been done on the effect of subtle changes of the bite angle in a series of ligands with similar electronic properties and steric size, thus solely examining the influence of the bite angle. The series of xanthene based diphosphine ligands designed in our group were thought to be very suitable for studying the bite angle effect for this reaction [5].

We tested the selectivity of our ligands in the rhodium catalysed hydroformylation of 1-octene (Table 4) [5]. DPEphos, having a calculated natural bite angle of 102.2° induced an enhanced, though

Table 4 Hydroformylation of 1-octene*

Ligand	β_n	Linear/ branched	% Linear aldehyde	% isomerization	Reaction rate [†]
DPEphos	102	6.7	87.0	0	250
3	109	34	94.2	3	168
4	109	41	93.0	4.7	445
5	112	53.5	97.7	0.5	800
DBFphos	131	3	71	5.5	125
BISBI	123	80.5	89.6	9.3	850

* Conditions: $T = 80^\circ\text{C}$, $\text{CO}/\text{H}_2 = 1$, total pressure 10 bar, substrate/Rh = 674, ligand/Rh = 2.2, $[\text{Rh}] = 1.78 \text{ mM}$. No hydrogenation product was observed.

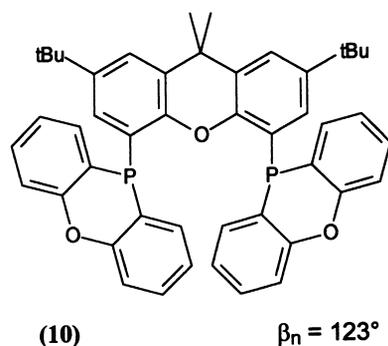
[†] Expressed as the turnover frequency (mol aldehyde/mol Rh/h).

moderate selectivity (compared to most diphosphines), but no isomerisation was detected. The ligands with a one atom bridge between the aromatic rings of the backbone **1–9** have calculated natural bite angles near 110° and showed a very high regioselectivity and a very low rate of isomerisation to internal alkenes. DBFphos [18], having a calculated natural bite angle of 131.1° proved not to be very selective, probably because the bite angle was too large to form a chelating complex. The ultimate test for a catalyst to check its selectivity towards the linear aldehyde is the hydroformylation of styrene, since this is a substrate with a distinct preference for the formation of the branched aldehyde due to the stability of the 2-alkyl-rhodium species, induced by the formation of an η^3 -benzyl complex. The hydroformylation of styrene with (**5**)Rh (our most selective catalyst) resulted in relatively high selectivity for the linear aldehyde (a linear to branched ratio of 2.35 was obtained).

Under these mild reaction conditions, the selectivities toward the linear aldehyde observed for **3–4** and especially **5** are considerably higher than that observed for BISBI. This is mainly due to the very low amount of isomerisation of 1-octene. The linear to branched ratios of our ligands are very close to that of BISBI. Furthermore, no hydrogenation was observed. Even though the linear to branched ratio is 80.5 for BISBI, the selectivity towards the linear aldehyde amounts to only 89.6% due to the relatively high isomerisation of 1-octene to 2-octene (under these conditions).

The catalytically active complexes could be synthesised by facile exchange of PPh_3 in $(\text{PPh}_3)_3\text{Rh}(\text{H})(\text{CO})$ with the diphosphines. Subsequent bubbling CO through a solution of (diphosphine)Rh(H)(CO)(PPh₃) led to displacement of the remaining PPh₃. Recent *in situ* high-pressure IR experiments [37] have shown that ligands **1–9** form mixtures of bis-equatorial and equatorial-apical isomers, which rapidly equilibrate. Especially for ligands having small bite angles and electron donating substituents the proportion of the 'unwanted' e-a isomer can be substantial, but the preference for linear aldehyde remains relatively high for such systems.

Xantphos ligands having still wider bite angles are obtained when rigid, cyclic substituents are used, as in **10** (Scheme 7). The wide bite angle now leads to a high propensity to isomerisation, while the high selectivity to linear product is retained. As a result internal alkenes can now be hydroformylated to linear aldehydes [38]. For octene-2 the linear to branched ratio is 9 and for octene-4 this value is 4.4 (conditions: 120°C , 2 bar CO/H₂, ligand/Rh = 5, octene/Rh = 637, [Rh] = 1 mM). At higher pressures of CO less linear aldehyde is formed, because the rate of isomerisation decreases. This is the first rhodium catalyst containing phosphines giving such high selectivity for linear aldehydes from internal alkenes. Certain phosphites have been known for quite some time to give such selectivities [39].



Scheme 7

CONCLUSION

The bite angle of bidentate ligands is an important additional parameter that has a pronounced effect on rate and selectivity of metal catalysed reactions. The diphosphine ligands based on xanthene backbone, inducing large bite angles, give unprecedented selectivities and reactivities in several important reactions. This can be achieved by the stabilisation of a crucial intermediate of the reaction cycle, as was shown in

the hydrocyanation reaction in which a tetrahedral complex was stabilised. Also in the hydroformylation reaction stabilisation of the desired bis-equatorial coordination mode in a trigonal bipyramidal starting rhodium complex was found to be predominant. Steric interactions between the ligand and the substrate were shown to result in high selectivities for the linear product in the palladium catalysed allylic alkylation.

REFERENCES

- 1 B. Cornils, W. A. Herrmann, eds. *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH Weinheim: New York/Basel/Cambridge/Tokyo (1996).
- 2 G. W. Parshall, S. D. Ittel. *Homogeneous Catalysis: the Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd edn. Wiley, New York (1992). P. W. N. M. van Leeuwen, G. van Koten. *Catalysis an Integrated Approach to Homogeneous Heterogeneous & Industrial Catalysis* (J. A. Moulijn, P. W. N. M. van Leeuwen R. A. van Santen, eds), Chap. 6. Elsevier, Amsterdam (1995).
- 3 P. W. N. M. van Leeuwen, K. Morokurna, J. H. van Lenthe, eds. *Theoretical Aspects of Homogeneous Catalysis; Applications Of Ab Initio Molecular Orbital Theory*. Kluwer Academic Publishers, Dordrecht (1995).
- 4 C. A. Tolman. *Chem. Rev.* **77**, 313 (1977).
- 5 M. Kranenburg, Y. E. M. van der Burgt, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje. *Organometallics* **14**, 3081 (1995).
- 6 W. Goertz, P. C. J. Kamer, P. W. N. M. van Leeuwen, D. Vogt, W. Keim. *Chem. Commun.* 1521 (1997).
- 7 M. Kranenburg, P. C. J. Kamer, P. W. N. M. van Leeuwen, D. Vogt, W. Keim. *Chem. Commun.* 2177 (1995).
- 8 P. C. J. Kamer, P. W. N. M. van Leeuwen. In *Organic Synthesis Via Organometallics* (G. Helmchen, J. Dibo, D. Flubacher, B. Wiese, eds), p. 229. Vieweg, Braunschweig/Wiesbaden (1997).
- 9 M. Kranenburg, P. C. J. Kamer, P. W. N. M. van Leeuwen, B. Chaudret. *Chem. Commun.* **3**, 73 (1997).
- 10 M. Kranenburg, P. C. J. Kamer, P. W. N. M. van Leeuwen. *Eur. J Inorg. Chem.* 25 (1998).
- 11 M. Kranenburg, P. C. J. Kamer, P. W. N. M. van Leeuwen. *Eur. J Inorg. Chem.* 155 (1998).
- 12 C. P. Casey, G. T. Whiteker. *Isr. J. Chem.* **30**, 299 (1990).
- 13 C. P. Casey, G. T. Whiteker, M. G. Melville, L. M. Petrovich, J. A. Gavney, D. R. Powell. *J. Am. Chem. Soc.* **114**, 5535 (1992).
- 14 G. Zhu, X. Zhang. *J. Org. Chem.* **63**, 3133 (1998).
- 15 D. L. Thorn, R. Hoffmann. *J. Am. Chem. Soc.* **100**, 2079 (1978).
- 16 K. Angermund, W. Baumann, E. Dinjus, R. Fornika, H. Görls, M. Kessler, C. Krüger, W. Leitner, F. Lutz. *Chem. Eur. J.* **3**, 755 (1997).
- 17 P. Dierkes, P. W. N. M. van Leeuwen. *J. Chem. Soc. Dalton Trans* 1519 (1999).
- 18 M. W. Hünel, D. Jakubik, E. Rothenberger, G. Schroth. *Chem. Ber.* **124**, 1705 (1991).
- 19 E. S. Brown. In *Aspects Of Homogeneous Catalysis* (R. Ugo, ed.), Vol. 2, pp. 57–78 Reidel (1974); W. C. Drinkard Jr. German Patent OLS 1,806,096; Netherlands Patent 68 15560; Belgian Patent 723,126; *Chem. Abstr.* **71**, 30092 (1969).
- 20 P. Albanese, L. Benzoni, G. Carniso, A. Crivelli. Italian Patent 869,900; *Chem. Abstr.* **78**(13), 5701 (1973).
- 21 P. S. Elmes, W. R. Jackson. *Aust. J. Chem.* **35**, 2041 (1982).
- 22 W. Keim, A. Behr, H.-O. Lühr, J. Weißer. *J. Cat.* **78**, 209 (1982).
- 23 R. J. McKinney, D. C. Roe. *J. Am. Chem. Soc.* **108**, 5167 (1986).
- 24 J. E. Bäckvall, O. S. Andell. *Organometallics* **5**, 2350 (1986).
- 25 A. L. Casalnuovo, T. V. RajanBabu, T. A. Ayers, T. H. Warren. *J. Am. Chem. Soc.* **116**, 9869 (1994).
- 26 W. Keim, A. Behr, J. P. Bioul, J. Weißer. *Erdöhl, Kohle, Erdgas, Petrochemie* **35**, 436 (1982).
- 27 J. Tsuji, H. Takahashi, M. Morikawa. *Tetrahedron Lett.* 4387 (1965).
- 28 B. M. Trost, T. Verhoeven. *Comprehensive Organometallic Chemistry* (G. Wilkinson, ed.), p. 799, Vol. 8. Pergamon, Oxford, UK (1982).
- 29 B. M. Trost, B. Breit, S. Peukert, J. Zambrano, J. W. Ziller. *Angew. Chem. Int. Eds. Engl.* **34**, 2386 (1995).
- 30 M. P.T. Sjögren, S. Hansson, B. Åkermark, A. Vitagliano. *Organometallics* **13**, 1963 (1994).

- 31 B. M. Trost, D. J. Murphy. *Organometallics* **4**, 1143 (1985).
- 32 T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Kguchi, K. Hirotsu. *J. Am. Chem. Soc.* **106**, 158 (1984).
- 33 R. J. van Haaren, H. Oevering, B. B. Coussens, G. P.F. van Strijdonck, J. N.H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen. *Eur. J. Inor. Chem* (1999).
- 34 P. W. N. M. van Leeuwen, G. J. R. Buisman, A. van Ropy, P. C. J. Kamer. *Recl. Trav. Chim. Pays-Bas* **113**, 61 (1994).
- 35 P. Dierkes, S. Ramdeehul, L. Barloy, A. De Cian, J. Fischer, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. A. Osborn. *Angew. Chem. Int. Engl. Ed.* **37**, 3116 (1998); S. Ramdeehul, P. Dierkes, R. Aguado, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. A. Osborn. *Angew. Chem Int. Engl. Ed.* **37**, 3118 (1998).
- 36 M. J. Burk, M. F. Gross. *Tetrahedron Lett.* **35**, 9363 (1994).
- 37 L. A. van der Veen, M. D.K. Boele, F. Bregman, P. C. J. Karner, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, H. Schenk, C. Bo. *J. Am. Chem. Soc.* **120**, 11616 (1998).
- 38 L. A. van der Veen, P. C. J. Kamer, P. W. N. M. van Leeuwen. *Angew. Chem. Int. Ed. Engl.* **38**, 336 (1999).
- 39 P. W. N. M. van Leeuwen, C. F. Roobeek. British Patent Application 2,068,377 (1980).