Accounts

Bite Angle Effects in Hydroformylation Catalysis†

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Recent advances in rhodium catalyzed hydroformylation using xanthene-based ligands will be reviewed. The calculated natural bite angles of the ligands discussed are in the range 100—123°. While the general trend is clear—higher l:b ratios at wider angles, small changes in the bite angle do not exhibit a regular effect on the selectivity of the reaction. The same is true for the rate of CO dissociation; the larger the rate of the CO dissociation, the larger the rate of hydroformylation, but for small changes the effects do not comply with this rule.

Keywords Bite angle effects, hydroformylation, xanthene-based Ligand

Introduction

Homogeneous catalysis with organo-transition metal complexes has become increasingly important in the process industry.[1] The development of organo-transition 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 organo-transition metal complexes is dependent on the ligand environment of the metal. By changing the ligands the performance of the catalyst can be directed and sometimes the effects can even be predicted. 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 organo-transition metal chemistry has evolved catalyst development from trial and error into rational design.

Recently, emphasis has been put on the influences of specific geometries of ligands around the catalytic center on the rate and selectivity of the reaction.[5-14] A reaction path can be influenced by ligands that stabilize selectivcly thc initial geometry, the transition state or the final geometry of a complex. For instance the course and rate of catalytic reactions can be directed by forcing the geometry of the complex towards a structure that resembles the transition state.

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, stabilize 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 destabilize 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 but also even alternative reaction pathways can become accessible. Already in the late seventies 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]

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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 favoring bite angles around 110° can be used to stabilize a bisequatorial coordination mode in trigonal bipyramidal Rh(I) complexes. Also these ligands tend to stabilize 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 center.[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 rhodium catalyzed hydroformylation as an example of such effect in catalytic reactions that are optimized 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 and Whiteker,[12] are useful parameters that 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 which can be reached within an energy barrier of 12.56 kJ·mol^{-1}. 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 actual 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 in 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 *ca*. 35°. It should be noted that the absolute values of the calculations will be dependent on the used force field, but the relative results and, therefore, the observed trends will be the same.

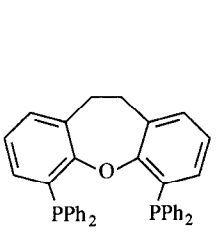
Table 1 Natural bite angles (β) and the flexibility range calculated for the xantphos ligands

X, in bridge	Ligand	β_n, deg.	Flexibility range
H,H	DPEphos	102	86—120
C_2H_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

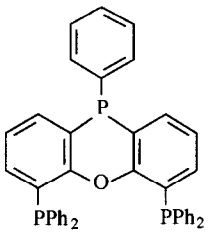
The X-ray crystal structure of the free Xantphos ligand shows that only very little adjustment of the structure is necessary to form a chelate; the orientation of the diphenyl-phosphine-moieties is nearly ideal. The observed P··P distance in the free ligand is 0.408 nm, while MM studies indicate that a decrease of the P··P distance to 0.384 nm is necessary for chelation with a P-Rh-P angle of 112°, a decrease of only 0.024 nm. 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 *ca*. 166° 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.

The ligands **1**—**9** have been applied in a variety of catalytic reactions, such as hydrocyanation of alkenes,

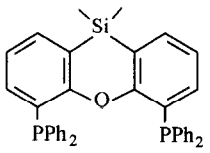
allylic alkylations, cross coupling reactions,[5-14, 18-20] *etc*. In hydrocyanation and hydroformylation the effect was according to expectations.[5-7] The results in palladium chemistry were often not as expected, but recently for allylic alkylation we have come to grip with the chemistry.[20] In other coupling reactions the outcome remains unpredictable, but trial and error often turns out to be worthwhile.



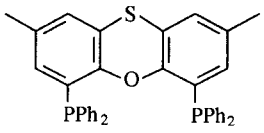
Homoxantphos (**1**)



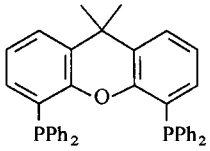
Phosxantphos (**2**)



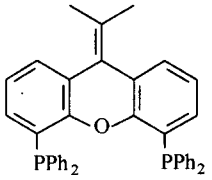
Sixantphos (**3**)



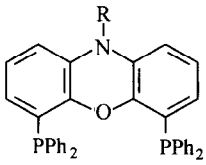
Thixantphos (**4**)



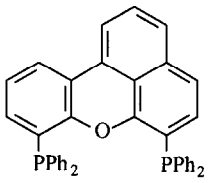
Xantphos (**5**)



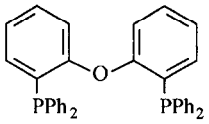
Isopropxantphos (**6**)



R=Bn, Benzylnixantphos (**7**)
R=H, Nixantphos (**8**)



Benzoxantphos (**9**)



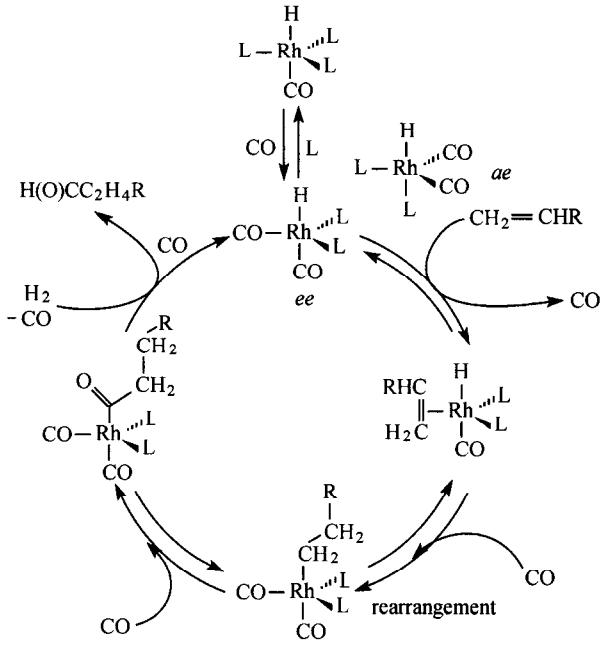
DPEphos

Hydroformylation

1-*Alkenes* Rhodium catalyzed 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 catalyzed reactions in industry.[1]

The generally accepted mechanism for the rhodium triphenylphosphine catalyzed reaction as originally proposed by Heck and Breslow is shown in Scheme 1. 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 triphenylphosphine based catalyst has two isomeric

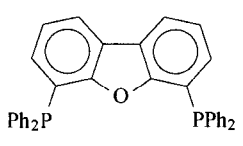
Scheme 1 Rhodium catalyzed hydroformylation



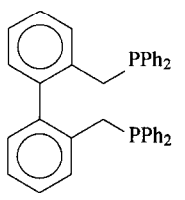
structures in which the phosphine ligands coordinate in a bis-equatorial (*ee*) fashion and an equatorial-axial (*ae*) fashion. Bidentate ligands can give rise to these two types of bipyramidal complexes, Scheme 1, depending on their natural bite angle. The majority of diphosphines known in literature 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.[21]

It was emphasized that diphosphine ligands that enforce bite angles around 120° would stabilize the bisequatorial coordination mode in the trigonal bipyramidal Rh(I) complexes. Casey and coworkers were the first to report that the bite angle of bidentate diphosphines can have a dramatic influence on the regioselectivity of the rhodium catalyzed 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) and found that the bite angle of this ligand is ~ 120° and that the preferential mode of co-ordination is bisequatorial. For the bisequatorially coordinated BISBI, a linear to branched aldehyde ratio as high as 66:1 was reported, while equatorially-axially coordinating dppe gavea 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 base bisphosphine ligands designed in our group were thought to be very suitable for studying the bite angle effect for this reaction.[5,22] We tested the selectivity of our ligands in the rhodium catalyzed hydroformylation of 1-octene (Table 2).



DBFphos



BISBI

DPEphos, having a calculated natural bite angle of 102°, induced an enhanced, though moderate selectivity (compared to mostdiphosphines), but no isomerization was detected. The ligands with an one-atombridge 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 isomerization to internal alkenes. DBFphos (dibenzofuran backbone),[23] having a calculated natural bite angle of 131°, 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 rhodium catalyzed hydroformylation of styrene using **5** (our most selective catalyst) resulted in relatively high selectivity for the linear aldehyde (a linear to branched ratio of up to 2.35 was obtained).

Under these mild reaction conditions, the selectivities toward the linear aldehyde observed for **3**—**9** and especially **9** 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, as at lower temperatures BISBI show no isomerization at all).

In order to know the intrinsic preference of a catalyst for linear alkyl formation we report the selectivity for linear aldehyde calculated by including the amount of 2-octene side product. Scheme 2 shows how the side product 2-octene can improve the l:b ratio. The linear alkyl is mainly converted to linear aldehyde, while the branched alkyl partially generates 2-octene. Since 2-octene is far less reactive in the hydroformylation, its formation is irreversible on the time-scale of the experiments.

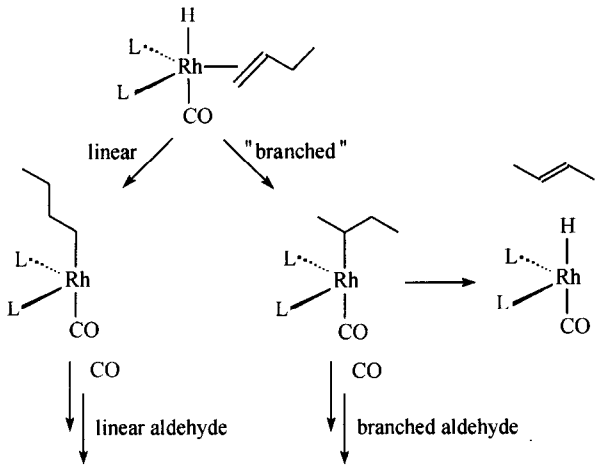
The catalytically active complexes could be synthesized by facile exchange of PPh_3 in $(PPh_3)_3Rh(H)(CO)$ with the diphosphines. Subsequent bubbling CO

Table 2 Hydroformylation of 1-octene using xantphos ligands

Ligand	β_n, deg.	l:b ratio[b]	Linear aldehyde (%)[b]	Isomer (%)[b]	Tof[b,c]
DPEphos[d]	102	6.7	87.0	0	250
1	102	8.5	88.2	1.4	37
2	108	14.6	89.7	4.2	74
3	109	34.6	94.3	3.0	81
4	110	50.0	93.2	4.9	110
5	111	52.2	94.5	3.6	187
6	113	49.8	94.3	3.8	162
7	114	50.6	94.3	3.9	154
8	114	69.4	94.9	3.7	160
9	121	50.2	96.5	1.6	343
DBFphos[d]	131	3	71	5.5	125
BISBI[d]	123	80.5	89.6	9.3	850

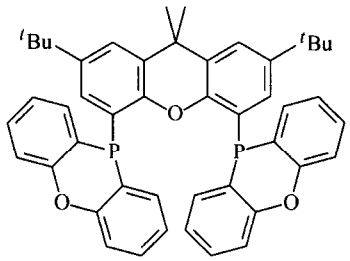
[a] Conditions: $CO/H_2 = 1$, $P(CO/H_2) = 2 \times 10^6$ Pa, ligand/Rh = 5, substrate/Rh = 637, [Rh] = 1.00 mol/L, number of experiments = 3. In none of the experiments was hydrogenation observed. [b] Linear over branched ratio, percent linear aldehyde, percent isomerization to 2-octene, and turnover frequency were determined at 20% alkene conversion. [c] Turnover frequency = (mol of aldehyde) (mol of Rh)$^{-1}$ h^{-1}. [d] $P(CO/H_2) = 10^6$ Pa

Scheme 2 Formation of 2-alkene



through a solution of (diphosphine)Rh(H)(CO)(PPh_3) led to displacement of the remaining PPh_3. Recent in situ high-pressure IR experiments (vide infra) 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" *ea* isomer can be substantial, but the preference for linear aldehyde remains relatively high for such systems.

2-Alkenes Xantphos ligands having still wider bite angles are obtained when rigid, cyclic substituents are used, as in **10**. 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.[24,25] For octene-2 the linear to branched ratio is 9 and for octene-4 this value is 4.4 (conditions: 120℃, 2×10^5 Pa CO/H_2, ligand/Rh = 5, octene/Rh = 637, [Rh] = 1 mmol/L). 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. Fluoroalkyl phosphites have been known for quite some time to give such selectivities[26] and in the last decade many diphosphites have been reported which do the same.[27-29]



10 $\beta_n = 123°$

Mechanistic studies The detailed mechanism governing the higher linearity for wider bite angles is still unclear. The rate-determining step in the hydroformylation of 1-octene with xantphos-type ligands is in an early stage in the catalytic cycle. Dissociation of CO, alkene coordination, and migratory insertion are relevant for the determination of the rate. So far, only the first step has been studied separately.[22,30] An experimental set-up was introduced enabling the measurement of the rate con-

stants for CO dissociation from the (diphosphine)-Rh $(CO)_2H$ complexes. By changing the ^{12}CO ligands for isotopically pure ^{13}CO ligands, the carbonyl absorptions in the IR spectra of the (diphosphine)$Rh(CO)_2H$ complexes shift 30—40 cm^{-1} to lower energy.

The rate constants k_1 for the dissociation of ^{13}CO from the (diphosphine)$Rh(^{13}CO)_2H$ complexes were determined by monitoring the exchange of ^{13}CO for ^{12}CO by exposing the ^{13}CO labeled complexes to a large excess of ^{12}CO, so any dissociated ^{13}CO will be replaced quantitatively by ^{12}CO.

To investigate the possible effect of the natural bite angle on the rate of CO dissociation from the (diphosphine)$Rh(CO)_2H$ complexes ^{13}CO exchange was measured for complexes containing ligands **2**, **4** and **6**. The exchange of ^{13}CO for ^{12}CO in the (diphosphine)Rh-$(^{13}CO)_2H$ complexes was monitored by rapid-scan HP IR spectroscopy at 40℃. The $^{13}CO/^{12}CO$ exchange was initiated by adding a large excess of ^{12}CO. The difference between the reactivity of the *ee* and *ea* isomers of the (diphosphine)$Rh(^{13}CO)_2H$ complexes cannot be determined, since the exchange between ee and ea isomers is several orders of magnitude faster than the rates of ^{13}CO dissociation, as is evident from the NMR spectra. The observed rate constants, k_1, are listed in Table 3.

Table 3 Kinetics of ^{13}CO dissociation of (diphosphine)$Rh(^{13}CO)_2H$ complexes[a]

Ligand	β_n, deg.	P (^{12}CO), 10^5 Pa	k_1, h^{-1}	Rate[c]
2	108	25	177	74
4	110	25	206	110
4[b]		25	200	
6	113	20	182	162
6		25	185	
6		30	181	
10	123	25	1200	1560

[a] Reaction conditions: [(diphosphine)$Rh(^{13}CO)_2H$] = 2.00 mmol/L in cyclohexane, $P(^{13}CO) = 1 \times 10^5$ Pa, $P(H_2) = 4 \times 10^5$ Pa, T = 40℃, diphosphine/Rh = 5. [b] [(diphosphine)Rh-$(^{13}CO)_2H$] = 3.00 mmol/L. [c] Rate of hydroformylation at 80℃, 2×10^6 Pa.

It is commonly accepted that CO exchange in (diphosphine)$Rh(CO)_2H$ complexes proceeds *via* the dissociative pathway. The decay of the carbonyl resonances of the (diphosphine)$Rh(^{13}CO)_2H$ complexes indeed followed simple first-order kinetics. This clearly confirms that reformation of the (diphosphine)Rh-$(^{13}CO)_2H$ complex via k_{-1} pathway is suppressed effectively, and all dissociated ^{13}CO is replaced by ^{12}CO. The experiments with ligand **6** at different ^{12}CO partial pressure show that the rate of CO displacement is independent of the CO pressure. Furthermore, the rate is also independent of the (diphosphine)$Rh(^{13}CO)_2H$ complex concentration, as demonstrated by the experiments with ligand **4**. It can therefore be concluded that CO dissociation for these complexes proceeds by a purely dissociative mechanism and obeys a first-order rate-law.

Table 3 shows that there is only a weak correlation between the rate of CO dissociation and the natural bite angle. The rate constants k_1 for ligands **2**, **4**, and **6** do not differ significantly and cannot explain the trend inobserved hydroformylation activities. Ligand **10** gives both the fastest CO exchange as the rate of hydroformylation. The comparison of the k_1 values for ligand **2**, **4**, **6** and **10** with the turnover frequencies depicted in Table 3, reveal that the rates of CO dissociation, measured at 40℃, are higher than the hydroformylation rates at 80℃. Since reaction rates increase approximately at most an order of magnitude with a temperature rise of 20 degrees, the CO dissociation rate at 80℃ is at most 100 times as fast as the hydroformylation reaction, *i.e.* CO dissociation represents a considerable part of the activation barrier.

In this study no influence of the natural bite angle on the rate of formation of the (diphosphine)$Rh(CO)H$ complexes (k_1) was found, implying that the activation energy for the formation of these complexes is not affected significantly. Therefore, the increase in hydroformylation rate with increasing bite angle must originate from an increase in the concentration of these four-coordinate complexes, or from a decrease in the activation energy for alkene coordination (if this step were rate-determining), or a lower energy of the alkene complex, or a faster migratory insertion.

It is not likely that increasing the bite angle would lower the activation energy for alkene coordination. Increasing the bite angle results in increased steric congestion around the rhodium center and consequently in more steric hindrance for the alkene entering the coordination sphere. What kind of electronic effect the widening of the bite angle has on the activation energy for alkene coordination is unclear, since it depends on the bonding mode of the alkene. Rhodium to alkene back-donation is

promoted by narrow bite angles, while alkene to rhodium donation is enhanced by wide bite angles.

Widening the bite angle of a *cis* bidentate in a square planar complex would certainly accelerate a migration reaction, but is is not clear how this would work out in a trigonal bipyramid having the diphosphine as a bis-equatorial ligand.

Conclusion

The bite angle of bidentate ligands is an important additional parameter that has a pronounced effect on rate and selectivity of metal catalyzed reactions. The diphosphine ligands based on xanthene backbone, inducing large bite angles, give unprecedented selectivities and reactivities in several important reactions. For hydroformylation this can be achieved by the stabilization of the desired bisequatorial coordination mode in a trigonal bipyramidal starting rhodium complex or stabilization of a crucial intermediate of the reaction cycle that escapes direct observation. The former turned out to be not essential and most likely steric interactions between the ligand and the substrate at a later stage of the reaction result in high selectivities for the linear product.

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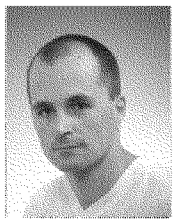

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