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Mini Review

Synthesis of chiral triazolinylidene and imidazolinylidene transition metal complexes and first application in asymmetric catalysis

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Abstract

Deprotonation of chiral triazolium salts and reaction of the resulting nucleophilic carbenes with suitable metal precursors leads to (carbene)transition metal complexes. These contain, depending on the geometry of the complex and the arrangement of the different ligands, a stereogenic center at the metal atom or an axis of chirality with diastereomeric excesses of up to 97%. The application of soluble and immobilized (carbene)transition metal complexes as catalysts in an asymmetric hydrosilylation reaction has been examined.

Keywords: Nucleophilic carbenes; Chiral triazolinylidenes; Chiral imidazolinylidenes; Immobilized triazolium salts; Asymmetric catalysis

1. Introduction

Carbenes are usually reactive and electrophilic intermediates which cannot be isolated. The discovery of nucleophilic carbenes by Wanzlick et al. in the 1960s [1] and their first application as ligands in organometallic chemistry [2] were the basis for chiral carbene complexes as possible catalysts in asymmetric synthesis. The isolation and characterization of the first stable imidazolinylidenes was performed in 1991 by Arduengo et al. [3], who also reported on an imidazolidinylidene later on [4]. In 1995, we isolated a stable triazolinylidene [5], and Alder et al. published the synthesis of the first acyclic stable amino carbene in 1996 [6].

The isolation of these compounds lead to a renaissance of nucleophilic carbenes. They can be used as prebuilt ligands in organometallic chemistry or be formed in situ originating from precursors as the corresponding salts or electron-rich olefins. Complexes of various transition metals and main group elements have been published so far [7].

The first chiral carbene complexes bearing imidazolidinylidene ligands were introduced by Lappert et al. in 1983 [8], later on, we reported on complexes containing chiral imidazolinylidenes and triazolinylidenes. The synthesis of these complexes as well as their application as catalysts in an asymmetric hydrosilylation reaction will be described in this account.

2. Synthesis of chiral triazolium salts

4*H*-1,2,4-triazol-1-ium salts (**1**) are versatile precursors for stable nucleophilic carbenes as 4,5-dihydro-1*H*-1,2,4-triazol-5-ylidenes, or triazolinylidenes [5]. Chiral triazolium salts have been used as catalysts for asymmetric benzoin condensations [9] and *Stetter* reactions [10] and for the preparation of carbene complexes of different transition metals [11]. Two major routes were applied for the synthesis of these carbene precursors, depending on the desired substitution pattern.

1,4-Disubstituted triazolium salts (**1**) were prepared in analogy to a method by Boyd et al. [12,13]. Starting from an alkyl or aryl hydrazine (**2**), the bisformyl hydrazines (**3**) could be obtained using the mixed anhy-

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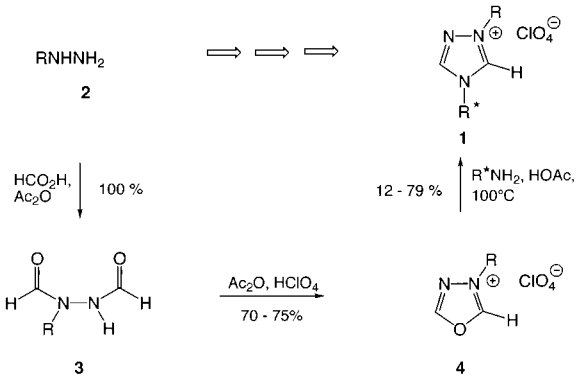
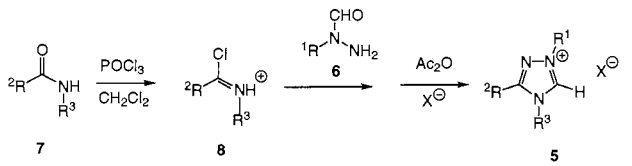
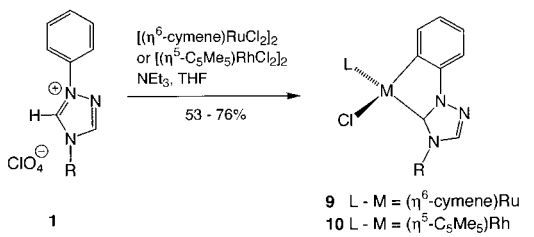


Scheme 1.



Scheme 2. General method for the synthesis of 3,4-disubstituted 1-alkyl-4*H*-1,2,4-triazol-1-ium salts.



Scheme 3. Preparation of *ortho*-metalated (*N*-phenyltriazolinylidene)ruthenium(II) (**9**) and -rhodium(III) (**10**) complexes.

dride of formic acid and acetic acid. Condensation of the bisformyl hydrazines with acetic anhydride and $HClO_4$ afforded the corresponding oxadiazolium salts (**4**). The last step of the synthesis was the *ring opening ring closure* reaction (*RORC*-reaction) using a chiral primary amine, in which the oxygen atom is substituted by the amine (Scheme 1).

In order to obtain 3,4-disubstituted 1-alkyl-4*H*-1,2,4-triazol-1-ium salts (**5**), *N*-alkyl-*N*-formyl hydrazines (**6**) were prepared from alkyl hydrazines and methyl formate [14] as starting material for the one pot procedure [15]. The method is based on the reaction of these hydrazines with an imidoyl chloride (**8**) which can be prepared in situ. The cyclization was achieved using acetic anhydride and anion exchange then yielded the desired triazolium perchlorates or tetraphenylborates (**5**) (Scheme 2).

Based on these two synthetic methods, the chiral triazolium salts as starting materials for the (triazolinylidene)metal complexes were obtained.

3. Chiral (triazolinylidene)ruthenium(II) and -rhodium(III) chelate complexes

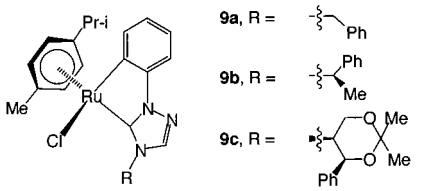
Free rotation about a carbene-carbon metal bond, a possible reason for low enantiomeric excesses when employing chiral carbenes as ligands in catalysis, may be reduced by the use of chelating ligands. Examples of chelate complexes with nucleophilic carbenes have been reported by Hitchcock et al. [16], who obtained ruthenium complexes containing *ortho*-metalated *N*-arylcarbene ligands. In order to introduce further chirality information into a catalyst, additionally to the chiral ligand, the creation of a stereogenic metal center is one possibility. We reported on the diastereoselective synthesis of ruthenium(II) and rhodium(III) complexes containing chiral *ortho*-metalated *N*-phenyltriazolinylidene ligands and a stereogenic center at the transition metal [11b].

2-Phenyltriazolium perchlorates were used as precursors, which, upon in situ deprotonation, afforded the corresponding carbenes. Reaction of these carbenes with *chloro*-bridged dinuclear complexes $[(\eta^6\text{-cymene})\text{-}RuCl_2]_2$ and $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ yielded *pseudo*-tetrahedral mononuclear complexes with the *ortho*-metalated *N*-phenylcarbene as chelating ligand (Scheme 3).

3.1. Ruthenium(II) complexes

The ruthenium(II) complexes were obtained as water and air stable yellow solids in yields of 70–76%. Due to the *pseudo*-tetrahedral arrangement of the ligands, a stereogenic center at the metal atom is created, leading to the existence of two diastereomers in the case of chiral carbene ligands (Table 1).

Table 1
Yields, diastereomeric excesses and optical rotation values of the ruthenium complexes **9**



9	Yield (%)	de [a] (%)	de [a,b] (%)	$[\alpha]_D^{25}$ (*c*, $CHCl_3$)
9a	76	–	–	–
9b	70	87	≥96 ((R_{Ru})-**9b**)	+337 (0.1)
			≥96 ((S_{Ru})-**9b**)	−25 (0.1)
9c	76	95	≥96 ((R^*_{Ru})-**9c**) [c]	−169 (0.1)
			≥96 ((S^*_{Ru})-**9c**) [c]	+79 (0.1)

[a] Determined by ^{1}H-NMR spectroscopy (300 MHz).

[b] After separation of the diastereomers by column chromatography.

[c] The absolute configuration was not determined, (R^*_{Ru})-**9c** major diastereomer, (S^*_{Ru})-**9c** minor diastereomer.

The diastereomeric excesses of the complexes **9b** and **9c** were determined by ^{1}H-NMR spectroscopy to be 87% and 95%, respectively. A separation of diastereomers could be achieved by column chromatography to yield the diastereomerically pure compounds. The relative and therefore also absolute configuration of the major diastereomer of **9b** was assigned to R_{Ru} by means of X-ray structure analysis (Fig. 1).

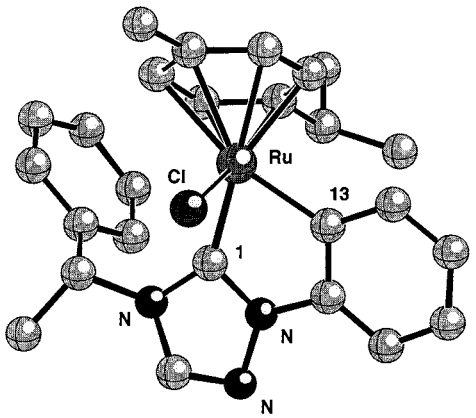
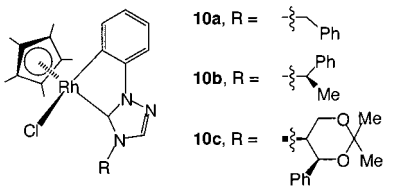


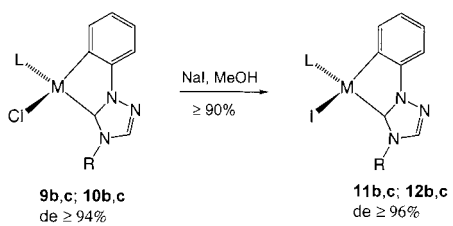
Fig. 1. Molecular structure of (R_{Ru})-**9b**. Selected bond lengths (Å) and angles (°): Ru–C1, 2.025(4); Ru–C13, 2.076(4); Ru–Cl, 2.427(1); C1–Ru–C13, 76.8(2); C1–Ru–Cl, 86.2(1); C13–Ru–Cl, 86.4(1).

Table 2
Yields, diastereomeric excesses and optical rotation values of the rhodium complexes **10**

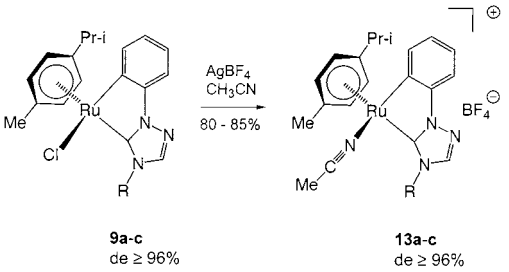


10	Yield (%)	de [a] (%)	de [a,b] (%)	$[\alpha]_D^{25}$ (*c*, $CHCl_3$)
10a	65	–	–	–
10b	57	50	94 ((R^*_{Rh})-**10b**) [c]	+366 (0.1)
			95 ((S^*_{Rh})-**10b**) [c]	+26 (0.1)
10c	53	83	≥96 ((R^*_{Rh})-**10c**) [c]	–104 (0.1)

[a] Determined by ^{1}H-NMR spectroscopy (300 MHz).
[b] After separation of the diastereomers by column chromatography.
[c] The absolute configuration was not determined, (R^*_{Rh})-**10b**,**c** major diastereomer, (S^*_{Rh})-**10b** minor diastereomer.



Scheme 4. Substitution of chlorine by iodine.



Scheme 5. Preparation of cationic ruthenium(II) complexes **13**.

3.2. Rhodium(III) complexes

In analogy to the preparation of the ruthenium(II) complexes, the rhodium(III) complexes were formed in diastereomeric excesses of 50% (**10b**) and 83% (**10c**), the values being lower than those obtained for the ruthenium compounds (Table 2).

As described above, the separation of diasteromers could be achieved by column chromatography, but in this case, epimerization in solution occured slowly so that the separation was not complete. These difficulties were overcome by an halogene exchange form chlorine to iodine.

3.3. Substitution reactions

Reaction of the ruthenium(II) and rhodium(III) complexes **9** and **10** with an excess of NaI led to the corresponding complexes **11** and **12** bearing an iodine atom instead of the chlorine atom (Scheme 4).

The (iodo)rhodium(III) complexes **11** and **12** were found to be stable towards epimerization, and in case of the major diasteromers of **11b**,**c** and **12b**,**c** no change in the diasteromeric excess was observed. For the minor diastereomers, the diasteromeric excess of the product was lower than that of the starting material, therefore indicating a partial epimerization during the reaction.

The chlorine atom of the ruthenium(II) complexes could also be removed employing $AgBF_4$ as dehalogenating agent in acetonitrile, yielding the chiral cationic complexes **13a–c** (Scheme 5).

A comparison of the optical rotation values for the chlorine complexes on one hand and the iodine and cationic complexes on the other hand indicates that the substitution reactions proceed with retention of configuration [17] (Table 3).

In summary, we have synthesized diastereo- and enantiomerically pure (triazolinylidene)ruthenium(II) and -rhodium(III) chelate complexes containing a stereogenic center at the metal atom as possible catalysts in enantioselective synthesis.

Table 3
Yields, diastereomeric excesses and optical rotation values for the substitution reactions

11–13	Yield (%)	de [a] (%)	$[\alpha]_D^{25}$ (c, $CHCl_3$)
(S_{Ru})-**11b**	94	≥96	+346 (0.1)
(S^*_{Ru})-**11c**	91	≥96	−147 (0.1)
(S^*_{Rh})-**12b**	94	≥96	+379 (0.1)
(S^*_{Rh})-**12c**	90	≥96	−216 (0.1)
(R_{Ru})-**13b**	85	≥96	+254 (0.07)
(S_{Ru})-**13b**	83	≥96	+35 (0.07)
(R^*_{Ru})-**13c**	80	≥96	−68 (0.1)

[a] Determined by ^{1}H-NMR spectroscopy (300 Hz).

4. Axial chirality in square-planar carbene metal complexes

Tetrahedral complexes containing a stereogenic center at the metal atom, as described above, or octahedral complexes with helical chirality are well known [18]. Square-planar complexes containing a chirality information additional to that within the ligand sphere are rare. Complexes bearing planar ligands with C_1-symmetry, such as triazolinylidenes, in an orientation perpendicular to the reference plane of the complex show such a chirality. Other examples of these ligands are guanosins [19] and tetrazoles [20], and whereas the existence of different diasteromers for this complexes has been described, only an insufficient proposal for a nomenclature has been developed [19].

We reported a more comprehensive concept of classification based on axial chirality, comparable to atropisomers in organic chemistry [21]. The axis is represented by the metal–ligand bond, and the two perpendicular planes are the reference plane of the complex and the plane of the ligand, respectively. The priorities can be assigned according to the CIP rules [22] looking along the metal–ligand bond, and termed as R_a and S_a. For a schematic classification, the different non-carbene ligands are abbreviated as **a**, **b** and **c**, with priorities **a** > **b** > **c** > carbene, and ball (o) higher priority than stick (|) within a carbene ligand. Using the CIP rules, it could certainly be possible that the carbene does not have the lowest priority. Complexes of type **A**, **B**, and **C** containing one carbene-type ligand can be chiral or achiral, depending on the arrangement of the different ligands (Fig. 2).

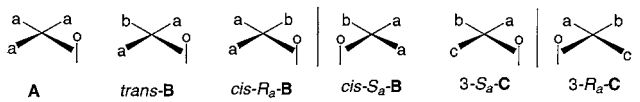


Fig. 2. Complexes of type **A**, **B**, and **C** with one planar ligand.

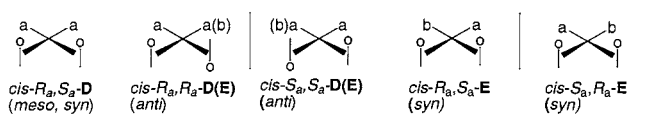


Fig. 3. *cis*-Complexes of type **D**, **E** with two planar ligands.

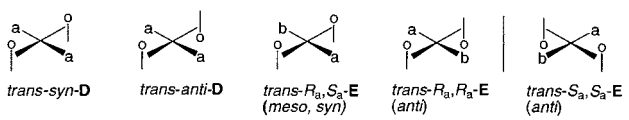


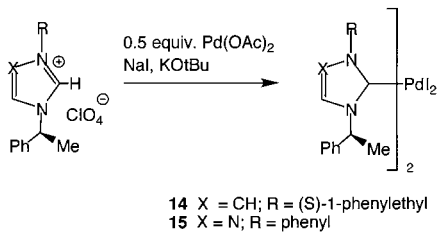
Fig. 4. *trans*-Complexes of type **D**, **E** with two planar ligands.

Complexes **A** and *trans*-**B** with a mirror-plane within the molecule are achiral, whereas complexes as *cis*-**B** and **C** contain one axis of chirality so that two enantiomers would be formed, respectively. They have to be described by the configuration of this axis and by the arrangement of the different ligands. The numeral (e.g. in 3-C) indicates the priority of the ligand opposite to the ligand with the highest priority, according to the IUPAC rules, in order to describe the sequence of the different ligands [18]. Other complexes may contain two identical carbene-type ligands, which can be arranged in a *cis*- or *trans*-form, and two other ligands, which may be identical or different. The configuration of the carbene ligand opposite to ligand **a** (with highest priority) is mentioned first for complexes of type **E** (Fig. 3).

Three different types of *cis*-isomers are possible. Complex **D**, where the carbene ligands have the same orientation (*syn*-form) and with two identical ligands a is a *meso*-form due to the presence of two identical axes of chirality within the molecule. With different orientations of the carbene-type ligands (complexes *cis-anti*-**D** and *cis-anti*-**E**), two enantiomers are formed. It makes no difference if there is only one type of additional ligand (*cis-anti*-**D**) or if there are two different ones (*cis-anti*-**E**). A *syn*-orientation of the carbene-type ligands with two different other ligands **a** and **b** as in *cis-syn*-**E** leads to a destruction of the symmetry which is present in *cis-syn*-**D** (*meso*) and therefore to the existence of two enantiomers.

The different *trans*-isomers can also be chiral or achiral depending on the arrangement of the ligands. The two *trans*-**D** isomers (*anti* and *syn*) with one other ligand a are achiral, whereas exchange of one ligand **a** with **b** breaks the symmetry and leads to one *meso*-form (*trans-syn*-**E**) and two enantiomers (*trans-anti*-**E**) (Fig. 4). Complexes bearing three or four or different carbene-type ligands can also be explained employing this nomenclature, which is therefore an efficient method of describing square-planar complexes containing C_1-symmetrical ligands perpendicular to the square-plane of the complex.

Table 4
Yields of the preparation of dicarbenediiodapalladium(II) complexes **14** and **15**



14 X = CH; R = (S)-1-phenylethyl
15 X = N; R = phenyl

	Yield (*trans*-product) (%)	Yield (*cis*-product) (%)
14	89	9
15	82	8

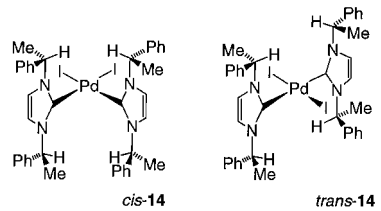


Fig. 5. *cis*- and *trans*-isomer of complex **14**.

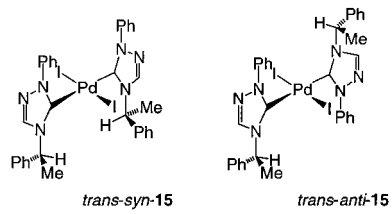


Fig. 6. *trans-syn* and *trans-anti*-isomer of complex **15**.

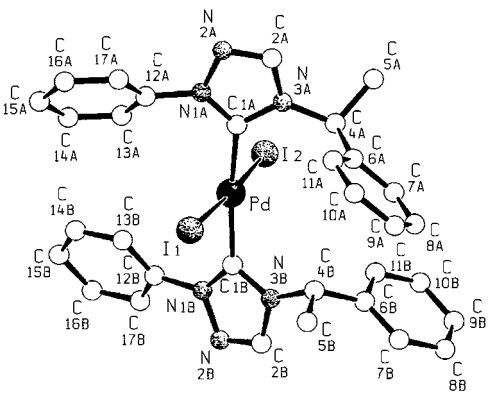


Fig. 7. SCHAKAL-plot of *trans-syn*-**15**.

5. Chiral (imidazolinylidene)- and (triazolinylidene)palladium(II) complexes

Mononuclear and dinuclear palladium(II) complexes bearing achiral nucleophilic carbenes as ligands have been published by Herrmann et al. [23], Bertrand et al. [24], and Caló et al. [25]. We reported on a synthetic procedure employing chiral imidazolinylidene and triazolinylidene ligands in order to obtain square-planar palladium(II) complexes which contain an axis of chirality [11a]. Mononuclear compounds bearing two carbene ligands were prepared by the reaction of $Pd(OAc)_2$ with two equivalents of an imidazolium or triazolium salt and an excess of NaI and KO*t*Bu in yields of more than 90% (Table 4).

Both *trans* and *cis* isomers were formed, which could be separated by column chromatography. For the C_2-symmetrical chiral imidazolinylidene ligands, only one *cis* and one *trans* complex (**14**) were obtained (Fig. 5), whereas with the C_1-symmetrical triazolinylidenes the number of possible isomers (**15**) increases due to the loss of symmetry in the ligand.

In the *trans* isomer *trans*-**15**, the two chiral groups can either point in the same direction (*trans-syn*-**15**) or in different directions (*trans-anti*-**15**) (Fig. 6).

Complex *trans-syn*-**15** was crystallized and the structure in the solid state was determined, therefore confirming the configuration and conformation measured by NMR spectroscopy (Fig. 7).

As for the *trans* compound, both *syn* and *anti* isomers are formed for the *cis* complex *cis*-**15**. The *anti* isomer exists as two diasteromers whereas only one *syn* isomer is possible (*meso* form) (Fig. 8). A distinction of *syn* and *anti* isomers was possible by NMR spectroscopy so that the diasteromeric excess (de = 35%) and the *anti*/*syn* ratio (7:1) could be determined (Table 5).

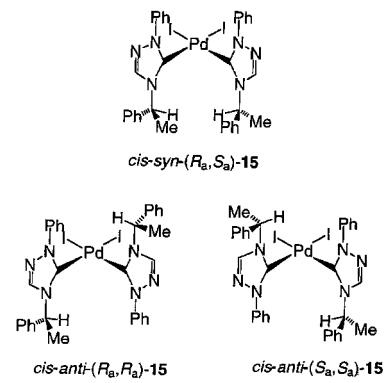
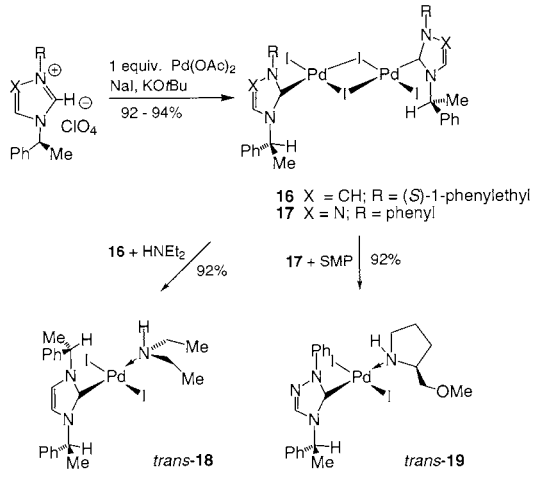


Fig. 8. *Cis-syn* and *cis-anti*-isomers of complex **15**.

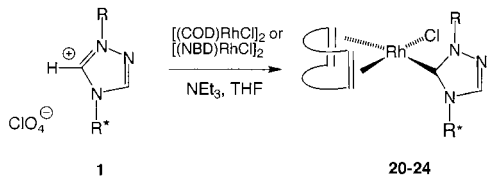
Table 5
Syn/*anti* ratios of *trans*- and *cis*-**15**

	syn-Product (%)	*anti*-Product (%)
trans-**15**	28	72
cis-**15**	12	88 [a]

[a] de (*cis-anti*-**15**) = 39%.

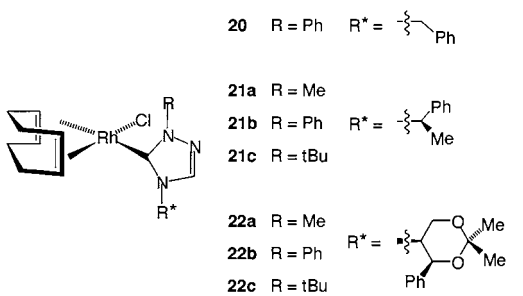


Scheme 6.



Scheme 7. Preparation of rhodium(COD) and -NBD complexes.

Table 6
Yields and diastereomeric excesses (de) of rhodium(COD) complexes **20–22**



20–22	Yield (%)	de (%) [a]
20	90	–
21a	70	41
21b	95	40
21c	78	36
22a	79	93
22b	95	91
22c	65	97

[a] Determined by ^{1}H-NMR spectroscopy.

Dinuclear palladium(II) complexes **16** and **17** were formed when only one equiv. of the imidazolium or triazolium salt was used for the preparation (Scheme 6). Addition of Lewis basic ligands as amines, phosphanes [26], or other carbenes to these dinuclear complexes **16** and **17** lead to mononuclear compounds with a *trans* configuration, e.g. (amino)(carbene)diiodopalladium(II) complexes *trans*-**18** and *trans*-**19** without an axis of chirality. Further chirality information could be introduced into the molecule by using a chiral amine, as SMP [27] in *trans*-**19**. Thus, the directed synthesis of possible catalysts with two different chiral ligands could be performed.

6. Chiral (triazolinylidene)rhodium(I) complexes

Square-planar rhodium(I) carbene complexes with a chiral imidazolidinylidene or imidazolinylidene have been described by Lappert et al. [8] and Herrmann et al. [28]. Using a C_1-symmetrical chirality triazolium salt and dinuclear rhodium(COD) or rhodium(NBD) complexes [29], we observed a hindered rotation around the carbene carbon metal bond and reported on the diastereoselective synthesis of such complexes with an axis of chirality [11c] (Scheme 7).

6.1. Rhodium(COD) complexes

(Carbene)(chloro)rhodium(COD) complexes **20–22** were prepared by reaction of a triazolium salt with $[(COD)RhCl]_2$ in THF with NEt_3 in yields of 65–95%. Calculation of the barrier for rotation of the carbene carbon-rhodium bond at the MP2/TZVP//RI-DFT/SV(P) level yielded an energy 93 kJ mol^{-1} for complex **20** [11c]. This was consistent with the hindered rotation found by NMR spectroscopy, with a splitting of the benzylic protons for complex **20** and the existence of two diastereomers for complexes **21** and **22** (Table 6).

Diastereomeric excesses of up to 97% (determined by ^{1}H-NMR spectroscopy) could be achieved using the (4*S*,5*S*)-2,2-dimethyl-4-phenyl-1,3-dioxanyl residue as chiral substituent R* with the best value for the bulky *t*-butyl group (**22c**). For the (*R*)-1-phenylethyl residue, only lower values of de = 36–41% were observed (**21a–c**). The major diastereomer of **22a** was crystallized and its structure in the solid state determined by X-ray structure analysis. The configuration of the axis of chirality could be assigned as (S_a) for complex **22a** with the dioxane ring in chair conformation pointing away from the rhodium atom (Fig. 9).

6.2. Rhodium(NBD) complexes

In analogy to the rhodium(COD) complexes **20–22**, rhodium(NBD) complexes **23–24** were prepared in yields of 75–95%. These compounds did not show the same hindrance of rotation about the carbene carbon–rhodium bond as the rhodium(COD) complexes. For instance, for the achiral benzyl group (compound **23**) no splitting of the benzylic protons was observed in the ^{1}H-NMR spectrum at room temperature (Table 7).

These findings were again supported by MP2/TZVP//RI-DFT/SV(P) calculations with a rotational barrier of 58 kJ mol^{-1} for compound **23**, much lower than that for the comparable rhodium(COD) complex **20** (93 kJ mol^{-1}). This is probably due to the decreased steric interaction of the triazolinylidene with a NBD ligand which is of smaller size compared to a COD ligand. Upon cooling of the NMR sample of complex **23** to −40°C, the broad signal for the benzylic protons in the ^{1}H-NMR spectrum sharpened and now appeared as two doublets indicating hindered rotation [30]. Nevertheless, complex **24c** with the most bulky achiral substituent R, a *t*-butyl group, showed hindered rotation at room temperature and a diastereomeric excess of 87%. In order to increase the steric hindrance and therefore the rotational barrier in the rhodium(NBD) complexes, the chlorine atom was exchanged with iodine using NaI in MeOH (Table 8).

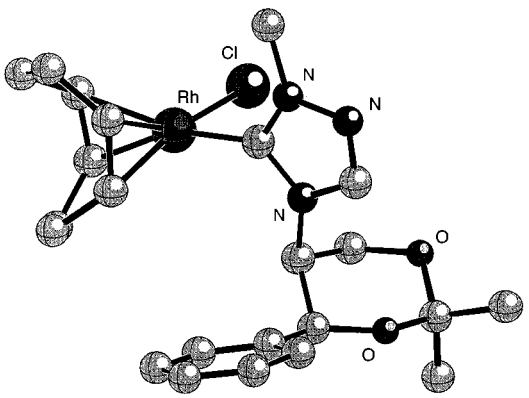
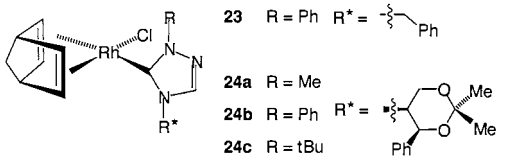


Fig. 9. Molecular structure of (S_a)-**22a**. Selected bond lengths (Å) and angles (°): Rh–C(carbene), 2.004(7); Rh–Cl, 2.366(2); Cl–Rh–C(carbene), 88.3(2).

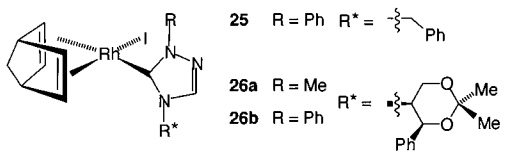
Table 7
Yields and diastereomeric excesses (de) of rhodium(NBD) complexes **23** and **24**



23/24	Yield (%)	de (%) [a]
23	95	[b]
24a	93	[b]
24b	95	[b]
24c	75	87

[a] Determined by ^{1}H-NMR spectroscopy.
[b] Due to broad signals (rotation of the ligand), a diastereomeric excess could not be determined.

Table 8
Yields and diastereomeric excesses (de) of rhodium(NBD) complexes **25** and **26**



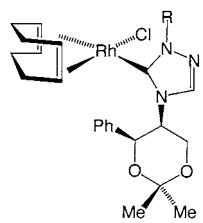
25/26	Yield (%)	de (%) [a]
25	90	–
26a	70	87
26b	83	87

[a] Determined by ^{1}H-NMR spectroscopy.

Several methyl ketones were converted into the corresponding alcohols **27–30** with diphenylsilane and 1 mol% of the catalysts and consequent quenching with methanol containing 1% of *p*-toluenesulfonic acid

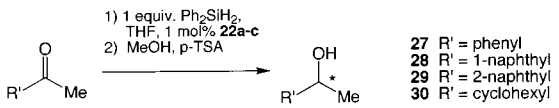
7. Catalytic asymmetric hydrosilylation

The hydrosilylation of ketones, alkenes, and alkynes using achiral rhodium complexes of nucleophilic carbenes has been described by Nile et al. [31] and Lappert et al. [32] in the 1970s and 1980s. Herrmann et al. reported on the enantioselective hydrosilylation of ketones with chiral (imidazolinylidene)rhodium(I) catalysts. Enantiomeric excesses of up to 32% could be achieved with an increasing enantioselectivity with decreasing temperature [28]. We investigated the potential of the (triazolinylidene)rhodium(I) complexes **22a–c** containing an axis of chirality which are described above as catalysts in an enantioselective hydrosilylation reaction [33] (Fig. 10).



22a R = Me, de = 93%
22b R = Ph, de = 91%
22c R = ^{t}Bu, de = 97%

Fig. 10. Axially-chiral (triazolinylidene)rhodium(COD) complexes **22**.



Scheme 8. Asymmetric hydrosilation of methyl ketones to afford the alcohols **27**–**30**.

(Scheme 8). THF was the best solvent for the reaction concerning yield and enantioselectivity and was preferably used in only small amounts. The observed enantioselectivity was independent of reaction time or amount of catalyst; the reaction conditions giving the highest enantioselectivities for each system are summarized in Table 9.

In order to achieve a yield of at least 40%, reaction times of up to 10 days were necessary, influenced by the steric demand of the ketone and of the catalysts and by the reaction temperature. The enantiomeric excesses were between 20% and 44% after optimization of reaction temperature with similar results being observed for aromatic and aliphatic ketones. The configuration of the resulting alcohol depended on the achiral group R at *N*1 of the triazolinylidene ligand. For example, both enantiomers of 1-cyclohexylethanol **30** could be obtained with enantiomeric excesses of 43–44% without any change of the chirality information within the catalyst (entries 7–9, Table 9) [34]. An optimum reaction temperature had to be found for each combination of catalyst and ketone; a decreased enantioselectivity both with increasing and decreasing temperature with respect to the optimum conditions was observed. This non-linear temperature effect (principle of isoinversion) was at first found by Scharf et al. for a Paterno–Büchi reaction [35] and later on also for a hydrosilylation reaction with rhodium(NBD) complexes and chiral cyclic monophosphonite ligands [36].

In case of the chiral (triazolinylidene)rhodium(I) complexes, the *Eyring* plots [37] $\ln[R]/[S]$ against $1/T$ of several systems were also found to show two linear regions intersecting at the inversion point T_{inv} which represents the optimum temperature. These temperature of inversion varied between $+42$°C and -10°C (Fig. 11).

Table 9
Reaction conditions, yields and enantiomeric excesses of the hydrosilylation reaction

Entry	Catalyst	Alcohol	Temperature (C)	Time	Yield (%)	ee (%)
1	**22a**	27	22	4 h	90	20 (*S*)
2	**22c**	27	11	6 days	60	40 (*R*)
3	**22a**	28	42	4 h	80	37 (*R*)
4	**22b**	28	2	10 days	40	32 (*R*)
5	**22a**	29	2	5 days	90	19 (*S*)
6	**22c**	29	22	16 h	40	24 (*R*)
7	**22a**	30	10	6 days	75	44 (*S*)
8	**22b**	30	2	4 days	80	43 (*S*)
9	**22c**	30	22	3 days	70	43 (*R*)

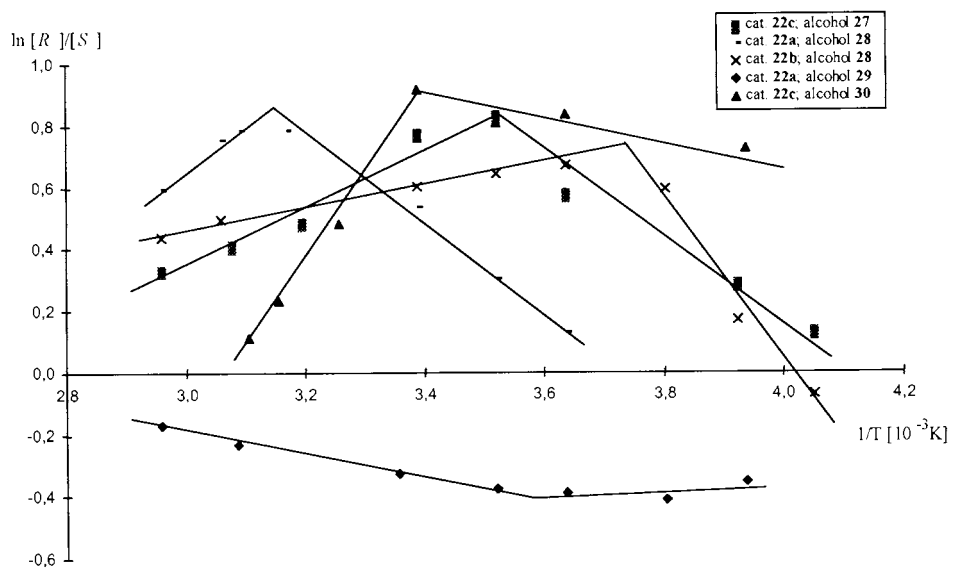


Fig. 11. Eyring plots.

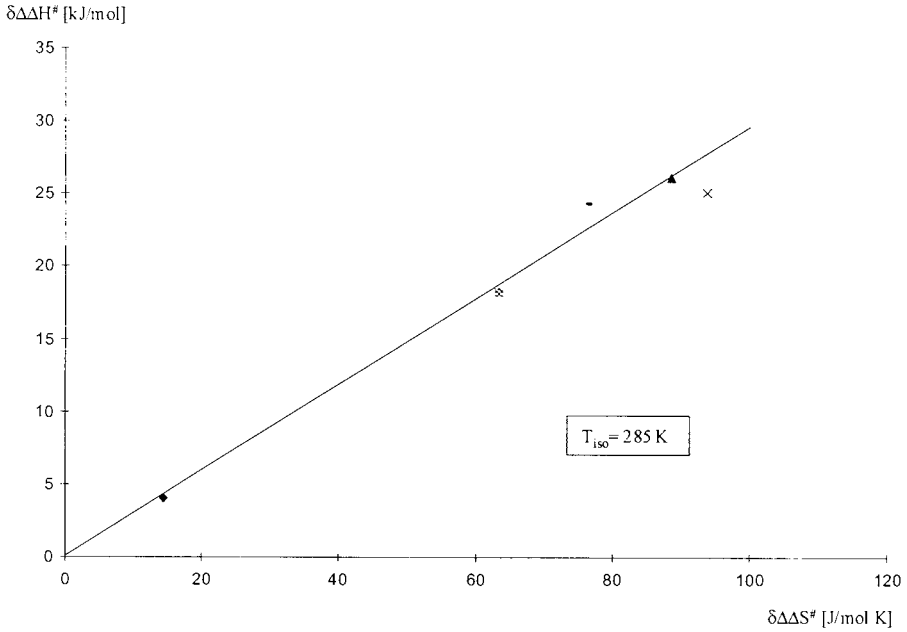


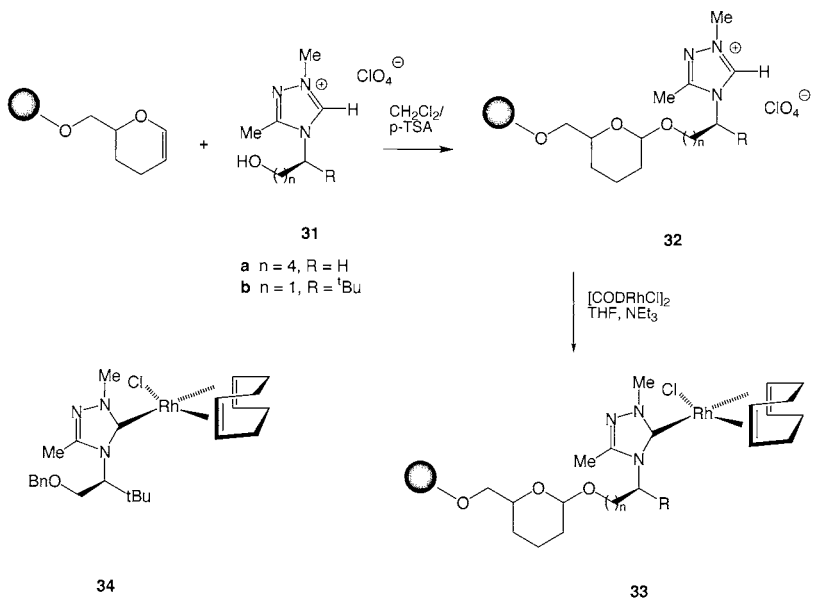
Fig. 12. Temperature of isoinversion.

The $\delta\Delta\Delta H^{\#}$ against $\delta\Delta\Delta S^{\#}$ plot (values calculated out of the *Eyring* plots) was found to be linear with a slope of 285 K ($T_{iso} = 13°C$) (Fig. 12). The best enantioselectivities for a (triazolinylidene)rhodium(I) catalyst are therefore to be expected at about the temperature of isoinversion of 13°C.

The enantioselectivity of the hydrosilylation reaction is highly dependent on the reaction temperature and the achiral substituent of the chiral ligand. These results show the influence of the axis of chirality on the outcome of the reaction compared to rhodium(COD) complexes of C_2-symmetrical chiral imidazolinylidene ligands (higher enantioselectivity with lower temperatures) [28].

8. Immobilized (triazolinylidene)rhodium(I) complexes

Immobilized chiral rhodium complexes, e.g. with a chiral phosphine ligand (DIOP) attached to a *Merrifield*



Scheme 9. Preparation of (triazolinylidene)rhodium(COD) complexes **33** and **34**.

Table 10
Yields and enantiomeric excesses of the hydrosilylation reaction [a1]

Catalyst	Run	Yield (%)	ee (%) [e1] (*R*-**27**)
33a [b1]	1	95	–
	2	95	–
	3	85	–
33b [c1]	1	80	24
	2	75	24
	3	70	23
34 [d1]		85	17

[a] 24 h room temperature, 1 mmol acetophenone.
[b] 200 mg resin **33a**.
[c] 400 mg resin **33b.**
[d] 1 mol% **34**.
[e] Determined by gas chromatography (CP-CHIRASIL-DEX CB).

resin [38] as introduced by Kagan et al. [39], have been used as catalysts in asymmetric hydrosilylation reactions [40].

In order to attach chiral triazolium salts as precursors for chiral carbene ligands to a resin, a functional group had to be introduced into the side chain of the molecule. We used *O*-benzyl protected aminoalcohols as starting materials for the synthesis according to Scheme 2 with subsequent removal of the protecting group [11d]. The generally used attachment of an alcohol to the *Merrifield* resin was not possible due to the higher acidity of the ring proton compared to the alcohol proton. The tetrahydropyranyl (THP) ether linkage, introduced by Thompson and Ellman [41] was chosen in order to have an acid-mediated attachment and a base-stable linker [42] (Scheme 9).

Between 10% and 50% of the active sites could be loaded with a triazolium salt (**31**), depending on the steric demand of the substituent R and the chain length (n). The reaction of these carbene precursors (**32**) with a base and $[(COD)RhCl_2]_2$ led to immobilized (triazolinylidene)rhodium(I) complexes **33** as catalysts for a hydrosilylation reaction. For a comparison between the homogeneous and heterogeneous reaction, complex **34** was prepared with a diastereomeric excess of 78%. Complexes **33a**,**b** and **34** were tested as catalysts of the hydrosilylation of acetophenone leading to 1-phenylethanol **27** as already described above (Scheme 8, Table 10).

The solid-supported catalysts **33** could be re-used after filtration under nitrogen atmosphere with only slowly decreasing yields for each run (95%–85%, 80%–70%), which are comparable to the yields of the homogeneous reaction with a similar amount of catalyst **34**. The enantiomeric excess of 17% for **34** was exceeded by resin **33b** with ee = 23–24% for several runs. In summary, we have accomplished the first immobilization of a precursor to a chiral nucleophilic carbene and have shown the possible re-use of the catalyst.

9. Conclusion

A methodology for the preparation of triazolium salts bearing different chiral and achiral substituents has been developed. These and imidazolium salts were used as precursors for the preparation of chiral (carbene)metal complexes. Ruthenium and rhodium complexes with a stereogenic center at the metal as well as rhodium and palladium complexes containing an axis of chirality have been prepared. A first application of the soluble or immobilized compounds in an asymmetric hydrosilylation was examined with moderate enantiomeric excesses of up to 44%. One reason for a loss of enantioselectivity when employing complexes with an axis of chirality could be partial epimerization of the catalytic species. A possibility to overcome this problem should be the use of chelating ligands, comparable to the *ortho*-metalated ruthenium complexes. The preparation of such complexes and the development of other catalytic applications especially C–C coupling reactions is subject of current studies in our laboratory.

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