

Review

Coordination geometry and bio-inspired ligands: useful concepts in homogeneous catalysis? A conceptual view

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In honour of the 70th birthday of Professor Josef J. Ziolkowski.

Abstract

It is a truism that ligands play a dominant role in homogeneous transition metal based catalysis. However, finding and predicting the right ligand, to a large extent, is still determined by trial and error. To practise homogeneous catalysis a better concept of general applicability is needed.

The coordination geometry seems to play an important role. Bidentate and tridentate ligands are presented postulating that a distinguished coordination geometry is required for catalysis to occur.

Monodentate ligands based on trivalent phosphorus have been studied extensively, whereas oxygen-, nitrogen- and sulphur-containing ligands have been neglected compared to phosphorus. Based on our research carried out over many years a conceptual view by the author is given presenting O–O, S–O, N–O, N–N–N, P–N–P and S–N–S ligands and elucidating to their catalytic behaviour. It is recommended for future research to pay more attention to the coordination geometry and to bio-inspired ligands.

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Keywords: Bio-inspired ligands; Ligands; Olefins; Coordination geometry in catalysis

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1. Introduction

Homogeneous, transition metal-based catalysis has seen a rapid and prosperous growth in the past decades. This success was certainly stimulated and supported by organometallic chemistry, which is the scientific backbone. In spite of all the advancements, which have been made, selecting and tailoring ligands to a large extent, is still determined by trial and error.

To practise homogeneous catalysis a better concept of understanding and general applicability is needed. If one looks at bio-catalysis based on metals two things are obvious: (a) nature prefers multidentate ligands; (b) nature prefers oxygen-, nitrogen- and sulphur-containing ligands.

Looking back at more than 40 years of experience in homogeneous catalysis, I want to emphasize two concepts, which I feel have been neglected in the past:

- impact of coordination geometry,
- use of bio-inspired ligands.

For experimental details see the references given.

2. Impact of coordination geometry

Bonding/coordination and dissociation of ligands are general principles guiding ligand design. They determine the coordination geometry and the geometry changes. For instance, depending on the nature of ligands nickel complexes with the coordination number of four can be square planar or tetrahedral. An equilibrium exists between the two isomers as is well demonstrated in the literature. In [Scheme 1](#) examples for four and five coordinated complexes and their structures are

Four coordination (square planar versus tetrahedral)

nickel acetylacetonate	Ni(CO) ₄
square planar	tetrahedral
NiCl ₂ [Ph ₂ P(CH ₂) ₂ PPh ₂]	NiCl ₂ [Ph ₂ P(CH ₂) ₃ PPh ₂]
square planar	tetrahedral

Five coordination (trigonal bipyramidal versus square pyramidal)

Fe(CO) ₅	Co(TPN) ₂
trigonal bipyramidal	square pyramidal
Ni(TPN) ₂	
trigonal bipyramidal	
TPN = N[CH ₂ CH ₂ P(C ₆ H ₅) ₂] ₃	

Scheme 1. Examples for four and five coordinated complexes.



Scheme 2. Bidentate ligand in *cis* and *trans* coordination.

shown. Five coordinated complexes can be trigonal bipyramidal and square pyramidal.

[Scheme 1](#) contains monodentate (carbon monoxide), bidentate (acetylacetonate) and tridentate (TPN) ligands.

In the past many monodentate ligands have been studied in great detail. Bidentate, in particular multidentate ligands have not attracted the same attention. For instance, the major share of homogeneous catalysts applied by industry is based on monodentate phosphorus ligands as is evident from hydroformylation based on XRh(CO)(R₃P)₂ complexes. Only lately, ligands such as cyclopentadienyl (as metallocenes) or ligands containing multibidentate nitrogen groups have found practical application.

2.1. Bidentate ligands

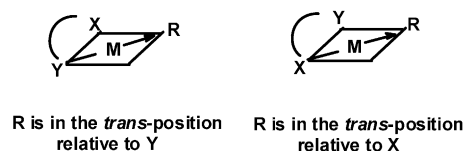
Since 1965, we are investigating the potential of bidentate ligands in C–C-linkage reactions of olefins. Our interest centered around unsymmetrical chelate ligands possessing electronically non-identical heteroatoms X–Y. The preferred metal was four-fold coordinated nickel. In square planar structures, the ligand X–Y can coordinate in *cis* and *trans*-position ([Scheme 2](#)).

If the bonding occurs in *cis*-position, one can differentiate whether a group R is in *cis*- or *trans*-position with respect to X and Y as is shown in [Scheme 3](#).

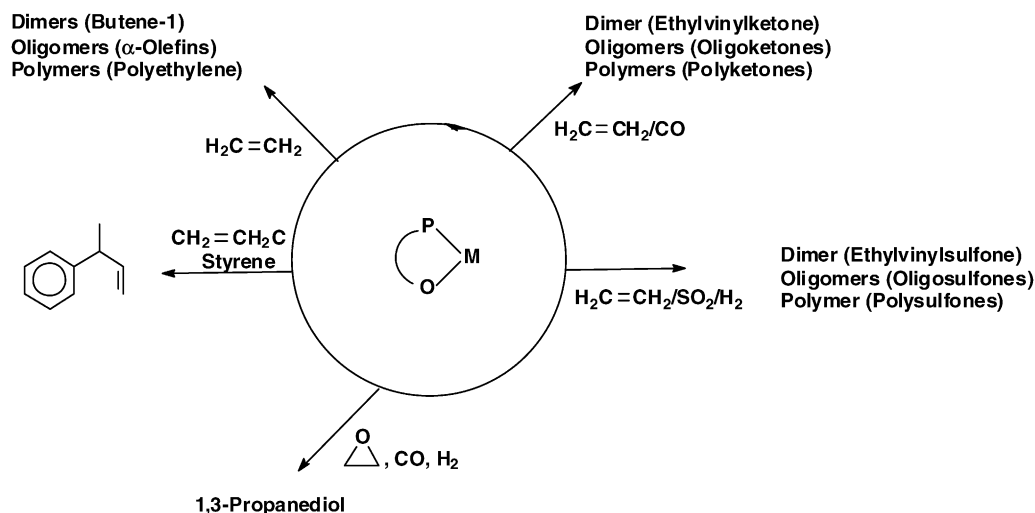
In consecutive reactions, for instance insertions, it can be important whether the group R stands *trans* to X or *trans* to Y (*trans* effect).

In addition, the bonding in bidentate ligands X–Y can be hemilabile opening a pathway to switch the *cis* and *trans* positions.

The working horse in our studies has been the heteroditopic bidentate ligand P–O [1]. Surprisingly, this ligand



Scheme 3. Bidentate ligands stabilising *cis* or *trans* positions.



Scheme 4. P–O-ligands in C–C-linkage reactions.

can be used to catalyse a variety of reactions depicted in Scheme 4.

With ethylene butene-1 or linear α -olefins (SHOP-process of Shell) or polyethylene can be obtained [1,2].

The reaction of ethylene with carbon monoxide yields ethylvinylketone, oligoketones and/or polyketones [3,4].

Olefins and SO_2/H_2 yield sulfonic acids a reaction paralleling hydroformylation [5]. In addition, ethylene reacts with SO_2 giving *trans*-but-2-enylsulfone and/or polysulfone [6].

The dimerization of ethylene and styrene results in the formation of 3-phenylbut-1-ene [7].

Finally, ethylene oxide and CO/H_2 can be converted to 1,3-propanediol [8].

The question arises: “What enables the P–O-ligand to catalyze so different reactions as shown in Scheme 4?” We believe and postulate that an explanation rests with the ability of P–O to stabilize square planarity and to coordinate in *cis*-position.

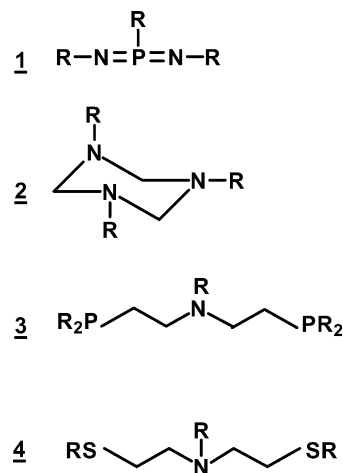
2.2. Tridentate ligands

The bonding of tridentate ligands can be very complex. For instance, they can coordinate in single, two-fold and triple mode as is known from biological systems [9]. They can be hemilabile [10] and can form bridges to two or more metals.

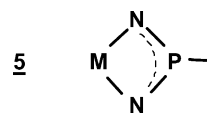
In trigonal bipyramidal complexes apical or equatorial bonding of the bidentate ligand is feasible (Berry-mechanism) [11]. In octahedral geometry meridional and facial coordination is possible. Systematic investigations with tridentate ligands in homogeneous catalysis are scarce. However, a few very interesting reactions with tridentate ligands have been reported in the literature: decarbonylation [12], dehydrogenation [13], polymerization [14,15]. Especially noteworthy in the context of this paper is the work by Gibson [15],

who has reported that five coordinated FeCl_2 complexes with 2,6-*bis*(imino)pyridine ligands can be trigonal bipyramidal or square pyramidal, which relates to their activity. Interestingly, iron analogues of Brookhart’s nickel-diimine catalysts were inactive for olefin polymerization. It was reasoned [16] that the iron’s tetrahedral coordination sphere does not allow for olefin insertion (in contrast to nickel’s square planar one).

We have looked at C–C-linkage reactions of olefins applying three heteroatoms containing ligands **1** [17], **2** [18], **3** [19] and **4** [20]

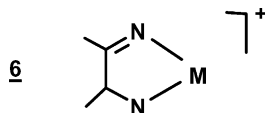


The complex **1** coordinates to nickel and palladium in square planar geometry **5**.

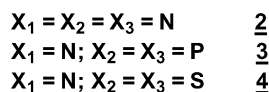
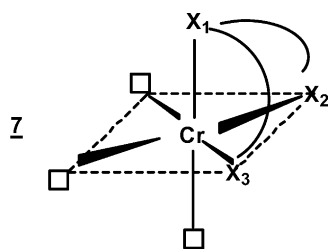


As early as 1981 we could show that **5** with ethylene yield novel polyethylenes whose physical properties lie between

those of high-pressure polyethylene and “EPDM”. G. Fink could explain that the structure of the polyethylene derived from **5** can be understood by migratory insertion (chain walking) [21]. Ten years later Brookhart reported that cationic complexes of type **6**, which show similarities to **5**, were very active in the ethylene polymerization [22]. Brookhart’s finding was a breakthrough attracting the attention to the value of ionic complexes in catalysis.



The complexes **2** [18], **5** [19] and **4** [20] in combination with chromium trimerized ethylene to 1-hexene in high yields. We postulate that this high selectivity is due to facial coordination in octahedral geometry leaving three free coordination sides for olefin coordination and concomitant trimerization as is shown in **7** [23]. To our great disappointment the X-ray structures of $\text{CrCl}_3[\text{HN}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2]$ [19] and $\text{CrCl}_3[\text{C}_2\text{H}_5\text{SCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{SC}_2\text{H}_5]$ [20] gave meridional coordination. However, it must be born in mind that these structures represent only that of the procatalyst. It is also possible that in solution or upon reaction with MAO facial coordination results.



2.3. Tetradentate ligands

Tetradentate ligands can exist in various forms:

- open-chain $[\text{H}_2\text{N}(\text{CH}_2\text{CH}_2)\text{N}(\text{CH}_2\text{CH}_2)\text{N}(\text{CH}_2\text{CH}_2)_2\text{NH}_2]$,
- cyclic (phthalocyanines, porphyrins),
- tripod $[\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3]$.

Many papers in organometallic chemistry deal with tetradentate ligands. Especially cyclic ones have been studied in oxidation reactions. Many researchers have attempted to model natural enzymes possessing tetradentate ligands like coenzyme F430 or coenzyme B₁₂ [24]. Salen complexes have been studied in asymmetric, nucleophilic and electrophilic reactions [25]. However, only a few systematic studies have been carried out with tetradentate A–B–C–D lig-

ands with various heteroatom combinations in cyclic or open structures.

3. Bio-inspired ligands

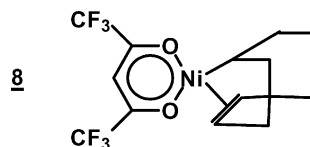
The use of P-containing ligands has been very successful in coordination chemistry and homogeneous catalysis. However, considering biological systems oxygen-, nitrogen- and sulphur-containing ligands are used. Ligands based on trivalent phosphorus, to our knowledge, are unknown. Therefore, it is strongly recommended to researchers in the field of organometallic chemistry and homogeneous transition metal based catalysis to include ligands mimicked after nature in their investigations.

In our research, we only sporadically have included “bio-inspired” ligands. The use of tridentate ligands is presented above.

In the following, some results with the bidentate ligands O–O, S–O, N–O, S–S, shedding light on catalysis amenable, will be elucidated. Some of the results have not been published outside of dissertations before, but reference is given to the experimental part.

3.1. O–O-Ligands

The reaction of *bis*cyclooctadiene nickel with hexafluoroacetylacetonate yielded complex **8** [26].

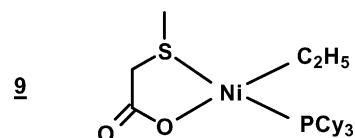


Complex **8** was active in the oligomerization of ethylene. Interestingly, **8** also dimerized α -olefins (propene, 1-butene and higher α -olefins) to highly linear dimers. To our knowledge this is the only complex known to do this [1,26].

3.2. S–O-Ligands

The reaction of *bis*cyclooctadienenickel with 2-mercaptobenzoic acid gave a catalyst, which oligomerized ethene to linear α -olefins [27].

In her thesis [28], Drießen-Hölscher investigated S–O-ligands for the alternating polymerization of ethene with CO. The ligands 2-mercaptobenzoic acid and 2-mercaptopropionic acid in combination with nickel yielded polyketones in good yields [28]. A complex **9** could be isolated and spectroscopically characterised.



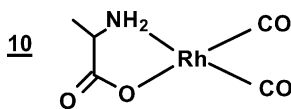
Complex **9** supports the *cis*-chelating nature of the S–O-ligand. Its diamagnetism is also indicative for square planar geometry.

3.3. N–O-Ligands

N–O-ligands have been of interest in organometallic chemistry and homogeneous catalysis, especially in C–C linkage reaction of olefins. Groß describes in his thesis various N–O-ligands, which oligomerize and polymerize ethene [29]. In collaboration with Cavell we have reported that N–O-ligands are well suited to polymerize ethene and copolymerize ethene/CO [30]. Mitsui Chemicals [31], Brookhart [32], Grubbs [33a] and Du Pont [33b] also have reported catalysts, which are very active and selective in C–C-linkage reactions. N–O-nickeldiazene complexes could also be used in our group to polymerize ethylene [34].

3.3.1. Aminoacids as ligands

A catalyst consisting of $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ /alanine cooligomerized ethylene and CO to oligoketones $\text{CH}_3\text{CH}_2(\text{COC}_2\text{H}_4)_x\text{H}$ ($x=1-5$) [35]. A complex **10** could be isolated and characterised spectroscopically.

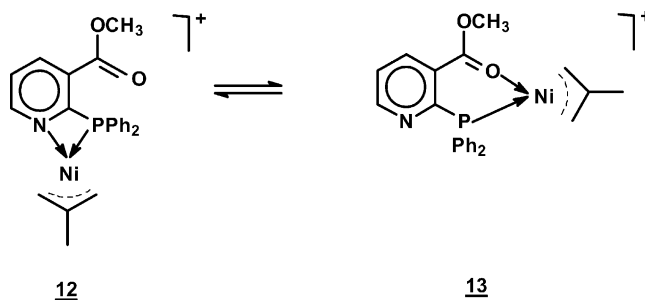
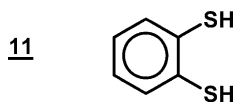


Besides alanine a series of other α -aminoacids such as glycine, leucine, proline, serine could be applied. These results are very encouraging to investigate other ligands known in biological systems.

3.4. S–S-Ligands

Sulfur is a frequently used ligand in biological systems. The organometallic chemistry with S-containing ligands is rich. In homogeneous catalysis examples are less common. Thereby, S–S-ligands should be well suited to stabilise selected coordination geometry as square planar in Ni(II)-complexes. Cavell and coworkers have demonstrated impressively that S–S-ligands are very active oligomerization catalysts [36].

Using sulfanyl ligands, we found that strongly chelating ligands like **11** show no catalysis in linking ethylene and ethylene/CO [37]. However, good catalysts could be obtained using non-chelating thiols. Here one can speculate whether hemilability and geometry change are a requisite for catalytic behaviour. A demonstration of such hemilabile equilibria between three heteroatoms is given in complexes **12** and **13** [38].



4. Conclusion

A delicate interplay of ligands and metals determines activity and selectivity of transition metal catalysed homogeneous reactions. In the past, great attention has been paid to trivalent phosphorus ligands. Heteroatom (O, S, N) containing ligands have been neglected to some extent. The following recommendation is given to researchers in the field of organometallic chemistry and homogeneous catalysis:

“More emphasis should be devoted to coordination geometry and to bio-inspired ligands”.

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