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Chiral *N*-heterocyclic carbene-transition metal complexes in asymmetric catalysis

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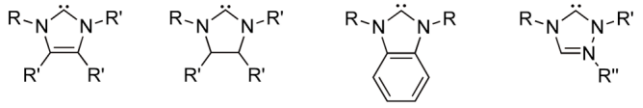
Abstract—Syntheses and applications of chiral *N*-heterocyclic carbenes are reviewed. The common features of successful enantioselective catalysts are identified, and the outlook for further investigations is discussed.

Contents

1. Introduction

Imidazolylidenes **A**, imidazolinylidenes **B**, benzimidazolylidenes **C**, triazolinylidines **D**, and related carbenes readily complex with transition metals.[1,2] These ligands are excellent σ-donors and form rather strong metal–carbon bonds; therefore, catalysts containing these ligands often have better air and thermal stability than complexes containing phosphines.[3,4] The use of such ligands in catalysis has lead to major advances particularly in the area of Ru-catalyzed alkene metathesis[5,6] and Pd-catalyzed C–C bond forming reactions.[7]



imidazolylidene **A** imidazolinylidene **B** benzimidazolylidene **C** triazolinylidene **D**

There are a variety of methods for forming carbenes from the corresponding azolium salts and these have been reviewed.[2,8,9] The procedure used most often is deprotonation of the corresponding azolium salt to give the free carbene. Surprisingly, there are very few reports in the literature on the pK_a of azolium salts. The pK_a's of *N*,*N*-dialkylimidazolium salts have been reported to be about 20 in THF and 23 in DMSO, making the carbene significantly more basic than a typical amine.[10,11] Despite this, imidazolylidenes are most often generated by treatment of the corresponding imidazolium salt with KO^{t}Bu (pK_a ~16). Deprotonation of azolium salts with this base is likely driven by the precipitation of halide salts or the formation of imidazolylidene complexes. We have found no reports on the pK_a's of triazolium, benzimidazolium or 4,5-dihydroimidazolium salts to give triazolinylidenes, benzimidazolylidenes or imidazolinylidenes, respectively; possibly this is because accurate determination of pK_a's for these compounds would be complicated by the potential reactivity of the free carbenes generated.

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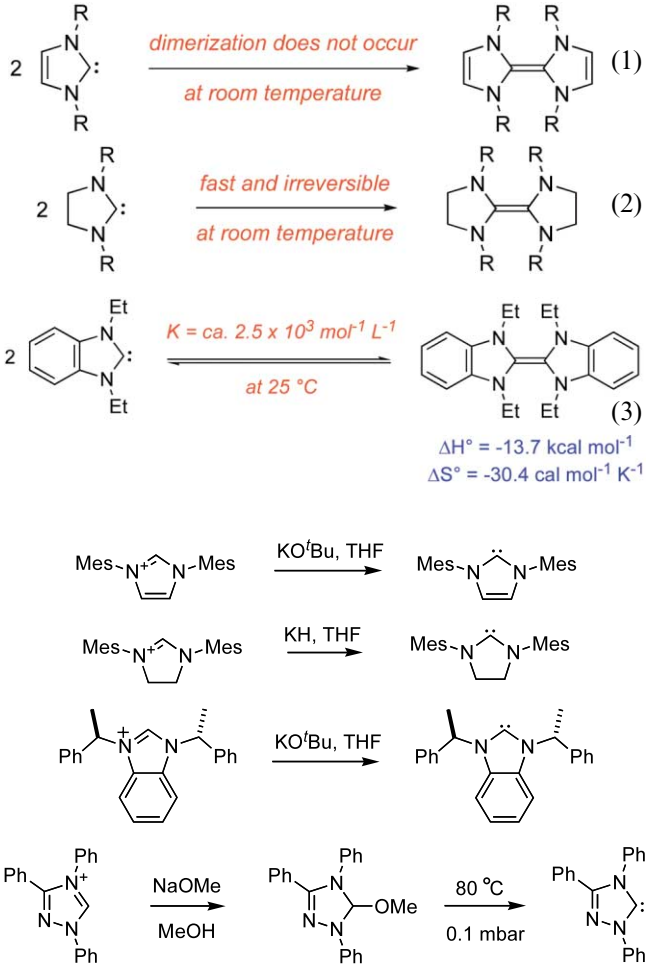
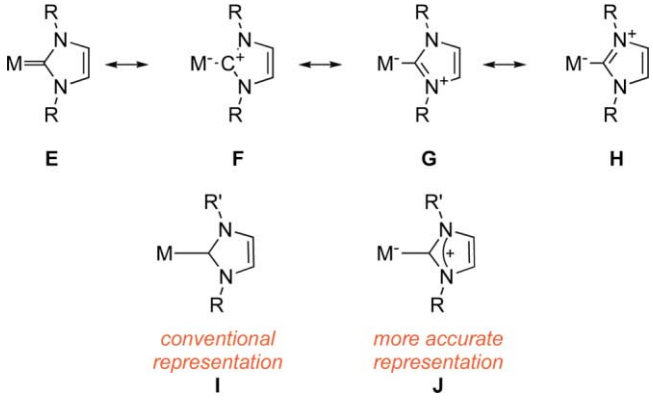
Stable carbenes of all four types shown in Scheme 1 have been isolated and characterized, but in organometallic chemistry the trend is that only imidazolylidenes are isolated prior to reaction with a desirable complex precursor. Dimerization of imidazolylidenes is estimated to be enthalpically favorable by approximately 4 kcal/mol, but this apparently does not offset the unfavorable entropic consideration (reaction 1).[12] Conversely, imidazolylidenes dimerize rapidly and irreversibly to form electron-rich alkenes as shown in reaction 2 unless the carbene carbon is shielded by extremely bulky substituents.[1,13] This difference in the tendencies of imidazolylidenes and imidazolinylidenes to dimerize has been attributed to several factors including the aromaticity of the former and the {calculated} lower singlet ground state to triplet excited state energy difference for the latter ($\sim$80 kcal/mol for imidazolylidines and $\sim$70 kcal/mol for imidazolinylidenes).[14] Benzimidazolylidenes have intermediate behavior relative to imidazolylidenes and imidazolylidines; an equilibrium between one of these free carbenes and the corresponding alkene dimer has been shown to favor the alkene by approximately 5 kcal/mol (reaction 3), though the position of similar equilibria will clearly be affected by steric factors associated with the R-functionalities.[15]



Scheme 1. Formation of an imidazolylidene, an imidazolinylidene, a benzimidazolylidene, and a triazolinylidene via deprotonation. The last example involves deprotonation then trapping (Mes = 2,4,6-trimethylphenyl).

Free carbenes can displace several different types of ligands including bridging halides, alkenes, carbonyls, arenes and phosphines to give carbene complexes.[2,8] Thermodynamic studies of these reactions can be complicated by dimerization and other side reactions of the carbenes. It is therefore unsurprising that most of the data that has been accumulated to date relates to imidazolylidenes, since these are readily accessible and least prone to dimerization. Symmetrical imidazolylidenes tend to form stronger bonds to Ru[16,17] or Co[18] than electron-rich phosphines unless the carbenes are extremely bulky. *N*,*N*-Dialkylimidazolylidenes are reported to have stronger metal to carbon bonds than the *N*,*N*-diaryl-ligands of comparable size.[16,17] Displacement of phosphine ligands by imidazolylidenes allows for the formation of a wide variety of complexes.

Electron-rich carbenes complexed to metals are good σ-donors and very poor π-acceptors because the proximal nitrogen atoms preferentially donate electron density into the empty orbital on the carbon atom. Thus, of the valence bond representations **E** to **H** (shown for the particular case of imidazolylidene complexes) contributing forms **G** and **H** are probably the most important, and **E** is the least. Most researchers represent complexes of electron-rich carbenes using diagrams like **I**. This is less accurate than representations like **J**, for instance, but diagrams in the style of **I** are preferred, presumably because they avoid complications regarding the actual charge of the complex. For the latter reason, diagrams in the conventional representation **I** are used throughout this review.



Complexes of electron-rich carbenes are robust and active catalysts for several different reactions[19–28] especially alkene metathesis.[5] They are modified under some conditions that facilitate metalation,[29–32] reductive elimination,[33,34] and CO insertion,[35] but these complicating side reactions are uncommon. A natural progression in this field is to asymmetric catalysis. However, there are few guiding principles for the development of useful chiral carbene ligands. These ligands are quite different from diarylphosphines in that they are unlikely to be able to present edge-to-face orientations of aromatic substituents, a common structural feature in useful, chiral phosphine ligands.[36] Topographical features of carbene ligands that are desirable for asymmetric catalysis must be identified. The area is really in a formative stage, searching for these key features. Several chiral *N*-heterocyclic carbene complexes have been developed, they have

been used in a limited number of asymmetric transformations, and a few have given high enantioselectivities. This review summarizes the state of the art in this area.

2. Chiral imidazolylidine complexes

2.1. Syntheses

Imidazolium salts, the usual precursors to imidazolylidine complexes, are generally synthesized by a ring-forming reaction, or via alkylation. Symmetrical imidazolium salts can be prepared by first forming 1,4-diazobutadienes (DABs) via condensation of an amine with glyoxal, then treatment of the DAB with paraformaldehyde and HCl.[37] This method works well for many, but not all, amines. A one-pot condensation of amines, paraformaldehyde and glyoxal under acidic conditions has also been used for the synthesis of symmetrical imidazolium salts.[38] Unsymmetrical imidazolium salts are typically prepared by alkylating monosubstituted imidazoles with an appropriate alkyl halide.[39] Chiral imidazolium salts have been synthesized by these methods and typical examples are shown in Chart 1. The structures illustrated reflect familiar themes in asymmetric syntheses: the use of pinene- and camphor-derived chiral auxiliaries, oxazolines from optically active amino acids, atropisomerism in binaphthyl systems, and the planar chirality of ferrocene.

Chiral imidazolium salts can be converted into transition metal complexes by treatment with a base in the presence of a transition-metal precursor as in reactions 4 and 5, or by treatment of the imidazolium salt with a complex containing basic ligands as in reactions 6–8.[40–42] Wanzlick and Öfele used the latter method to synthesize the first imidazolylidene complexes.[43,44]

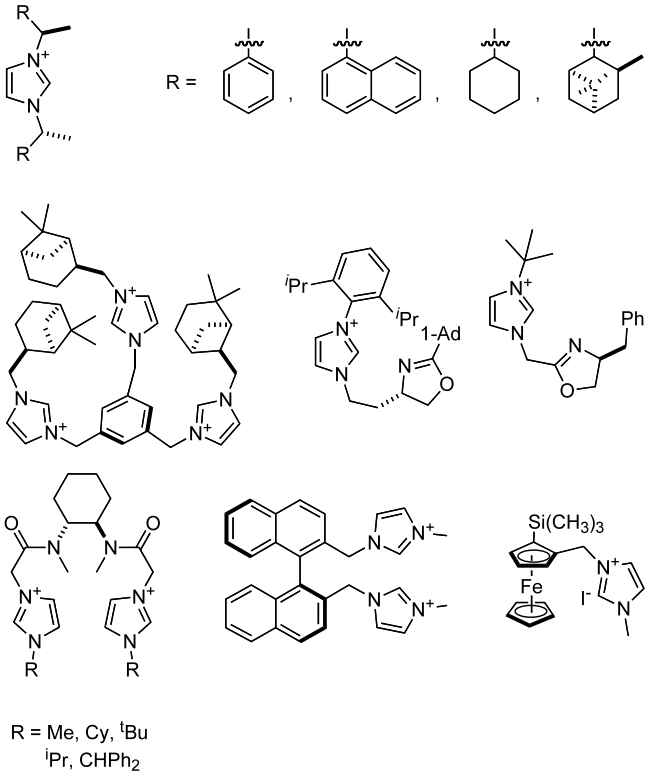
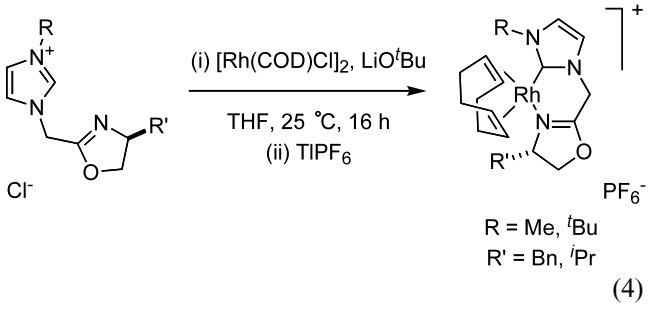


Chart 1. Symmetrical and unsymmetrical chiral imidazolium salts.



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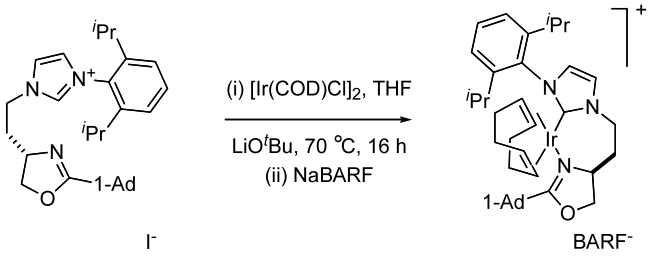

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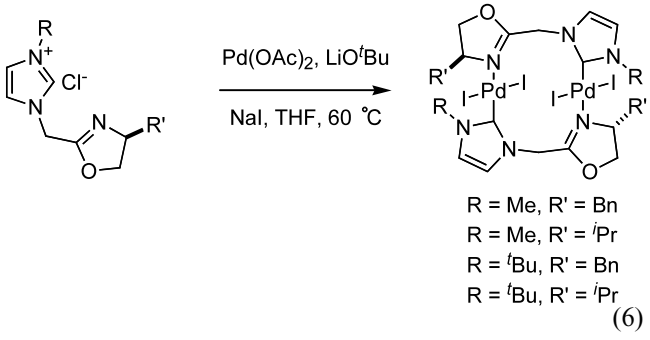

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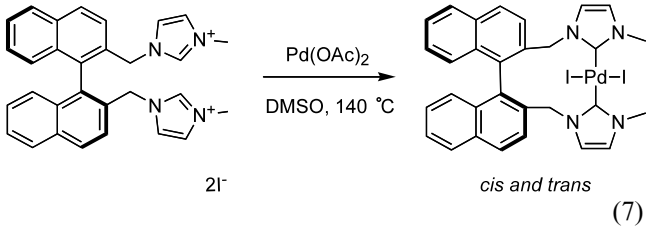

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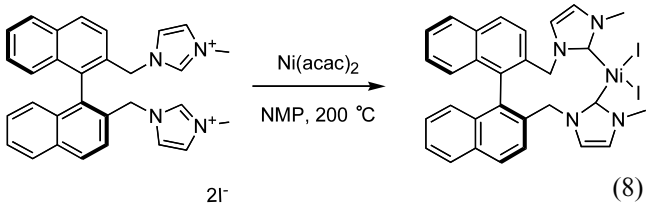
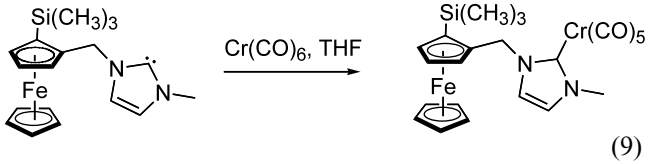


(8)

Reactions 6–8 are ones in which the carbenes are formed in situ, but preformed, isolated carbenes can be used to replace labile ligands on a suitable complex precursor. Examples of this kind of process are shown in reactions 9–14.[38,45,46]



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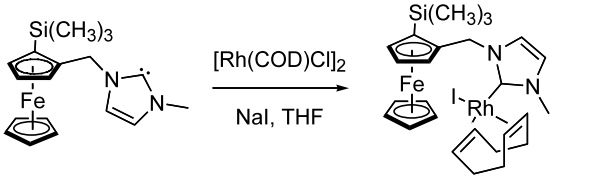

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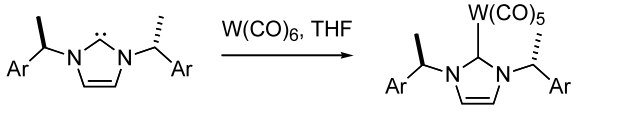
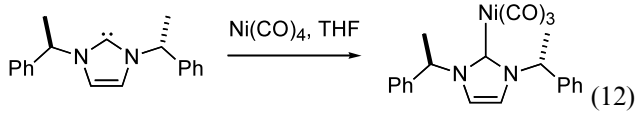


Ar = Ph, 2-Nap (11)



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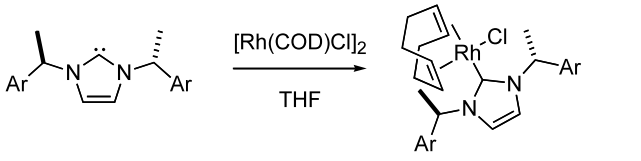

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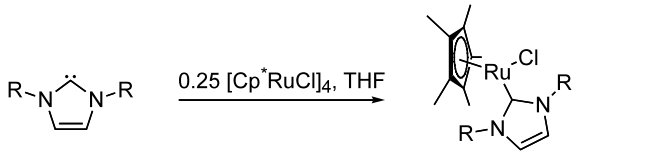
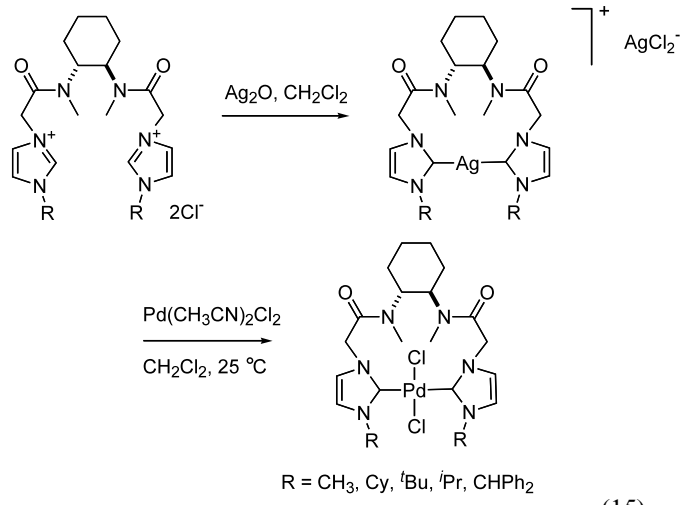
Ar = Ph, 2-Nap (13)



(14)

Transfer of carbene ligands from silver[47] is also an effective way to form carbene complexes that has been applied to chiral forms (reaction 15).[48] The driving force for this reaction is the formation of insoluble silver salts. This method can be particularly useful if the ligand precursors have protons of comparable acidity to the imidazolium C–H, and treatment with base is not productive.



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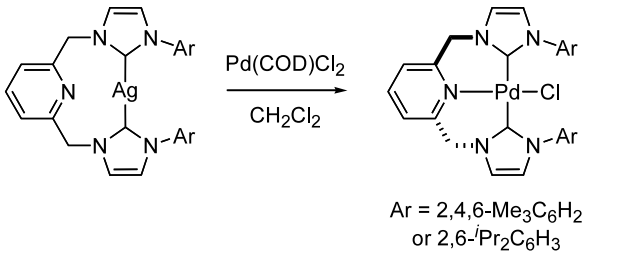


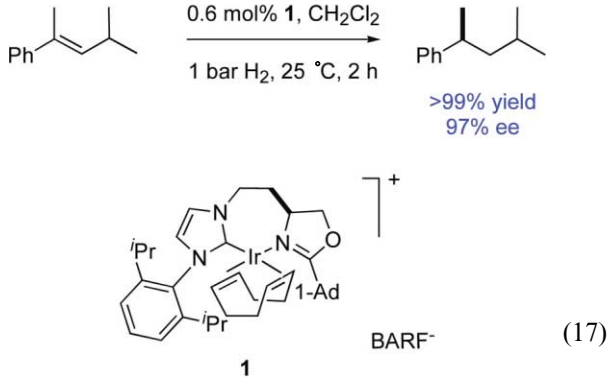
(16)

In reaction 15, the backbone chirality of *trans*-1,2-diaminocyclohexane should enforce a twist of the carbene arms. Similar atropisomeric chirality can be induced without backbone chirality, as shown in reaction 16.[49] The enantiomers of the product in that reaction were differentiated using a chiral additive in an NMR experiment, but they were not otherwise resolved.

2.2. Applications

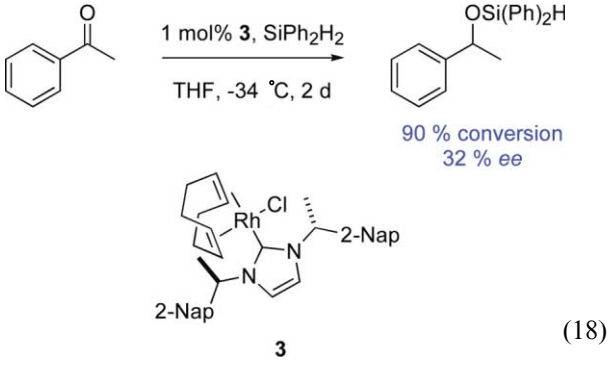
There are relatively few reports on the use of chiral imidazolylidene complexes in asymmetric catalysis, and only one catalyst and reaction combination leads to enantiomeric excesses of >90%: the hydrogenation of unfunctionalized alkenes using the iridium catalyst **1**.[41] Conveniently, this reaction occurs at room temperature and 1 bar of H_2 (reaction 17).[50] High enantioselectivities can be obtained for several substrates under ambient pressures of H_2. The data obtained are comparable with the best phosphine or phosphite-oxazoline iridium complexes, which typically require pressures of 50 bar H_2.[51–53] A small library of complexes related to **1** was prepared using other carbene and oxazoline substituents. In screening experiments, complex **1** was the best in most cases, and some relatively small changes to the ligand were shown to have dramatic effects on the yields and enantioselectivities obtained.

Other examples of asymmetric catalysis using chiral imidazolylidine complexes have provided much lower enantioselection than the hydrogenation processes illustrated above. For instance, the rhodium complexes **3**



(17)

(2 = 2-Nap) mediate hydrosilylation of methyl ketones, but with only 32% ee at best (reaction 18).[54] Similarly, the hydrosilylation of acetophenone using the ferrocenyl-based complex **2** gave racemic product in low yields.[45]



(18)

3. Chiral imidazolinylidene complexes

3.1. Syntheses

As outlined above, imidazolinylidenes are usually prepared by deprotonation of 4,5-dihydroimidazolium salts.[55,56] Chiral 4,5-dihydroimidazolium salts can be prepared from 1,2-diamines having stereogenic centers in the backbone, in the nitrogen substituents, or both (Chart 2).

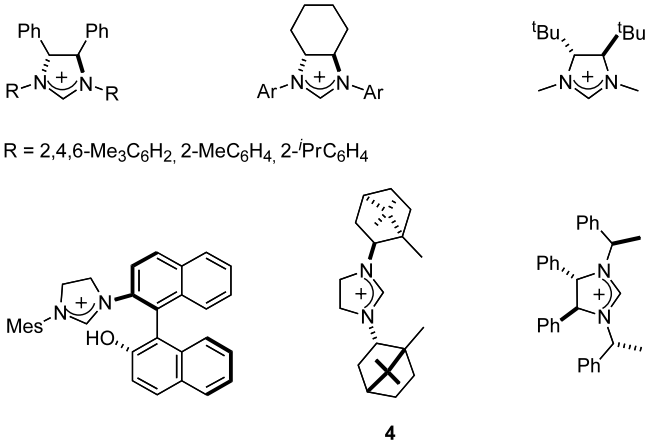
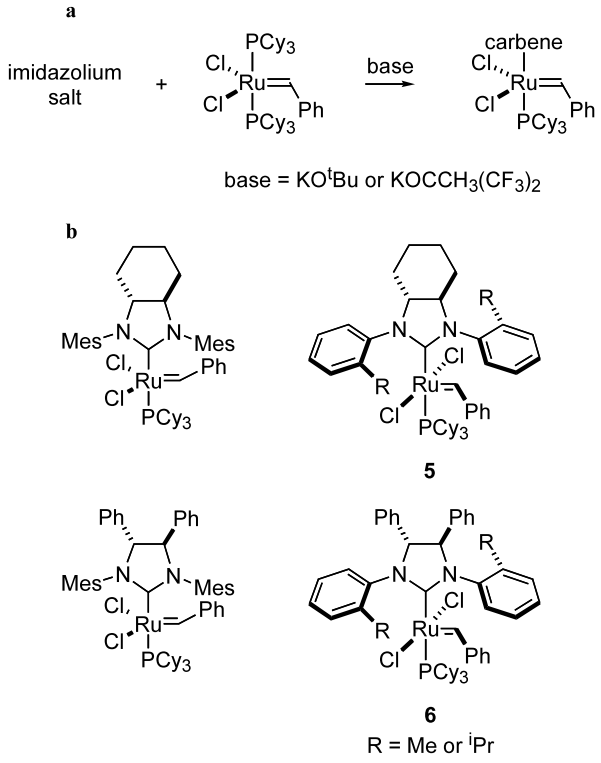


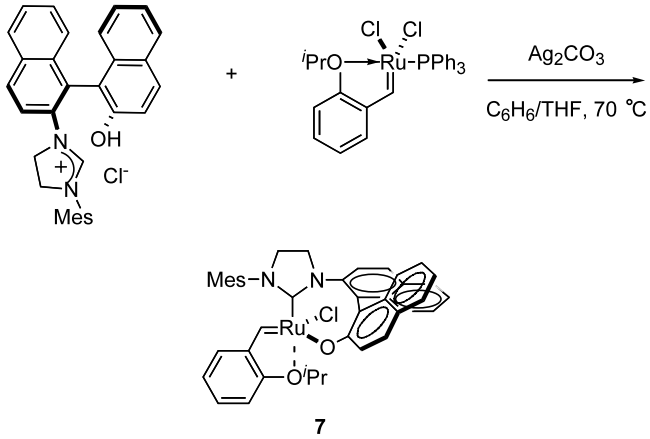
Chart 2. Chiral imidazolium salts with stereogenicity in the backbone, the *N*-substituents, or both.

Imidazolinylidines can be formed from salts like those shown above in the presence of a complex precursor. Scheme 2 shows a general approach, which has been used to make a series of ruthenium complexes.[57,58] Systems **5** and **6** cleverly use the backbone stereogenicity to induce atropisomeric chirality in the unsymmetrical *N*-aryl substituents.



Scheme 2. (**a**) General approach to ruthenium imidazolylidine complexes; and (**b**) some of the complexes formed.

Reaction 19 shows a modification of the process delineated in Scheme 2. The main difference is a peripheral phenolic oxygen that coordinates to the ruthenium and locks the aromatic group into a chiral, twisted conformation in the product complex **7**.[59]



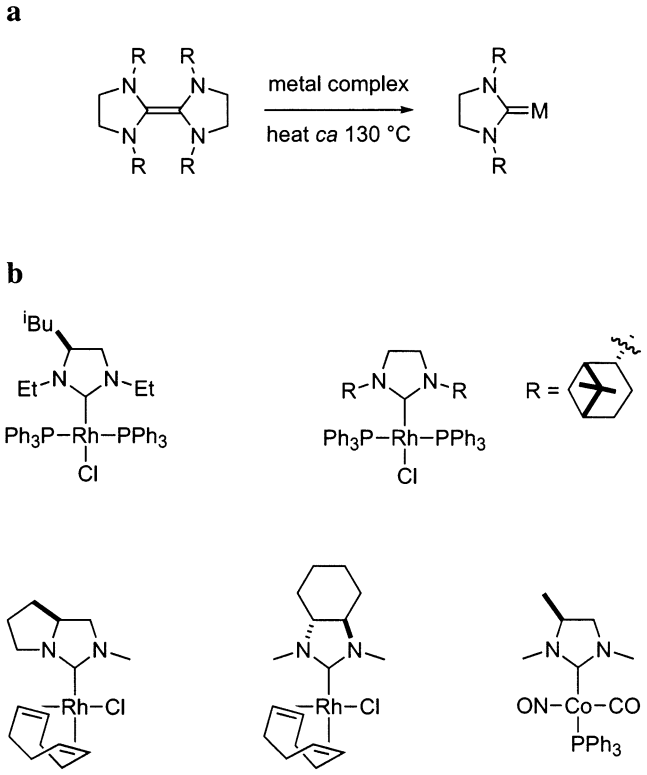
(19)

Formation of imidazolinylidines in situ, i.e. in the presence of metal complex precursors, is a reasonable strategy to suppress competing dimerization reactions of the

carbene. Ironically, the very first chiral imidazolinylidene complexes were synthesized by Lappert et al. by the reverse of this process: heating the corresponding dimers, highly electron-rich alkenes, in the presence of a complex precursor.[13] That work was performed prior to the isolation of the first stable *N*-heterocyclic carbenes. Scheme 3 describes the approach, in general terms, and shows some of the chiral complexes that have been prepared.

3.2. Applications

The chiral imidazolinylidine ruthenium alkylidene complexes shown in Scheme 2 and reaction 8 have been used in asymmetric alkene metathesis reactions; in fact, this is the most studied application of these ligands. By far the majority of alkene metathesis reactions do not involve formation of stereogenic centers, hence these particular transformations are special cases designed to prove feasibility. Both ring-closing (reaction 20 and Fig. 1),[58,59] and ring-opening[59] (reactions 21 and 22) variants of the metathesis process have been devised in which desymmetrization occurs. Fig.1 summarizes the optimization studies that led to the experiment shown in reaction 20. These indicated: (i) the 1,2-diphenylethylenediamine backbone gave higher enantioselectivities than the 1,2-diaminocyclohexane; (ii) higher ee's were also obtained when the 2-methylphenyl or 2-*iso*-propylphenyl *N*-substituents were used in place of the mesityl group; and (iii) higher enantioselectivities but lower conversions were obtained for the iodo-complex



Scheme 3. (**a**) A general approach to ruthenium imidazolylidine complexes from electron-rich alkenes; and (**b**) some of the complexes formed.

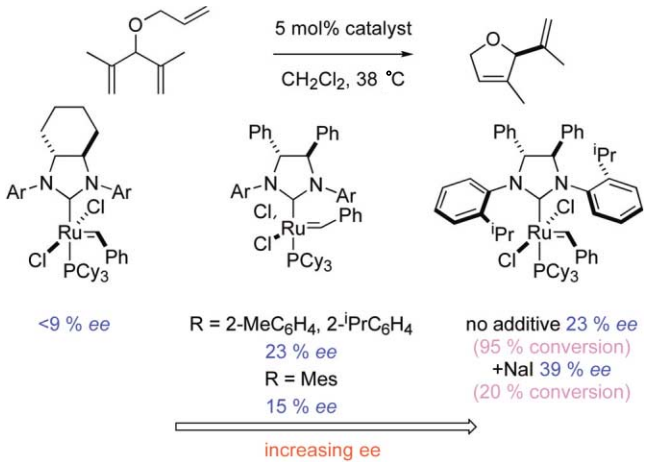
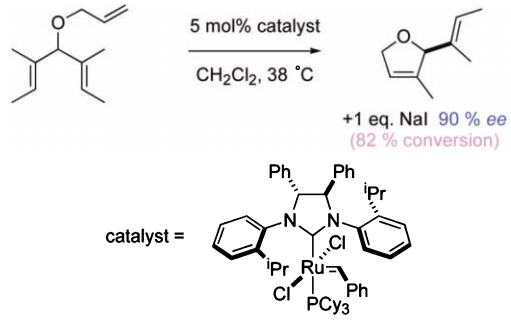


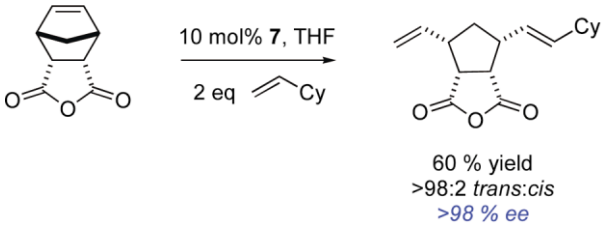
Figure 1. Optimization of enantioselectivities in a ring closing metathesis reaction.

relative to the chloro one. However, the significance of these data should not be exaggerated because the conclusions are based on small enantioselectivity differences in a multivariable situation.



(20)

Complex **7** has been used in four asymmetric metathesis reactions; two ring closures and two ring openings. Enantioselectivities were not reported for the ring closing reactions, but the ring opening transformations gave enantioselectivities in the 95–98% range (reactions 21 and 22). It is possible that the enantioselectivities of these reactions increase with time, at the expense of yield, if the minor enantiomer reacts with the excess alkene faster than the major one. It would have been informative to quote relative rates of formation of the enantiomers, but the authors did not comment on this. They did comment on the robust character of the catalyst, however. It is air stable, can be subjected to chromatography on silica gel in air, used in undistilled solvents, and recovered at the end of the reaction.



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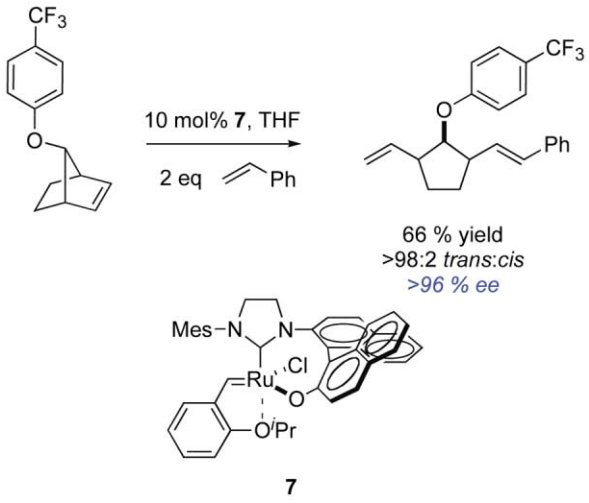
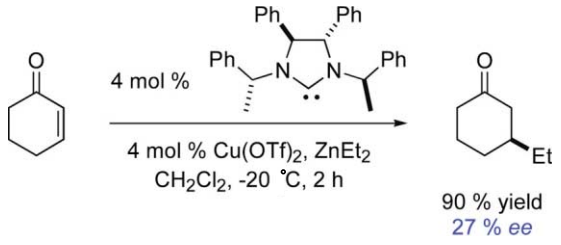


(22)

The asymmetric conjugate addition of diethylzinc to cyclohexenone in reaction 23 relies on generation of a chiral imidazolinylidine complex in situ from $Cu(OTf)_2$ and a dihydroimidazolium salt. Enantioselectivities of up to 27% were obtained.[60] These data indicate there was little difference between the system containing stereogenicity only in the backbone and the one containing stereogenicity in both the backbone and on nitrogen. However, only one stereoisomer was studied so it is impossible to be certain of the extent of matching and mismatching effects[61] in this system. A similar transformation, but involving a ligand with only backbone chirality, was developed in which a silver imidazolinylidene complex was used as a carbene transfer agent producing ee's of up to 23% (reaction 24).[62]



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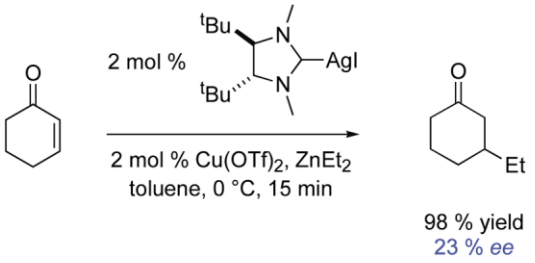
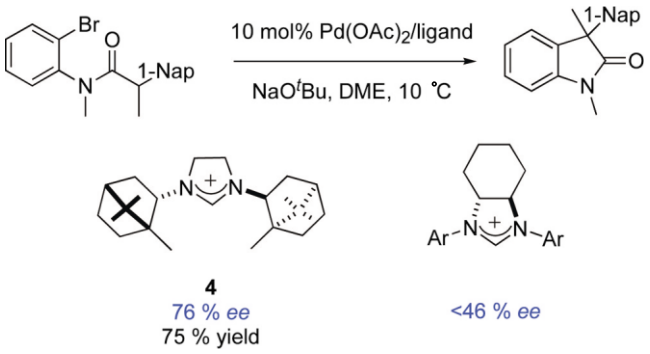


(24)

Intramolecular palladium-mediated coupling of an enolate onto an aromatic bromide facilitates formation of chiral oxindoles. Hartwig et al. made the process asymmetric by producing chiral imidazolinylidines in situ. Enantioselectivities of up to 76% were obtained (reaction 25).[63] The best ligand identified was **4**; this has chiral *N*-substituents and gave better results than similar ligands with stereogenicity in the backbone. This leads to a common-sense conclusion that, in the absences of additional factors, it is desirable to locate the stereogenic centre as close as possible to the reacting center.



(25)

4. Chiral benzimidazolylidene complexes

Benzimidazolylidenes can be formed by deprotonation of the corresponding benzimidazolium salt with an appropriate base, and isolated. Benzimidazolium salts can be synthesized via the condensation of a 1,2-diaminobenzene derivatives with an orthoester or via alkylation.[64,65] Some chiral 2*H*-benzimidazolium salts are shown in Chart 3. However, so far there are no reports of these being used in asymmetric catalysis.

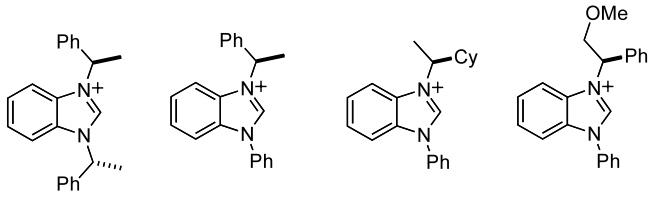


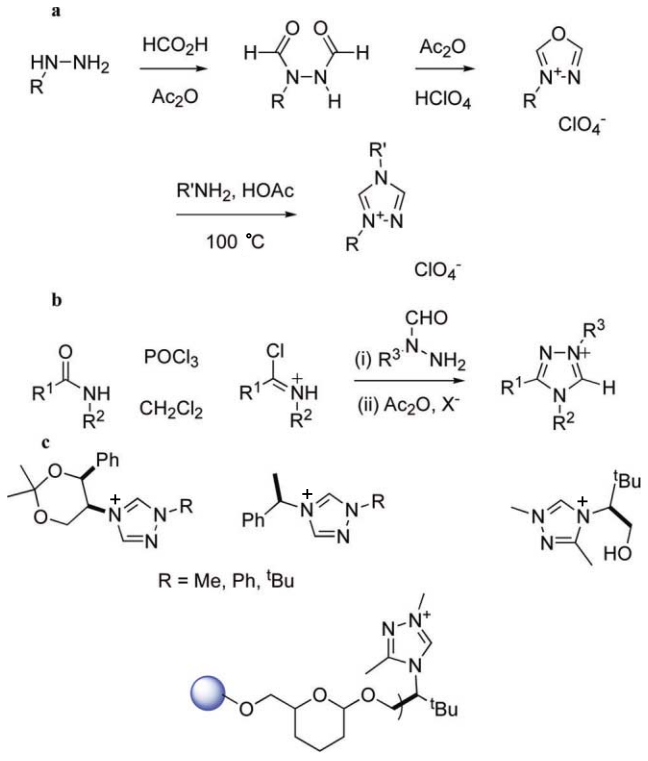
Chart 3. Chiral benzimidazolium salts.

5. Chiral triazolinylidene complexes

5.1. Syntheses

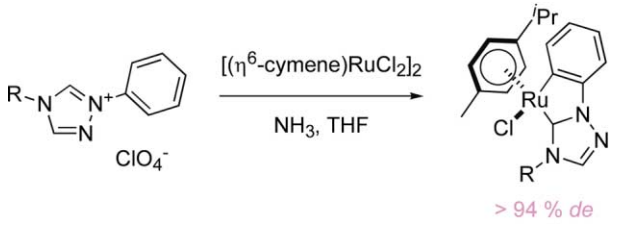
Triazolium salts are usually synthesized by one of two methods.[9] 1,4-Disubstituted forms are prepared by condensation of alkyl hydrazines with *N*,*N*′-diformylhydrazines, then reaction with an amine. 3,4-Disubstituted 1-alkyl-4*H*-1,2,4-triazol-1-ium salts are also prepared from *N*-formylhydrazines and imidoyl chlorides. Scheme 4 shows these two methods, and shows some of the chiral triazolium salts that have been prepared. They all have only one chiral group attached to the triazolium ring, and they were all isolated as their perchlorate salts.[9]

Triazolinylidenes are typically formed either by deprotonation of a triazolium salt, or by thermal elimination of an alcohol from an alkoxytriazole.[9] Complexes of these carbenes are usually made by generating the carbene in the presence of a complex precursor, rather

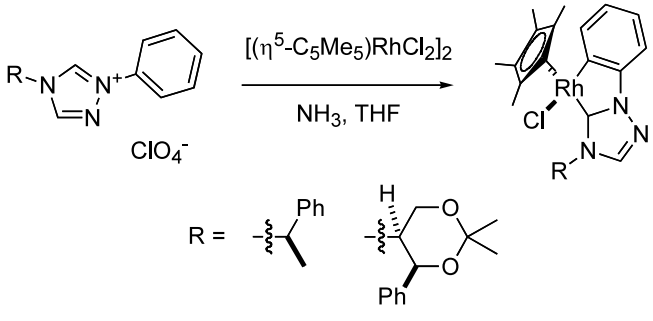


Scheme 4. Synthesis of (**a**) 1,4-disubstituted triazolium salts; (**b**) 3,4-disubstituted 1-alkyl-4*H*-1,2,4-triazol-1-ium salts; and (**c**) some perchlorate salts prepared using these methods.

than via isolation of the free ligand. Chiral rhodium, ruthenium and palladium complexes have been synthesized from triazolium salts.[9] The triazolium ring is not symmetric, so diastereomeric mixtures of complexes with an axis of chirality are formed, in many cases with high diastereoselectivities (reactions 26 and 27).

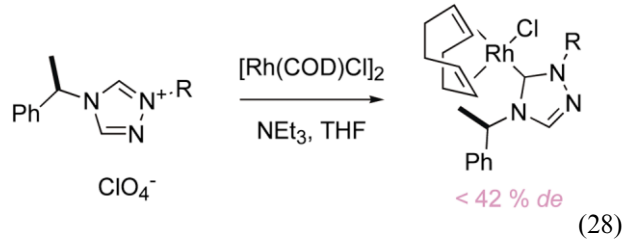


(26)

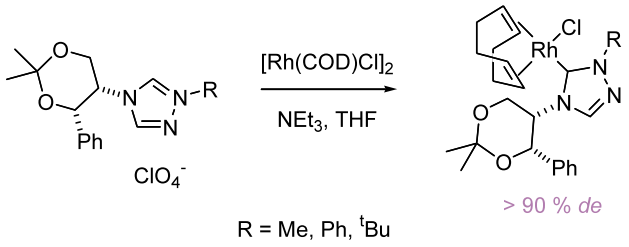


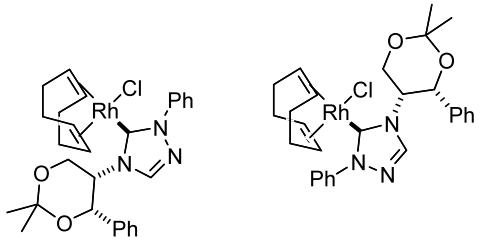
(27)

Other syntheses of chiral triazolinylidene complexes also proceed via deprotonation of the corresponding azolium salt in situ. A surprisingly weak base, triethylamine, is effective in these transformations (reactions (28) and (29)).



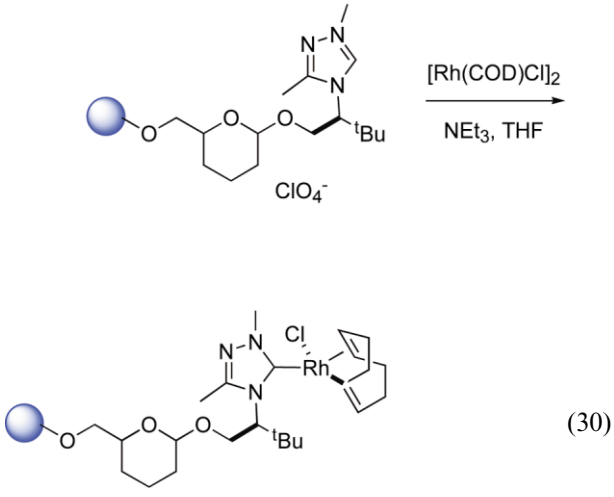
(28)





(29)

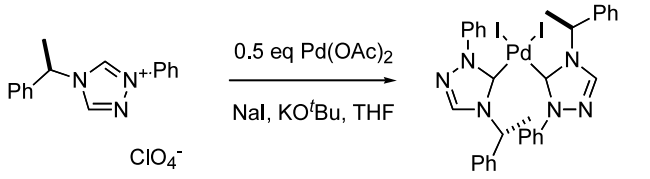
The robust characteristics of *N*-heterocyclic carbene complexes could mean that catalysts of this type could be recycled without loss of activity. One of the most convenient ways to recycle them is via attachment to solid supports. Once attached, the strong metal to carbene bonds should minimize leaching of the metal from the supports; reaction 30 is important in this regard.



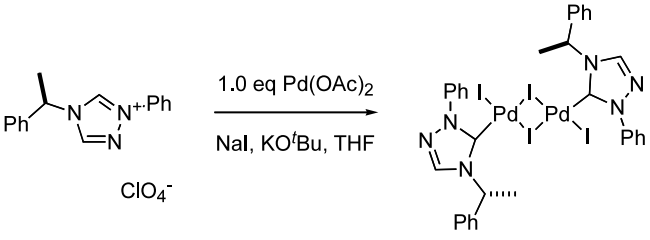
(30)

Reactions 31 and 32 illustrate how monometallic and dimetallic chiral triazolinylidene complexes can be formed selectively by adjusting the stoichiometry of a reaction. Treatment of the bimetallic products with amines, including chiral amines, cleaves them into

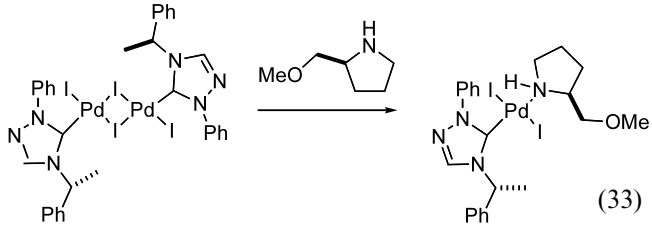
monomeric complexes with only one carbene ligand (reactions 33 and 34).



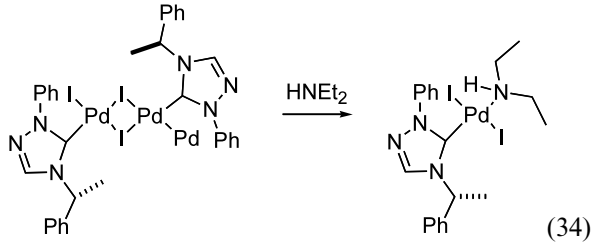
(31)



(32)



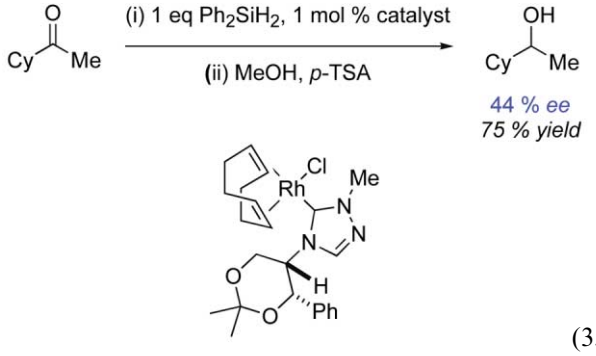
(33)



(34)

5.2. Applications

Despite the variety of chiral triazolinylidene complexes that have been formed, only two asymmetric reactions have been reported. The first was an unspecified Heck reaction which gave a product in only 8% ee.[66] The other is the asymmetric hydrosilylation of a series of methyl ketones, where low enantioselectivities were obtained (reaction 35).[67]



(35)

6. Conclusions

There are only two catalytic processes in which chiral *N*-heterocyclic carbene ligands have provided high enantioselectivies: iridium-mediated hydrogenation of unfunctionalized alkenes,[41] and desymmetrizing metathesis reactions.[58,59] These reactions feature imidazolylidine and imidazolinylidine complexes, respectively. No applications of chiral benzimidazolylidene complexes have been reported, and the one process that has been cited for triazolinylidene complexes was not highly enantioselective. Triazolinylidene complexes can be more difficult to apply in asymmetric catalysis because they are unsymmetrical and this results in formation of diastereomers on complexation. Even if diastereomerically pure complexes are obtained, stereoisomerism via rotation about the metal–carbon bond is a possibility for some complexes.

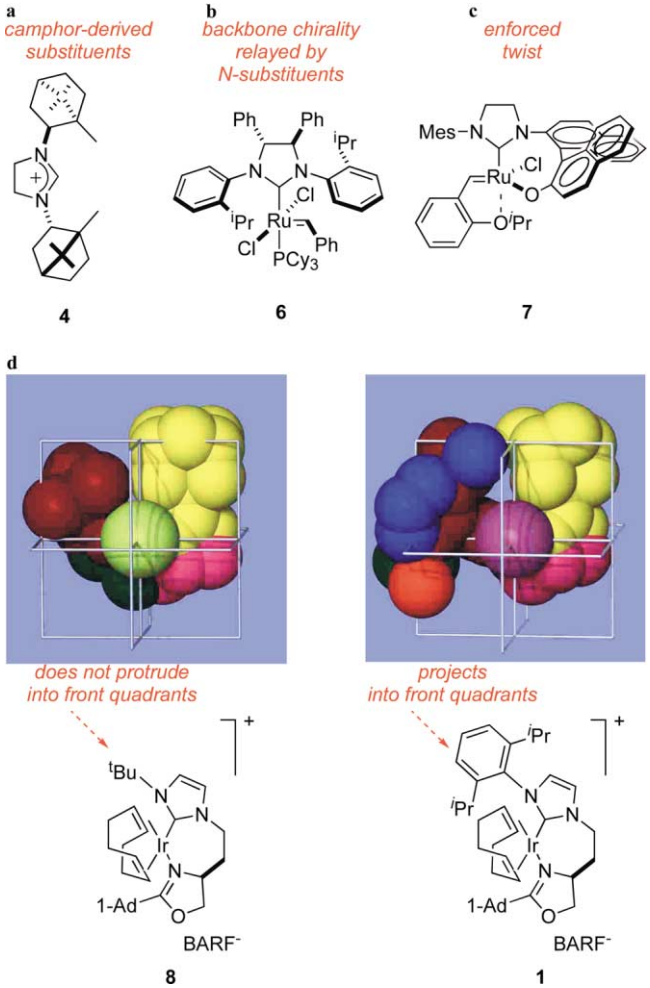


Figure 2. Some common features of effective *N*-heterocyclic ligands for asymmetric catalysis. (**a**) Camphor-derived *N*-substituents; (**b**) backbone stereogenicity relayed via *N*-substituents; (**c**) a catalyst with an unusual twist; and (**d**) the complex **8** has no presence 'in front' of the metal, but the homolog **1** does and is far more enantioselective in hydrogenations (atoms in the space filling diagram are colored according to the quadrants they occupy).

There are grounds for optimism regarding applications of chiral *N*-heterocyclic carbenes in asymmetric catalysis, despite the current lack of examples and the limitations identified above. The successful examples include both monodentate and chelating ligands. There is, and there is unlikely to be, one single key structural feature that can be associated with high enantioselectivities, but some trends are emerging. Monodentate ligands can be effective if they have large (e.g. camphor-derived) *N*-substituents. Conversely, monodentate carbene ligands with only backbone stereogenicity can give high enantioselectivities in ring-closing metatheses if the core asymmetry is amplified via preferred conformations of *N*-substituents, e.g. for complexes **5** and **6**. The unusual twisted geometry of complex **7** makes this a highly enantioselective catalyst for ring opening metatheses (Fig. 2).

In the asymmetric hydrogenations of unfunctionalized alkenes using iridium imidazolylidine-oxazoline ligands, a steric presence in six of the octants about the metal center was identified as a favorable molecular feature.[50] This same study also demonstrated the screening small libraries of well-designed chiral complexes can be highly effective for catalyst discovery and optimization. In this regard *N*-heterocyclic carbene complexes can be more easily obtained than similar phosphine containing materials. Overall, progress in this field will not be easy, but it seems evident that chiral *N*-heterocyclic carbenes provide exciting avenues for the development of new asymmetric catalysts.

Acknowledgements

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