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Catalytic asymmetric C–H activation of sp^3 hybridized C–H bonds by means of carbenoid C–H insertions: applications in organic synthesis

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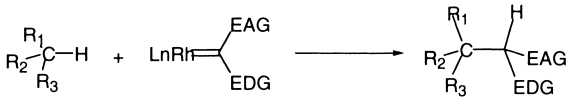
Abstract

The development of practical catalytic asymmetric methods for selective C–H activation could revolutionize the approaches used for the construction of complex organic compounds [1]. In this review, our progress in achieving a practical and catalytic method for asymmetric intermolecular C–H activation using rhodium carbenoid intermediates will be described (Eq. (1)) [2]. The inherent advantage of the carbenoid method over traditional C–H activation processes is the ease of achieving a catalytic cycle. Efficient reactions using chiral catalyst loadings of 1% or less are readily achieved. In order for the carbenoid-induced C–H activation to be useful in organic synthesis, issues of enantioselectivity, diastereoselectivity and regioselectivity need to be controlled. We have demonstrated that rhodium carbenoids containing both electron donor and acceptor groups are ideal reagents for selective C–H functionalization of hydrocarbons [3]. The synthetic potential of this chemistry will be illustrated by examples in which the C–H activation is used as a surrogate for some of the classic C–C bond-forming reactions of organic synthesis. These classic reactions will include the Michael reaction, the aldol reaction, the Mannich reaction and the Claisen rearrangement.



EAG = electron accepting group (CO_2Me)
EDG = electron donating group (aryl, vinyl)

(1)

Keywords: Catalytic asymmetric; Rhodium carbenoid; C–H activation

1. Background of C–H activation

The development of practical laboratory methods for catalytic C–H activation has been a long-term goal of the organometallic chemical community [1]. The most extensively studied strategy for C–H activation has been the use of highly reactive metal complexes that undergo oxidative addition across a C–H bond. Several metal complexes have been developed that are capable of such oxidative additions. The most extensively studied system is the iridium complex **1**

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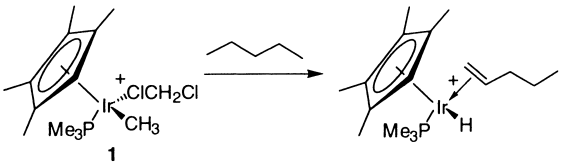
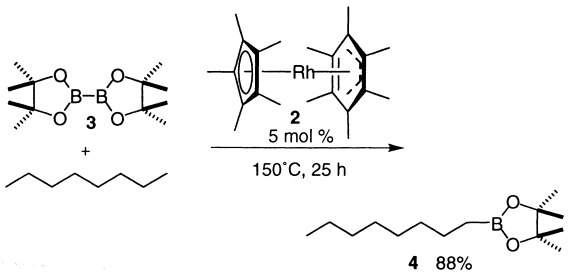
(Eq. (2)), whose C–H activation chemistry has been elegantly explored in landmark studies by Arndtsen et al. [1b]. The extension of this strategy into a truly practical C–H functionalization protocol has been very challenging because it is virtually impossible to achieve a catalytic cycle. The starting complexes are very high energy and their regeneration to complete the catalytic cycle is highly unfavorable.



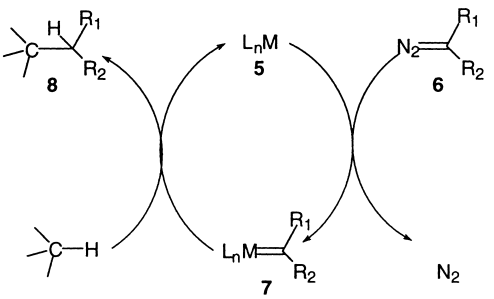
(2)

In recent years alternate methods have been explored, to achieve C–H activations that are more synthetically useful. A breakthrough result was recently described by Hartwig using rhodium catalyst **2** to catalytically couple linear alkanes with borane **3** through a C–H insertion process to give good yields of linear alkylboranes **4** (Eq. (3)) [4].



(3)

A third method for C–H activation is the insertion of a metal-carbenoid intermediate across a C–H bond. In general, this reaction has not been classified as a C–H activation process [1,5,6], presumably because the carbenoid rather than the metal is inserting across the C–H bond. This process, however, offers a unique opportunity for the development of practical processes for functionalization of non-activated C–H bonds. A major advantage of metal-carbenoid-induced C–H activation over the more traditional approaches is that a catalytic cycle is extremely favorable (Eq. (4)) [6]. The driving force for the cycle is derived from the carbenoid precursor, typically a diazo compound (**6**). The catalyst **5** is reasonably stable, but catalyzes the loss of nitrogen from the diazo compound to form the high-energy metal-carbenoid intermediate **7**. The metal-carbenoid intermediate then undergoes the C–H activation step by inserting the carbene into the C–H bond and releasing the functionalized product **8** and regenerating the catalyst **5**. This catalytic cycle is so favorable that reactions with low catalyst loading can be realistically contemplated.



(4)

Originally the catalysts used for decomposition of diazo compounds were copper based, and the resulting copper-carbenoid intermediates showed little tendency towards clean C–H insertions [7]. In the 1970s, however, Teyssie and co-workers introduced dirhodium tetracarboxylates as catalysts for diazo decomposition, and discovered that the resulting rhodium carbenoids have a greater tendency to undergo C–H insertion reactions, compared to the copper catalysts [8]. Impressive advances have been made in asymmetric intramolecular C–H insertions of diazo compounds [6]. In general, five-membered rings are formed, although the formation of other ring sizes can occur in exceptional cases. Competition studies have been used to confirm the insertion preferences for $3^\circ > 2^\circ \gg 1^\circ$ C–H bonds [6]. This selectivity is very intriguing because it is opposite to that observed with the traditional organometallic C–H activation [1,4]. Extensive studies on the effect of substituents have been carried out, and C–H activation was found to be favored adjacent to electron donating groups such as alkyl and silyl ethers, as well as azido substituents [6]. It was also determined that electron withdrawing groups such as esters and acetoxy groups disfavor C–H activation at adjacent C–H bonds [6].

In contrast to the intramolecular C–H insertions, the intermolecular reaction has not enjoyed widespread application. Indeed up until very recently, the intermolecular C–H insertion was not considered to be of

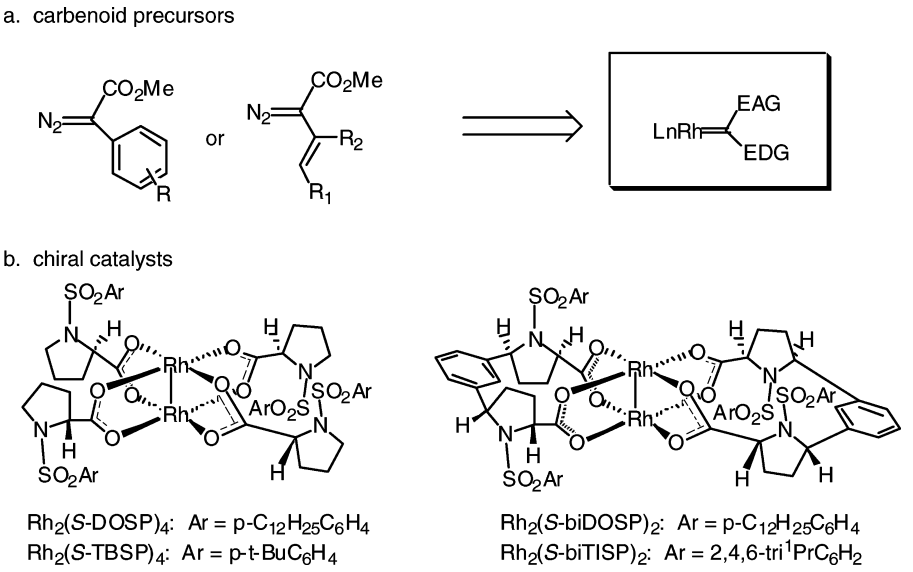
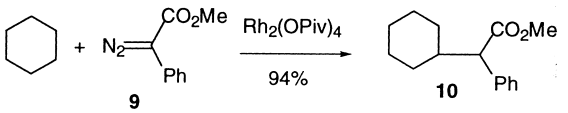


Fig. 1. Carbenoid percursors and chiral catalysts.

great synthetic utility [6,9]. The major difficulty with the intermolecular reactions is that the most widely studied carbenoids derived from alkyl diazoacetates are very prone to dimerization unless an efficient trap is present [10]. Furthermore, this class of carbenoid is not very chemoselective in intermolecular C–H insertions [9,11]. Consequently, in order for the intermolecular C–H insertion to become a practical reaction, it was necessary to develop carbenoid intermediates with improved chemoselectivity.

For some time, my group has been exploring a new class of rhodium carbenoid intermediates which contain both donor and acceptor substituents (Fig. 1) [12]. The presence of the donor group stabilizes the highly electron deficient carbenoid such that their reactions are much more chemoselective than is typically seen with the usual carbenoids, which lack the donor group [13]. These donor–acceptor substituted carbenoids undergo highly diastereoselective cyclopropanations, and when the reactions are catalyzed by the dirhodium tetraprolinate catalysts, Rh_2(*S*-TBSP)$_4$ and Rh_2(*S*-DOSP)$_4$ high asymmetric induction can be achieved [14]. Second generation catalysts that show great promise for this chemistry are the bridged prolinate catalyst Rh_2(*S*-biDOSP)$_2$ and Rh_2(*S*-biTISP)$_2$ [15].

The above observations led us to explore the possibility that these more stabilized carbenoids would be capable of undergoing much more selective C–H insertions than had been seen with the traditional carbenoids. An early comparison study between methyl phenyldiazoacetate (**9**) and ethyl diazoacetate (**11**) revealed that this was indeed the case (Eqs. (5) and (6)) [16]. Under identical conditions using dirhodium tetrapivalate as catalyst, phenyldiazoacetate **9** underwent C–H insertion into cyclohexane to form **10** in 94% yield while only a 10% yield of **12** was obtained from the reaction with ethyl diazoacetate (**11**).



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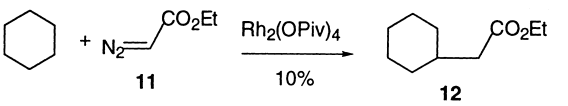


(6)

Rh_2(*S*-DOSP)$_4$ catalyzed decomposition of methyl phenyldiazoacetate (**9**) in the presence of hydro-

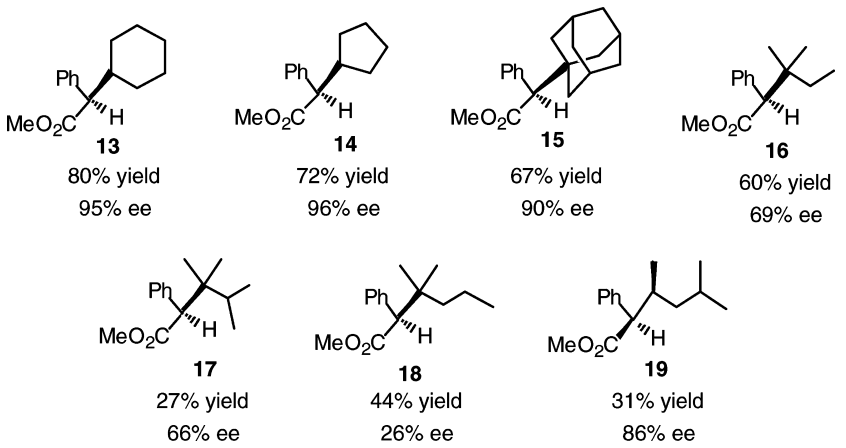
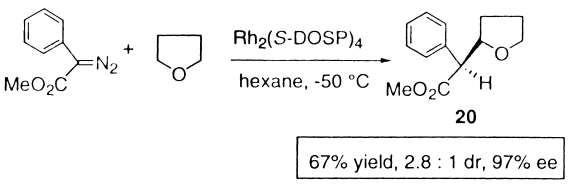


Fig. 2. Rh_2(*S*-DOSP)$_4$ catalyzed C–H activation of various hydrocarbons by **9**.

carbons revealed that highly enantioselective C–H insertions were possible [3b]. Furthermore, a delicate balance existed between insertion into methylene and methene C–H bonds. The results of C–H insertions with various substrates are summarized in Fig. 2. The reactions with cyclohexane and cyclopentane are very efficient resulting in C–H insertion products **13** and **14** in greater than 90% ee. The carbenoid reactions with adamantane, 2-methylbutane and 2,2-dimethylbutane resulted in clean insertions into the methene C–H bonds but the yield and enantioselectivity of the C–H insertion products **15–17** decreased as the methene site became more crowded. The formation of only two products **18** and **19** from the reaction of 2-methylpentane is most informative. The sites of attack are the methene site and the less crowded methylene position. Thus, the C–H insertion selectivity between methylene and methene sites is controlled by a delicate balance of steric and electronic effects. A major difference between the carbenoid C–H insertions and the more traditional C–H activations is that insertions into a methyl C–H bond is rarely observed with the donor–acceptor substituted carbenoids.

Much more facile C–H insertions occur at sites that are either allylic or adjacent to a heteroatom [3b]. A spectacular example of this effect is the reaction with tetrahydrofuran (THF, Eq. (7)). An effective reaction can be carried out at −50 °C using just two equivalents of THF in hexane as solvent. Under these conditions, the insertion product **20** is formed as a 2:8:1 diastereomeric mixture in 67% yield, where the major diastereomer is produced in 97% ee.



(7)

Competition experiments between various alkanes and THF revealed a remarkable range of reactivity towards C–H insertion [3b]. The room temperature reaction with THF is favored by a factor of >2000 over the reaction with cyclohexane, which in turn is favored by a factor of 13 over the reaction with 2-methylbutane. After normalizing for the number of sites available in each compound this would indicate that the methylene C–H bond of cyclohexane and the methene C–H bond of 2-methylbutane have roughly equivalent reactivity towards the C–H insertion. In the case of 2,2-dimethylbutane, the reactivity is considerably decreased, presumably because the insertion site is sterically crowded. On the basis of these reactivity patterns, 2,2-dimethylbutane was developed as a suitable inert solvent for this chemistry, since it does not have reactive C–H bonds and is non-polar (Fig. 3).

Kinetic deuterium isotope effects of 2–3 for cyclohexane and THF demonstrate that C–H bond cleavage

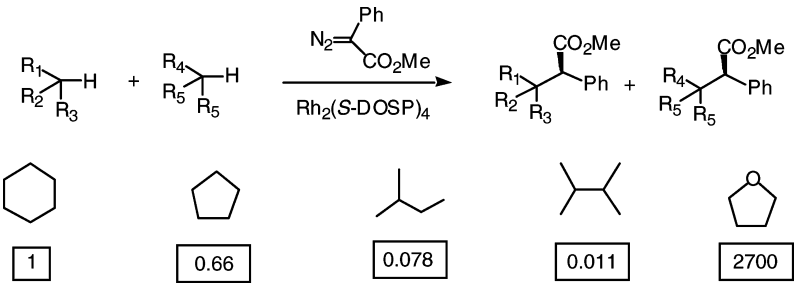


Fig. 3. Relative rates of C–H insertion.

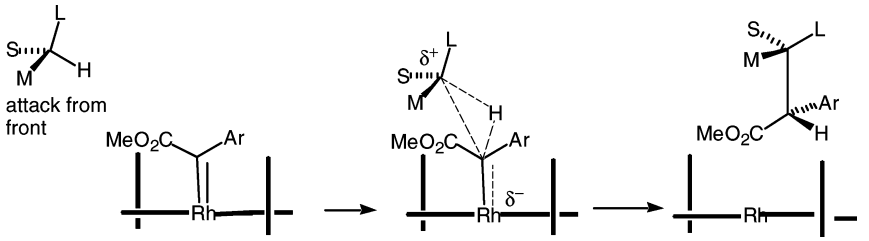
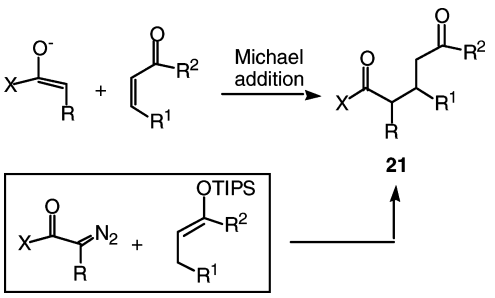


Fig. 4. Predictive model for asymmetric induction with Rh_2(S-DOSP)4 catalyst.

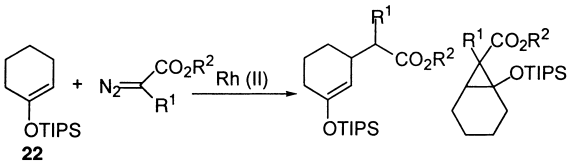
is involved in the rate determining step, but the extent of the cleavage is limited [3b]. Definitive kinetic data have been rarely obtained for metal catalyzed decomposition of diazo compounds, and this is also the case for these intermolecular C–H insertions. Consequently, a well-developed mechanistic interpretation of this reaction is not available at this time. However, an excellent predictive model of the stereochemical outcome of this reaction has been proposed [3b] and this is shown in Fig. 4. Due to the high symmetry of the catalysts, they can be simply viewed as a catalyst wall with two blocking groups, indicated by the thickened lines [3b]. The reaction is viewed as a concerted non-synchronous C–H insertion with build-up of positive charge on carbon [3b]. The actual orientation of approach of the trapping agent is not known, but it is considered to be quite specific. The orientation illustrated in Fig. 4, is predictive not only of the absolute stereochemistry but also of the relative stereochemistry, as will become apparent in later sections of this review.

Having determined that the intermolecular C–H activations are viable on hydrocarbons, our recent studies have focused on demonstrating that the C–H activation can be a surrogate for some of the classic C–C bond-forming reactions in organic synthesis. Allylic C–H insertions of vinyl ethers would be an intriguing proposition because the resulting product after silyl deprotection would be a 1,5-dicarbonyl compound **21** (Scheme 1). The usual C–C bond-forming strategy for the synthesis of 1,5-dicarbonyl compounds is the Michael reaction (for a general review on the asymmetric Michael addition, see [17]). Even though there have been some exciting advances in the use of chiral bases or Lewis acids to induce asymmetry in the Michael reaction, the control of relative stereochemistry is still problematic [17].



Scheme 1.

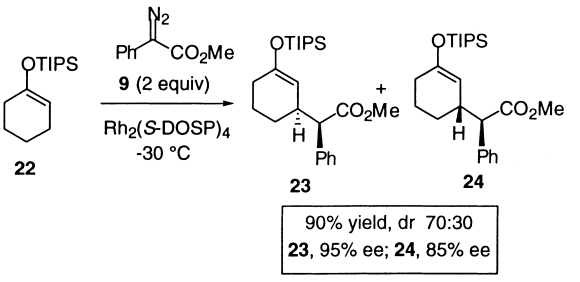
Vinyl ethers are excellent substrates for cyclopropanation with the traditional carbenoids such as those derived from diazoacetates [18], but the carbenoids derived from aryldiazoacetates are more sterically discriminating [19]. This is clearly seen on comparing the reaction of ethyl diazoacetate and methyl phenyldiazoacetate with trisiopropylsiloxycyclohexene (**22**) (Eq. (8)) [20]. Rhodium(II) octanoate catalyzed reaction of ethyl diazoacetate with the silyl enol ether **22** results in a strong preference for cyclopropanation over C–H insertion by a ratio of 96:4 [20]. The Rh_2(*S*-DOSP)$_4$ catalyzed reaction improved the ratio to 76:24, but still cyclopropanation dominates [20]. In contrast, the reaction with methyl phenyldiazoacetate results in exclusive formation of the C–H insertion products [20].



Cat.	R^1	R^2	C-H insertion : cyclopropanation
Rh_2(OOct)$_4$	H	Et	4 : 96
Rh_2(*S*-DOSP)$_4$	H	Et	24 : 76
Rh_2(*S*-DOSP)$_4$	Ph	Me	100 : 0

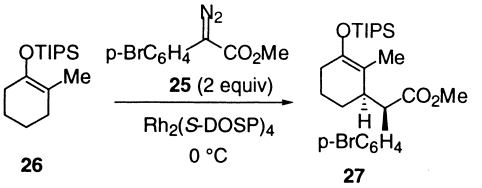
(8)

In addition to the high chemoselectivity of the C–H insertion of **22** by **9**, the reaction also occurs with high asymmetric induction [20]. The Rh_2(*S*-DOSP)$_4$ catalyzed reaction results in the formation of a 70:30 mixture of the two diastereomers **23** and **24** in 90% yield, where the major diastereomer **23** is formed in 95% ee and the minor diastereomer **24** is formed in 85% ee.



(9)

Further examples of the potential of this chemistry are seen in the reactions of the methyl bromophenyldiazoacetate (**25**) with the silyl enol ethers **26** and **28** as substrates [20]. The reaction with **26** results in improved diasterocontrol compared to the reaction with **18** and the major diastereomer **27** is formed in 89% ee (Eq. (10)). This example demonstrates the selectivity that is possible in this chemistry because **26** contains three allylic sites, yet reaction occurs at only a single site. The reaction with the benzo-fused system **28** (Eq. (11)) is an intriguing example because the corresponding Michael reaction to form **29** is not feasible because the requisite enone would be the keto tautomer of 1-naphthol. In this case, the major diasteromer **29** of the C–H insertion product is formed in 90% ee.



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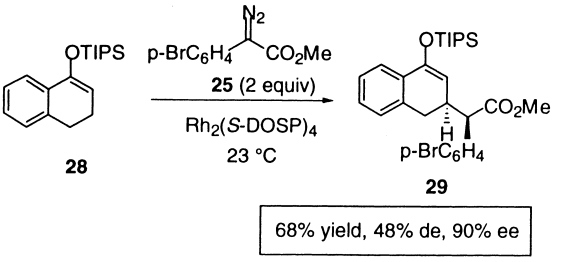
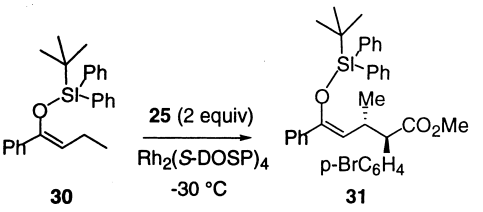


(11)

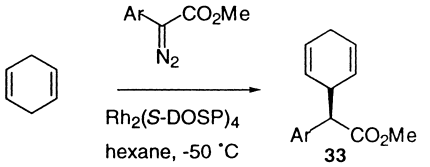
In order to have highly diasteroselective reactions, the substituents at the methylene site need to be considerably different in size [20]. The acyclic system **30** meets this requirement, and the C–H insertion with this substrate generates essentially a single diastereomer of **31** in 84% ee (Eq. (12)) [20].



(12)

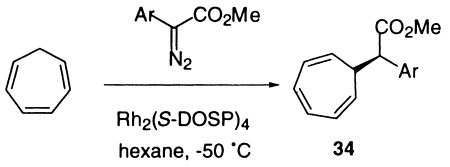
Allylic C–H activation of simple alkenes would generate γ,δ-unsaturated carbonyl compounds **32**. The classic method for preparing such compounds is the Claisen rearrangement of allyl vinyl ethers, and this reaction is especially effective at controlling the relative stereochemistry of the two new stereogenic centers (for a review, see [21]). A systematic study was undertaken to determine if the allylic C–H activation could be a stereoselective surrogate of the Claisen rearrangement (Scheme 2).

Allylic C–H activation of 1,4-cyclohexadiene [22] and 1,3,5-cycloheptatriene [23] is a very effective reaction. The C–H insertion products **33** and **34** are produced in high yield and enantioselectivity. However, these examples generate only a single stereocenter and do not address the issue of whether the carbenoid-induced C–H activation would be effective as a surrogate of a diastereoselective Claisen rearrangement.



Ar	Yield, %	ee, %
p-chlorophenyl-	84	95
p-methylphenyl-	84	94
p-methoxyphenyl-	69	93
2-naphthyl-	64	92

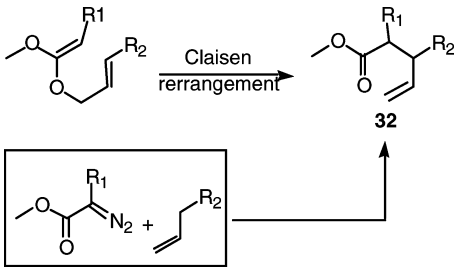
(13)



Ar	Yield, %	ee, %
phenyl	55	95
p-chlorophenyl-	64	95
p-methylphenyl-	60	94
2-napthyl-	53	91

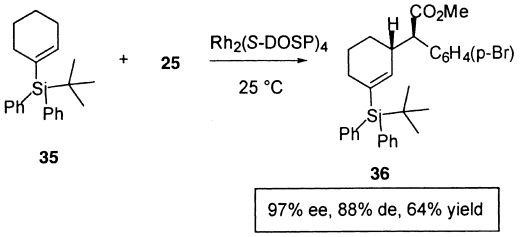
(14)

The first report on allylic C–H activation of a simple alkene gave a mixture of products [24]. The $Rh_2(S\text{-DOSP})_4$ catalyzed reaction of **9** with cyclohexene gave a 1:1 diastereomeric mixture of C–H activation products as well as competing cyclopropanation.



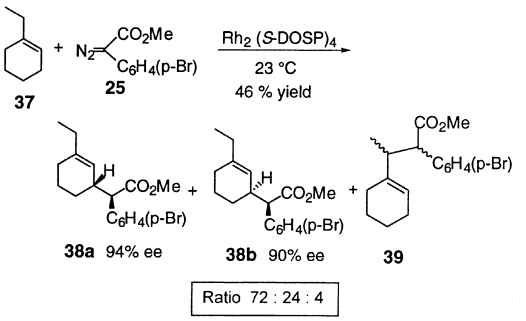
Scheme 2.

In order to eliminate the cyclopropane formation, the alkene needs to be more sterically crowded, while good size differentiation between the two methylene substituents is required to control the diastereoselectivity. This was achieved by using the silyl substituted cyclohexene **35**, whose $Rh_2(S\text{-DOSP})_4$ catalyzed reaction with **9** generated the C–H insertion product **36** in 88% de and 97% ee [25].



(15)

This reaction has been applied to a range of cyclic and acyclic alkenes [23] and the reaction displays remarkable regiocontrol. For example, a very challenging substrate is 1-ethylcyclohexene (**37**), which contains three allylic methylene sites (Eq. (16)). The majority of the product is derived from C–H insertion at the less crowded endocyclic methylene position (**38a** and **38b**), while only a trace of C–H insertion at the exocyclic methylene site (**39**) is observed. A 3:1 mixture of diastereomers **38a** and **38b** are formed in 94 and 90% ee, respectively.



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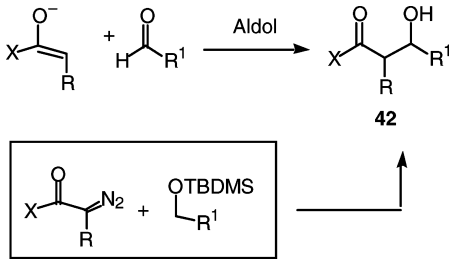
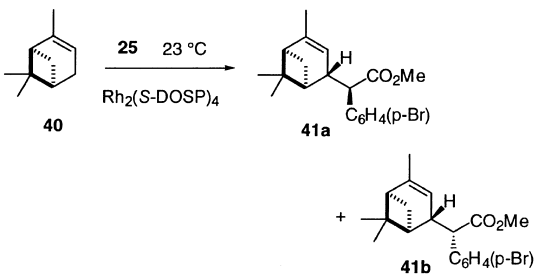


Scheme 3.

With appropriate substrates, the allylic C–H activation displays considerable kinetic resolution and enantiomer differentiation. An example of this is shown in the reaction with (α)-pinene (Eq. (17)). The reaction of (+)-(α)-pinene (**40**) with **25** (two equivalents) catalyzed by Rh_2(*S*-DOSP)$_4$ is the matched reaction because this results in a very efficient transformation in which **41a** is formed in 93% yield and 96% de. The reaction catalyzed with Rh_2(*R*-DOSP)$_4$ is less effective and **41a** and **41b** are formed in 62% combined yield and the major diastereomer is **41b**. When the Rh_2(*S*-DOSP)$_4$ catalyzed reaction is carried out with (±)-(α)-pinene (10 equivalent), a mixture of **41a** and **41b** is formed in 52% yield and the major diastereomer **41a** is formed in 99% ee. The high enantioselectivity is due to a combination of kinetic resolution and enantiomer differentiation.



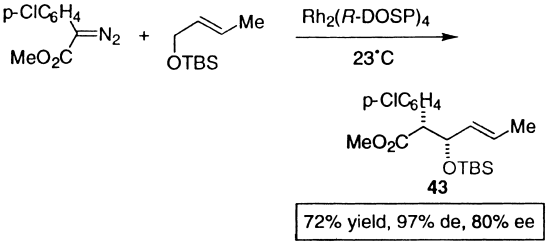
Substrate	Catalyst	yield, %	ratio, **41a** : **41b**	ee, **41a**, %
(+) (0.5 equiv)[a]	Rh_2(*S*-DOSP)$_4$	93	98 : 2	–
(+) (0.5 equiv)[a]	Rh_2(*R*-DOSP)$_4$	62	24 : 76	–
(±) (10 equiv)[b]	Rh_2(*S*-DOSP)$_4$	52	88 : 12	99

a: reaction temperature, 23 °C
b: reaction temperature, 0 °C

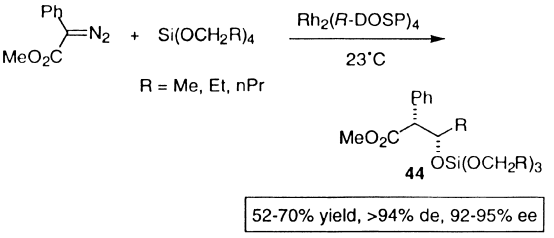
(17)

Carbenoid C–H insertion α to oxygen would generate protected β-hydroxy esters **42** (Scheme 3). The classic C–C bond-forming method for the synthesis of β-hydroxy esters is the aldol reaction. The relative stereochemistry can be predictably controlled by using enolates of defined geometry. Wonderful chiral auxilaries [26] and more recently, chiral catalysts (for a general review of catalytic enantioselective aldol reactions [27]) have been developed for asymmetric aldol reactions. Still, many of the catalytic asymmetric aldol reactions have limited substrate specificity and do not generally occur with very low catalyst loading. Thus, it was intriguing to explore if the C–H insertion a to oxygen could offer advantages over the classic aldol reaction.

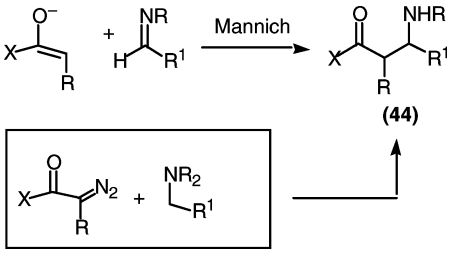
Even though the diastereoselectivities of the C–H insertions are substrate dependent, certain silyl ethers results in very efficient C–H insertions with very high diastereoselectivity [28a,28b]. *Trans* allyl silyl ethers are exceptional substrates, which lead to C–H insertion products in 96–98% de and 70–85% ee [28a]. An illustrative example is shown in Eq. (18) [28a]. Tetraalkoxysilanes are even better substrates because in this case the C–H insertion products **43** are formed in >94% de and 92–95% ee (Eq. (19)) [28b]. These reactions are highly diastereoselective because there is good size differentiation between the two substituents on the methylene group.



(18)



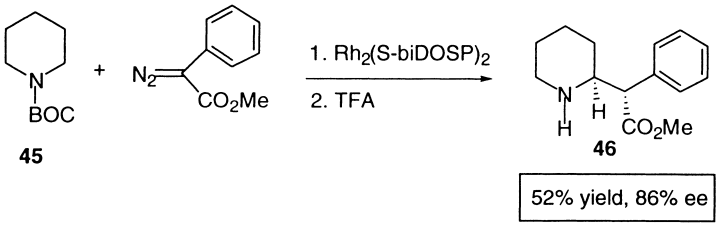
(19)



Scheme 4.

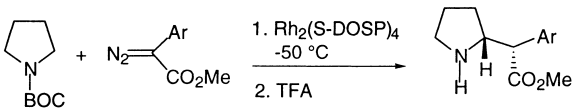
A fourth example of the synthetic potential of C–H insertion is as a surrogate for the Mannich reaction (Scheme 4) [29]. This could be achieved by a selective C–H insertion α to nitrogen leading to the formation of β-amino acid derivatives (**44**). Considerable advances have been made in developing catalytic asymmetric Mannich reactions, but achieving this and also controlling the relative stereochemistry has met with only limited success to date [29].

The reaction of methyl phenyldiazoacetate with *N*-BOC-piperidine (**45**) is a good illustration of the potential of this chemistry because it leads to the direct synthesis of *threo*-methylphenidate (**46**) [30]. The most efficient rhodium carboxylate catalyst for carrying out this tranformation is Rh_2(*S*-biDOSP)$_2$, which results in the formation of a 71:29 mixture of the readily separable *threo* and *erythro* diastereomers. The *threo* diastereomer is produced in 52% isolated yield and 86% ee (Eq. (20)). This approach is considerably shorter than other reported asymmetric syntheses of *threo*-methylphenidate using traditional reaction sequences [31].



(20)

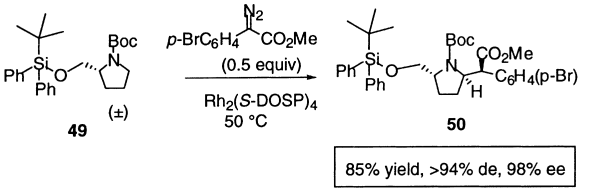
In contrast to the reaction with *N*-BOC-piperidine, the reaction with *N*-BOC-pyrrolidine (**47**) is highly stereoselective [30]. Rh_2(*S*-DOSP)$_4$ catalyzed reaction of various aryl diazoacetates with *N*-BOC-pyrrolidine at −50 °C generates the C–H insertion products **48** in greater than 90% ee and 90% de (Eq. (21)).



Ar	Yield, %	de, %	ee, %
Ph	72	92	94
4-ClPh	72	94	94
4-MePh	67	94	93
2-naphthyl	49	92	93

(21)

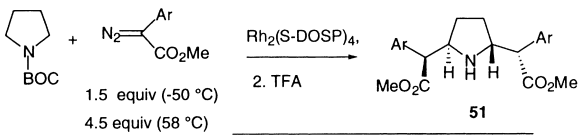
The 2-substituted pyrrolidines are very interesting substrates for C–H activation because they can display very impressive levels of kinetic resolution and enantiomer differentiation [32]. An example, which convincingly demonstrates the potential of such chemistry, is the reaction of the (±)-silylated alcohol **49**, which results in a single diastereomer of the C–H insertion product **50** in 85% yield and 98% ee. The stereoselectivity of this substrate is so well controlled that one enantiomer of **49** results in a very clean C–H insertion while the second enantiomer of **49** is essentially unreactive.



(22)

The reaction with *N*-BOC-pyrrolidine may be taken a step further by inducing a double C–H insertion sequence. This results in the formation of elaborate C-2 symmetric bases as single diastereomers with control of stereochemistry at four stereogenic centers. The enantioselectivities of the products are higher than what is obtained for the single C–H

insertion products, presumably because kinetic resolution is occurring in the second C–H insertion step.



Ar	yield, %	ee, %
Ph	78	97
p-Cl-Ph	50	96
p-Me-Ph	51	96
2-Naphthyl	40	88
p-MeO-Ph	62	97

(23)

In summary, C–H activation by means of a rhodium carbenoid-induced C–H insertion offers numerous opportunities in organic synthesis. The reactions are very practical transformations that can be carried out using conventional glassware and equipment. The chemistry is highly chemoselective, which is critical for a broadly useful C–H activation protocol. There is a delicate balance between C–H activation at secondary versus tertiary C–H sites which is goverened by electronic and steric factors. Allylic positions and sites α to oxygen and nitrogen are strongly favored for C–H activation. The most striking feature of the C–H activation is that it is tolerant to many functional groups, including *cis* and *trans* alkenes, aromatic rings, ethers, acetates, and *N*-BOC functionality. The chemistry is routinely highly enantioselective, with most reactions occurring in >90% ee. Furthermore, if appropriate substrates are used, highly diastereoselective reactions are also feasible. The success of this chemistry rests on the use of carbenoid systems that contain both donor and acceptor substituents. The future challenge for this chemistry will be to broaden the range of carbenoid systems that display this critical requirement.

Acknowledgements

Several post-doctoral associates, graduate students and undergraduate students have made major contributions to the chemistry described in this review. Without their dedication and ingenuity, this chemistry would not have reached its current level of broad synthetic utility. These studies were generously supported by the National Science Foundation (CHE 0092490), the National Institutes of Health (DA-06303 and DA-05886) and by A. Johnson & Johnson Focused Giving Grant.

References

[1] (a) A.E. Shilov, G.B. Shul'pin, Chem. Rev. 97 (1997) 2879;
(b) B.A. Arndtsen, R.G. Bergman, T.A. Mobley, T.H. Peterson, Acc. Chem. Res. 28 (1995) 154;
(c) C. Jia, T. Kitamura, Y. Fujiwara, Acc. Chem. Res. 34 (2001) 633.
[2] H.M.L. Davies, E.G.J. Antoulinakis, Organomet. Chem. 45 (2001) 617–618.
[3] (a) H.M.L. Davies, T.J. Hansen, Am. Chem. Soc. 119 (1997) 9075;
(b) H.M.L. Davies, T. Hansen, M.R. Churchill, J. Am. Chem. Soc. 122 (2000) 3063.
[4] (a) K.M. Waltz, J.F. Hartwig, Science 277 (1997) 211;
(b) H. Chen, S. Schlecht, T.C. Semple, J.F. Hartwig, Science 287 (2000) 1995;
(c) K.M. Waltz, J.F. Hartwig, J. Am. Chem. Soc. 122 (2000) 11358.
[5] Y. Guari, S. Sabo-Etienne, B. Chaudret, Eur. J. Inorg. Chem. (1999) 1047.
[6] M.P. Doyle, M.A. McKervey, T. Ye, In Modern Catalytic Methods for Organic Synthesis with Diazo Compounds, Wiley/Interscience, New York, 1998, pp. 112–162.
[7] G. Mass, In Topics in Current Chemistry, Vol. 137, Springer, New York, 1987, pp. 75–254.
[8] (a) R. Paulissen, H. Reimlinger, E. Hayez, A.J. Hubert, P. Teyssie, Tetrahedr. Lett. 14 (1973) 2233;
(b) A. Demonceau, A.F. Noels, A.J. Hubert, P.J. Teyssie, Chem. Soc., Chem. Commun. (1981) 688.;
(c) A. Demonceau, A.F. Noels, A.J. Hubert, P. Teyssie, Bull. Soc. Chim. Belg. 93 (1984) 945;
(d) A. Demonceau, A.F. Noels, A.J. Hubert, P.J. Teyssie, Mol. Catal. 49 (1988) L13.
[9] (a) T. Ye, M.A. McKervey, Chem. Rev. 94 (1994) 1091;
(b) D.M. Spero, J. Adams, Tetrahedr. Lett. 33 (1992) 1143.
[10] (a) M.P. Doyle, D. van Leusen, W.H. Tamblyn, Synthesis (1981) 787;
(b) D.S. Wulfman, B.W. Pearce, R.S. McDaniel Jr., Tetrahedron 32 (1976) 1251.
[11] (a) L.T. Scott, G.J.J. DeCicco, Am. Chem. Soc. 96 (1974) 322;
(b) R.A. Ambramovitch, J.J. Roy, Chem. Soc., Chem. Commun. (1965) 542;
(c) J. Adams, M.-A. Poupart, L. Greainer, C. Schaller, N. Quimet, R. Frenette, Tetrahedr. Lett. 30 (1989) 1749;
(d) H.J. Callott, F. Metz, Tetrahedr. Lett. 23 (1982) 4321;
(e) H.J. Callott, F. Metz, Nouv. J. Chimie 9 (1985) 167;
(f) A. Domenceau, A.F. Noels, J.L. Costa, A. Hubert, J. Mol. Catal. 58 (1990) 21.
[12] H.M.L. Davies, Curr. Org. Chem. 2 (1998) 464.

[13] H.M.L. Davies, S.A. Panaro, Tetrahedron 56 (2000) 4871.
[14] H.M.L. Davies, Eur. J. Org. Chem. (1999) 2459;
H.M.L. Davies, Aldrichim. Acta 30 (1999) 105.
[15] H.M.L. Davies, S.A. Panaro, Tetrahedr. Lett. 40 (1999) 5287.
[16] H.M.L. Davies, L.M. Hoeges, J.J. Matasi, T. Hansen, D.S. Stafford, Tegrahedr. Lett 39 (1998) 4417.
[17] M. Yamaguchi, E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), in: Comprehensive Asymmetric Catalysis, Vol. III, Springer, Berlin, 1999, pp. 1121–1139.
[18] H.U. Reissig, Top. Curr. Chem. 144 (1988) 73.
[19] H.M.L. Davies, P. Bruzinski, D.K. Hutcheson, N. Kong, M.J. Fall, J. Am. Chem. Soc. 118 (1996) 6897.
[20] H.M.L. Davies, P.J. Ren, Am. Chem. Soc. 123 (2001) 2071.
[21] P. Wipf, in: B.M. Trost (Ed.), Comprehensive Organic Synthesis, Vol. 5, Pergamon Press, Oxford, 1991, pp. 827–874.
[22] H.M.L. Davies, D.G. Stafford, T. Hansen, Org. Lett. 1 (1999) 233.
[23] H.M.L. Davies, D.G. Stafford, T. Hansen, Tetrahedr. Lett. 41 (2000) 2035.
[24] P. Muller, S. Tohill, Tetrahedron 56 (2000) 1725.
[25] H.M.L. Davies, Q. Jin, P. Ren, Chem. Lett. (2001).
[26] (a) C.H. Heathcock, in: J.D. Morrison (Ed.), Asymmetric Synthesis, Vol. 3, Academic Press, San Diego, CA, 1984 (Chapter 2);
(b) D.A. Evans, Aldrichim. Acta 15 (1982) 23.
[27] S.G. Nelson, Tetrahedr. Asymm. 9 (1998) 357.
[28] H.M.L. Davies, E.G. Antoulinakis, T. Hansen, Org. Lett. 1 (1999) 383;
(b) H.M.L. Davies, E.G. Antoulinakis, Org. Lett. 2 (2000) 4153.
[29] S.E. Denmark, O.J.-C. Nicaise, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprhensive Asymmetric Catalysis, Springer, Berlin, 1999, pp. 954–958.
[30] H.M.L. Davies, T. Hansen, D. Hopper, S.A. Panaro, J. Am. Chem. Soc. 121 (1999) 6509.
[31] (a) D.L. Thai, M.T. Sapko, C.T. Reiter, D.E. Bierer, J.M. Perel, J. Med. Chem. 41 (1998) 591;
(b) Y. Matsumura, Y. Kanda, K. Shirai, O. Onomura, T. Maki, Org. Lett 1 (1999) 175.
[32] H.M.L. Davies, C. Venkataramani, Org. Lett. 3 (2001) 1773.