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Review

Trans-chelating diphosphines, the elusive ligands!

Zoraida Freixa *, Piet W.N.M. van Leeuwen [1]

Institute of Chemical Research of Catalonia (ICIQ), Avda. Països Catalans 16, 43007 Tarragona, Spain

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Contents

Abstract

The development of chelating diphosphine ligands has been a prolific research area for several decades, but quite surprisingly, from the plethora of diphosphines that are currently known, only a handful of them are able to coordinate preferentially in a *trans*-fashion (P–M–P angle close to 180°). The most representative ones, together with their most relevant reactivities and catalytic applications will be presented herein.

Although some sophisticated backbones are currently known, a truly and only *trans*-coordinating diphosphine remains elusive. Apparently, the inherent flexibility associated with the required large backbones always left other coordination modes accessible. *Cis*-monodentates, dimeric species or bimetallic compounds are additional escape routes for the desired species. Nevertheless, on the way to this illusory goal compounds with surprising and fascinating reactivities and coordination modes have been encountered which surely have contributed to widen the knowledge of coordination chemistry.

Keywords: Diphosphines; *Trans*-ligands; Ligands design; Homogeneous catalysis

1. Introduction

The development of chelating diphosphine ligands has been a prolific research area for several decades. This progress had a great impact on the advance of organometallic and coordination chemistry, and it was triggered by the need of more effective systems for homogeneous catalysis, especially since the middle of the 20th century which saw the concomitant development of this methodology for industrial applications.

In the early 1970s many scientists, intrigued by the reactivity of square-planar d^8 transition metal compounds, dedicated many efforts to stabilize such species. Obviously, in addition to *cis*-ligands, *trans*-chelating diphosphines seemed

* Corresponding author. Tel.: +34 977920200; fax: +34 977920221.
E-mail addresses: zfreixa@iciq.es (Z. Freixa), pvanleeuwen@iciq.es (P.W.N.M. van Leeuwen).
[1] Tel.: +34 977920227; fax: +34 977920221.

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an obvious target as well. Initial backbones consisted of simple long hydrocarbon chains, but the possibility of different coordination modes and oligomer formation rendered somewhat disappointing results [1–4]. A more promising option arrived at this early stage with a more sophisticated phenanthrene based backbone developed by Venanzi et al. [5].

Simultaneously, the rapid growth of goal-designed *cis*-coordinating diphosphines with potential application in the industrially relevant asymmetric hydrogenations overshadowed the emerging *trans*-diphosphines [6,7]. From then on the majority of the diphosphines were designed to coordinate in a *cis*-manner (with a P–M–P angle of 90°) in transition metal complexes.

The development, in the 1990s of new diphosphines stabilizing wider bite angles (around 120°), such as BISBI and Xantphos meant to coordinate in equatorial–equatorial positions in trigonal-bipyramid geometries, constituted a real milestone in homogeneous catalysis. These diphosphines were initially developed for and tested in hydroformylation reactions, but they also showed unprecedented behaviour in many catalytic reactions [8–15].

Still and quite surprisingly, from the plethora of diphosphines that are currently known, even nowadays only a handful of them are able to coordinate preferentially in a *trans*-fashion (P–M–P angle close to 180°). The most representative ones, together with their most relevant reactivities and catalytic applications will be presented herein. The use of simple long-chain backbones (with or without further functionalities as alkene, alkyne or polyethers) [16–18] will not be explicitly mentioned here as they have been already covered in previous review articles [19].

In order to locate the two phosphorus atoms at the adequate distance for a *trans*-chelation mode, the ligands should contain relatively large backbones. As will be shown in the following sections, this accounts for the main drawbacks; either an excessive flexibility that allows other coordination modes (*cis*-monomers, dimers, oligomers or dinuclear species[2]) or *ortho*-metallation of the backbone leading to a polydentate P–X_n–P (X = C, N) coordination frustrate the attempts.

The current designs of *trans*-diphosphines try to avoid some of these concomitant drawbacks. Although some sophisticated backbones are currently known, it turned out that after so many years of research, a truly and only *trans*-coordinating diphosphine remains elusive. Nevertheless, on the way to this illusory goal compounds with surprising and fascinating reactivities and coordination modes have been encountered which surely have contributed to widen the knowledge of coordination chemistry.

[2] Dimers will be used along the text when there is a bridging ligand other than the diphosphine between the two metals. Bimetallic or dinuclear species is reserved for species in with the only bridging ligand is the diphosphine coordinating in a η^1-manner to each metal.

2. Main *trans*-diphosphines

2.1. General description of the known ligands: Main coordination modes and their X-ray structures

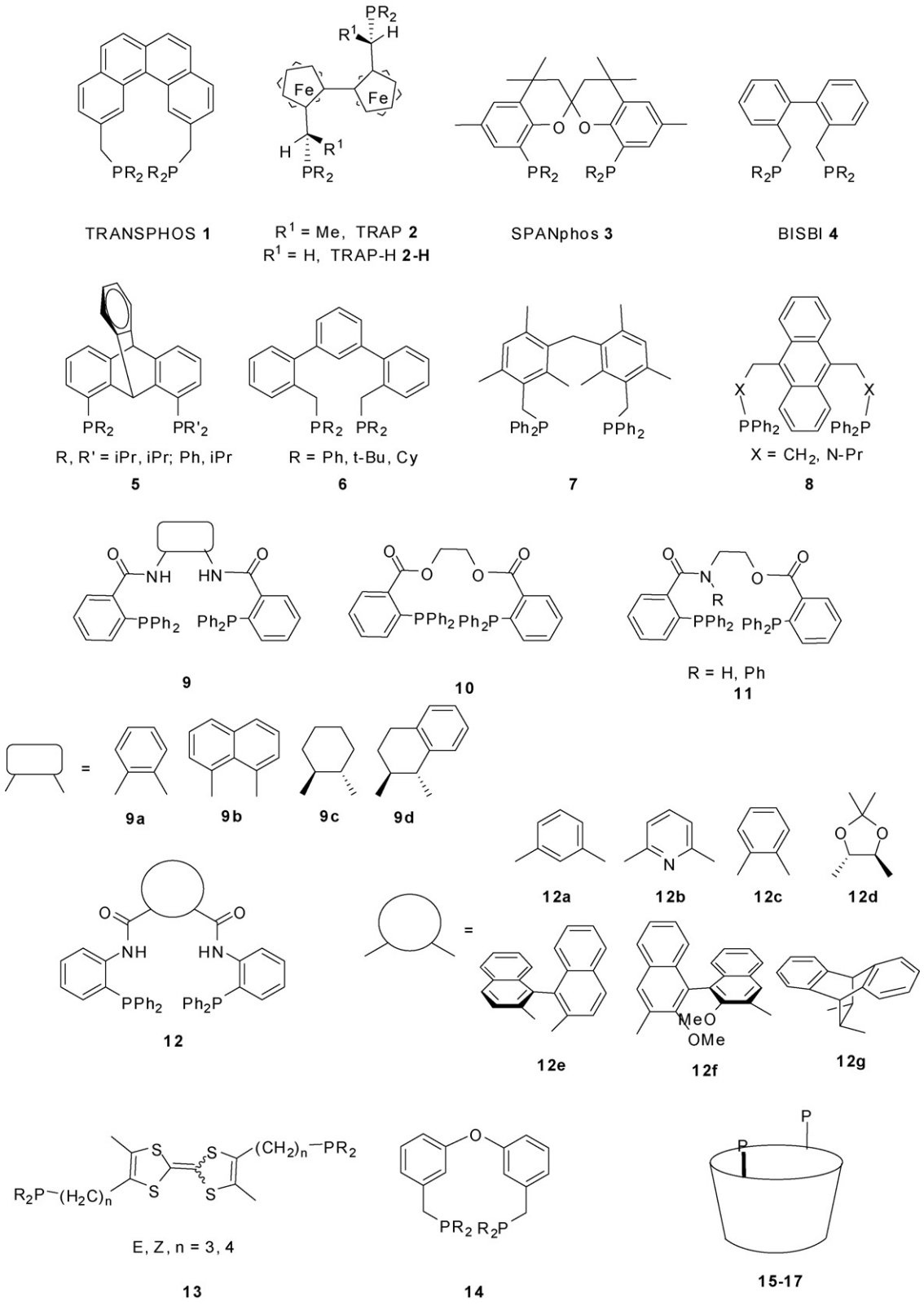
Although the first well characterized complex containing a *trans*-chelating diphosphine dates from 1961 [20], it was not until 1976 that Venanzi published what is considered the first example of a diphosphine designed to be a *trans*-ligand [5]. Fairly, it deserved years later the meaningful name of TRANSPHOS (**1** in Scheme 1). Already in the first publication the authors claimed that their interest was driven to stabilize square-planar compounds due to the potential reactivity of such a unsaturated organometallic species and its forthcoming applications in catalysis [5]. The ligand, the backbone of which consists on a phenanthrene unit, was described as "a fairly innocent ligand of rigid structure which places inert organic matter above and below the plane of the complex" (they focused on square-planar complexes).

The synthetic route toward the ligand consists on eight steps with a low global yield of around 7% (Scheme 2) [5].

This early ligand is probably still nowadays the better studied representative (from an organometallic point of view) of the *trans*-coordinating diphosphines. In fact the exhaustive studies performed by Venanzi and co-workers resulted in a series of 19 papers in Helvetica Chimica Acta related to the characterization and reactivity of its derivatives [5,21–37]! Numerous complexes with different coordination numbers and geometries have been synthesized and the structure of many of them has been elucidated by means of X-ray diffraction (Table 1). The published structures comprise complexes containing ten different metals and coordination numbers ranging from two (linear complexes) to six (octahedral compounds). The marked preference of this ligand to form *trans*-coordinating complexes is clear from the large number of these type of complexes which X-ray structure has been solved, but there are also some examples of tetrahedral and trigonal species (with P–M–P angles of only 120–150°) and even one X-ray structure of a *cis*-compound has been found! (P–Pt–P angle 105°) and many more have been spectroscopically characterized [32,38].

Also oligomeric species of undefined nature have been observed as minoritary by-products in the synthesis of Pt**1**Cl_2 and Pd**1**Cl_2. By reaction of $Pt(C_2H_4)_3$ with **1** some dinuclear species of formula $(Pt(C_2H_4)_2)_2$**1** with the ligand bridging between two metals have been characterized [32]. In spite of the size of the chelate ring, there are even examples of Pt hydrido-bridged dimeric compounds with the ligand coordinating in a *cis*-manner to each metal center [35]!

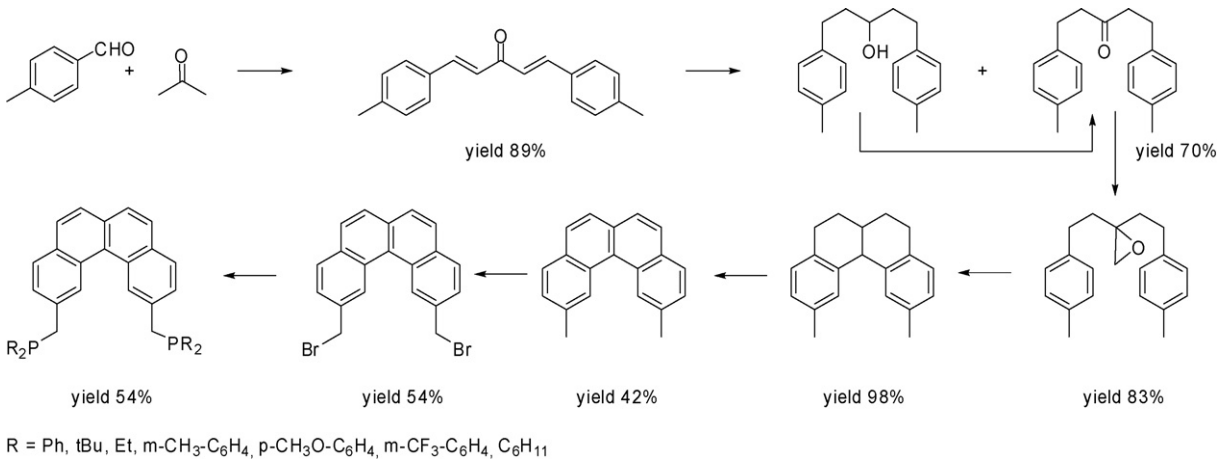
Analysis of the different X-ray structures of ligand **1** showed in all cases, the phenanthrene unit of the backbone significantly deviated from planarity due to steric interactions between the H(1) and H(12). A tilt angle "β" is defined as the dihedral angle between the two terminal aromatic phenyl rings. Values of β vary from 17° to 36°. On the other hand, the ligand occurs in two distinct conformations. In one group of compounds the C(19)-P(1) and C(20)-P(2) vectors point to the same side of the mean phenanthrene plane (these are called P-type, P for parallel).



Scheme 1. Structures of the most representative *trans*-chelating diphosphine ligands[3].

In the other group, these vectors point to opposite sides of this plane (called A-type, A for antiparallel), Scheme 3 [36,44]. In a general manner, the presence of the methylene groups of the backbone accounts for the observed flexibility of the ligand as

[3] The different ligands have been grouped per families. Along the text, when a specific derivative is mentioned it will be identified with the number of the generic ligand family preceded by a label recalling its particularity (i.e. **Cy-6** to refer to the biscyclohexylphosphine derivative of ligand **6**).



Scheme 2. Synthetic route toward TRANSPHOS ligand **1**. Yields specified for R = Ph.

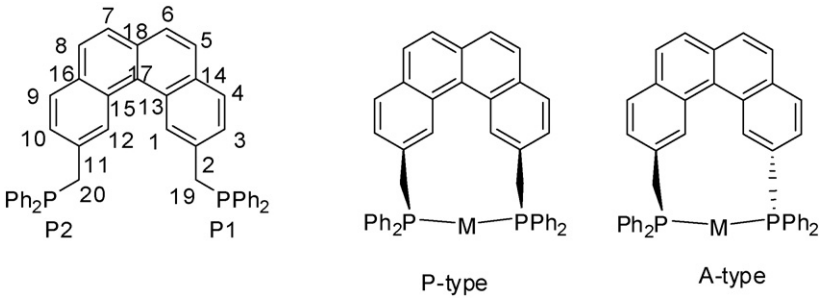
it allows the existence of two different conformations, A and P. Conformations of type A have been encountered for bite angles larger than 160° and conformation type-P is present when the P–M–P angle is smaller than 140°. The middle range angles 140°–160° can be attained by both conformations.

Although it only appeared 15 years later, the other outstanding representative of the family of *trans*-ligands is, undoubtedly, the diphosphine TRAP **2** developed by Ito et al. [45]. Untill today, it still represents the only successful example of a chiral *trans*-chelating ligand for asymmetric catalysis. The backbone is based on a bis-ferrocenyl unit, and it possesses planar chirality as well as stereogenic centers (Scheme 4). The ligand (Ph derivative, **Ph-2**) is synthesized in an enantiomerically pure form in four steps from (*S*)-1-(*N*,*N*-

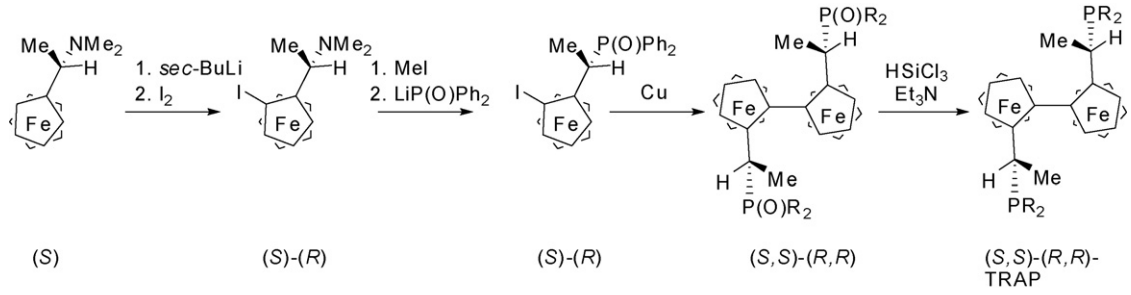
Table 1
Structures (X-ray) of ligand **1** published in the CCDC

Ligand	CN	Complex	CCDC code	Distance P–P (Å)	Angle P–M–P (°)	Reference
1 R = Ph	3	$[(AgL)_2F]^+[BF_4]^-$	BIWVEI	4.60	143.5	[39]
				4.66	144.9	
1 R = Ph	3	$PtLCl_2$	BZPNPU	3.57	104.7	[38]
1 R = Ph	3	$AgL(SnCl_3)$	CAMREN	4.61	142.2	[40]
1 R = Ph	4	$AgL(NO_3)$	CAMRIR	4.65	148.6	[40]
1 R = Ph	4	$AgLClO_4$	CAMROX	4.67	151.5	[40]
1 R = Ph	4	$HgLI_2$	CAYBIN	4.77	146.0	[41]
1 R = Ph	4	$HgLI_2$	CAYBOT	4.44	125.6	[41]
1 R = tBu	3	AgLBr	CORTOS10	n.r.[a]	141.6	[33]
1 R = tBu	3	AgLCl	CORTUY10	n.r.[a]	142.6	[33]
1 R = tBu	3	$AgL(ClO_4)$	CORVAG10	n.r.[a]	161.5	[33]
1 R = Ph	4	PtLHCl	HCPPPT10	4.56	176.2	[35]
1 R = Ph	5	$RuLCl(NO)_2$	JAXHIZ	4.846	164.1	[42]
1 R = Et	2	$[AgL]^+[ClO_4]^-$	KAHFAA	4.76	167.6	[34]
1 R = Et	4	$NiLCl_2$	KOWHAF	4.43	176.2	[43]
1 R = Et	4	$PdLCl_2$	KOWHEJ	4.61	177.4	[43]
1 R = Et	4	$PtLCl_2$	KOWHIN	4.58	177.1	[43]
1 R = Ph	4	$PdLCl_2$	PCPPB10	4.64	175.6	[24]
1 R = Ph	3	AgLCl	PMBPAG10	4.56	140.7	[40]
1 R = Ph	3	AuLCl	PMBPAU	n.r.[a]	176[b]	[44]
1 R = Ph	3	CuLCl	PMBCU	n.r.[a]	132[b]	[44]
1 R = Ph	4	RhL(CO)Cl	PMBZRH20	4.62	174.7	[24]
1 R = Ph	5	RuL(CO)Cl(NO)	RUNCPP10	4.78	167.7	[27]
1 R = Ph	6	$IrLCl_3(CO)$	TCIRPP10	4.81	170.6	[31]
1 R = Ph	0	L	VAZYOK	5.71	–	[36]
1 R = tBu	0	L	VAZZAX	6.09	–	[36]
1 R = Ph	4	$PtLCl_2$	ZZZBJV	n.r.[a]	175.7	[24]
1 R = Ph	4	IrL(CO)Cl	ZZZBJY	n.r.[a]	174.7	[24]
1 R = Ph	4	IrL(CO)Cl	ZZZBJY10	4.61	173.9	[31]

CN: coordination number around the metal center.
[a] n.r. data not reported.
[b] More accurate unavailable.



Scheme 3. TRANSPHOS conformations.



Scheme 4. Synthetic route for TRAP ligand **2**.

dimethylamino)ethylferrocene with an overall yield of 51% [45–47].

As a consequence of the research interests of that period, the effort was not especially focused on characterization of TRAP organometallic complexes but more directed towards their catalytic applications. In spite of this, several X-ray structures have been published over the years. All of them, except the ligand oxide, show square-planar geometries (Table 2). Although there are no crystal structures published with the ligand occupying relative *cis*-positions, already in the first publication of the ligand, the concomitant formation of *trans*- and *cis*-Pt(II) complexes in a ratio 20:1 was reported [45]. Also, a characterized *cis*-Ru species was postulated as being involved in the catalytic activity of hydrogenation reactions (vide infra) [48].

Another of the few examples of chiral *trans*-diphosphines is SPANphos, **3**, which was developed by Freixa [52]. The backbone consists on a bis-chromane unit, and, although it does not include any stereogenic carbon atom, it does contain a spiro center. The molecule shows a global C_2-symmetry, and initially it was thought that the rigidity of the backbone will suffice to locate the two phosphorus atoms at a rather large distance as to ensure that only *trans*-chelating species will be formed. The ligand is synthesized (as a racemate) in only three steps from simple starting reagents with nearly quantitative yields (Scheme 5) [52].

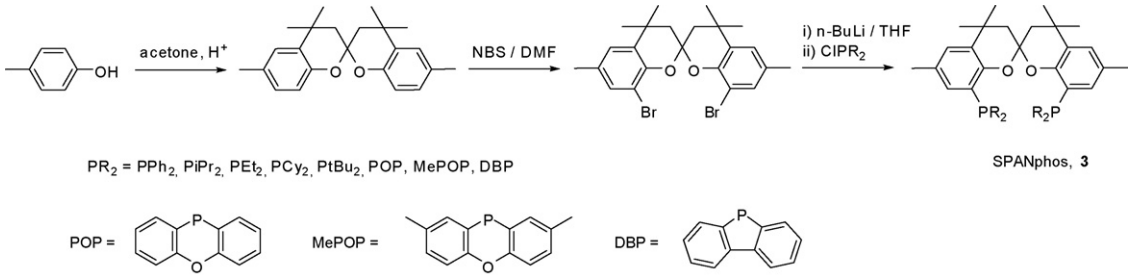
The enantiomeric diphosphines could be resolved, although it was only accomplished by the expensive complexation with chiral cyclometallated-Pd compounds (Scheme 6) [53].

SPANphos was initially introduced as a *trans*-ligand due to the many examples in which it behaved as such (without traces of *cis*-compounds ever present) [54] and its reluctance to perform *trans*- to *cis*-isomerizations under catalytic conditions [55,56]. Recently a more detailed study showed that its flexibility was larger than anticipated [57]. The authors proposed the reaction of a putative *trans*-ligand with $[Rh(nbd)_2][BF_4]$

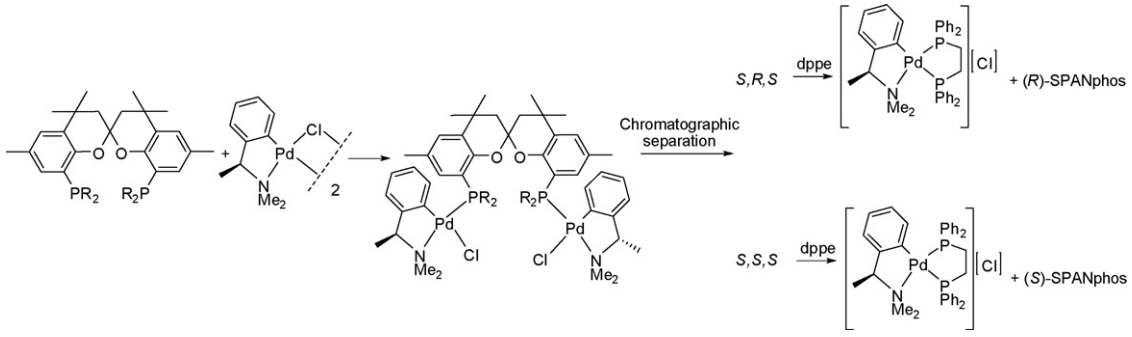
Table 2
Structures (X-ray) of ligand **2** published in the CCDC

Ligand	CN	Complex	CCDC code	Distance P–P (Å)	Angle P–M–P (°)	Reference
2 R = iPr	0	L oxide	JEFQAM	5.10	–	[49]
2 R = Et	4	$PdLBr_2$	JEFQEQ	4.59	166.7	[49]
2 R = Et	4	$PdLBr_2$	JEFQEQ01	4.50	166.4	[50]
2 R = Bu	4	$PdLBr_2$	JEFQIU	4.59	165.6	[49]
2 R = iBu	4	$PdLBr_2$	JEFQOA	4.61	163.1	[49]
2 R = iPr	4	$PdLBr_2$	JEFQUG	4.68	167.5	[49]
2 R = Bu	4	RhL(CO)Cl	LECTOC	4.57	164.4	[51]
2 R = Ph	4	$PdLBr_2$	ZISNUK	4.62	163.6	[46]
2 R = Furyl	4	RhL(CO)Cl	ZISPAS	4.36	161.0	[46]

CN: coordination number around the metal center.



Scheme 5. Synthesis of SPANphos (**3**) ligands.



Scheme 6. SPANphos: enantiomers resolution.

(nbd = 2,5-norbornadiene) in polar solvents as the final test to be passed. Under this stringent conditions directing towards the formation of *cis*-complexes (the presence of a strong *cis*-enforcing ligand as nbd and the polarity of the solvent), SPANphos derivatives led, much to the authors' surprise, to *cis*-complexes! This proved that the strain energy of the ligand in a *cis*-coordination mode was not as high as anticipated, but it could be overruled by the chelate effect and the stabilization of a *cis*-species with dipole moment.

The capability of the ligand to locate the two phosphorus at large distances (even larger than the one needed for a *trans*-complexation) was already known as several bimetallic (i.e. $Rh_2(cod)_2Cl_2L$, L = **Ph-3**, **DBP-3**, **iPr-3**; cod = 1,4-cyclooctadiene) and dinuclear species (i.e. $Rh_2(\mu\text{-}Cl)_2L(CO)_2$ and $Pd_2(\mu\text{-}Cl)_2LMe_2$ L = **Ph-3**) containing the ligand were known (Table 4) [56–58].

A conformational analysis of the different X-ray structures of the SPANphos complexes revealed that the ligand can adopt diverse conformations due to the flexibility of the central rings. Although four out of six atoms of each chromane unit are retained in one plane, the position of the CH_2 and spiro carbon atoms with respect to this plane renders already four possible arrangements (for each half of the backbone!), Fig. 1.

Semiempirical (AM1) and DFT (B3LYP/6-31G) performed on the spiro bischroman backbone (spirobi[2*H*-1-benzopyran],3,3′,4,4′-tetrahydro-4,4,4′,4′-tetramethyl) confirmed that all the conformations encountered in the X-ray structures correspond to the seven local minima identified within 10 kcal mol^{-1} from the global minima (Table 3). The different conformers are described according to the conformation adopted by each one of the central rings using the nomenclature described in Fig. 1 [57].

Table 3
Conformational analysis of spirobischroman and examples of X-ray structures where these conformations are found in the backbone of **3**

Backbone conformation							
Conformer	Boat Boat	Boat Twist	Envelope spiro Envelope spiro	Twist Twist	Envelope CH_2 Envelope CH_2	Envelope spiro Twist	Envelope spiro Envelope spiro
Example	RhCy-3(nbd)+	RhPh-3(nbd)+	RhiPr-3(cod)2Cl2	POP-3	PtPh-3Cl2	iPr-3	RhDBP-3(cod)2Cl2
Distance H_{C18}–H_{C9} (Å)	4.24	4.73	5.35	5.42	5.75	6.04	6.58
Energy (AM 1)	+1.7	+1	0	0	+0.3	+2.4	+5.8
Energy (B3LYP/6-31G)	+4.2	+2.0	0	0	0	+4.3	+9.2

Calculated energies in kcal mol^{-1}.

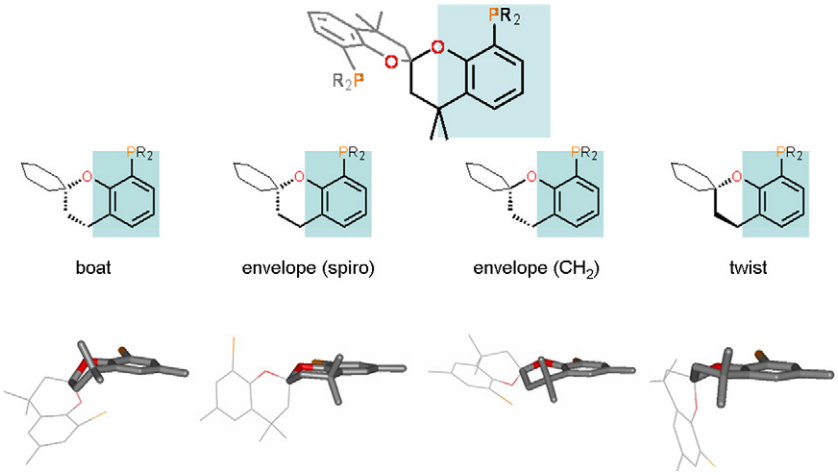


Fig. 1. Possible conformations of each chroman unit.

This conformational analysis, together with calculations performed on the full *cis*- and *trans*-complexes of SPANphos allowed the authors to conclude that although the ligand retains a preference for *trans*-complexes, this energetic preference is not as high as initially thought.

Actually, the ability of ligands **3** to coordinate in a *cis*-manner was confirmed with the synthesis of several *cis*-Pd(0) compounds containing the ligand **3** and the strong acceptor tetracyanoethylene (tcne) (PdL(tcne) L = **Ph-3**, **iPr-3**, **Cy-3**, **DBP-3**, Table 4) [59].

BISBI ligand, initially developed at the Eastman Kodak laboratories [63–67], had a great impact as one of the pioneering wide bite angle diphosphines, with huge relevance (together with Xantphos) in the understanding of this effect in catalysis, especially in the hydroformylation reaction. Nevertheless, it should not be considered as a "designed to be" *trans*-diphosphine, as in fact it was conceived to coordinate in equatorial–equatorial mode in bipyramidal species (P–M–P angle of 120°), or maybe it was not the result of design at all. It contains a bis-phenyl backbone, and early molecular mechanics calculations already showed that in fact it is a rather flexible ligand that can accommodate a broad range of chelation angles (calculated bite angle = 113°, accessible bite angles within 3 kcal/mol 92°–155°) [9,68]. As assessed by Pringle et al. [69], the published crystal structures of the ligand bear out this prediction. Although two X-ray structures are described as containing BISBI coordinated in a *trans*-manner ($FeL(CO)_3$ [70] and $RuLH_2(CO)(PPh_3)$ [71]) in both cases heavy distortions from ideal structures were observed, and the experimental bite angles are rather smaller than 180° as to be expected in a *trans*-coordination mode (Table 5, entries JETTAD and JABSIO). The decision to include BISBI in this section is because its capability to reach wider bite angles cannot be yet ruled out as it was never strongly pursuit (to the best of our knowledge, neither any square planar nor linear structure has been ever published). This is especially true after Pringle and co-workers reported on a BISBI analogue containing instead of diphenylphosphine groups the bulkier 9-phosphacyclo[3,3,1]non-9-yl or di-*tert*-buthylphosphine moieties [69,72]. The former showed to coordinate in a *trans*-fashion in square-planar Pd(II), Ni(II) and Pt(II) complexes with bite angles that fall out of the expected range for BISBI (Table 5). In the case of the $PtLCl_2$ complex both *cis*- and *trans*-isomers have been characterized by X-ray diffraction (FEWXAH and FEWWOU in Table 4) and spectroscopic techniques, and a *trans*- to *cis*-isomerization in solution has been observed showing that in fact, the *cis*-complex is thermodynamically more stable. For the *tert*-butyl derivative, neither *cis*- nor *trans*-chelating species have been observed when it was reacted with $[Rh_2(cod)(\mu\text{-}Cl)_2]$; instead dinuclear or monodentate complexes were formed, which was attributed to the steric bulk of the substituents [72].

As it happened with BISBI, Xantphos and DPEphos ligands had always been considered wide bite angle diphosphines. Several review articles summarize their outstanding behaviour in many catalytic reactions and their main coordination compounds [10–14,73–75]. Accordingly, they will not be explicitly mentioned here nor included as presumed *trans*-diphosphines, but it is necessary to mention that several X-ray structures of Pd in which Xantphos coordinates in a *trans*-manner without the assistance of the oxygen of the backbone have been also published and should be surely possible also for DPEphos [76–79].

In recent years several groups, challenged by the synthesis of a truly *trans*-diphosphine, published interesting backbone designs, of which the real potential still needs to be revealed. In an effort to understand its coordination and catalytic properties, Gelman studied a barrelene based roof-like diphosphine initially developed by Pacciello et al. at BASF (ligand **5**) [83–87]. X-ray structures of its Pd(II) complexes showed that the ligand in fact spans *trans*-positions, although a strong distortion from the ideal square-planar geometry toward a butterfly-like environment of the Pd center was observed. This deformation was attributed to the strain of the eight-membered ring formed upon chelation. In fact, the observed P–Pd–P angles are rather small for an ideal *trans*-coordination (ECEQAF, ECEQEJ and CEQJAK in Table 6). Just this year one platinum structure of ligand **iPr-5** has been published that should be better defined as a *cis*-complex (Table 6) [87]!

Unexpectedly, Gelman observed that ligand **5** also forms very stable dinuclear species in which the strain of the ligand is some-

Table 4
Structures (X-ray) of ligand **3**

Ligand	CN	Complex	CCDC code	Distance P–P (Å)	Angle P–M–P (°)	Reference
3 R = Ph	4	$[RhL(nbd)]^+[BF_4]^-$	ICUKEX	3.50	97.9	[57]
3 R = iPr	4	$[RhL(nbd)]^+[BF_4]^-$	ICUKIB	3.52	95.6	[57]
3 R = Cy	4	$[RhL(nbd)]^+[BF_4]^-$	ICUKOH	3.55	96.3	[57]
3 R = iPr[a]	4	$Rh_2LCl_2(cod)_2$	ICUKUN	6.61	–	[57]
3 R = DBP[a]	4	$Rh_2LCl_2(cod)_2$	ICULAU	7.61	–	[57]
3 R = iPr	0	L	ICULEY	5.80	–	[57]
3 R = POP	0	L	ICULIC	6.51	–	[57]
3 R = tBu	0	L	ICULOI	6.17	–	[57]
3 R = Cy	4	$[RhL(nbd)]^+[BF_4]^-$	ICULUO	3.56	95.6	[57]
3 R = Ph	0	L	WABXED	4.99	–	[52]
3 R = Ph	4	$PtLCl_2$	WABXIH	4.60	171.9	[52]
3 R = Ph	4	RhL(CO)Cl	XASDEB	4.60	173.8	[56]
3 R = Ph[b]	4	$Rh_2L(\mu\text{-}Cl)_2(CO)_2$	XASDIF	6.09	–	[56]
3 R = Ph[b]	4	$Pd_2L(\mu\text{-}Cl)_2Me_2$	–	6.11	–	[56,58]
3 R = Ph[c]	4	PdL(*p*-C_6H_4CN)Br	–	4.59	161.8	[60]
				4.59	161.6	
3 R = Ph	4	$PdLCl_2$	–	4.62	175.4	[61]
3 R = Ph	5	$RhLCl_2H$	–	4.63	176.4	[62]
3 R = iPr	5	$RhLCl_2H$	–	4.66	175.6	[62]
3 R = DBP	4	RhL(CO)Cl	–	4.53	163.4	[62]
3 R = Cy[c,d]	3	PdL(tcne)	–	3.61	101.0	[62]
				3.61	100.8	
3 R = DBP[c,d]	3	PdL(tcne)	–	3.70	106.1	[62]
				3.70	106.4	
3 R = iPr[d]	3	PdL(tcne)	–	3.79	107.6	[62]
3 R = Ph[c,d]	3	PdL(tcne)	–	3.77	106.7	[62]
				3.77	107.0	
3 R = Ph	3	CuLCl	–	4.04	128.5	[62]

CN: coordination number around the metal center.
[a] Bimetallic species.
[b] Dimer.
[c] Two molecules in the unit cell.
[d] tcne = tetracyanoethylene.

Table 5
Structures (X-ray) of ligand **4**

Ligand	CN	Complex	CCDC code	Distance P–P (Å)	Angle P–M–P (°)	Reference
4[a] R = Ph	5	$IrLH(CO)(PPh_3)$	BIQKIV	4.04	124.2	[80]
4[b] R = 9-ph	4	RhL(CO)Cl	FEWWIO	4.55	162.1	[69]
4[b] R = 9-ph	4	$PdLCl_2$	FEWWOU	4.56	163.6	[69]
4[b] R = 9-ph	4	$NiLCl_2$	FEWWUA	4.39	164.6	[69]
4[b] R = 9-ph	4	$PdLCl_2$	FEWXAH	3.52	101.8	[69]
4 R = Ph	6	$RuLH_2(CO)(PPh_3)$	JABSIO	n.r.[c]	144.6	[71]
4 R = Ph	5	$FeL(CO)_3$	JETTAD	4.26	151.9	[70]
4 R = Ph	5	$RhLH(CO)(PPh_3)$	JUDZOX	4.08	124.8	[9]
4 R = Ph	5	$IrLH(CO)_2$	JUDZUD	3.95	117.9	[9]
4 R = Ph	5	$IrLH(CO)(PPh_3)$	NUZVOT	3.90	119.2	[81]
4 R = tBu[d]	4	$Rh_2LCl_2(cod)$	RADMOZ	6.58	–	[72]
4 R = Ph	0	L	SORFUA	6.73	–	[82]
4 R = Ph	6	$MoL(CO)_4$	SORGAH	4.03	103.5	[82]

CN: coordination number around the metal center.
[a] Tetrachlorinated backbone.
[b] 9-ph = 9-phosphacyclo[3.3.1]non-9-yl.
[c] Data not reported.
[d] Dinuclear compound.

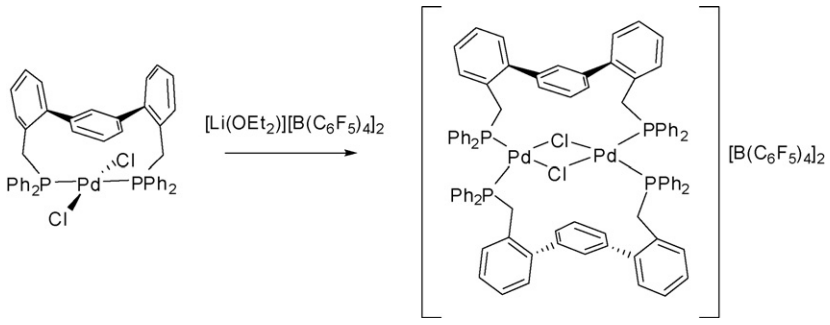
Table 6
Structures (X-ray) of ligands **5–14** published in the CCDC

Ligand	CN	Complex	CCDC code	Distance P–P (Å)	Angle P–M–P (°)	Reference
5 R = iPr	4	$PdLCl_2$	ECEQAF	4.55	154.9	[84]
5 R = Ph, iPr	4	$PdLCl_2$	ECEQEJ	4.05	150.4	[84]
5[a] R = iPr	4	$Pd_2L(\mu\text{-}Cl_2)Cl_2$	ECEQIN	5.91	–	[84]
5[a] R = Ph, iPr	4	$Pd_2L(\mu\text{-}Cl_2)Cl_2$	CEMPEQ	5.77	–	[86]
5[a] R = iPr	4	$Rh_2L(\mu\text{-}Cl_2)(CO)_2$	CEMPIU	5.88	–	[86]
5 R = iPr	4	$PdLCl_2$	CEQJAK	4.52	154.1	[115]
5[a] R = Ph, iPr	4	$Pd_2L(\mu\text{-}Cl_2)Cl_2$	CERTID	5.77	–	[86]
5 R = iPr	4	$PtLCl_2$	–	3.79	109.3	[87]
6 R = Ph		$PdLCl_2$	OBUTEL	4.63	173.0	[88]
6 R = Ph	4	$NiLCl_2$	OBUTIP	4.48	174.8	[88]
6[a] R = Ph	4	$Pd_2L_2(\mu\text{-}Cl)_2$	OBUTOV	6.59	–	[88]
6[b] R = Ph	4	PdLBr	XEMSOY	4.59	169.5	[89]
7 R = Ph	4	$PdLCl_2$	HENSEZ	4.63	178.9	[91]
8[c] X = CH_2	4	$[RhL(CO)Cl]_3$	IGUYUE	4.64 4.63 4.63	173.8 175.2 175.2	[94]
8 X = CH_2	2	$[AgL]^+[ClO_4]^-$	TUTQOO	4.88	177.9	[93]
8 X = NPr	2	$[AgL]^+[ClO_4]^-$	IBAYUF	4.79	169.9	[92]
8 X = NPr	2	$[CuL]^+[ClO_4]^-$	TUTQEE	4.31	154.0	[93]
8 X = NPr	2	$[AuL]^+[ClO_4]^-$	TUTQII	4.63	171.6	[93]
9a	0	L	AJIFII	7.79	–	[98]
9a[d]	4	PtL	AJIFOO	3.581	106.26	[98]
9a	4	$PdLCl_2$	AJIFUU	4.678	178.41	[98]
9a	4	RhL(CO)Cl	NALGUD	4.653	173.44	[97]
9a[d]	4	PdL	QETFAX	3.581	105.44	[104]
9b	0	L	IVONIQ	5.393	–	[105]
9b	0	Loxide	IVONOV	5.742	–	[105]
9b[e,f]	4	$Ru_2L(\eta^6\text{-}p\text{-cymene})_2Cl_2$	IVIPAK	9.182 9.215	–	[105]
9c	0	L	CEMPOZ	10.718 9.916	–	[106]
9c[d]	4	PdL	FENRAS	3.493	102.47	[103]
9c	4	$PtLCl_2$	IZAHUM	3.489	101.15	[102]
9c[e]	4	$Pt_2L(C_3H_5)_2$	CEMPIT	9.504	–	[106]
9d	0	L	KEGRIY	4.792	–	[116]
11 R = Ph	4	$PtLI_2$	MOVMEP	4.648	178.40	[99]
11[a] R = Ph	6	$Rh_2L(\mu\text{-}I)_2(COMe)_2I_2$	MOVMIT	7.967	–	[99]
11[a] R = Ph	6	$Rh_2L(\mu\text{-}I)_2(COMe)_2I_2$	MOVMOZ	7.399	–	[99]
12b	4	$PtLCl_2$	NURGAY	4.635	174.43	[101]
12g	4	$PdL(C_3H_5)$	ZIBVUB	3.859	110.57	[100]
13 $n = 3$	6	$WL(CO)_4$	NEMFER	4.927	177.36	[107]
13 $n = 3$	6	$WL(CO)_4$	NEMFIV	4.913	169.15	[107]
13 $n = 3$	6	$MoL(CO)_4$	NEMFOB	3.906	99.85	[107]
13 $n = 4$	6	$WL(CO)_4$	NEMFUH	4.934	176.20	[107]
13 $n = 4$	6	$WL(CO)_4$	NEMGAO	4.905	172.58	[107]
14	3	AgLCl	FENGUA	4.619	145.61	[110]
14	4	$PdLCl_2$	IDOGOY	4.659	176.50	[112]
14	4	$PtLBr_2$	FUFFAN	4.639	179.46	[113]

CN: coordination number around the metal center.
[a] Dimer.
[b] Metallated compound (terdentate P–C–P).
[c] Trimeric compound.
[d] Tetradentate P–N–N–P coordination.
[e] Dinuclear compound.
[f] Two independent molecules in the crystal cell.

how released compared to the mononuclear structures [84,86]. These complexes (of formula $M_2(\mu\text{-}X)_2X_2$**5**) can be selectively formed through a "ring-expansion" reaction by addition of an excess of metal to the pre-synthesized mononuclear M**5**X_2. Several X-ray structures of these dimeric complexes have been published (ECEQIN, CEMPEQ, CEMPIU, CERTID in Table 6).

Not all the *trans*-chelating diphosphines were "designed to be". As frequently happens in science serendipity played a role



Scheme 7. Dimers formation with ligand **6**.

as well. Terphenyl based ligand **6** was initially designed by Protasiewicz to act as a terdentate P–C–P pincer-type ligand after cyclometallation of the central benzene ring [88]. Attempts to promote this C–H activation were unsuccessful and the ligand behaved in fact as a *trans*-spanning diphosphine as confirmed by X-ray analysis of a Ni(II) compound (Table 6 entry OBUTIP). A new ligand containing a more reactive Br on the C-1 position of the central ring was later on synthesized in order to achieve a pincer-type complex with the same backbone (Table 6 entry XEMSOY) [89].

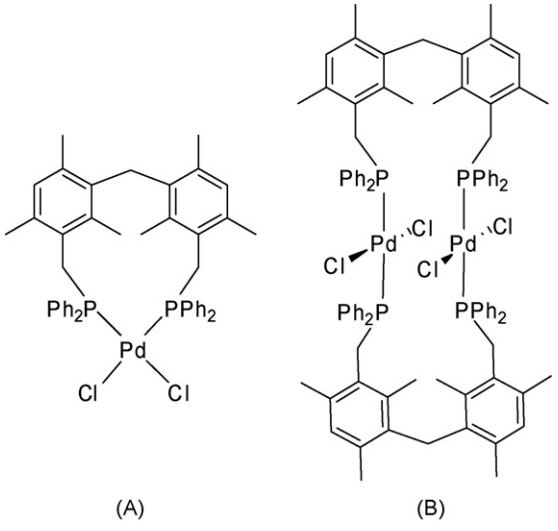
When *trans*-Pd**Ph-6**Cl_2 was reacted with $[Li(OEt_2)][B(C_6F_5)_4]$ in order to promote the halide dissociation (and cyclometallation), a new dicationic dimeric species was isolated. Crystals of this compound suitable for X-ray diffraction were obtained showing a peculiar structure (Scheme 7) and proves that ligand **6** can accommodate the two phosphorus atoms at distances as large as 6.6 Å [88]!

Although there is no evidence of such a species, the efficiency of ligand **6** for cross-coupling reactions (vide infra) together with the broadening observed in the ^{1}H NMR spectra of Pd**Ph-6**Cl_2 suggests that the flexibility of the ligand can also accommodate a *cis*-chelating mode [90].

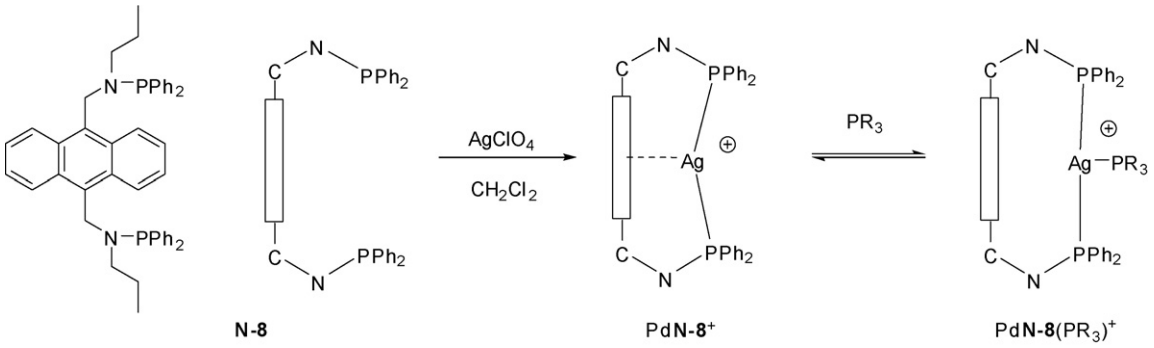
Following a thoroughly opposite approach, Süss-Fink designed bis(3-diphenylphosphino)methyl)-2,4,6-trimethylphenyl)methane ligand **7** pursuing a *trans*-coordination of the two phosphorus atoms while avoiding the possibility of *ortho*-metallation [91]. All *ortho*-positions in the benzylic rings of the backbone are blocked by methyl groups. The only X-ray structure published of this novel ligand (Pd**7**Cl_2, HENSEZ in Table 6) represents certainly a square-planar palladium complex with a nearly linear arrangement of the two phosphorus atoms. In fact, to the best of our knowledge, it is one of the widest bite angles ever reported for a chelating diphosphine (angle P–Pd–P of 178.86°). Nevertheless, variable temperature NMR experiments performed on a C_6D_6 solution of the *trans*-complex showed the emergence of a new signal at temperatures over 70 °C. The nature of this species has not been elucidated, due to the reversibility of the process when lowering the temperature, but a binuclear *trans*-complex or the mononuclear *cis*-compound were postulated as the most plausible options (see Scheme 8) (for catalytic implications vide infra).

Anthraceno based ligands **N-8** (X = N-Pr) were initially designed in view of their photoluminiscent properties, being the *trans*-coordination mode an indirect requisite to allow their use as molecular switches [92,93]. The emissive ligand **N-8** reacted with Ag^+, Cu^+ and Au^+ to give the non-emissive cationic *trans*-complexes [Ag**N-8**]$^+$, [Cu**N-8**]$^+$ and [Au**N-8**]$^+$ respectively (IBAYUF, TUTQEE and TUTQII in Table 6). Their X-ray structures show P–M–P angles (154°–172°) slightly smaller than 180°, with the metal atom slightly moved toward the middle aromatic ring of the anthracene framework. In fact an endocyclic metal complex with metal-η^6-anthracene coordination is proposed in view of the observed carbon-metal distances, and confirmed by means of ab initio and DFT calculations, which is thought to be responsible for the fluorescence quenching after metal coordination. Accordingly, addition of PR_3 to the solution of [M**8**]$^+$ immediately triggered an intense fluorescence due to the formation of a P-tricoordinated complex in which the hapticity to the anthracene is cleaved (Scheme 9).

Although the analogue ligand **C-8** (X = CH_2) formed a *trans*-complex with silver with the same stoichiometry [Ag**C-8**]$^+$, it did form completely different species with the gold and copper precursors, and it reacted with half an equivalent of [$Rh_2(\mu$-$Cl)_2(CO)_2$] to form not the expected *trans*-Rh**C-8**(CO)Cl, but a cyclic trimeric calix-shaped structure (IGUYUE in Table 5, Scheme 10) [94]. In fact, analysis of the X-ray structure of the complex [Ag**C-8**]$^+$ revealed a much wider P-Ag-P angle



Scheme 8. *Cis*-monomer (A) and *trans*-binuclear (B) proposed to be in equilibrium with *trans*-Pd**7**Cl_2 at temperatures over 70 °C.



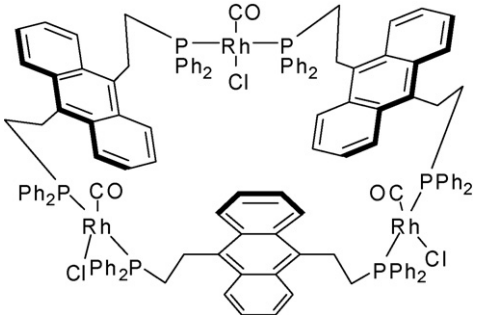
Scheme 9. Molecular switch generated by ligand Ag**N-8** complexes.

of 177.9° than the one encountered in [Ag**N-8**]$^+$ (TUTQOO and IBAYUF in Table 6) which should account for a weaker metal-η^6-arene bond [94]. As confirmed by ab initio and DFT calculations, the N–P bonds present in ligand **N-8** have an important contribution in the formation of the complexes with arene-metal hapticity and they could be responsible for the preferential formation of *trans*-complexes versus oligomers with this ligand.

Exploiting the methodology developed by Trost et al. [95,96], Süss-Fink applied his modular approach to generate a family of *trans*-diphosphine ligands **9**–**11** by using different spacers and combining amide and ester linkages [97–99]. Ligands **9**–**11** are (as Trost's ligands) 2-diphenylphosphino benzoic acid derivatives formed by condensation with different diamines (**9**), diols (**10**) and aminoalcohols (**11**). Also the so called "invertomers" of ligands **9** can be obtained following an analogous strategy, but reversing the sense of the amide linkage, as published by Trost [100], and extended by Feringa et al. [101]. The corresponding polydentate ligands **12** can be synthesized by a simple condensation of 2-diphenylphosphinoaniline with different diacylchlorides.

The capability of ligands **9**–**12** to form *trans*-coordinating complexes has been largely demonstrated. Many square-planar *trans*-complexes as IrL(CO)Cl, RhL(CO)Cl, $PtLCl_2$, $PtLI_2$ or $PdLCl_2$ have been characterized by means of spectroscopic techniques and several X-ray structures confirmed the ligand arrangement (see Table 6) [97–99,101,102].

Nevertheless, slightly different coordination properties could be expected depending on the spacer and the linkage (amide or ester) used. In fact, this was observed already in the first



Scheme 10. Trimeric structure of *trans*-Rh**C-8**(CO)Cl.

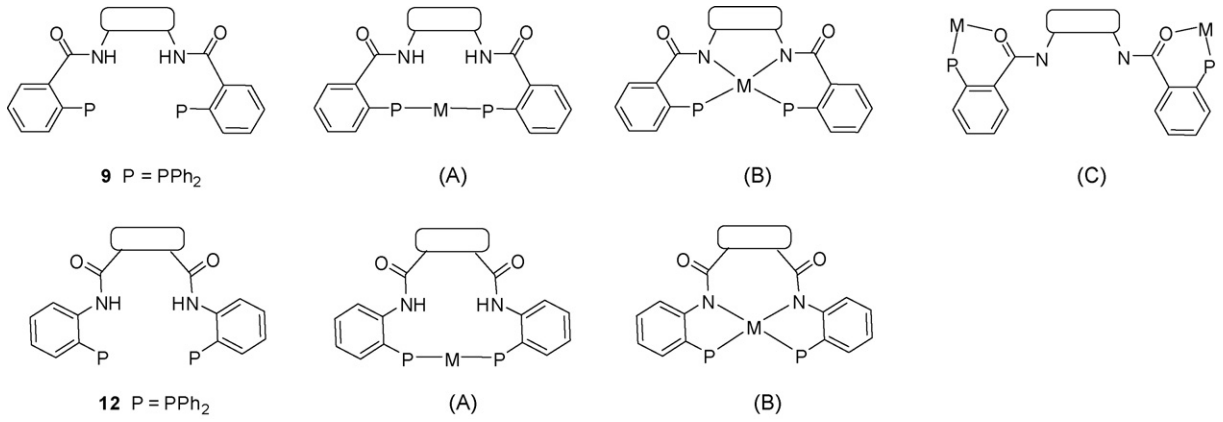
example published by Feringa et al. [101]. Ligand **12a**, showed by NMR the formation of mixtures of different species when reacted with $PdCl_2(CH_3CN)_2$ but in contrast, ligand **12b** formed both with Pd(II) and Pt(II) precursors quantitatively the *trans*-dichloride complexes. The X-ray structure of the Pt**12b**Cl_2 has been published and shows a P–Pt–P angle of 174.4° (NURGAY in Table 6).

Ligands **9** and **12** showed several coordination modes, which is not surprising, as they are in fact polydentate ligands. They can act also as a tetradentate P–N–N–P donor in an square-planar environments (after deprotonation of the amide nitrogens) as was demonstrated by NMR and MS analysis of the corresponding Ni**12b** complex [101], and in several X ray structures of the corresponding PdL and PtL complexes with ligands **9a** and **9c** (AJIFOO, QETFAX, FENRAS in Table 6, B in Scheme 11) [98,103,104].

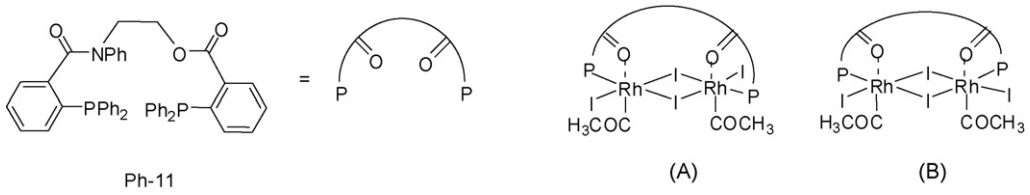
In the case of ligands **9**, also some structures in which the ligand acts as P,O bis-chelate coordinated to two different metals, with very large P–P distances, have been observed (C in Scheme 11) [105,106]. This should be attributed to the adequate disposition of the donor atoms (P,O) to form a *cis*-chelate, together with the extreme flexibility of the backbone. This flexibility is clearly reflected in the X-ray structures of the free ligands **9** which show P–P distances ranging from 4.8 to 10.7 Å! (AJIFII **9a**, IVONIQ **9b**, CEMPOZ **9c** and KEGRIY **9d** in Table 6), and in the fact that even one structure of a *cis*-$PtLCl_2$ complex is known for ligand **9c** (IZAHUM in Table 6) [102].

Some flexibility should account also for ligands **10**–**12**, as dimeric structures of rhodium with large P–P distances have been observed for ligand **Ph-11** (MOVMIT and MOVMOZ in Table 6). In these complexes the ligands can occupy either "anti" or "syn" coordination sites with respect to the two metal centers (A and B in Scheme 12) [99]. In these structures the two metal centers are in octahedral environments sharing one side through the two bridging iodides. The sixth coordination site of each rhodium is supposed to be occupied by the acyl oxygens of the backbone.

Aiming at the construction of nanoelectronic devices, Gachot et al. developed new diphosphines containing a tetrathiafulvalene (TTF) unit in the backbone. These ligands (**13**) should generate after metal complexation metalamacrocycles with multiple redox sites [107]. Diphosphines **13** were synthesized as a mixture of *cis*- and *trans*-isomers on the tetrathiafulvalene core.



Scheme 11. Different coordination modes observed for complexes of ligands **9** and **12**. P–P chelate (A), P–N–N–P tetradentate (B) or bis(P–O) dinuclear (C). M represents the metal with its remaining ligands.



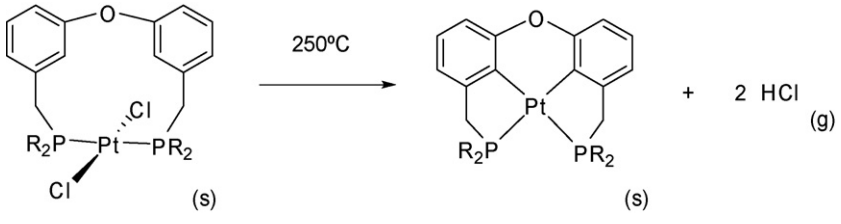
Scheme 12. Dimeric rhodium(III) structures observed for ligand **Ph-11**.

Attempts to separate them were unfruitful, as the TTF fragments are prone to isomerization in solution upon light exposure or in presence of traces of acid. When ligands **13** were reacted with one equivalent of *cis*-$M(CO)_4$(pyridine)$_2$ (M = Mo, W) they formed a mixture of mono- and oligomeric species from which the mononuclear compounds could be isolated in an overall yield of 20–30%. NMR analysis of the mononuclear fraction that contain the expected $M13(CO)_4$ complexes showed that in fact both *trans*- and *cis*-mononuclear compounds were formed in a ratio 5/2. X-ray structures of both type of structures have been published (Table 6).

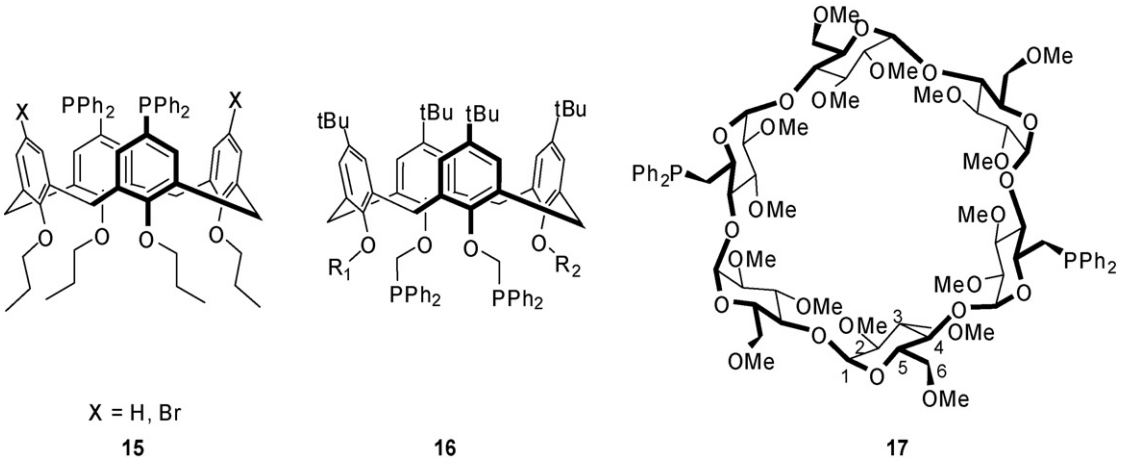
Diphosphine **14** is an early example of *trans*-chelating ligand forming (as TRANSPHOS **1**) after coordination a 12-membered chelate ring [108]. The design was originally intended to arrive at a more readily accessible version of **1** in order to study the mechanism of the double cyclometallation. Actually ligand **14**, compared to **1**, has two additional rotating bonds, which should provide the diphosphine with the flexibility needed for a *trans*- to *cis*-isomerization (needed to complete the double metallation, Scheme 13).

Several studies were also directed to unravel how the increased flexibility of ligand **14** compared to **1** would affect its tendency to form *trans*-coordinating complexes concluding that it does not have a detrimental effect [109,110]. Many *trans*-complexes of ligand **14** have been synthesized as Ni**14**X_2 (X = Cl, I, NCS, CN), Pd**14**X_2 (X = Cl, Br, I, ONO, N_3), Pt**14**X_2 (X = Br, I, Cl), Pt**14**HCl, Pt**14**HBr, Ag**14**Cl or Rh**14**(CO)Cl and fully characterized by spectroscopic techniques [110–113]. The data analysis suggested that ligand **14** forms exclusively monomeric species in high yields with Ni(II) and Pd(II). On the other hand, with Pt(II) the relative yield of *trans*-monomer versus *cis*-monomer and oligomers is highly dependant on the metal precursor used and the reaction conditions. The formation of *trans*-Pt**14**Cl_2 is most efficiently achieved when weakly polar solvent mixtures are used (i.e. MeCN/toluene 1/100). In very polar HCl/H_2O mixtures mostly *cis*-polymers are formed (as had already been observed for other *trans*-diphosphines, since polar solvents are more likely to yield *cis*-complexes) [114].

Surely one of the most sophisticated backbones (due to their spectacular tridimensionality) used to construct *trans*-diphosphines are the cyclodextrine and calix[4]arene derivatives extensively developed by Matt and co-workers [117–128]. This ambitious design is aimed at the construction of catalysts locating the metal center in close proximity (or even included) in a



Scheme 13. Double metallation of complex *trans*-Pt**14**Cl_2.



Scheme 14. *Trans*-diphosphines constructed on upper (**15**) and lower (**16**) rim functionalized calix[4]arenes and on cyclodextrines **17**.

cavity in order to modify the activity or selectivity of the systems (see Scheme 14).

Several cone-shaped calix[4]arene scaffolds, both upper and lower rim functionalized, containing phosphine moieties have been synthesized. We will focus on the ones containing two phosphine moieties tethered in distal positions as they are supposed to favour the *trans*-chelation, and after complexation, position the metal center at the center of the cavity entrance [121–129]. Lower rim bifunctionalized calix[4]arenes offer the additional advantage that there are two further sites where other groups can be easily appended to assist in the coordination (and/or catalysis).

Concerning upper rim functionalized calix-[4]-arenes **15**, several mononuclear complexes in which the ligand coordinates in a *trans*-manner have been synthesized with different metal geometries. Examples range from the linear [Ag(**H-15**)][BF_4], several square-planar Pt and Pd compounds ([Pt(**H-15**)H(PPh_3)][BF_4] or [Pd(**H-15**)(py)Me][BF_4] py = pyridine) to the octahedral Ru(**H-15**)$(CO)_2Cl_2$ [129]. Spectroscopic data suggested that the metal was located in the entry of the cavity in all these *trans*-structures. In the case of coordination numbers higher than two, it was also proposed that one of the additional ligands was in fact included into the calix[4]arene core. This could be confirmed by the X-ray structure of Ru(**H-15**)$(CO)_2Cl_2$ which clearly shows the entrapment of one metal carbonyl unit inside the cavity (Scheme 17).

Nevertheless, the flexibility of the ligand accounts for other possible geometries. For instance, with Pt(II) both *cis*-(OBOSAA in Table 7) and *trans*-mononuclear complexes have been synthesized, and unless the reaction was performed in high dilution, oligomeric species were also obtained [124].

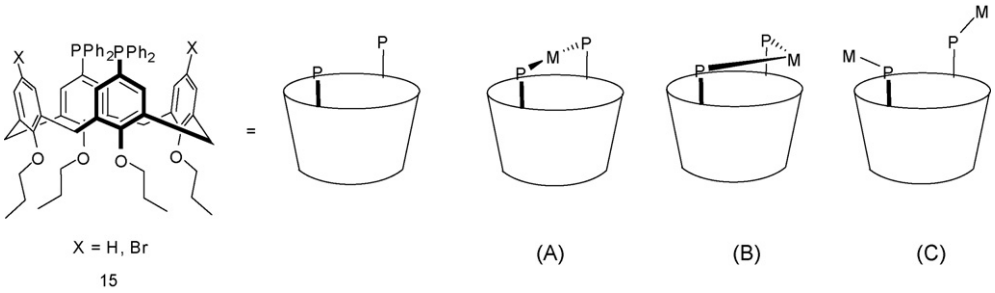
Dinuclear complexes in which the ligand bridges between two metal centers have been also selectively obtained. Reaction of **H-15** with [Ru(*p*-cymene)Cl_2]$_2$ with one equivalent of ligand rendered the dinuclear species Ru_2(**H-15**)(*p*-cymene)$_2Cl_4$, a highly symmetrical C_{2v}-structure as confirmed by NMR spectroscopy (C in Scheme 15) [124].

In fact, with these ligands, although very interesting inclusion *trans*-complexes have been obtained, more effort has been dedicated to the study of structures with smaller bite angles. For instance, *cis*-[Rh(**H-15**)(nbd)][BF4], Ni(**H-15**)Br_2, [Ni(**Br-15**)Cp][BF_4] (Cp = cyclopentadienyl), [Pd(**H-15**)(η3-Me-allyl)][BF_4] or *cis*-Pt(**Br-15**)Cl_2 have been synthesized and most of them could be analyzed by means of X-ray diffraction

Table 7
Structures (X-ray) of ligands **15-17** published in the CCDC

Ligand	CN	Complex	CCDC code	Distance P–P (Å)	Angle P–M–P (°)	Reference
15 X = H	6	$RuL(CO)_2Cl_2$	JISXOY	4.80	172.2	[129]
15 X = Br	4	$PtLCl_2$	OBOSAA	3.46	99.7	[124]
15 X = H	4	$[PdL(Me\text{-}allyl)]^+[BF4]^-$	OBORUT	3.66	103.3	[124]
15 X = H	4	$NiLBr_2$	IDIKEM	3.82	110.4	[122]
15[a] X = Br	5	NiLCp	JAMZED	3.48 3.46	104.7 103.7	[123]
16 R = $CONEt_2$	4	PtLHCl	TUNHOZ	4.48	164.3	[127]
16 R = $CONEt_2$	3	PtL(tcne)	NEHSAU	3.54	101.4	[126]
17	6	$RuL(CO)_2Cl_2$	PABZOI	4.84	175.3	[130]
17	4	$PdLCl_2$	PABZUO	4.71	171.8	[130]
17	3	$AgL(CH_3CN)$	TIFJEX	4.86	142.9	[119]

CN: coordination number around the metal center.
[a] Two independent molecules in the crystal cell.



Scheme 15. Different coordination modes of ligands **15**: mononuclear *trans*- (A) and *cis*- (B) and dinuclear (C). M represents the metal with its remaining ligands.

(Table 7). Analysis of these structures demonstrate that these ligands can also form highly unsymmetrical *cis*-compounds in which the metal is bent to one side of the cavity [122–124].

The interest of such *cis*-complexes lies on their particular structural features. It has been established that there is an intrinsic molecular motion during which the P–M–P angle widens and shrinks while the metal crosses in front of the cavity from one side of the calixarene axis to the other (Scheme 16). Remarkably the widest bite angle (speculated to be only around 130°) is achieved when the metal crosses the calix arene axis. Apparently this mechanism is responsible of the outstanding performance of these ligands in several catalytic reactions as ethylene and propene dimerization, orthogonal tandem oligomerisation in the production of linear low-density polyethylene (LLDPE), and several cross-coupling reactions [121,122,128]. Although it is surely a very interesting and worth to mention example of a bite angle effect in catalysis, its detailed analysis falls outside the scope of this review.

A priori, lower rim bis-functionalized calix[4]arenes **16** are a more adequate design for a *trans*-chelating diphosphines. Moreover, apart from the phosphine groups tethered on distal sites through CH_2 spacers, other neighboring auxiliary functions have been attached, namely ethers, esters and amides (some of them even incorporating chiral groups!).

Trans-complexes of the type $[ML][BF_4]$ (M = Ag and Au) have been characterized, but more interestingly, reaction of ligands **16** with $PtHCl(PPh_3)_2$ or $PtH(thf)(PPh_3)_2$ rendered, respectively, corresponding *trans*-Pt**16**HCl and *trans*-Pt**16**$HPPh_3$, in which the hydride ligand is directed into the calixarene cavity [126]! X-ray analysis of the complex *trans*-Pt**16**HCl proved that these inclusion *trans*-complexes are also possible with this type of ligands (TUNHOZ in Table 6) [127].

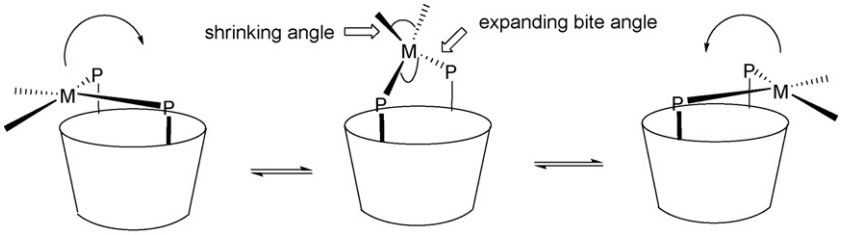
In contrast with complexes of the same stoichiometry with other *trans*-diphosphines (as TRANSPHOS) these ligands do not show *trans*- to *cis*-isomerization in solution, which could be an issue for catalytic reactions in with *trans*-coordination needs to be retained.

For instance, this complex does not react with tcne (tcne = tetracyanoethylene), but after activation of the complex with $AgBF_4$ (the chloride is then replaced by one of the carbonyl groups of the additional functionalities) a new *trans*-complex in which the hydride is no longer inside the cavity is formed, and it becomes accessible to species in solution. This complex does react with tcne and the insertion product *cis*-[Pt**16**(tcne)] has been isolated and characterized by means of X-ray diffraction (NEHSAU in Table 7) [126].

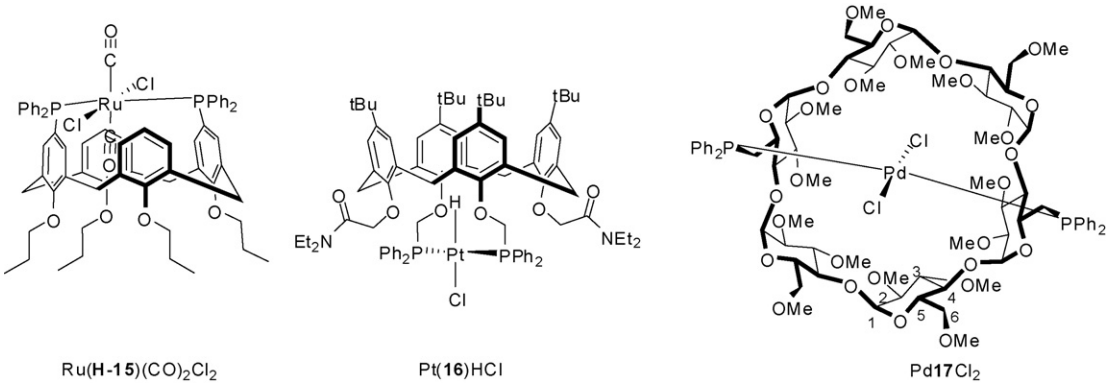
Actually, also with these ligands several mononuclear *cis*-complexes and dinuclear species have been synthesized (i.e. [Pd**16**(η^3-Me-allyl][BF_4] [125], [Rh**16**(nbd)][BF_4] [131], [Ru**16**(*p*-cymene)Cl][BF_4] [131], [Pt**16**(tcne)] [126], [Ru_2**16**(*p*-cymene)$_2Cl_4$] [131]).

In summary biphosphine-calix[4]arene derivatives **15** and **16** render structures rather flexible as to be considered pure *trans*-chelating diphosphines. Many structures with narrower angles and in which the ligands act as a bridge between two metals have been characterized. On the other hand the formation of interesting *trans*-complexes in which one of the additional ligands is included in the cavity avoiding *trans–cis*-isomerization converts them in unique *trans*-chelators (at least from a reactivity point of view).

To the best of our knowledge there are no *cis*-complexes reported of cyclodextrine based diphosphines **17**. Remarkably, these diphosphines also demonstrated a marked tendency to form *trans*-complexes confining the metal in the entry of the cavity and some ligands (especially chlorides) included in it (see Scheme 17) [130]. In this case, the ligand entrapment is supposed to be assisted by weak interactions with the H5 of the cyclodextrine. The molecular structure of two examples of this type of complexes has been analyzed by X-ray diffraction (Pt**17**Cl_2 and Ru**17**$(CO)_2Cl_2$, Table 6) [130]. In the latter, in which the ligand



Scheme 16. Proposed dynamics in *cis*-complexes of ligand **15**.



Scheme 17. Examples of *trans*-chelating inclusion complexes obtained with ligands **15-17**.

spans *trans*-position in an octahedral compound, two chlorides are located inside the cavity! The reactivity of ligand **17** with Ag precursors was also studied in order to analyze ligand exchange processes inside the cavity [119].

2.2. Relevant NMR-data of complexes containing *trans*-diphosphines

The NMR spectra of coordination complexes containing *trans*-chelating diphosphines are, of course, basically analogous to the ones of related complexes with two monophosphines in *trans*-coordination sites. Nevertheless, the structural information that can be inferred from them makes it worth to highlight here some of their peculiarities. In most of the cases, the proper analysis of the NMR spectra of the carefully chosen complexes would suffice to state if the ligands are capable to coordinate in a *trans*-manner. Whether the formed complex is a *trans*-mononuclear or a *trans*-oligomer has to be assessed by other techniques (vapor pressure osmometry, DOSY, Gel Permeation Chromatography, X-ray analysis, etc.), but surely a distinction between *trans*- or *cis*-complexes can be clearly made by simple inspection of their NMR spectra.

In Table 8 a list of the most relevant data of several *trans*-complexes with ligands **1**–**15** is presented to exemplify the trends discussed here.

At first instance one might think that the most relevant spectroscopic information concerning the coordination mode of a ligand would come from its ^{31}P NMR spectra, and indeed this is the case, but usually only if the diphosphine is coordinated to a magnetically active metal (vide infra). The value of the ^{31}P–^{31}P coupling constant is clearly indicative of a *trans*- or *cis*-relative arrangement of the two phosphorus atoms, but most of the times, due to the absence of asymmetry in the ligand, this coupling constant cannot be observed in the phosphorus signals. In these cases, most of the structural information comes from inspection of the ^{13}C{^{1}H}- and ^{1}H NMR spectra of the backbone.

It has been known since the early 60s that "virtual coupling" can be observed in spectra of other nuclei, initially only in the ^{1}H NMR spectra, of some transition metal complexes containing two coordinated phosphines [132,133]. This phenomenon, which was later also observed in the corresponding ^{13}C{^{1}H} NMR spectra became an important tool for geometry assignments [134]. From a practical point of view (leaving aside the theory behind it) [132,134–139], as a result of the large ^{31}P–^{31}P coupling experienced by two phosphorus atoms in mutually *trans*-positions of an organometallic compound, the C atoms (and H attached to them) of the backbone can appear in the corresponding NMR spectra as "virtual triplets" and rarely as more complex spectra, because the P–P coupling constant is usually much larger than the other constants involved. Although this phenomenon can be extended to the whole molecule, in Table 7 only the ones reported for the methylene groups directly connected to phosphorus (if they are) are presented. This phenomenon is called "virtual coupling" because even though the longer range $J_{P'-C}$ or $J_{P'-H}$ are close to zero, lines due to this second phosphorus are observed in the ^{13}C- or ^{1}H NMR spectrum, respectively, caused by the strong ^{31}P–^{31}P coupling. So the carbon and proton nuclei are "virtually" coupled to a "triplet" set of

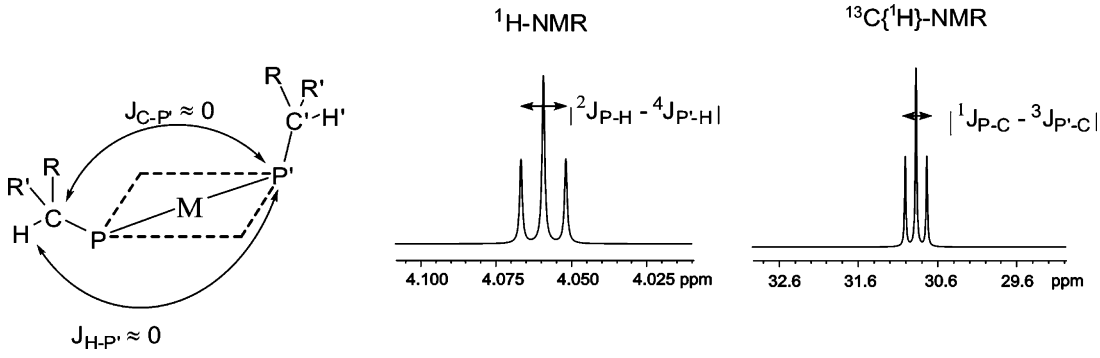


Fig. 2. Virtual coupling in *trans*-complexes.

Table 8
Relevant NMR data of complexes containing ligands **1-17**

L	Complex	^{31}P NMR			^{1}H NMR[a]				^{13}C NMR[a]		Solvent	Reference
		δ (ppm)	$^{1}J_{P-M}$ (Hz)	$^{2}J_{P-P}$ (Hz)	δ (ppm)	$J\|^{2}J_{H-H}\|$ (Hz)	$J\|^{2}J_{P-H}+^{4}J_{P'-H}\|$ (Hz)	$J\|^{3}J_{M-H}\|$ (Hz)	δ (ppm)	$J\|^{1}J_{P-C}+^{3}J_{P'-C}\|$ (Hz)		
1 R = Ph	L	−8.7							36.7	15.9[b]	nd	[21]
1 R = Ph	$NiLCl_2$	6.5			3.93		7.3				nd	[21,29]
1 R = Ph	$NiLBr_2$	12.1			4.22		10.3				nd	[21]
1 R = Ph	$NiLI_2$	8.8			4.70		8.8		41.8	29.3	nd	[21]
1 R = Ph	$NiL(NCS)_2$	14.9			3.80		9.1		33.4	29.3	nd	[21]
1 R = Ph	$PdLCl_2$	19.7			4.30		9.1				nd	[21]
1 R = Ph	$PdLBr_2$	16.0			4.56		8.1				nd	[21]
1 R = Ph	$PdLI_2$	5.7			5.00		7.8				nd	[21]
1 R = Ph	$PtLCl_2$	16.8	2602		4.32		9.6	28.2			nd	[21]
1 R = Ph	$PtLBr_2$	12.6	2492		4.57		8.9	34.1			nd	[21]
1 R = Ph	$PtLI_2$	4.1	2429		4.98		8.8	31.3			nd	[21]
1 R = Ph	CuLI	−4.7			3.98		6.4				CD_2Cl_2	[22]
1 R = Ph	CuLCl	−4.5			3.89		6.7				CD_2Cl_2	[22]
1 R = Ph	$CuLNO_3$	−4.5			3.73		6.1				CD_2Cl_2	[22]
1 R = Ph	AgLI	2.6	378, 437[c]		3.93		6.7				$CDCl_3$	[22]
1 R = Ph	AgLCl	6.2	411, 474[c]		3.93		5.9				$CDCl_3$	[22]
1 R = Ph	AgLBr	7.1	408, nd									
1 R = Ph	$AgLNO_3$	8.0	461, 536[c]		4.10		nd				$CDCl_3$	[22]
1 R = Ph	$AgL(BF_4)$	12.1	515, 593[c]		4.15		nd				$CDCl_3$	[22]
1 R = Ph	$AgL(ClO_4)$	10.5	507, 585[c]								$CDCl_3$	[40]
1 R = Ph	$AgL(SnCl_3)$	8.5	418, 481[c]								$CDCl_3$	[40]
1 R = Ph	AuLI	38.1			4.63		7.9				$CDCl_3$	[22]
1 R = Ph	AuLCl	40.9			4.70		9.1				$CDCl_3$	[22]
1 R = Ph	$AuLNO_3$	43.0			4.49		8.5				$CDCl_3$	[22]
1 R = Ph	RhL(CO)Cl	28.2	124		5.28 3.64	14.0	9.0				$CDCl_3$	[23]
1 R = Ph	RhL(CO)Br	26.0	123		5.39 3.80	13.8	nd				$CDCl_3$	[23]
1 R = Ph	RhL(CO)I	22.9	122		5.58 4.08	14.0	8.0				$CDCl_3$	[23]
1 R = Ph	RhL(CO)(NCS)	28.0	125		4.68 3.75	13.5	9.0		36.7	25.0	$CDCl_3$	[23]
1 R = Ph	$[RhL(CO)(CH_3CN)][BF_4]$	28.0	120		4.42	nd	nd				Acetone-D6	[23]
1 R = Ph	$RhL(CO)(CH_3CN)$				3.67 3.19	13.0	6.0				$CDCl_3/C_6D_6$	[23]
1 R = Ph	IrL(CO)Cl	21.7			5.23 3.82	13.8	9.5				$CDCl_3$	[23]
1 R = Ph	IrL(CO)Br	19.0			5.35 3.98	13.8	9.5				$CDCl_3$	[23]
1 R = Ph	IrL(CO)I	14.5			5.56 3.98	14.0	9.0				$CDCl_3$	[23]
1 R = Ph	IrL(CO)(NCS)	21.2			4.66 3.94	13.6	9.1				$CDCl_3$	[23]
1 R = Ph	$[IrL(CO)(CH_3CN)][BF_4]$	22.1			4.62	nd	nd		37.0	30.9	$CDCl_3$	[23]
1 R = Ph	$IrLHCl_2(CO)$	6.5			5.42 3.72	13.2	9.0				$CDCl_3$	[23]
1 R = Ph	$IrLHBr_2(CO)$	−5.4			4.71 3.64	14.2	nd				$CDCl_3$	[23]
1 R = Ph	$IrLHI_2(CO)$	−21.7			4.60 4.05	14.5	8.0				$CDCl_3$	[23]
1 R = Ph	$IrLH_2(CO)$	0.1			5.28 4.18	12.0	8.5				$CDCl_3$	[23]
1 R = Ph	$[IrLH_2(CO)(CH_3CN)][BF_4]$	4.5			4.50 4.20	13.0	6.0				$CDCl_3$	[23]
1 R = Ph	$[IrLH_2(CO)_2][BF_4]$	−3.2			4.44	8.8					$CDCl_3$	[23]
1 R = Ph	$FeL(CO)_3$	76.1			4.19	9.1					Acetone (i.c. C_6D_6)	[26]
1 R = Ph	$RuL(CO)_3$	49.5			4.16		8.2				$CDCl_3$	[26]
1 R = Ph	RuLCl(NO)	31.5			5.10 4.14	13.8	7.3 11.3				C_6D_6	[27]
1 R = Ph	RuLCl(NO)(CO)	36.7			5.17 3.88	14.2	9.5 11.6				CD_2Cl_2	[27]
1 R = Ph	$PtLH(PPh_3)$	18.8	2730		3.94		8.0	43.0			C_6D_6	[38]
1 R = *p*-tolyl	$NiLCl_2$	6.8			3.90		10.1				nd	[29]
1 R = *p*-tolyl	$NiL(NCS)_2$	14.9			3.75		9.8				nd	[29]
1 R = *p*-tolyl	$PdLCl_2$	19.6			4.29		9.2				nd	[29]
1 R = *p*-tolyl	$PtLCl_2$	16.4	2577		4.30		9.3	29.3			nd	[29]

Table 8 (*Continued*)

L	Complex	^{31}P NMR			^{1}H NMR[a]				^{13}C NMR[a]		Solvent	Reference
		δ (ppm)	$^{1}J_{P-M}$ (Hz)	$^{2}J_{P-P}$ (Hz)	δ (ppm)	$J\|^{2}J_{H-H}\|$ (Hz)	$J\|^{2}J_{P-H}+^{4}J_{P'-H}\|$ (Hz)	$J\|^{3}J_{M-H}\|$ (Hz)	δ (ppm)	$J\|^{1}J_{P-C}+^{3}J_{P'-C}\|$ (Hz)		
1 R = *p*-MeO-C_6H_4	$NiLCl_2$	4.16			3.85		11.0				nd	[29]
1 R = *p*-MeO-C_6H_4	$NiL(NCS)_2$	13.5			3.76		10.3				nd	[29]
1 R = *p*-MeO-C_6H_4	$PdLCl_2$	17.6			4.25		8.6				nd	[29]
1 R = *p*-MeO-C_6H_4	$PtLCl_2$	14.7	2552		4.25		9.2	29.0			nd	[29]
1 R = *p*-CF_3-C_6H_4	$NiLCl_2$	8.3			3.97		10.1				nd	[29]
1 R = *p*-CF_3-C_6H_4	$NiL(NCS)_2$	14.4			3.85		10.1				nd	[29]
1 R = *p*-CF_3-C_6H_4	$PdLCl_2$	21.4			4.34		8.9				nd	[29]
1 R = *p*-CF_3-C_6H_4	$PtLCl_2$	18.6	2640		4.36		8.9	30.2			nd	[29]
1 R = C_6H_{11}	$NiLCl_2$	9.4			3.34		9.7				nd	[29]
1 R = C_6H_{11}	$NiL(NCS)_2$	27.4			3.32		9.1				nd	[29]
1 R = C_6H_{11}	$PdLCl_2$	26.7			3.75		7.6				nd	[29]
1 R = C_6H_{11}	$PtLCl_2$	18.9	2416		3.79		7.9	28.1			nd	[29]
1 R = C_6H_{11}	PtLHCl	34.9	2781		3.86		7.4	37.5			nd	[29]
1 R = *t*-Bu	$NiL(NCS)_2$	41.1			3.82 2.93	14.0	n.d. 9.0				nd	[29]
1 R = *t*-Bu	$PdLCl_2$	42.1			5.03 2.93	13.7	8.0 6.0				nd	[29]
1 R = *t*-Bu	$PtLCl_2$	29.5	2419		5.10 2.97	13.5	9.0 5.0	n.d. 48			nd	[29]
1 R = *t*-Bu	PtLHCl	59.1	2836		n.d.						nd	[29]
1 R = Ph	$HgL(NO_3)_2$	45.6	5710								$CDCl_3$	[41]
1 R = Ph	$HgLCl_2$	29.1	4671								$CDCl_3$	[41]
1 R = Ph	$HgLBr_2$	23.5	4219								$CDCl_3$	[41]
1 R = Ph	$HgL(SCN)_2$	33.2	4189								$CDCl_3$	[41]
1 R = Ph	$HgLI_2$	14.9	3624								$CDCl_3$	[41]
1 R = Ph	$HgL(CN)_2$	15.0	2914								$CDCl_3$	[41]
2 R = Ph	$PtLCl_2$	21.4	2612		4.06		7.3		30.89	28	$CDCl_3$	[45,46]
2 R = p-MeO-C_6H_4 R′ = Ph	$PtLCl_2$	20.7 21.4	2550–2600 2600–2650	490	4.03		n.d.		30.91	27	$CDCl_3$	[46]
2 R = Ph	$PdLCl_2$	25.1			4.08		6.8		30.90	18	$CDCl_3$	[45,46]
2 R = Ph	$PdLBr_2$	29.9			4.10		7.1		33.25	19.2	$CDCl_3$	[46]
2 R = Ph	$PdLI_2$	27.8			4.07		n.d.		36.35	19.3	$CDCl_3$	[46]
2 R = Ph	IrL(CO)Cl	21.0 40.4		344							$CDCl_3$	[46]
2 R = Ph	RhL(CO)Cl	26.2 48.1	129 126	355							$CDCl_3$	[46]
2-H R = Et	RhL(CO)Cl	20.8 26.5	119 120	340							$CDCl_3$	[141,142]
2 R = 2-furyl	RhL(CO)Cl	4.5 12.3	135 133	394							$CDCl_3$	[46]
3 R = iPr	$[AgL][NO_3]$	20.7	482, 556[c]								$CD_3C(O)CD_3$	[59]
3 R = Ph	PdL(*p*-C_6H_4CN)Br	20.9 14.6	431								$CDCl_3$	[54]
3 R = POP	PdL(*p*-C_6H_4CN)Br	−22.5 −23.8	485								$CDCl_3$	[54]
3 R = Ph	$PtLCl_2$	17.6	2723								$CDCl_3$	[52]
3 R = Ph	RhL(CO)Cl	22.3 26.5	132 132	365							CD_2Cl_2	[56]
3 R = Ph	RhL(CO)I	25.6 21.7	129 118	359							CH_2Cl_2[d]	[54]
4[e] R = 9-ph	$PtLCl_2$	9.9	2500								CD_2Cl_2	[69]
4[e] R = 9-ph	RhL(CO)Cl	22.1 15.4	122 122	350							CD_2Cl_2	[69]
4[e] R = 9-ph	$PdCl_2$	13.6									CD_2Cl_2	[69]
4 R = Ph	$RuLH(CO)(PPh_3)$	58.8 56.1	232									[71]
5 R = iPr	$PdLCl_2$	33.9							[f]		$CDCl_3$	[84]
5 R = iPr, R′ = Ph	$PdLCl_2$	38.1 14.47							[f]		$CDCl_3$	[84]
5 R = iPr	RhL(CO)Cl	61.7	171								$CDCl_3$	[86]
6 R = Ph	$PdCl_2L$	16.1									$CDCl_3$	[88]
6 R = Cy	$PdCl_2L$	59.7									$CDCl_3$	[90]
6 R = tBu	$PdCl_2L$	28.3									$CDCl_3$	[90]
6 R = Ph[g]	$PdCl_2L$	26.3			2.91	13	n.d.				$CDCl_3$	[89]

Table 8 (*Continued*)

L	Complex	^{31}P NMR			^{1}H NMR[a]				^{13}C NMR[a]		Solvent	Reference
		δ (ppm)	$^{1}J_{P-M}$ (Hz)	$^{2}J_{P-P}$ (Hz)	δ (ppm)	$J\|^{2}J_{H-H}\|$ (Hz)	$J\|^{2}J_{P-H}+{}^{4}J_{P'-H}\|$ (Hz)	$J\|^{3}J_{M-H}\|$ (Hz)	δ (ppm)	$J\|^{1}J_{P-C}+{}^{3}J_{P'-C}\|$ (Hz)		
							n.d.					
					3.21							
6 R = Cy[g]	$PdCl_2L$	33.7			2.53	13	n.d.				$CDCl_3$	[89]
							n.d					
					2.84							
6 R = tBu[g]	$PdCl_2L$	55.1			2.69	13	n.d.				$CDCl_3$	[89]
							n.d					
					2.93							
7	$PdLCl_2$	20.56			3.51	13	8.4				$CDCl_3$	[91]
					4.45							
N-8	$[AgL][ClO_4]$	43.59	537, 643[c]								$CDCl_3$	[92]
9a	RhL(CO)Cl	37.1	130								$CDCl_3$	[97]
9b	RhL(CO)Cl	35.5	135								$CDCl_3$	[97]
9c	RhL(CO)Cl	35.7	130								$CDCl_3$	[97]
9a	$PdLCl_2$	24.0									$CDCl_3$	[98]
H-11	IrL(CO)Cl	27.1									$CDCl_3$	[99]
Ph-11	IrL(CO)Cl	27.9									$CDCl_3$	[99]
Ph-11	$PtLI_2$	11.9	2702								$CDCl_3$	[99]
12b	$PtLCl_2$	15.4	2457						[f]		$CDCl_3$	[101]
12b	$PdLCl_2$	19.4							[f]		$CDCl_3$	[101]
H-15	$PtLCl_2$	20.6	2584		6.74[h]		10.5[h]				$CDCl_3$	[124]
H-15	$[AgL][BF_4]$	10.4	503, 580[c]								$CDCl_3$	[129]
H-15	$PtLH(PPh_3)$	24.2	2706								$CDCl_3$	[129]
H-15	PdLMe(py)	27.0			6.62[h]		9[h]				CD_2Cl_2	[129]
H-15	$RuLCl_2(CO)_2$	12.9			6.82[h]		n.d.[h]				CD_2Cl_2	[129]
H-15	$RuLCl_2(CO)_2$	42.4			6.75		10				CD_2Cl_2	[129]
16 R = C(O)NEt_2	PtLHCl	22.7	3122						70.24	51	$CDCl_3$	[126,127]
16 R = C(O)NEt_2	$PtLH(PPh_3)$	14.38	2879						73.21	52	$CDCl_3$	[126,127]
16 R = C(O)NEt_2	$[AuL][BF_4]$	36.9							72.01	41	$CDCl_3$	[126]
16 R = C(O)NEt_2	$[AgL][BF_4]$	−0.9	542, 469[c]						n.d	n.d	$CDCl_3$	[126]
16 R = (*R*)-C(O)NHCHMePh	$PtLH(PPh_3)$	15.9	2879						74.17	60	$CDCl_3$	[126]
16 R = CH_2OMe	$PtLH(PPh_3)$	15.6	2843						73.02	55	$CDCl_3$	[126]
16 R = C(O)OEte	PtLHCl	23.8	3148								$CDCl_3$	[126]
16 R = C(O)NEt_2	$[RhL(CO)][BF_4]$	18.1	127						72.99	43	$CDCl_3$	[126]
16 R = (*R*)-C(O)NHCHMePh	$[RhL(CO)][BF_4]$	20.7	132	331	5.68	12	8	0	73.35	46	CD_2Cl_2	[126]
		14.26	132		5.32		9	2				
					5.46	12	12	0				
					5.31		12	3				
17	RhLCl(CO)	17.9	132		2.84	n.d	n.d		35.83	22.4	C_6D_6	[130]
					3.65							
17	PdLMeCl	19.4			2.77		n.d.		37.3	24.7	C_6D_6	[130]
17	$RuL(CO)_2Cl_2$	12.4			2.54		n.d.		33.5	28.0	$CDCl_3$	[130]
17	$[AgL(CH_3CN)][BF_4]$	7.6	458, 529		2.52		n.d.				CD_3CN	[119]
17	$[AgL(C_6H_5CN)][BF_4]$	8.7	458, 529		3.30–3.35		n.d.				CD_3CN	[119]

nd: not determined or not specified in the original reference.

[a] Chemical shift of the C or CH_2 (if there is) of the backbone directly bonded to P.

[b] $|^{1}J_{P-C}|$.

[c] $|^{1}J_{107Ag-P}|$, $|^{1}J_{109Ag-P}|$.

[d] Unlocked spectra.

[e] 9-ph = 9-phosphacyclo[3,3,1]non-9-yl.

[f] The splitting in virtual triplets of several C atoms is reported, but the spectra are not assigned.

[g] Cyclometallated P–C–P ligand.

[h] *m*-H of *o*-Ar-P, $|^{3}J_{P-H}+{}^{5}J_{P'-H}|$.

phosphorus nuclei (see Fig. 2). For intermediate cases, detailed coupling constants can be deduced from the spectra by computer simulation.

In ^{13}C NMR spectra a spins system of type AXX′ (A = C; X, X′ = P) is attributed for the observed triplets. Strictly speaking, this signal will appear as a 1:2:1 triplet if $|^{n}J_{C-P} - {}^{n+2}J_{C-P'}|^2 < 8^2J_{P-P'}\Delta\nu_{1/2}$[4] (which will be the case for large ^{31}P–^{31}P *trans*-coupling constants and nearly null $^{n+2}J_{C-P'}$) [136]. The separation between the first and the third line corresponds to $|^{n}J_{P-C}+{}^{n+2}J_{P'-C}|$, and it is the value usually reported ($|^{1}J_{P-C}+{}^{3}J_{P'-C}|$ for the carbon directly attached to P) [136,139].

For the ^{1}H NMR spectra the spin system is described as $A_nXX'A'_n$ (A, A′ = H; X = P). In this case, the resulting signal is also a 1:2:1 triplet when $|^{n}J_{H-P}-{}^{n+2}J_{CH-P'}|^2 < 2^2J_{P-P'}\Delta\nu_{1/2}$ [136]. The value of $|^{2}J_{P-H}+{}^{4}J_{P'-H}|$ can be directly deduced from the ^{1}H NMR spectra.

Some reported values for these coupling constants are presented in Table 8, and the presence of such signals constitutes an indication of the linear arrangement of the two phosphorus atoms. The situation can be more complex when, for instance in a *trans*-diphosphine containing directly attached CH_2 groups

[4] $\Delta\nu_{1/2}$ is related to the resolving power of the spectrometer.

in which the two H are not magnetically equivalent. In these cases, although the corresponding carbon spectra will appear as only one "virtual triplet" in the ^{13}C NMR, the spin system for the protons can be far more complicated. This situation is commonly observed in asymmetrically substituted square-planar complexes or when, for steric reasons, the backbone is constrained in a certain conformation [23,29].

One should be also be aware that although the presence of virtual triplets in the ^{13}C or ^{1}H NMR spectra is often taken as a proof of a *trans*-P–P arrangement, simulation shows that for instance $^{2}J_{P-P'} > 20$ Hz and the common $^{n}J_{P-C}$ and $^{n+2}J_{P'-C}$ coupling constants already apparent triplets will be observed. Indeed, the apparent coupling constants range from 1 through 5 Hz, the average of $^{n}J_{P-C}$ (0–20) and $^{n+2}J_{P'-C}$ (0–10), which often have opposite signs [134]. The appearance of virtual triplets for *cis*-complexes of nickel [140] or in the recently reported *cis*-complexes of SPANphos (**3**) provide evidence that care must be taken when using this as the only criterion [57].

Coupling with active metal centers can (in some cases) also univocally define the relative positions of phosphines coordinated to them. Especially indicative is, for instance, the analysis of the ^{31}P NMR spectra of the corresponding platinum(II) compounds. The value of the $J_{195Pt-P}$ (which can be extracted from the satellites observed in the ^{31}P NMR due to 33.8% abundance of active ^{195}Pt) can be directly correlated with the coordination mode of the diphosphine. Values below 3000 Hz (usually around 2500 Hz) are encountered for *trans*-diphosphines, and higher values (around 3600 Hz) for complexes in which the phosphines occupy *cis*-positions.

The value of the ^{31}P–^{31}P coupling constant is also relevant, as it should be large for two phosphorus atoms in relative *trans*-positions. Unfortunately, the coupling can only be observed when the two phosphorus are nonequivalent. With *trans*-diphosphines, this will be the case only in asymmetrically substituted complexes with chiral ligands, or if asymmetrically substituted diphosphines are used. Few examples have been reported (Table 8) but the available data (and also the one extracted from complexes with monophosphines) give us some indicative numbers. $^{2}J_{P-P'}$ *trans*-coupling constants over 300 Hz (300–500 Hz) are expected for square-planar Rh(I) or Ir(I) complexes, and values around 500 Hz for the corresponding Pt(II) or Pd(II) compounds.

2.3. Reactivity and catalysis

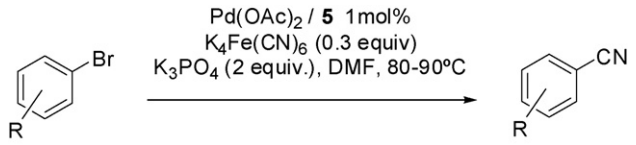
The study of the reactivity of *trans*-chelating diphosphines is crucial in order to evaluate the scope of these ligands in catalytic reactions. Most of the exhaustive reactivity studies were performed using the pioneering ligand TRANSPHOS on the early work of *trans*-diphosphines.

Ligand addition reactions of neutral small molecules as CO, SO_2 or PR_3 to *trans*-square-planar compounds of ligand **1** were initially studied due to their putative (at that time) implication in important organometallic catalytic cycles as hydroformylation, hydrogenation or oligomerisation. Reaction of *trans*-Ir**1**(CO)Cl or *trans*-[Ir**1**(CO)(CH_3CN)][BF_4] with CO (saturated solution) rendered a new species tentatively identified as the product of CO addition. Unfortunately attempts to isolate it led to the recovery of the starting material presumably by loss of CO. Nearly the same behaviour was observed when the addition of SO_2 to *trans*-Ir**1**(CO)Cl was studied. The situation was even worse for the addition of PPh_3 for which no reaction was observed. These studies indicated that the presence of ligand **1** in the rhodium and iridium complexes causes a significant destabilization of the five-coordinated species relative to the four-coordinated starting compounds [23].

Oxidative addition of O_2, H_2 or hydrogen halides to *trans*-MX(CO)**1** was also investigated, due to the potential catalytic implications [23]. It was expected that the ligand decreased the tendency to form six-coordinated species. In fact, complex *trans*-IrCl(CO)**1** reacted with O_2 only after 24 h at a pressure of 130 bar in only a 25% yield, and when the O_2 pressure was released, the compound reverted to the starting material. On the contrary, complexes *trans*-IrX(CO)**1** (X = Cl, Br, I) reacted smoothly with hydrogen halides to give the corresponding Ir(III) species $IrHX_2$(CO)**1**. In a similar manner, H_2 was oxidatively added to species *trans*-IrI(CO)**1** and *trans*-[Ir (CO)(CH_3CN)**1**][BF_4], concluding that the *trans*-chelating ligand allows the formation of six-coordinated species which are best formed if at least one of the donor atoms is hydrogen.

Migratory insertions and reductive eliminations from square-planar d^8 complexes have been extensively studied, because of their relevance to many catalytic processes [143,144]. Special attention has been dedicated to the effect of chelating diphosphines on the reaction rate. Both reactions require a *cis*-coordination of the two groups involved. In most cases, theoretical calculations point out that the chelating ligand widens its bite angle while the migration or elimination proceeds, although initially this effect has been overestimated. We must distinguish between migratory insertion reactions and reductive elimination reactions. A simplified picture leads to the conclusion that wide bite angle diphosphines enhance migratory insertion reactions by forcing the two migrating groups to be closer to one another [11,13,145–148]. Thus, this is an indirect steric effect of the bite angle [55,149]. Reductive elimination is clearly enhanced by an electronic bite angle effect. It must be noted that bulky substituents at phosphorus also widen the bite angle and in these instances a separation of steric and electronic effects is not possible [150]. When the two eliminating groups have strongly different character and overlapping orbitals that participate in the bond formation, the elimination takes the character of a migratory reductive elimination, and although electronic effects seem to dominate, in some extreme cases steric effects may play a role as well [55,149,151].

On an early example, the complex Pd**1**Me_2 was tested as a model reaction to study the mechanism of reductive elimination. This Pd-TRANSPHOS compound did not undergo reductive elimination of ethane, not even at 100 °C in Me_2SO, which was considered as a proof of the reaction mechanism and of the reluctance of the ligand for a *trans*- to *cis*-isomerization [144]. Surprisingly, years later, reductive elimination was observed from the related Pd**1**(S-*t*Bu)(*p*-C_6H_4-Me) [145]. In this case, the reactivity was be attributed either to a complex in which the ligand coordinates in a *cis*-manner, or the dissociation of one arm



Scheme 18. Cyanation of aryl bromides catalyzed by Pd/**5**.

of the ligand. This de-chelation could lead to either reductive elimination from a three-coordinate complex or isomerization of the complex to generate a highly reactive *cis*-compound.

A purely *trans*-chelating diphosphine coordinated to a square-planar d^8 complex, should be inactive for these reactions as they require two coordinative vacancies in relative *cis*-positions. Taking advantage of this situation, van Leeuwen et al. inferred from the lack of activity of SPANphos-Pd complexes (together with other evidences) an inner-sphere attack of the alcohol at the coordinated acetyl-carbon atom, as the chain transfer mechanism in Pd-catalyzed CO and ethene copolymerization [55].

2.3.1. Cross-coupling reactions (cyanation, Suzuki and Heck)

As the catalytic cycles of group 10 metal catalyzed cross-coupling reactions contain reductive elimination and oxidative addition reactions as elementary steps that seem to involve *cis*-Pd(II) species, it is logical to assume that *trans*- to *cis*-isomerization is a requisite for these reactions to proceed. Consequently, the activity of the putative *trans*-diphosphines in these reactions should be considered as a proof of their capability to form *cis*-complexes. In most of the cases, probably the outstanding catalytic performance observed for these ligands could be attributed to an extreme bite angle effect, caused by the active *cis*-species.

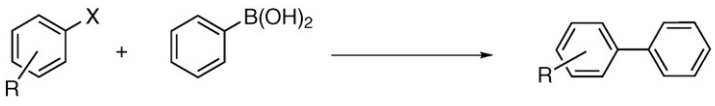
Alternatively an open arm mechanism or the involvement of dinuclear species has been postulated.

Nevertheless, the exceptional results obtained, and the lack of evidence of which is the real active species in each case, prompted us to summarize here the major trends observed.

One of the inherent peculiarities of *trans*-chelating ligands is that once coordinated they do physically "embrace" the metal. This steric protection is responsible for the lack of activity in certain situations (vide infra) but it could be advantageous in other cases. At least, according to Gelman, it accounts for the outstanding performance of the trypticene based ligand **5** when applied in catalytic cyanation of aryl halides (Scheme 18) [85]. This reaction, for which certain Pd catalysts showed to be effective, has the drawback that it is inhibited by high concentrations of cyanide anions, apparently due to the formation of inactive Pd(II)-dicyanide species which cannot be reduced to the active Pd(0) complexes [152,153]. Ligand **5** showed to catalyze the cyanation of a large variety of substrates efficiently under mild conditions, it circumvents the need for amines as co-ligands, and it can be performed without inert atmosphere in common solvents showing in nearly all the cases 99% conversion to the desired aryl-cyanide. The steric protection offered by the ligand to the Pd center against premature contact with cyanides accounts for the excellent activities observed. One might also argue that the wide bite angle accelerates the reductive elimination relative to side reactions giving palladium dicyanide, as is the case in hydrocyanation reactions [10,154,155].

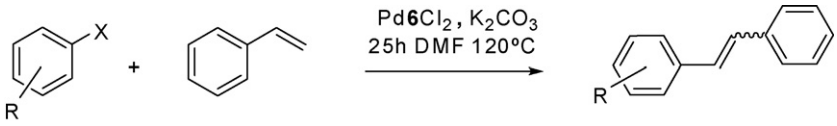
Ligands **5** and **6** (especially the Ph derivative of the latter) showed to be also effective in other cross-coupling reactions such as Suzuki coupling of phenylboronic acids with aryl-halides rendering the desired biphenyls in good to excellent yields [84,90]. In view of these results, Süss-Fink also tested the activity of other *trans*-complexes, namely Pd**7**Cl_2 and Pd**9a**Cl_2, in Suzuki couplings (see Scheme 19) [91,104]. In the case of ligand **7**, its performance was compared to an analogue with monophosphines *trans*-Pd(PPh_2-CH_2-2,4,6-$C_6H_2Me_3$)$_2$)Cl_2. Both systems showed similar productivities at 90 °C for the coupling reaction of 4-bromotoluene and 2,4,6-trimethylphenylbromide with phenyl boronic acid (full conversions after 18 h were obtained for the less hindered substrate). In contrast, at lower temperatures (30 °C) the monophosphine system showed an activity 15 times higher than the *trans*-chelate Pd**7**Cl_2 for the coupling of 4-bromotoluene and was the only active systems for the bulkier 2,4,6-trimethylphenylbromide. It has already been suggested above that this behaviour points to the activities observed at high temperature not to be due to the *trans*-species, but rather to *cis*- or dinuclear compounds, as they were also observed at high temperatures in isolated experiments (vide supra).

For ligand **9a**, strong evidences indicated also that the true catalyst does not contain the ligand in a *trans*-coordination manner. Although good activities were observed with the Pd**9a**Cl_2 system, it seems to isomerize to a *cis*-form under catalytic conditions. The *cis*-tetradentate complex Pd**9a** renders in fact a slightly more active system. Comparison of the Xantphos ligands also revealed that there is a subtle balance between activity and isolated intermediates [[76] and references therein]. In several amination reactions Xantphos gave a faster catalyst than does DPEphos, while the latter gives *cis*-intermediates and the former gives *trans*-intermediates as the isolated complexes.



X = Cl catalyst: Pd(OAc)$_2$/**5**, K_3PO_4, 12h dioxane 70ºC
X = Br catalyst: Pd**6**Cl_2 , Cs_2CO_3, 25h dioxane 100ºC
X = Br R = 4-Me, 2,4,6-trimethyl catalyst: Pd**7**Cl_2 , K_2CO_3, 18h toluene (90-30)ºC
X = Br R = 4-Me catalyst: Pd**9a**Cl_2 or Pd**9a**, K_2CO_3, 18h toluene (90-30)ºC

Scheme 19. Suzuki coupling catalyzed by Pd complexes of ligands **5**, **6**, **7** and **9a**.



Scheme 20. Heck reaction of aryl-bromides with styrene catalyzed by Pd**6**Cl_2.

Thus, *trans–cis*-isomerization followed by a very fast reductive elimination, may be more effective than the formation of a *cis*-intermediate that does not require isomerization, but undergoes the elimination more slowly.

The good results obtained with the use of ligand **6** in Suzuki couplings prompted the authors to test also these ligands for the Heck reaction of arylbromides with styrene (see Scheme 20) [90]. Surprisingly, in contrast with the results obtained for the bis(phenyl) and bis(*tert*-butyl) derivatives (**Ph-6** and **tBu-6**), the bis(cyclohexyl)phosphine analogue (**Cy-6**) was inefficient for all the substrates tested. As it is commonly accepted that a *trans*-chelated complex is inefficient for reductive elimination/oxidative addition [144] this disparity in efficiency is attributed either to a mechanism in which one of the phosphorus of the ligand dissociates from the metal center (happening with different readiness for the different ligands) or to their distinct capability to isomerize from a *trans*- to a *cis*-coordination manner.

2.3.2. *Rhodium catalyzed methanol carbonylation*

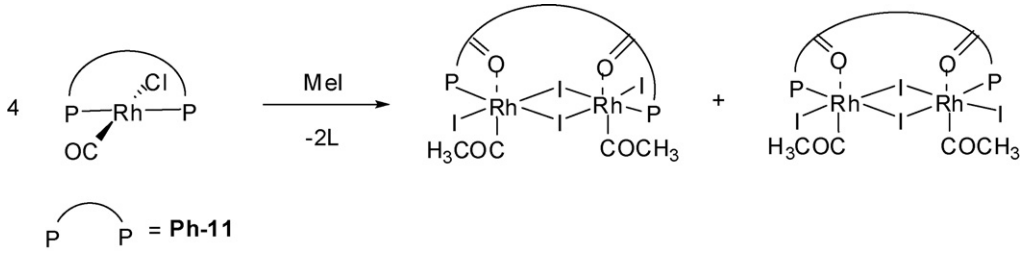
Methanol carbonylation is an industrially relevant catalytic reaction, because the product, acetic acid, is a bulk chemical commodity industrially used for a wide range of applications. The rate liming step is accepted to be the oxidative addition of MeI to a square-planar Rh(I) species. Even though the use of basic phosphines (i.e. PEt_3 [156,157] or methyl-2-diphenylphosphinobenzoate [158]) which increase the nucleophilicity of the rhodium center, was initially considered a very promising strategy, their instability under the harsh conditions of the process constituted a major drawback for their application. Attempts to circumvent the decomposition were undertaken by using bidentate diphosphines, which stabilize the active rhodium species by the chelate effect. A very interesting contribution was published by Süss-Fink with the use of ligands **9**–**12**, as they combined the chelate-effect with the good electron donating properties (assisted probably by a weak O–Rh interaction with the acyl groups of the backbone). A key point is also its capability to coordinate in a *trans*-manner, as then the active species will resemble the ones obtained with PEt_3 (*trans*-RhI(CO)$(PEt_3)_2$) [156,157].

When the corresponding rhodium complexes were tested in methanol carbonylation the activity obtained is ca. 2.5 times higher than that obtained with the phosphine-free Monsanto system under the same catalytic conditions [97,99,159]. The stability of the systems is evident by the ability to perform several runs without any noticeable loss in activity. From the residue of the reaction employing ligand **Ph-11**, the dinuclear isomeric compounds *cis*- and *trans*-Rh_2(**Ph-11**)(μ-$I)_2I_2(COCH_3)_2$ (Scheme 21) were isolated and characterized by X-ray diffraction (vide supra), in addition to the expected complex Rh(**Ph-11**)I(CO). Surprisingly, these species could be also isolated by treatment of the mononuclear Rh(**Ph-11**)(CO)Cl with an excess of MeI (Scheme 21) [99,159].

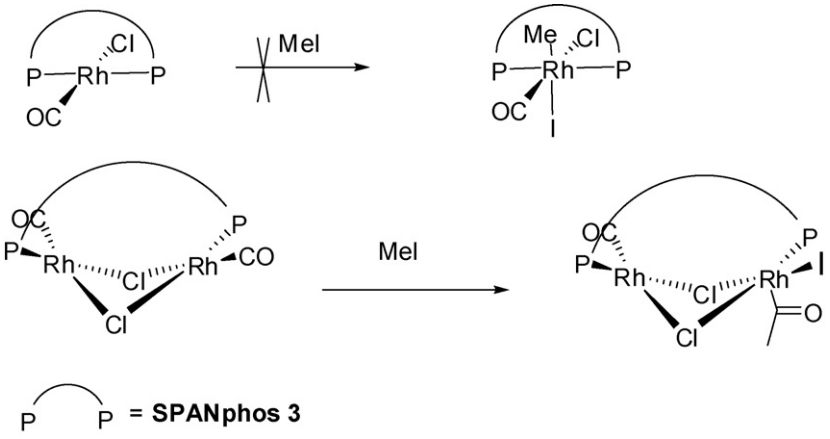
The proposed catalytic cycle is analogous to Monsanto's one, but it involves neutral species containing a *trans*-chelating diphosphine. Presumably, the isolated dinuclear compounds act as resting state for the acetyl complex [Rh(**Ph-11**)I_2(COMe)], generated by two of such molecules by loss of one diphosphine [97,99,159].

Another family of diphosphines displaying a *trans*-coordination mode, SPANphos **3**, has also been tested in this reaction [56,160]. Surprisingly, even though the corresponding *trans*-RhI(CO)**3** rendered systems as active as the Süss-Fink analogues, they showed no reaction in the oxidative addition of MeI (supposed to be the rate determining step). The observed catalytic activity has been attributed to dinuclear species formed under catalytic conditions. The pre-synthesized dinuclear compounds [Rh_2**3**$(\mu\text{-}Cl)_2(CO)_2$], react with MeI at 25 °C with a k_1 value of ca. 0.025 s^{-1} M^{-1} and currently they represent the fastest phosphine based systems reported for methanol carbonylation. According to spectroscopic and GC–MS analysis, the products of the MeI oxidative addition are dinuclear monoacetyl derivatives (Scheme 22).

The reactivity of dinuclear rhodium compounds toward MeI has been subject of study from the late 1970s [161,162]. Unfortunately, no kinetic data is available, but the corresponding mono-



Scheme 21. Synthesis of dinuclear Rh-complexes of ligand **Ph-11** by oxidative addition of MeI to *trans*-Rh(**Ph-11**)(CO)Cl.



Scheme 22. Reactivity of mono and dinuclear Rh-SPANphos complexes with MeI.

and bis-acetyl derivatives have been detected. The fact that the oxidative addition/migration at the second metal center becomes more difficult after the first one took place is a common observation, especially when the "open-book" conformation of the complexes is forced by the (bridging) ligands.

In fact, the possible involvement of dinuclear species in the Monsanto process was proposed already in the earliest studies, where the dimerization equilibrium of the acetyl derivative $[RhI_3(COMe)(CO)]^-$ was considered. The corresponding dinuclear species $[Rh_2I_6(CO)_2(COMe)_2]^{2-}$ was isolated in the form of its trimethylphenylammonium salt and characterized by X-ray diffraction. The possibility that neutral dinuclear methyl and acetyl Rh(III) species play an important role in the Monsanto process has very recently been reconsidered [163]. These neutral species should lead to faster CO migratory insertions and reductive eliminations than their anionic analogues, and surely in the future new ligands able to generate more active dinuclear systems for methanol carbonylation will be developed.

2.3.3. Enantioselective reactions

The success of chiral diphosphines in asymmetric catalysis is vested in their capability to create effectively an asymmetric environment for the active site of the catalyst. Different approaches have been contemplated: Asymmetry in the backbone, at the phosphorus atoms or in their substituents, or combinations of them. It is believed that, in general, the substituents at phosphorus are responsible for the construction of the adequate shape of the "chiral pocket", because they are the most exposed fragments of the ligand and the closest to the remaining coordination sites of the metal. The obvious strategy is then to locate the chirality directly in these substituents or at the phosphorus atom, but synthetically it does not constitute the most straightforward approach. Most commonly, chiral diphosphines are based on an asymmetric backbone, and their success relies on what is called an effective "transfer of chirality" from the backbone to the phosphorus substituents in order to fix them in a chiral manner (Fig. 3).

Theoretically, chiral *trans*-diphosphines should be superior to their *cis*-counterparts (provided that they are equally active for the same transformation) as there is no need to rely on a chirality transfer mechanism. Both the backbone and the phosphorus substituents are directly exposed to the remaining coordination sites of the metal and could contribute to the formation of the "chiral pocket". Unfortunately there are not many examples yet of chiral *trans*-diphosphines to back up this theory, but the extraordinary success of Ito's TRAP ligands in many asymmetric transformations should encourage scientists for further developments.

2.3.3.1. Asymmetric Michael addition. The chiral TRAP ligand **2** proved to activate efficiently 2-cyano carboxylates and amides as nucleophiles for enantioselective aldol and Michael reactions [164–168].

In the first publications on catalysis with TRAP ligands, which represent also the first enantioselective Michael addition catalyzed by a chiral transition metal complex, the reaction between α-cyano carboxylates and various vinyl ketones was reported [47,164,165]. Enantioselectivities ranging from 72 to 93% were obtained with all the derivatives tested (and showed to be strongly dependent on the nature of the ester group R^2) obtaining the best results with R = iPr. Based on these results, Nozaki et al. also applied a puta-

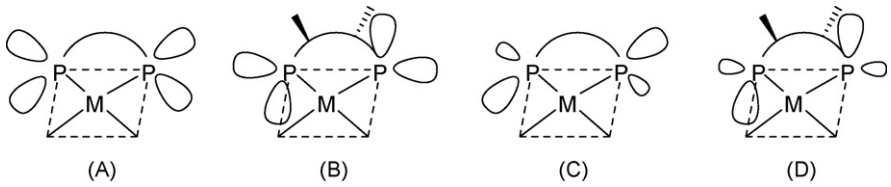
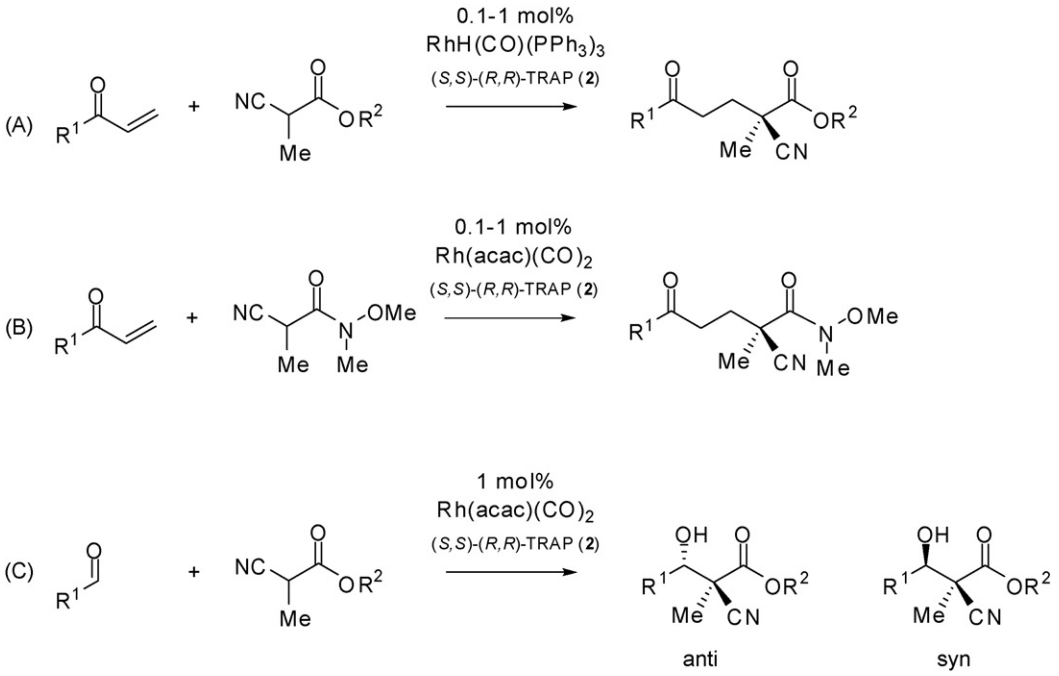


Fig. 3. Square-planar complexes containing *cis*-diphosphines. (A) Aquiral, (B) with chirality in the backbone, (C) chirality at the phosphorus atoms, and (D) chirality both in the backbone and at the phosphorus atoms.



Scheme 23. Asymmetric Michael (A and B) and aldol (C) reactions.

tive *trans*-diphosphine (*R*)-7,7′-bis(diphenylphosphinomethyl)-2,2′-dimethoxy-1,1′-binaphthyl to this reaction reporting enantioselectivities up to 73% [169]. When other "conventional" diphosphines where tested in this reaction (BINAP, DIOP CHIRAPHOS), the ee's never exceeded 17%.

The TRAP ligand also showed outstanding performance when Weinreb amides (α-cyano amides) were used as Michael nucleophiles (B in Scheme 23, ee 89–94%)[166] or in the related aldol reaction of 2-cyano propionates (C in Scheme 23, ee up to 94% for formaldehyde) [168,170].

It was postulated that the outstanding performance of the TRAP ligands in these reactions is related to its *trans*-coordination mode. The key for success is proposed to be a reaction mechanism involving activation of the nucleophile by coordination through the nitrogen atom of the cyano group, and a direct attack of the electrophile on the activated substrate, which implies a C–C formation rather distant from the metal center (around 4.6 Å!). The fact that more reproducible results were obtained when $Rh(acac)(CO)_2$ was used instead of $[RhH(CO)(PPh_3)_3]$ as a metal precursor, prompted the authors to propose a mechanism in which the coordinated acetylacetonate acts as the base to generate the active species containing the deprotonated enolate [168]. It was speculated that only a *trans*-chelating ligand would be suitable to create such a distant chiral environment (Fig. 4) capable of distinguishing between the bulkiness of the alkyl group R and the R^2 group of the enolate intermediate and simultaneously directing the attack of the Michael acceptor. Although the authors propose this theory, they also mention that *cis*-species could be responsible of the catalytic activity, as analysis of the product of the reaction of the ligand with $RhH(CO)(PPh_3)_3$ rendered a mixture of unidentified compounds

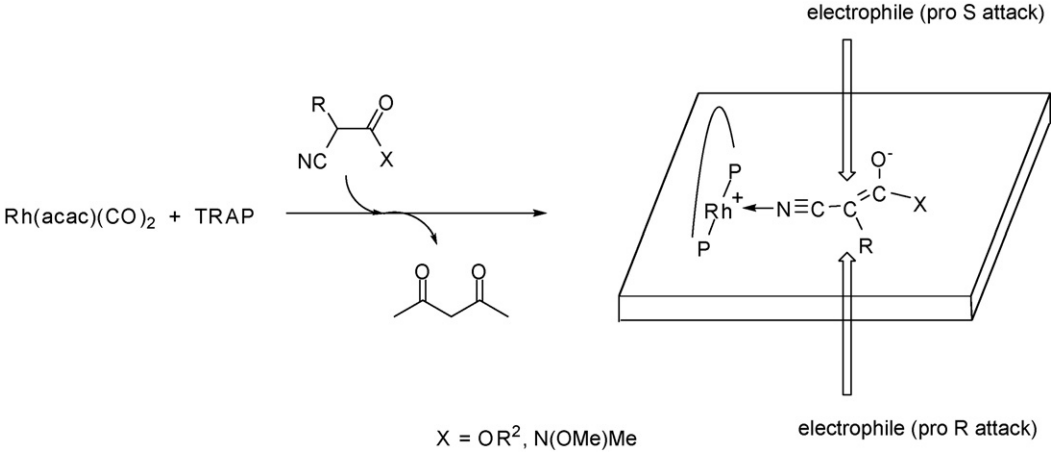
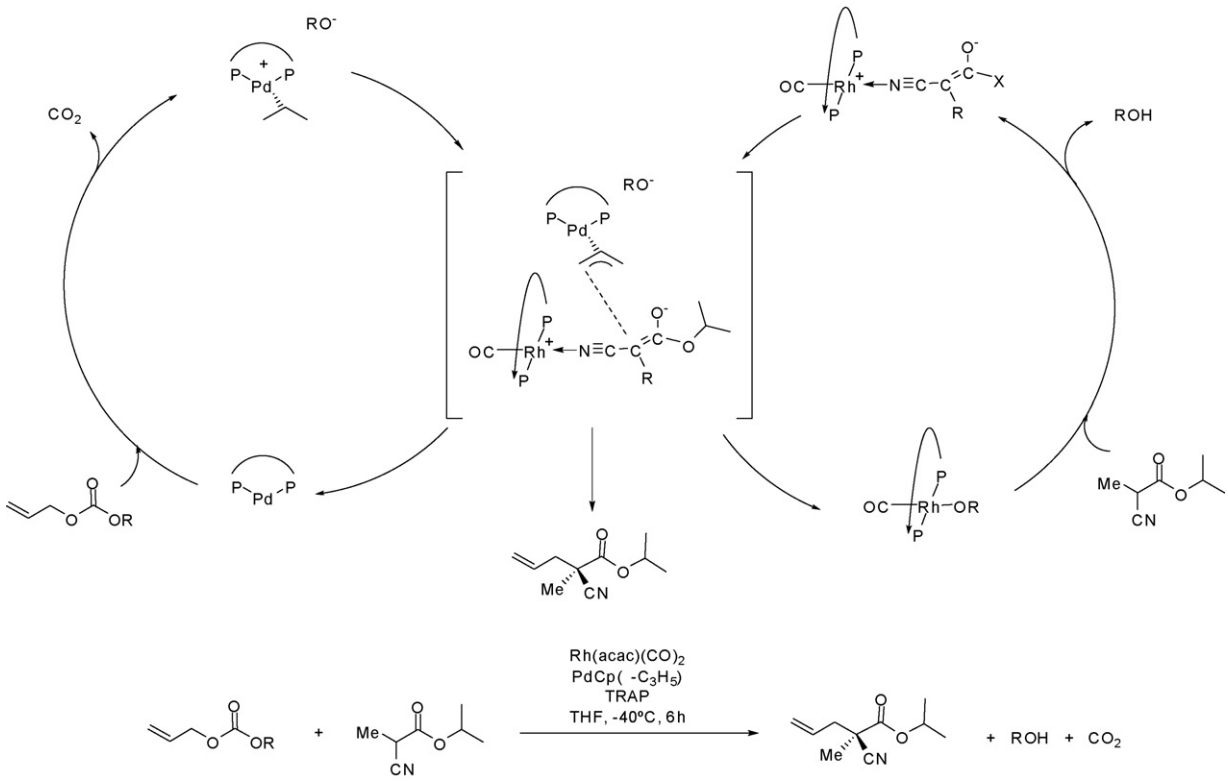
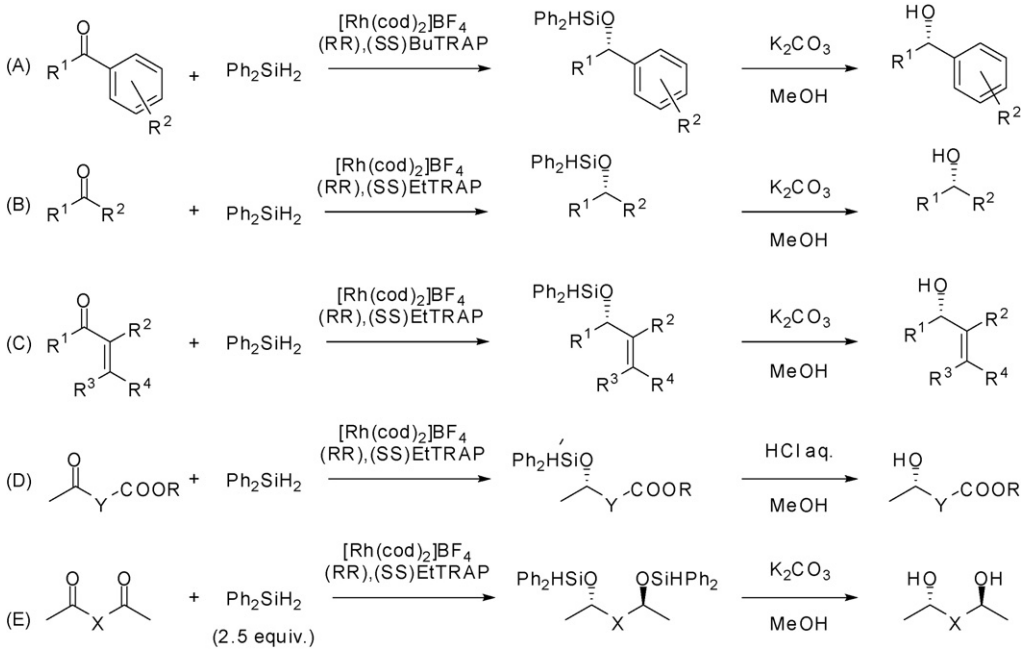


Fig. 4. Proposed mechanism for the activation of nucleophiles for asymmetric Michael and aldol reactions catalyzed by TRAP ligands.

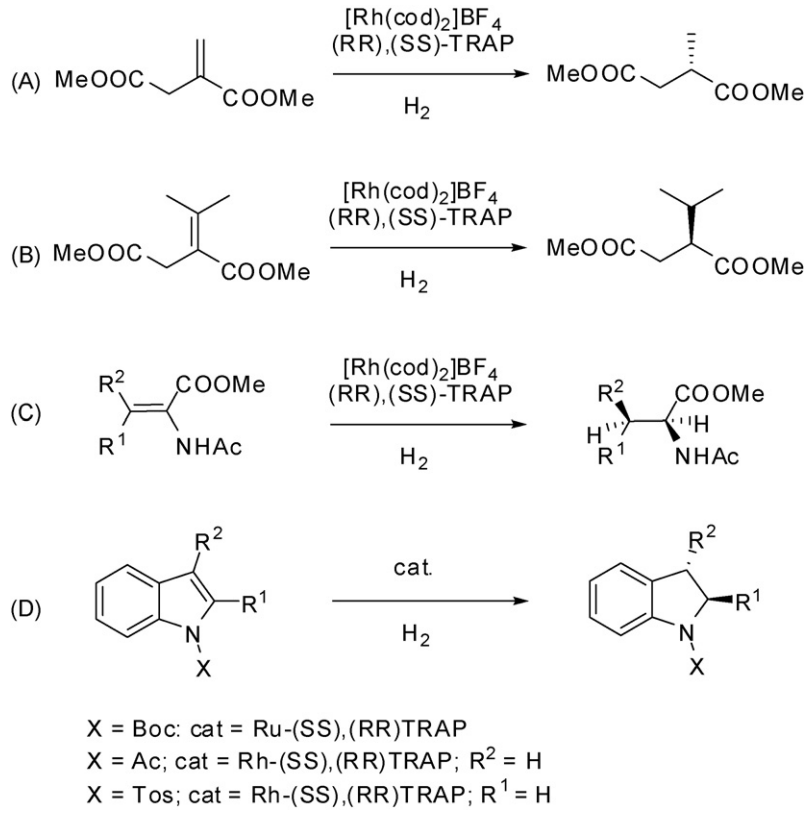


Scheme 24. Two-component Rh-Pd-TRAP catalyzed allylic alkylation of activated nitriles.

An exceptional and elegant example of this "asymmetric nucleophilic activation" and its potential to a wider range of catalytic reactions is the dual Rh-Pd-catalyzed allylic alkylation of activated nitriles (Scheme 24). In this special case, the electrophile is a π-allylpalladium(II) complex instead of the Michael acceptor! Enantioselectivities up to 99% with 93% yield were obtained, and high asymmetric induction was maintained even when the ligand in one (it does not matter which one!) of the catalytic systems was a non chiral diphosphine instead of TRAP [143].



Scheme 25. Asymmetric hydrosilylation of aryl- (A), alkyl- (B) and α,β-unsaturated (C) ketones, ketoesters (D) and symmetric diketones (E) catalyzed by Rh-TRAP systems.



Scheme 26. Asymmetric hydrogenation of dimethyl itaconate (A), dimethyl-2-isopropyllidene succinate (B), α-acetamidoacrylates (C) and protected indoles using TRAP containing catalysts.

2.3.3.2. Asymmetric hydrosilylation. In contrast with the results obtained for "conventional" chiral diphosphines, for which high enantioselectivities were only achieved for ketonic substrates containing a secondary coordinating functional group, TRAP ligands showed high enantioselectivities for the asymmetric hydrosilylation of a wide variety of substrates (Scheme 25) [51,171,172].

For example, acetophenone derivatives were hydrosilylated with enantioselectivities ranging 79–91% ee, but other arylketones also rendered enantiomeric excesses over 80%. For aliphatic ketones the ee ranged from 32 to 96%, and around 90% was obtained for α,β-unsaturated ketones. For ketoesters enantioselectivities up to 98% were also reported, and finally, for symmetrical diketones (to obtain optically pure diols) the best results not only in enantioselectivity but also in diastereoselectivity were obtained for 2,3-butanedione (dl/meso = 90/10, ee 95% (*S*,*S*)) and 3,3-dimethyl-2,4-pentadione (dl/meso = 96/4, ee 99% (*S*,*S*)).

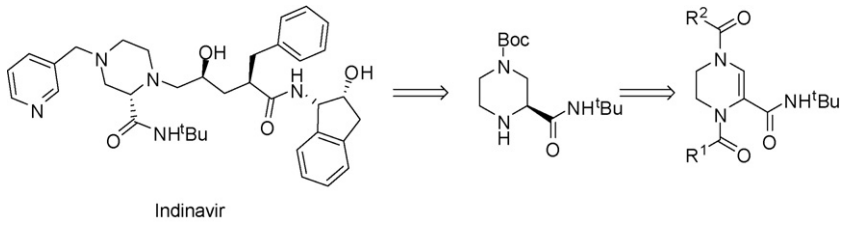
It is noteworthy that a variant of the TRAP ligands, Et-TRAP-H containing only planar chirality and no stereogenic carbon atoms, showed a performance superior to TRAP ligands in this reaction, and induced the same sense of enantioselection. This observation suggested that the stereodiscrimination is controlled by the planar chirality of the ligand [141,142].

2.3.3.3. Asymmetric hydrogenation. The TRAP ligands proved to be effective catalysts for the asymmetric hydrogenation of a variety of substrates ranging from activated olefins as acetamidoacrylates [173,174] or itaconates [175,176] to heteroaromatic compounds [48,170,177,178] with outstanding conversions and enantioselectivities. In all the cases, the success requires a careful choice of the TRAP derivative (the substituent on the phosphorus atom) and the reaction conditions, as a strong influence on both parameters is frequently reported.

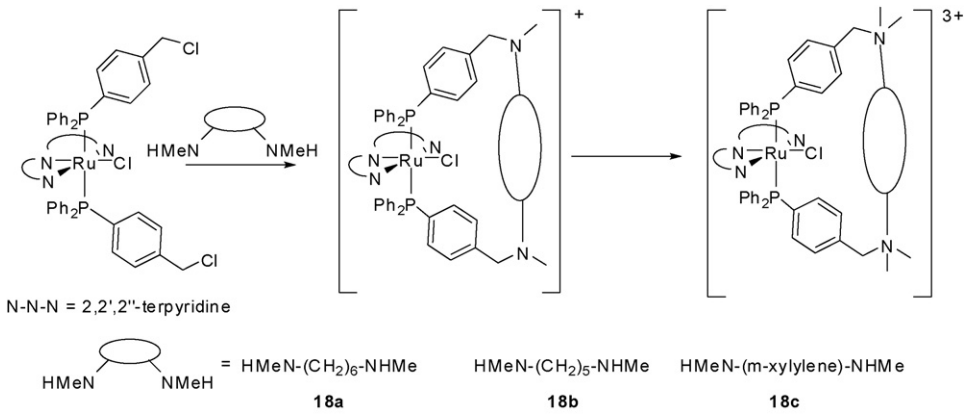
One of the first reports on asymmetric hydrogenation using TRAP derivatives concerns the hydrogenation of dimethyl itaconate (a benchmark reaction to test chiral ligands). In fact, it was hydrogenated with 96% ee when the ethyl derivative Et-TRAP was used as a ligand (A, Scheme 26). Also the tetrasubstituted derivative dimethyl-2-isopropylidene succinate was reduced with high enantioselectivities (up to 78% ee), but in this case the Bu-TRAP ligand showed the best performance (and opposite sense of the enantioselection) [175,176].

Analogously, TRAP ligands with linear alkylic substituents (ethyl and butyl) at the phosphorus atoms showed not only remarkable performance for the asymmetric hydrogenation of α-acetamidoacrylates, but they also induced unprecedented activities and enantioselectivities for the asymmetric hydrogenation of congested β,β-disubstituted α-acetamidoacrylates (conv. 100%, ee 77–88%) (C in Scheme 26) [173,174].

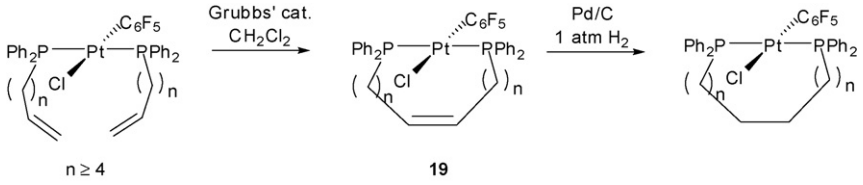
In the case of hydrogenation of more tricky heterocyclic compounds, such us protected indoles, both 2- and 3-substituted indoles have been successfully hydrogenated using TRAP ligands (conventional chiral diphosphines DIOP, BINAP, chiraphos, DuPhos etc, failed to give acceptable enantioselectivities) (D, Scheme 26). Remarkably, the best enantioselectivities



Scheme 27. Indavinir synthesis by asymmetric hydrogenation.



Scheme 28. Synthesis of ligands **18** by metal template.



Scheme 29. Example of construction of *trans*-chelating diphosphines by an intramolecular metathesis reaction.

were obtained when *N*-acetyl-protected-2-substituted indoles and *N*-tosyl-protected-3-substituted indoles were used as substrates, and opposite sense of stereoinduction was obtained [170,177,178]! However, the harsh conditions needed to remove those protective groups after hydrogenation, led the authors to develop a method for enantioselective hydrogenation of N-Boc protected 2- and 3-substituted indoles, which was achieved with enantioselectivities up to 95% and 94%, respectively, when using a Ru-TRAP based system (generated in situ from [Ru(*p*-cymene)Cl_2]$_2$ and PhTRAP[5]) [48].

An applied example of hydrogenation of heterocyclic compounds is the asymmetric hydrogenation of 1,4,5,6-tetrahydropyrazine-2-(*N*-*tert*-butyl)carboxamide to obtain (*S*)-4-(*tert*-butoxycarbonyl)piperazine-2-(*N*-*tert*-butyl) carboxamide, and important synthetic intermediate of Merck HIV protease inhibitor Indavinir (Crixivian). It proceeds at low pressures and temperatures (1 bar H_2, 50 °C) with full conversions and enantioselectivities up to 97% ee. It is remarkable that opposite stereoinductions were obtained depending on the P-substituents (Me or i-Bu) (Scheme 27) [179].

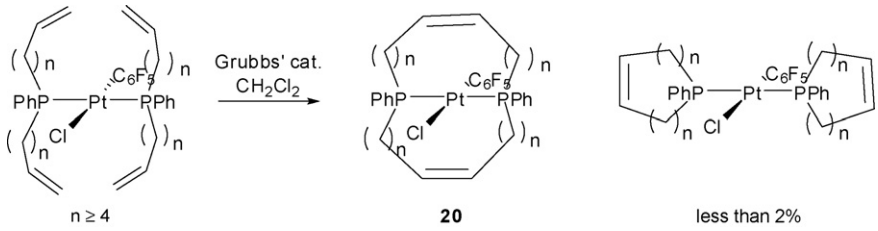
3. Special cases

Alternative strategies have been also considered for the construction complexes containing diphosphines coordinated in a *trans*-manner. They range from generating the covalent bidentate ligand from pre-coordinated monophosphines to the use of supramolecular interactions. Some representative examples will be mentioned in this section.

3.1. Trans-ligands "in situ" formed after metal-template

In an attempt to avoid the formation of dimers or dinuclear species when long-chain diphosphines were used as *trans*-chelators, Takeuchi designed a new approach that consisted in the formation of a *trans*-chelator by creating a "chemical connection" between two pre-coordinated functionalizated phosphines coordinated already in relative *trans*-positions of the metal cen-

[5] Although the spectroscopical data of complex formed by reaction of TRAP and [Ru(*p*-cymene)Cl_2]$_2$ proved the cis coordination manner of the ligand, the authors claim that in the active species, free of the *p*-cymene ligand, TRAP adopts a *trans*-coordination mode, responsible for the high stereoinduction.



Scheme 30. Construction of doubly connected *trans*-diphosphines by intramolecular metathesis reactions.

ter [180]. In spite of the seemingly ideal setup, the formation of dimeric species was observed when the rigid *meta*-xylylene spacer was used (see Scheme 28).

Using the same concept, but a different cyclization reaction, Gladysz constructed several *trans*-spanning diphosphines by means of intramolecular metathesis reactions. For that purpose, phosphines functionalized with terminal alkene groups were used. The resulting unsaturated *trans*-chelators could be subsequently hydrogenated by using Pd/C catalyst (Scheme 29) [181–183].

Also the possibility of using double-functionalized phosphines to construct the "double-bridged" *trans*-diphosphine, was successfully explored by Shima [184]. Surprisingly, the undesired by-products coming from intraligand metathesis were only observed when the carbon bridges would be too short to span *trans*-positions (Scheme 30).

3.2. Trans-ligands by supramolecular interactions

In the last few years, a fascinating new strategy emerged which makes use of supramolecular interactions for the construction of *cis*-chelating diphosphines [185–200]. The challenging synthesis of *trans*-chelating diphosphines has also been approached with this methodology. Different non-covalent interactions have been used either to create the backbone of the ligand or to fix it in a certain conformation. Nevertheless, one has to keep in mind that, when hydrogen-bonding or ionic interactions are used, the strongest interaction in the "supramolecular complex" may not be the non-covalent interaction of the backbone but rather the metal–phosphorus bond. When ionic interactions are used (which in certain cases can be as strong as covalent bonding!) the main drawback arises from the lack of directionality. In view of all this, one should remain skeptical about the feasibility of constructing ligands able to fix a *trans*- only coordination mode based on these non-covalent interactions. The use of a second metal–ligand interaction for the assembly arises as a most promising approach.

Although there are several "supramolecular diphosphines" that allow a *trans*-chelation mode, any example of purely *trans*-chelating ligand generated by supramolecular interactions cannot be found yet in the literature. Nevertheless, selected examples will be mentioned here to give some insight in the state of the art.

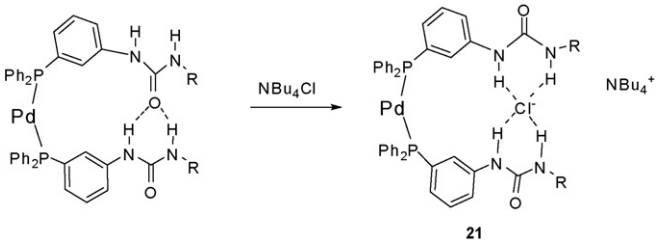
As it happens with "conventional" ligands, two different approaches can be considered; pre-synthesized and "in situ" formed "supramolecular *trans*-diphosphines. Pioneering examples of both strategies can be encountered in the literature.

The urea-containing phosphines reported by Reek and coworkers [185,192] and Love et al. [194] can be described as an example of "in situ" generated chelating ligands. The intramolecular hydrogen-bonding between the urea moieties, that exists when the phosphines are coordinated to a metal center, can be disrupted by the presence of an anion which widens the bite angle (see Scheme 31). This anion binding generates a new chelating ligand able to coordinate in a *trans*-manner, as demonstrated by the X-ray structure of the corresponding *trans*-[Pd**21**(Cl)Cl_2][N^nBu_4] [194]. Nevertheless, the existence of *cis*-complexes not only in the bis-urea metal precursors, but also when the anion is hydrogen-bonded to the ureas (as in [Pd**21**(Cl)(tcne)][N^nBu_4]) evidences that there is no strong preference for a *trans*-coordination.

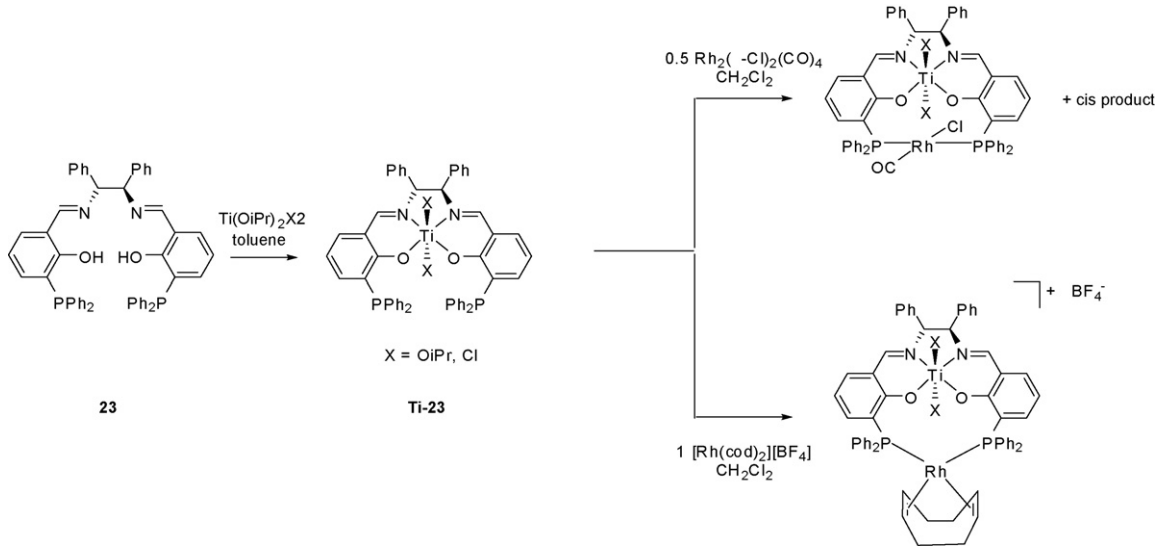
The use of ionic interactions to assemble monophosphorus ligands has been demonstrated recently by van Leeuwen [195]. An assembly of *meta*-substituted triphenylphosphane derivatives, connected by an ionic bond between their sulfonate and ammonium functional groups (**22**, $Ph_2P(3\text{-}C_6H_4\text{-}SO_3^-)$/$Ph_2P(3\text{-}C_6H_4\text{-}NH_3^+)$), has been proved to form *trans*-complexes, such as *trans*-Pd(**22**)$(CH_3)Cl$ or *trans*-Rh(**22**)(CO)Cl. However, the structure of a *cis*-complex, *cis*-Pt(**22**)Cl_2 has also been found, confirming that the non-directional nature of the ionic bond allows considerable flexibility of the bite-angle.

Metal template-assisted formation of wide bite angle diphosphines has been also addressed. The assembly metal has been used either to create the bidentate phosphine (by attaching two ditopic phosphines) or to fix a diphosphine in a certain conformation.

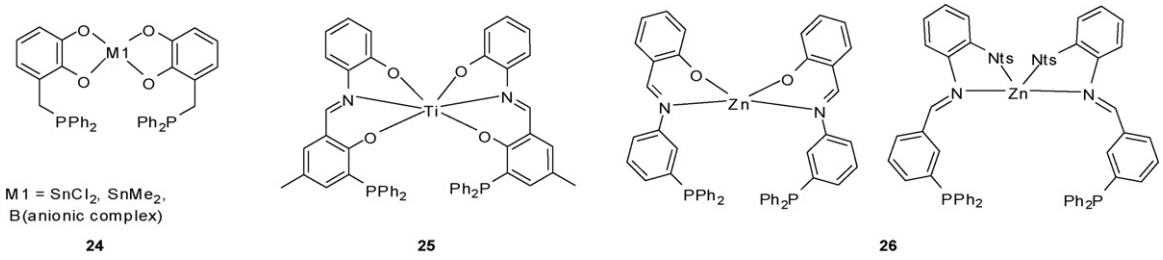
Börner published a chiral salen-containing diphosphine **23** for the construction of heterobimetallic complexes [201,202]. The ligand contains hard (O, N) as well as soft (P) donor to selectively form an early-late heterobimetallic complex. It is



Scheme 31. Urea-containing diphosphines able to anion binding.



Scheme 32. Complexation of salen-containing diphosphosphines.



Scheme 33. Wide bite angle diphosphines constructed by metal-templates.

remarkable that when the ligand reacted with Rh(I) or Pd(II) precursors various monomeric and oligomeric O–P chelates were formed. In contrast, if the ligand was pre-organized by titanium complexation to the hard donor atoms, not only the formation of P–O chelates was prevented, but in addition the ligand was conformationally restricted to coordinate to the soft metal. X-ray analysis of the bimetallic compound [Pd**Ti-23**I_2(μ-O)]$_2$ showed that the ligand coordinates to the Pd center in a *trans*-manner, but NMR analysis of a solution of *trans*-[Pd**Ti-23**I_2(μ-O)]$_2$ showed that it isomerizes to the corresponding *cis*-complex [202]. More recently, both *cis*- and *trans*-structures have been encountered for Rh(I) complexes of the templated ligand **23** (Scheme 32) [203].

Gudat et al. [196,197] and van Leeuwen et al. [198] also published recently the use of metal–bond interactions, not only to restrict the conformation (bite angle) of the backbone, but to assemble to monophosphines into a chelating ligand. Some examples by using different assembly metals (tin, boron, zinc and titanium) are shown in Scheme 33.

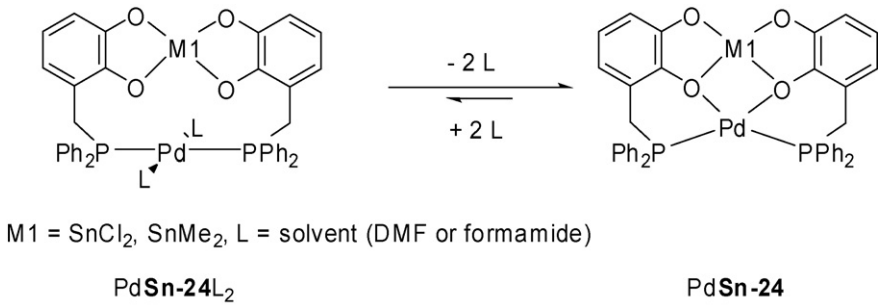
The capability of these structures to coordinate in a *trans*-manner has been established by means of NMR spectroscopy and X-ray diffraction (for Ag**B-24**) [197]. Unfortunately also for these ligands, structures having other coordination modes have been detected. For ligand **Sn-24** the X-ray structure of the complex Pd**Sn-24** has been published, showing that two of the oxygens of the backbone also coordinate to the active metal center (Scheme 34) [196]. Similar species have been postulated for ligand **25** and analogous diphosphines derived from 3-diphenylphosphino-2-hydroxy-5-methylbenzaldehyde as a result of their poor performance in hydroformylation reactions [198].

Although the existence of Pd(II) and Rh(I) *trans*-complexes with ligands **25-26**, has been confirmed by means of NMR spectroscopy, other coordination modes as *cis*-chelating or equatorial–equatorial in bipyramidal geometries have been also encountered [204].

4. Remarks on dimeric and dinuclear complexes

A clear distinction needs to be made between dinuclear complexes, in which there is no ligand other than the diphosphine bridging the two metals, and dimeric compounds if other ligands act also as a bridge between the two metal centers (Fig. 5).

As mentioned above on several occasions, both dinuclear and dimeric species are frequently encountered when working with "would-be trans" diphosphine ligands. Inspection of the published X-ray structures of such compounds (Tables 4–6) shows that they all show extremely long P–P distances (5.77–9.21 Å). For dinuclear complexes of type A and B in Fig. 5, this long distance is not a prerequisite for their formation, but it is rather a consequence of the large backbones used in



Scheme 34. Pd complexes of ligand **Sn-24**.

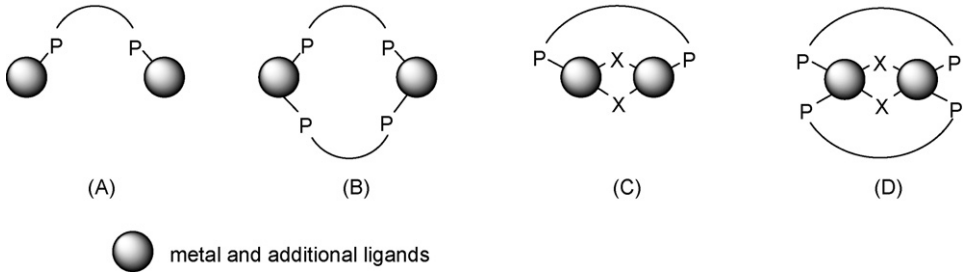


Fig. 5. Schematic representation of dinuclear (A, B) and dimeric (C, D) species.

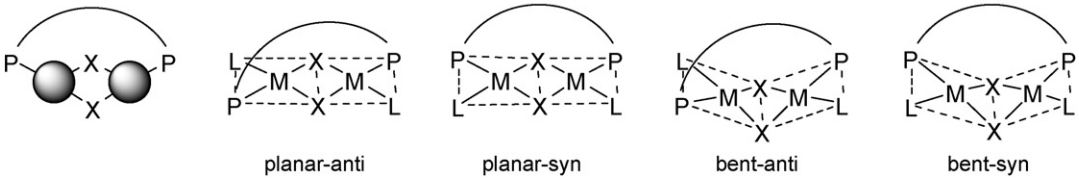


Fig. 6. Different isomers of dimeric structures type C.

these specific cases. The same types of structures A and B have been also observed with short chain diphosphines, even when they contained only one carbon in the backbone! (the large class of A-frame complexes belongs to this group [205–208], e.g. $PdCl_2(Ph_2PCH_2PPh_2)_2$ type B, P-P distance 3.3 Å).

Dimeric complexes, usually described as "edge-sharing dimers", are more closely related to *trans*-diphosphines than dinuclear species. They cannot be obtained unless a large backbone is used, as it is essential to locate the two phosphorus atoms at such distant positions. When only one diphosphine is acting as a bridge (type-C complexes) several structures can be formed. According to the specific conformation planar or bent compounds can be distinguished, and in both cases either anti or syn isomers are possible depending on the substitution pattern (Fig. 6).

Examples of all these complexes are found in the X-ray structures published of "*trans*-ligands": Ligand **Ph-11** formed complexes of formula Rh_2**Ph-11**$(\mu\text{-}I)_2(COMe)_2I_2$ as a mixture of isomers planar-anti and planar-syn (MOVMIT and MOVMOZ in Table 6, and Scheme 12). On the contrary, ligand **Ph-3** formed selectively dimers of type bent-anti with both Rh(I) and Pd(II) (Rh_2**Ph-3**$(\mu\text{-}Cl)_2(CO)_2$, and Pd_2**Ph-3**$(\mu\text{-}Cl)_2Me_2$ in Table 4) and ligands **5** formed selectively species with structure bent-syn of formula $(Pd_2L(\mu\text{-}Cl_2)Cl_2$ and $Pd_2L(\mu\text{-}Cl_2)Cl_2$ (ECEQIN, CEMPEQ and CEMPIU in Table 6).

As already mentioned by Azerraf [86], a possible "communication" between the two metal centers of such structures is intriguing, as these complexes could present a cooperative effect between the two metals, that often finds an expression in unique physical and chemical properties. If possible, this "communication" should be optimal for structures of the type bent, as the axial orbitals of the metal converge in the space. The fact that dimeric species of ligands **Ph-11** and **Ph-3** are putatively involved in the methanol carbonylation reaction (vide supra), reinforces this hypothesis and encourages further development of new ligands designed to selectively stabilize dimeric structures.

5. Conclusions

The synthesis of exclusively *trans*-spanning diphosphines has been pursued already for decades. From the early beginning, the potential of such ligands was recognized, as they will render organometallic complexes with unprecedented reactivities (or lack of reactivities!). Surprisingly, the design of the ideal ligand (easy synthesis being also a key point) remains undiscovered. Apparently, the inherent flexibility associated with the required large backbones always left other coordination modes accessi-

ble. *Cis*-monodentates, dimeric species or bimetallic compounds are additional escape routes for the desired species.

Far from being disappointing, the search for such *trans*-coordinating ligands rendered us several unusual and fascinating diphosphines. Although none of them could be called "purely and only *trans*-chelating" so far, they already served to discover unusual complexes and reactivities which otherwise would have remained unknown.

Surely future developments directed to the synthesis of *trans*-coordinating ligands will materialize. When found, we will learn about fascinating and unprecedented reactivities!

Acknowledgements

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References

[1] J.C. Briggs, C.A. Mcauliffe, W.E. Hill, D.M.A. Minahan, J.G. Taylor, G. Dyer, Inorg. Chem. 21 (1982) 4204.
[2] W.E. Hill, D.M.A. Minahan, J.G. Taylor, C.A. McAuliffe, J. Am. Chem. Soc. 104 (1982) 6001.
[3] A.J. Pryde, B.L. Shaw, B. Weeks, J. Chem. Soc., Chem. Commun. (1973) 947.
[4] A. Pryde, B.L. Shaw, B. Weeks, J. Chem. Soc., Dalton Trans. (1976) 322.
[5] N.J. Destefano, D.K. Johnson, R.M. Lane, L.M. Venanzi, Helv. Chim. Acta 59 (1976) 2674.
[6] R. Noyori, Angew. Chem. Int. Ed. 41 (2002) 2008.
[7] W.S. Knowles, Angew. Chem. Int. Ed. 41 (2002) 1999.
[8] M. Kranenburg, Y.E.M. van der Burgt, P.C.J. Kamer, P.W.N.M. van Leeuwen, Organometallics 14 (1995) 3081.
[9] C.P. Casey, G.T. Whiteker, M.G. Melville, L.M. Petrovich, J.A. Gavney Jr., D.R. Powell, J. Am. Chem. Soc. 114 (1992) 5535.
[10] M. Kranenburg, P.C.J. Kamer, P.W.N.M. van Leeuwen, D. Vogt, W. Keim, J. Chem. Soc., Chem. Commun. (1995) 2177.
[11] M. Kranenburg, P.C.J. Kamer, P.W.N.M. van Leeuwen, Eur. J. Inorg. Chem. (1998) 155.
[12] M. Kranenburg, P.C.J. Kamer, P.W.N.M. van Leeuwen, Eur. J. Inorg. Chem. (1998) 25.
[13] Z. Freixa, P.W.N.M. van Leeuwen, Dalton Trans. (2003) 1891.
[14] P.W.N.M. van Leeuwen, P.C.J. Kamer, J.N.H. Reek, P. Dierkes, Chem. Rev. 100 (2000) 2741.
[15] L.A. van der Veen, M.D.K. Boele, F.R. Bregman, P.C.J. Kamer, P.W.N.M. van Leeuwen, K. Goubitz, J. Fraanje, H. Schenk, C. Bo, J. Am. Chem. Soc. 120 (1998) 11616.
[16] H.D. Empsall, E. Mentzer, D. Pawson, B.L. Shaw, R. Mason, G.A. Williams, J. Chem. Soc., Chem. Commun. (1977) 311.
[17] R. Mason, G.R. Scollary, Aust. J. Chem. 31 (1978) 781.
[18] A.L. Balch, F. Neve, M.M. Olmstead, Inorg. Chem. 30 (1991) 3395.
[19] C.A. Bessel, P. Aggarwal, A.C. Marschilok, K.J. Takeuchi, Chem. Rev. 101 (2001) 1031.
[20] K. Issleib, G. Hohlfeld, Z. Anorg. Allg. Chem. 312 (1961) 169.
[21] N.J. Destefano, D.K. Johnson, L.M. Venanzi, Helv. Chim. Acta 59 (1976) 2683.
[22] D.K. Johnson, P.S. Pregosin, L.M. Venanzi, Helv. Chim. Acta 59 (1976) 2691.
[23] F.J.S. Reed, L.M. Venanzi, Helv. Chim. Acta 60 (1977) 2804.
[24] F. Bachechi, L. Zambonelli, L.M. Venanzi, Helv. Chim. Acta 60 (1977) 2815.
[25] P.N. Kapoor, L.M. Venanzi, Helv. Chim. Acta 60 (1977) 2824.
[26] R. Holderegger, L.M. Venanzi, Helv. Chim. Acta 62 (1979) 2154.
[27] R. Holderegger, L.M. Venanzi, F. Bachechi, P. Mura, L. Zambonelli, Helv. Chim. Acta 62 (1979) 2159.
[28] G. Balimann, L.M. Venanzi, F. Bachechi, L. Zambonelli, Helv. Chim. Acta 63 (1980) 420.
[29] P.N. Kapoor, P.S. Pregosin, L.M. Venanzi, Helv. Chim. Acta 65 (1982) 654.
[30] L.I. Elding, B. Kellenberger, L.M. Venanzi, Helv. Chim. Acta 66 (1983) 1676.
[31] E. Baumgartner, F.J.S. Reed, L.M. Venanzi, F. Bachechi, P. Mura, L. Zambonelli, Helv. Chim. Acta 66 (1983) 2572.
[32] P. Boron-Rettore, D.M. Grove, L.M. Venanzi, Helv. Chim. Acta 67 (1984) 65.
[33] M. Camalli, F. Caruso, S. Chaloupka, P.N. Kapoor, P.S. Pregosin, L.M. Venanzi, Helv. Chim. Acta 67 (1984) 1603.
[34] M. Camalli, F. Caruso, S. Chaloupka, L.M. Venanzi, Helv. Chim. Acta 71 (1988) 703.
[35] G. Bracher, B. Kellenberger, L.M. Venanzi, F. Bachechi, L. Zambonelli, Helv. Chim. Acta 71 (1988) 1442.
[36] H.-B. Bürgi, J. Murray-Rust, M. Camalli, F. Caruso, L.M. Venanzi, Helv. Chim. Acta 72 (1989) 1293.
[37] M. Camalli, F. Caruso, S. Chaloupka, E.M. Leber, L.M. Venanzi, Helv. Chim. Acta 73 (1990) 2263.
[38] G. Bracher, D.M. Grove, L.M. Venanzi, F. Bachechi, P. Mura, L. Zambonelli, Helv. Chim. Acta 63 (1980) 2519.
[39] M. Camalli, F. Caruso, L. Zambonelli, Inorg. Chim. Acta 61 (1982) 195.
[40] M. Barrow, H.B. Burgi, M. Camalli, F. Caruso, E. Fischer, L.M. Venanzi, L. Zambonelli, Inorg. Chem. 22 (1983) 2356.
[41] R.W. Kunz, P.S. Pregosin, M. Camalli, F. Caruso, L. Zambonelli, Helv. Chim. Acta 66 (1983) 1661.
[42] D.M.P. Mingos, D.J. Sherman, I.D. Williams, Transit. Metal. Chem. 12 (1987) 493.
[43] F. Bachechi, L. Zambonelli, Acta Crystallogr. C48 (1992) 788.
[44] M. Barrow, H.B. Burgi, D.K. Johnson, L.M. Venanzi, J. Am. Chem. Soc. 98 (1976) 2356.
[45] M. Sawamura, H. Hamashima, Y. Ito, Tetrahedron: Asymmetry 2 (1991) 593.
[46] M. Sawamura, H. Hamashima, M. Sugawara, R. Kuwano, Y. Ito, Organometallics (1995) 4549.
[47] Y. Ito, R. Kuwano, Phosphorus Sulfur Silicon Relat. Elem. 146 (1999) 469.
[48] R. Kuwano, M. Kashiwabara, Org. Lett. 8 (2006) 2653.
[49] R. Kuwano, M. Sawamura, S. Okuda, T. Asai, Y. Ito, M. Redon, A. Krief, Bull. Chem. Soc. Jpn. 70 (1997) 2807.
[50] F. Spindler, Private communication to CCDC.
[51] M. Sawamura, R. Kuwano, Y. Ito, Angew. Chem. Int. Ed. 33 (1994) 111.
[52] Z. Freixa, M.S. Beentjes, G.D. Batema, C.B. Dieleman, G.P.F. van Strijdonck, J.N.H. Reek, P.C.J. Kamer, J. Fraanje, K. Goubitz, P.W.N.M. van Leeuwen, Angew. Chem. Int. Ed. 42 (2003) 1284.
[53] Z. Freixa, M.S. Beentjes, G.D. Batema, C.B. Dieleman, P.C.J. Kamer, P.W.N.M. van Leeuwen, Paper Presented at the 225th ACS National Meeting, New Orleans, 2003.
[54] Z. Freixa, P.C.J. Kamer, P.W.N.M. van Leeuwen, unpublished results.
[55] P.W.N.M. van Leeuwen, M.A. Zuideveld, B.H.G. Swennenhuis, Z. Freixa, P.C.J. Kamer, K. Goubitz, J. Fraanje, M. Lutz, A.L. Spek, J. Am. Chem. Soc. 125 (2003) 5523.
[56] Z. Freixa, P.C.J. Kamer, M. Lutz, A.L. Spek, P.W.N.M. van Leeuwen, Angew. Chem. Int. Ed. 44 (2005) 4385.
[57] C. Jimenez-Rodriguez, F.X. Roca, C. Bo, J. Benet-Buchholz, E.C. Escudero-Adan, Z. Freixa, P.W.N.M. van Leeuwen, Dalton Trans. (2006) 268.

[58] F.X. Roca, Z. Freixa, C. Jimenez-Rodriguez, P.W.N.M. van Leeuwen, unpublished results.
[59] C. Jimenez-Rodriguez, Z. Freixa, P.W.N.M. van Leeuwen, unpublished results.
[60] Z. Freixa, P.C.J. Kamer, J. Fraanje, K. Goubitz, P.W.N.M. van Leeuwen, unpublished results.
[61] Z. Freixa, P.C.J. Kamer, M. Lutz, A.L. Spek, P.W.N.M. van Leeuwen, unpublished results.
[62] C. Jimenez-Rodriguez, J. Benet-Buchholz, E.C. Escudero-Adan, Z. Freixa, P.W.N.M. van Leeuwen, unpublished results.
[63] T.J. Devon, G.W. Phillips, T.A. Puckette, J.L. Stavinoha, J.J. Vanderbilt, for Eastman Kodak, US 4,694,109 (1986).
[64] T.A. Puckette, T.J. Devon, G.W. Phillips, J.L. Stavinoha, for Eastman Kodak Company, EP 4,879,416 (1989).
[65] G.O. Nelson, T.J. Devon, T.A. Puckette, J.L. Stavinoha, G.W. Phillips, J.J. Vanderbilt, for Eastman Kodak, EP 4,742,178 (1988).
[66] T.J. Devon, G.W. Phillips, T.A. Puckette, J.L. Stavinoha, J.J. Vanderbilt, for Eastman Kodak, WO 8,707,600 (1987).
[67] J.L. Stavinoha, G.W. Phillips, T.A. Puckette, T.J. Devon, for Eastman Kodak, EP 0,326,286 (1989).
[68] C.P. Casey, G.T. Whiteker, Israel J. Chem. 30 (1990) 299.
[69] M.R. Eberhard, K. Heslop, A.G. Orpen, P.G. Pringle, Organometallics 24 (2005) 335.
[70] C.P. Casey, G.T. Whiteker, C.F. Campana, D.R. Powell, Inorg. Chem. 29 (1990) 3376.
[71] R.X. Li, K.C. Tin, N.B. Wong, T.C.W. Mak, Z.Y. Zhang, X.J. Li, J. Organomet. Chem. 557 (1998) 207.
[72] L.J. Higham, K. Heslop, P.G. Pringle, A.G. Orpen, J. Organomet. Chem. 689 (2004) 2975.
[73] P.C.J. Kamer, J.N.H. Reek, P.W.N.M. van Leeuwen, Chemtech (1998) 27.
[74] P.C.J. Kamer, P.W.N.M. van Leeuwen, J.N.H. Reek, Acc. Chem. Res. 34 (2001) 895.
[75] M. Kranenburg, J.G.P. Delis, P.C.J. Kamer, P.W.N.M. vanLeeuwen, K. Vrieze, N. Veldman, A.L. Spek, K. Goubitz, J. Fraanje, J. Chem. Soc., Dalton Trans. (1997) 1839.
[76] M.A. Zuideveld, B.H.G. Swennenhuis, M.D.K. Boele, Y. Guari, G.P.F. van Strijdonck, J.N.H. Reek, P.C.J. Kamer, K. Goubitz, J. Fraanje, M. Lutz, A.L. Spek, P.W.N.M. van Leeuwen, J. Chem. Soc., Dalton Trans. (2002) 2308.
[77] J.J. Yin, S.L. Buchwald, J. Am. Chem. Soc. 124 (2002) 6043.
[78] V.V. Grushin, W.J. Marshall, J. Am. Chem. Soc. 128 (2006) 12644.
[79] K. Fujita, M. Yamashita, F. Puschmann, M.M. Alvarez-Falcon, C.D. Incarvito, J.F. Hartwig, J. Am. Chem. Soc. 128 (2006) 9044.
[80] F.A. Rampf, M. Spiegler, W.A. Herrmann, J. Organomet. Chem. 582 (1999) 204.
[81] C.P. Casey, E.L. Paulsen, E.W. Beuttenmueller, B.R. Proft, L.M. Petrovich, B.A. Matter, D.R. Powell, J. Am. Chem. Soc. 119 (1997) 11817.
[82] W.A. Herrmann, C.W. Kohlpaintner, E. Herdtweck, P. Kiprof, Inorg. Chem. 30 (1991) 4271.
[83] W. Ahlers, M. Röper, P. Hofmann, D.C.M. Warth, R. Pacciello, for BASF, WO 01/58,598 (2001).
[84] O. Grossman, C. Azerraf, D. Gelman, Organometallics 25 (2006) 375.
[85] O. Grossman, D. Gelman, Org. Lett. 8 (2006) 1189.
[86] C. Azerraf, S.M. Cohen, D. Gelman, Inorg. Chem. 45 (2006) 7010.
[87] C. Azerraf, O. Grossman, D. Gelman, J. Organomet. Chem. 692 (2007) 761.
[88] R.C. Smith, J.D. Protasiewicz, Organometallics 23 (2004) 4215.
[89] L.Q. Ma, R.A. Woloszynek, W.Z. Chen, T. Ren, J.D. Protasiewicz, Organometallics 25 (2006) 3301.
[90] R.C. Smith, C.R. Bodner, M.J. Earl, N.C. Sears, N.E. Hill, L.M. Bishop, N. Sizemore, D.T. Hehemann, J.J. Bohn, J.D. Protasiewicz, J. Organomet. Chem. 690 (2005) 477.
[91] L. Chahen, B. Therrien, G. Süss-Fink, J. Organomet. Chem. 691 (2006) 4257.
[92] F.B. Xu, L.H. Weng, L.J. Sun, Z.Z. Zhang, Z.F. Zhou, Organometallics 19 (2000) 2658.
[93] F.B. Xu, Q.S. Li, L.Z. Wu, X.B. Leng, Z.C. Li, X.S. Zeng, Y.L. Chow, Z.Z. Zhang, Organometallics 22 (2003) 633.
[94] F.B. Xu, Q.S. Li, X.S. Zeng, X.B. Leng, Z.Z. Zhang, Organometallics 21 (2002) 4894.
[95] B.M. Trost, D.L. Van Vranken, C. Brigel, J. Am. Chem. Soc. 114 (1992) 9327.
[96] B.M. Trost, D.L. Van Vranken, Angew. Chem. Int. Ed. 31 (1992) 228.
[97] S. Burger, B. Therrien, G. Süss-Fink, Helv. Chim. Acta 88 (2005) 478.
[98] S. Burger, B. Therrien, G. Süss-Fink, Eur. J. Inorg. Chem. (2003) 3099.
[99] C.M. Thomas, R. Mafua, B. Therrien, E. Rusanov, H. Stoeckli-Evans, G. Süss-Fink, Chem. Eur. J. 8 (2002) 3343.
[100] B.M. Trost, B. Breit, S. Peukert, J. Zambrano, J.W. Ziller, Angew. Chem. Int. Edit. 34 (1995) 2386.
[101] E.K. van den Beuken, A. Meetsma, H. Kooijman, A.L. Spek, B.L. Feringa, Inorg. Chim. Acta 264 (1997) 171.
[102] S. Burger, B. Therrien, G. Süss-Fink, Acta Crystallogr. E 60 (2004) m1163.
[103] K.R. Campos, M. Journet, S. Lee, E.J.J. Grabowski, R.D. Tillyer, J. Org. Chem. 70 (2005) 268.
[104] L. Chahen, L. Karmazin-Brelot, G. Süss-Fink, Inorg. Chem. Commun. 9 (2006) 1151.
[105] S. Burger, B. Therrien, G. Süss-Fink, Inorg. Chim. Acta 357 (2004) 1213.
[106] C.P. Butts, J. Crosby, G.C. Lloyd-Jones, S.C. Stephen, Chem. Commun. (1999) 1707.
[107] G. Gachot, P. Pellon, T. Roisnel, D. Lorcy, Eur. J. Inorg. Chem. (2006) 2604.
[108] U. Baltensperger, J.R. Gunter, S. Kagi, G. Kahr, W. Marty, Organometallics 2 (1983) 571.
[109] P.N. Kapoor, J. Organomet. Chem. 315 (1986) 383.
[110] W. Marty, P.N. Kapoor, H.B. Burgi, E. Fischer, Helv. Chim. Acta 70 (1987) 158.
[111] P.N. Kapoor, J. Organomet. Chem. 341 (1988) 363.
[112] L. Chahen, B. Therrien, G. Süss-Fink, Acta Crystallogr. E 62 (2006) M1270.
[113] H. Stoeckli-Evans, P.N. Kapoor, W. Marty, Acta Crystallogr. C 43 (1987) 2224.
[114] J.N. Harvey, K.M. Heslop, A.G. Orpen, P.G. Pringle, Chem. Commun. (2003) 278, and references therein.
[115] C. Azerraf, O. Grossman, D. Gelman, private communication to CCDC.
[116] Y.H. Cho, A. Fayol, M. Lautens, Tetrahedron: Asymmetry 17 (2006) 416.
[117] C. Jeunesse, D. Armspach, D. Matt, Chem. Commun. (2005) 5603.
[118] C. Dieleman, C. Jeunesse, D. Matt, Z. Krist. New Cryst. St. 216 (2001) 435.
[119] E. Engeldinger, D. Armspach, D. Matt, Angew. Chem. Int. Ed. 40 (2001) 2526.
[120] D. Armspach, D. Matt, Chem. Commun. (1999) 1073.
[121] D. Sémeril, M. Lejeune, D. Matt, New. J. Chem. 31 (2007) 502.
[122] M. Lejeune, D. Sémeril, C. Jeunesse, D. Matt, P. Lutz, L. Toupet, Adv. Synth. Catal. 348 (2006) 881.
[123] M. Lejeune, D. Semeril, C. Jeunesse, D. Matt, F. Peruch, P.L. Lutz, L. Ricard, Chem. Eur. J. 10 (2004) 5354.
[124] M. Lejeune, C. Jeunesse, D. Matt, N. Kyritsakas, R. Welter, J.P. Kintzinger, J. Chem. Soc., Dalton Trans. (2002) 1642.
[125] C. Jeunesse, C. Dieleman, S. Steyer, D. Matt, J. Chem. Soc., Dalton Trans. (2001) 881.
[126] C. Wieser, D. Matt, J. Fischer, A. Harriman, J. Chem. Soc., Dalton Trans. (1997) 2391.
[127] C. Wieser, D. Matt, L. Toupet, H. Bourgeois, J.P. Kintzinger, J. Chem. Soc., Dalton Trans. (1996) 4041.
[128] D. Semeril, M. Lejeune, C. Jeunesse, D. Matt, J. Mol. Catal. A 239 (2005) 257.
[129] C. Wieser-Jeunesse, D. Matt, A. De Cian, Angew. Chem. Int. Ed. 37 (1998) 2861.
[130] E. Engeldinger, D. Armspach, D. Matt, P.G. Jones, R. Welter, Angew. Chem. Int. Ed. 41 (2002) 2593.
[131] C. Dieleman, S. Steyer, C. Jeunesse, D. Matt, J. Chem. Soc., Dalton Trans. (2001) 2508.
[132] R.B. King, Inorg. Chem. 2 (1963) 936.

[133] J.M. Jenkins, B.L. Shaw, Proc. Chem. Soc. Lond. (1963) 279.
[134] A.W. Verstuyft, J.H. Nelson, L.W. Cary, Inorg. Chem. 15 (1976) 732.
[135] J.A. Rahn, L. Baltusis, J.H. Nelson, Inorg. Chem. 29 (1990) 750.
[136] D.A. Redfield, L.W. Cary, J.H. Nelson, Inorg. Chem. 14 (1975) 50.
[137] M. Fild, W. Althoff, J. Chem. Soc., Chem. Commun. (1973) 933.
[138] A. Pidcock, Chem. Commun. (1968) 92.
[139] W.H. Hersh, J. Chem. Educ. 74 (1997) 1485.
[140] R.T. Boere, C.D. Montgomery, N.C. Payne, C.J. Willis, Inorg. Chem. 24 (1985) 3680.
[141] R. Kuwano, T. Uemura, M. Saitoh, Y. Ito, Tetrahedron: Asymmetry 15 (2004) 2263.
[142] R. Kuwano, T. Uemura, M. Saitoh, Y. Ito, Tetrahedron Lett. 40 (1999) 1327.
[143] M. Sawamura, M. Sudoh, Y. Ito, J. Am. Chem. Soc. 118 (1996) 3309.
[144] A. Gillie, J.K. Stille, J. Am. Chem. Soc. 102 (1980) 4933.
[145] G. Mann, D. Baranano, J.F. Hartwig, A.L. Rheingold, I.A. Guzei, J. Am. Chem. Soc. 120 (1998) 9205.
[146] J.M. Brown, P.J. Guiry, Inorg. Chim. Acta 220 (1994) 249.
[147] J.E. Marcone, K.G. Moloy, J. Am. Chem. Soc. 120 (1998) 8527.
[148] M.J. Calhorda, J.M. Brown, N.A. Cooley, Organometallics 10 (1991) 1431.
[149] J. Ledford, C.S. Shultz, D.P. Gates, P.S. White, J.M. DeSimone, M. Brookhart, Organometallics 20 (2001) 5266.
[150] E. Zuidema, P.W.N.M. van Leeuwen, C. Bo, Organometallics 24 (2005) 3703.
[151] E. Zuidema, C. Bo, P.W.N.M. van Leeuwen, J. Am. Chem. Soc. 129 (2007) 3989.
[152] K.D. Dobbs, W.J. Marshall, V.V. Grushin, J. Am. Chem. Soc. 129 (2007) 30.
[153] M. Sundermeier, A. Zapf, M. Beller, Eur. J. Inorg. Chem. (2003) 3513.
[154] W. Goertz, P.C.J. Kamer, P.W.N.M. van Leeuwen, D. Vogt, Chem. Commun. (1997) 1521.
[155] W. Goertz, P.C.J. Kamer, P.W.N.M. van Leeuwen, D. Vogt, Chem. Eur. J. 7 (2001) 1614.
[156] J. Rankin, A.C. Benyei, A.D. Poole, D.J. Cole-Hamilton, J. Chem. Soc., Dalton Trans. (1999) 3771.
[157] J. Rankin, A.D. Poole, A.C. Benyei, D.J. Cole-Hamilton, Chem. Commun. (1997) 1835.
[158] D.K. Dutta, J.D. Woollins, A.M.Z. Slawin, D. Konwar, P. Das, M. Sharma, P. Bhattacharyya, S.M. Aucott, Dalton Trans. (2003) 2674.
[159] C.M. Thomas, G. Süss-Fink, Coord. Chem. Rev. 243 (2003) 125.
[160] M. Feliz, Z. Freixa, P.W.N.M. van Leeuwen, C. Bo, Organometallics 24 (2005) 5718.
[161] A. Mayanza, J.J. Bonnet, J. Galy, P. Kalck, R. Poilblanc, J. Chem. Res. (1980) 146.
[162] M.J. Doyle, A. Mayanza, J.J. Bonnet, P. Kalck, R. Poilblanc, J. Organomet. Chem. 146 (1978) 293.
[163] A. Haynes, P.M. Maitlis, I.A. Stanbridge, S. Haak, J.M. Pearson, H. Adams, N.A. Bailey, Inorg. Chim. Acta 357 (2004) 3027.
[164] M. Sawamura, H. Hamashima, Y. Ito, J. Am. Chem. Soc. 114 (1992) 8295.
[165] M. Sawamura, H. Hamashima, Y. Ito, Tetrahedron 50 (1994) 4439.
[166] M. Sawamura, H. Hamashima, H. Shinoto, Y. Ito, Tetrahedron Lett. 36 (1995) 6479.
[167] R. Kuwano, H. Miyazaki, Y. Ito, Chem. Commun. (1998) 71.
[168] R. Kuwano, H. Miyazaki, Y. Ito, J. Organomet. Chem. 603 (2000) 18.
[169] K. Inagaki, K. Nozaki, M. Takaya, Synlett (1997) 119.
[170] R. Kuwano, K. Kaneda, T. Ito, K. Sato, T. Kurokawa, Y. Ito, Org. Lett. 6 (2004) 2213.
[171] R. Kuwano, M. Sawamura, J. Shirai, M. Takahashi, Y. Ito, Tetrahedron Lett. 36 (1995) 5239.
[172] R. Kuwano, M. Sawamura, J. Shirai, M. Takahashi, Y. Ito, Bull. Chem. Soc. Jpn. 73 (2000) 485.
[173] R. Kuwano, M. Sawamura, Y. Ito, Bull. Chem. Soc. Jpn. 73 (2000) 2571.
[174] M. Sawamura, R. Kuwano, Y. Ito, J. Am. Chem. Soc. 117 (1995) 9602.
[175] Y. Ito, for NIPPON OIL Co., EP 0,663,382 (1995).
[176] R. Kuwano, M. Sawamura, Y. Ito, Tetrahedron: Asymmetry 6 (1995) 2521.
[177] R. Kuwano, M. Kashiwabara, K. Sato, T. Ito, K. Kaneda, Y. Ito, Tetrahedron: Asymmetry 17 (2006) 521.
[178] R. Kuwano, K. Sato, T. Kurokawa, D. Karube, Y. Ito, J. Am. Chem. Soc. 122 (2000) 7614.
[179] R. Kuwano, Y. Ito, J. Org. Chem. 64 (1999) 1232.
[180] R.A. Leising, J.J. Grzybowski, K.J. Takeuchi, Inorg. Chem. 27 (1988) 1020.
[181] N. Lewanzik, T. Oeser, J. Blumel, J.A. Gladysz, J. Mol. Catal. A 254 (2006) 20.
[182] E.B. Bauer, J. Ruwwe, J.M. Martín-Alvarez, T.B. Peters, J.C. Bohling, F.A. Hampel, S. Szafert, T. Lis, J.A. Gladysz, Chem. Commun. (2000) 2261.
[183] J. Ruwwe, J.M. Martin-Alvarez, C.R. Horn, E.B. Bauer, S. Szafert, T. Lis, D. Hampel, P.C. Cagle, J.A. Gladysz, Chem. Eur. J. 7 (2001) 3931.
[184] T. Shima, E.B. Bauer, F. Hampel, J.A. Gladysz, Dalton Trans. (2004) 1012.
[185] L.K. Knight, Z. Freixa, P.W.N.M. van Leeuwen, J.N.H. Reek, Organometallics 25 (2006) 954.
[186] F. Chevallier, B. Breit, Angew. Chem. Int. Ed. 45 (2006) 1599.
[187] M. Weis, C. Waloch, W. Seiche, B. Breit, J. Am. Chem. Soc. 128 (2006) 4188.
[188] W. Seiche, A. Schuschkowski, B. Breit, Adv. Synth. Catal. 347 (2005) 1488.
[189] B. Breit, Angew. Chem. Int. Ed. 44 (2005) 6816.
[190] B. Breit, W. Seiche, J. Am. Chem. Soc. 125 (2003) 6608.
[191] M. Kuil, P.E. Goudriaan, P.W.N.M. van Leeuwen, J.N.H. Reek, Chem. Commun. 45 (2006) 4679.
[192] A.J. Sandee, A.M. van der Burg, J.N.H. Reek, Chem. Commun. (2007) 864.
[193] M.J. Wilkinson, P.W.N.M. van Leeuwen, J.N.H. Reek, Org. Biomol. Chem. 3 (2005) 2371.
[194] P.A. Duckmanton, A.J. Blake, J.B. Love, Inorg. Chem. 44 (2005) 7708.
[195] H. Gulyás, J. Benet-Buchholz, E.C. Escudero-Adan, Z. Freixa, P.W.N.M. van Leeuwen, Chem. Eur. J. 13 (2007) 3424.
[196] S. Chikkali, D. Gudat, M. Niemeyer, Chem. Commun. (2007) 981.
[197] S.H. Chikkali, D. Gudat, F. Lissner, M. Nieger, T. Schleid, Dalton Trans. (2007) 3906.
[198] D. Rivillo, H. Gulyás, J. Benet-Buchholz, E.C. Escudero-Adan, Z. Freixa, P.W.N.M. van Leeuwen, Angew. Chem. Int. Ed. 46 (2007) 7247.
[199] V.F. Slagt, P.W.N.M. van Leeuwen, J.N.H. Reek, Chem. Commun. (2003) 2474.
[200] V.F. Slagt, M. Röder, P.C.J. Kamer, P.W.N.M. van Leeuwen, J.N.H. Reek, J. Am. Chem. Soc. 126 (2004) 4056.
[201] A. Kless, R. Kadyrov, A. Börner, J. Holz, H.B. Kagan, Tetrahedron Lett. 36 (1995) 4601.
[202] A. Kless, C. Lefeber, A. Spannenberg, R. Kempe, W. Baumann, J. Holz, A. Börner, Tetrahedron 52 (1996) 14599.
[203] M. Quirmbach, A. Kless, J. Holz, V. Tararov, A. Börner, Tetrahedron: Asymmetry 10 (1999) 1803.
[204] D. Rivillo, Z. Freixa, P.W.N.M. van Leeuwen, unpublished results.
[205] C.F. Xu, G.K. Anderson, Organometallics 13 (1994) 3981.
[206] J.A. Jenkins, J.P. Ennett, M. Cowie, Organometallics 7 (1988) 1845.
[207] C.B. Pamplin, S.J. Rettig, B.O. Patrick, B.R. James, Inorg. Chem. 42 (2003) 4117.
[208] A.L. Balch, in: L.H. Pignolet (Ed.), Homogeneous Catal. Met. Phosphine Complexes, Plenum, New York, 1983.