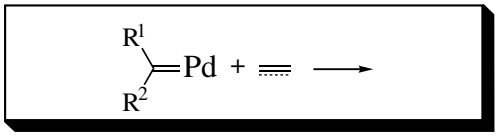


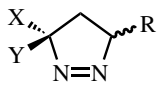
IV.9 Cyclopropanation and Other Reactions of Palladium-Carbene (and Carbyne) Complexes

OLIVER REISER

A. INTRODUCTION

The cyclopropanation of alkenes *via* carbene transfer from diazo compounds can be achieved by a variety of transition metals. The most popular catalysts for this transformation are based on copper(I) and rhodium(II) complexes, however, palladium(II) has been shown, as demonstrated first by Kirmse and Kapps,[1],[2] to be effective and even superior for certain substrates and reagents.[3],[4]

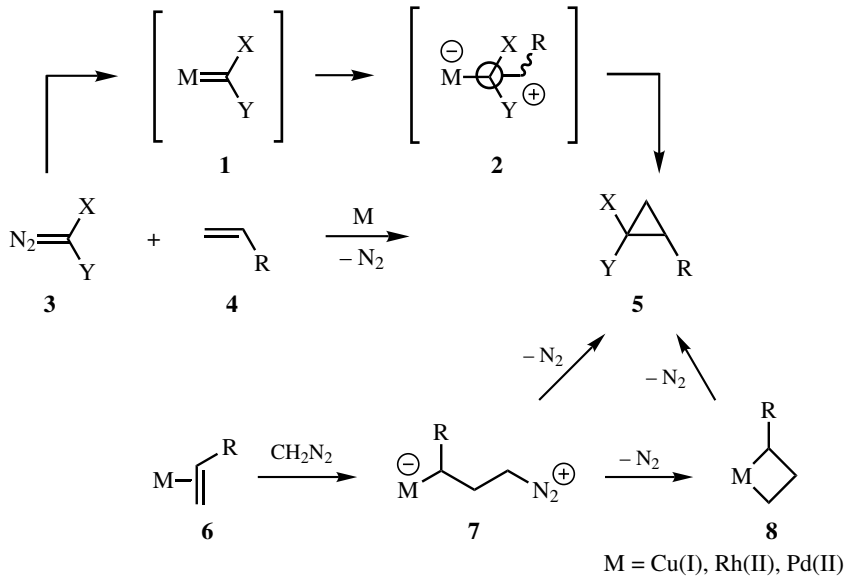
The general mechanistic picture for these carbene transfer reactions starts with the initial decomposition of the diazo compound **3** upon the influence of the metal (**Scheme 1**). Although not conclusively proven, there is strong evidence that metal carbene complexes **1** are formed, most prominently with copper and rhodium. These intermediates are attacked at the electrophilic carbene center by the alkene **4** to form **2**, which subsequently collapses to the cyclopropane **5**. However, there are distinctive differences in the range of reagents and substrates being employed in copper and rhodium catalyzed carbene transfer reactions compared to palladium. Due to the strong coordinating power of palladium(II) towards alkenes, electrophilic addition of the metal olefin complex **6** onto diazomethane to **7** followed by extrusion of nitrogen *via* metalocyclobutanes **8** or direct cyclopropane formation might be a plausible alternative.[5] Moreover, it was suggested that the reaction might take place by a 1,3-dipolar cycloaddition with palladium(II) acting as a Lewis acid followed by nitrogen extrusion from the pyrazoline **9**. Indeed, 1,3-dipolar cycloaddition readily takes place with alkenes bearing strong electron withdrawing substituents (CN, CO_2Et),[6] however, the overall mechanistic proposal for cyclopropane formation *via* this pathway has been distinctively ruled out at least for some cases.[7]



9

Formula 1

Handbook of Organopalladium Chemistry for Organic Synthesis, Edited by Ei-ichi Negishi
ISBN 0-471-31506-0



Scheme 1

The success of palladium catalyzed cyclopropanation reactions is strongly dependent on the substitution pattern of the employed alkene. Electron poor alkenes, most notably α,β-unsaturated carbonyl compounds and oxygen and nitrogen containing allylic derivatives display good reactivity while electron rich alkenes such as vinyl ethers usually give only low conversion. Terminal and strained alkenes are also good substrates, while the reactivity systematically drops with an increase of its substitution degree.

B. CYCLOPROPANATION OF α,β-UNSATURATED CARBONYL COMPOUNDS WITH DIAZOMETHANE

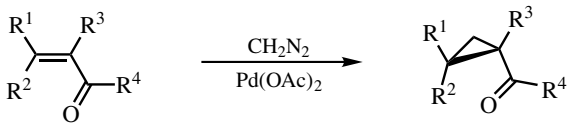
Palladium(II) salts are the catalysts of choice for cyclopropanations with diazomethane, giving especially good results with α,β-unsaturated aldehydes, ketones, esters or amides. α,α- and α,β-disubstitution is well tolerated, but trisubstituted alkenes do not react (**Table 1**).[5],[7]–[8]

In accordance with this substitution rule, **10**, **12**, **14** and **16** were cyclopropanated well with diazomethane/$Pd(OAc)_2$, while various trisubstituted steroidal ketones are not suitable substrates (**Scheme 2**).[7]

Cyclopropyl analogs of prostaglandins have been synthesized starting from α,β-unsaturated ketone **18a** and the corresponding allylic alcohol **18b (Scheme 3)**. While **19a** was obtained in excellent yield (92%, 2:1 mixture of diastereomers), **19b** was formed as a mixture of epimers in only 20% yield along with the methyl ether of **18a** (20%).[9]

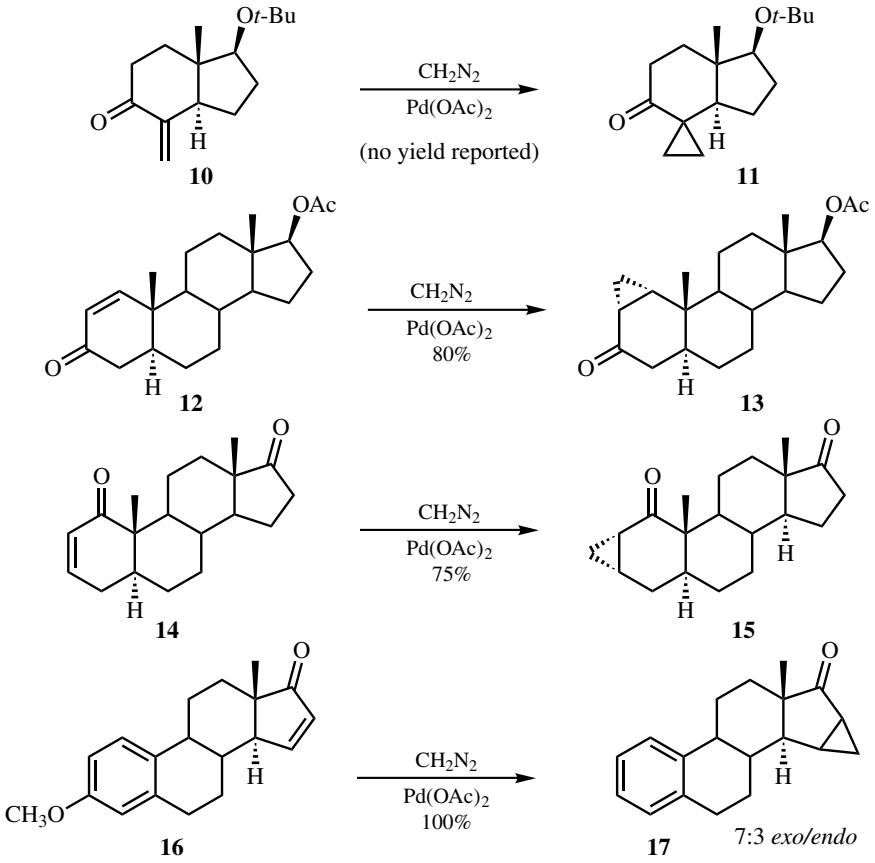
The synthesis of enantiomerically enriched cyclopropanes has been carried out successfully by attaching chiral auxiliaries to α,β-unsaturated carbonyl compounds. Using Oppolzer's sultam, a broad range of substituted amides **20** react with diazomethane to **21** in generally good yields and diastereoselectivities (**Table 2**). Moreover, the products can be easily raised to enantiopurity by recrystallization.[10],[11]

TABLE 1. Cyclopropanation of α,β-unsaturated carbonyl compounds with diazomethane

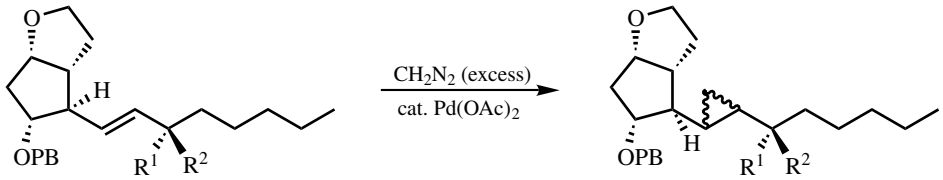


R^1	R^2	R^3	R^4	Yield (%)	Reference
$MeO_2C(CH_2)_3$	H	H	H	80	[5]
Ph	H	H	CH_3	85	[7]
Ph	H	H	Ph	98	[7]
H	H	H	OEt	82	[8]
H	Ph	H	OEt	85	[7]
CH_3	H	H	OEt	89	[7]
H	H	CH_3	OEt	88	[7]
Ph	H	H	OEt	90	[7]
CH_3	CH_3	H	CH_3	n.r.[a]	[7]
CH_3	CH_3	H	OEt	n.r.[a]	[7]

[a] no reaction.



Scheme 2



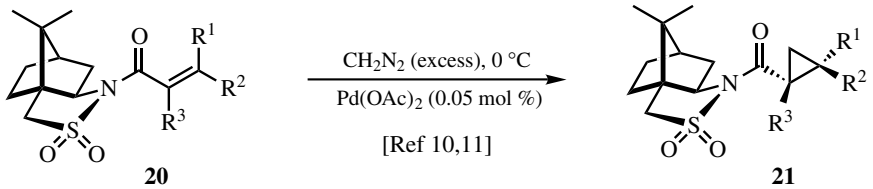
18a: R^1, R^2 = O
18b: R^1 = OH, R^2 = H

19a: R^1, R^2 = O
19b: R^1 = OH, R^2 = H

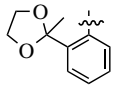
PB = *p*-phenylbenzoyl

Scheme 3

TABLE 2. Cyclopropanation of α,β-unsaturated amides modified by the sultam auxiliary with diazomethane

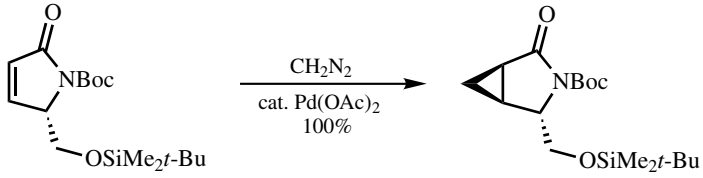


20 **21**

R^1	R^2	R^3	de (%)[a]	de (%)[b]	Yield(%)
H	Ph	H	86	99	73
H	2-MeO-Ph	H	92	99	73
H	3-MeO-Ph	H	72	98	63
H	3,4,5-$(MeO)_3$-Ph	H	67	98	62
H	4-(CN)-Ph	H	60	96	29
H	2-MeO-5-F-Ph	H	73	>99	45
H		H	63	99	11
H	2-Thienyl	H	88	99	71
H	4-Br-2-thienyl	H	68	88	59
H	2-Furyl	H	76	>99	67
H	Ferrocenyl	H	82	>96	76
H	Me	H	91	>99	72
H	Decyl	H	83	>99	62
H	Prop-l-enyl	H			—
Me	Me	H			—
H	Me	Me			—
H	Cl	H			—
Cl	H	H			—
CF_3	Me	H			—
H	CO_2Et	H			—
H	H	H			—

[a] crude mixture.
[b] after recrystallization.

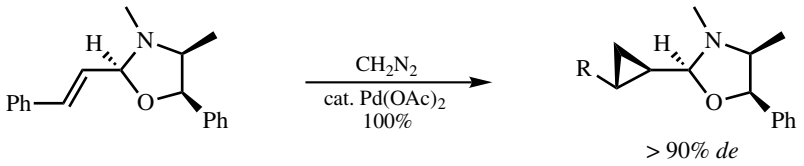
Again, only monosubstituted amides can be employed as substrates, while one additional substituent—no matter if electron donating or withdrawing—causes failure of the cyclopropanation. Consequently, the cyclic amide **22** combining the advantages of olefinic strain and α,β-unsaturated carbonyl compound could be cyclopropanated in excellent yield and good diastereoselectivity (9:1) (**Scheme 4**).[12],[13]



22 **23**

Scheme 4

The alkene **24** can be cyclopropanated with diazomethane in high yield, offering an attractive way to functionalize α,β-unsaturated aldehydes diastereoselectively by first forming the N,O-acetales with chiral amino alcohols (**Scheme 5**).[14]



> 90% *de*

24 **25**

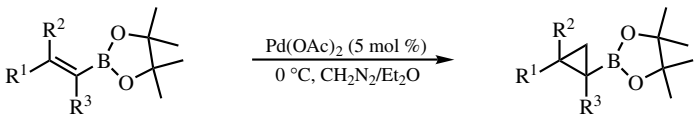
Scheme 5

Attempts to carry out carbene transfer reactions with chiral palladium catalysts were unsuccessful so far. Denmark et al. conducted a detailed study[15] in which cyclopropanations of α,β-unsaturated carbonyl compounds with diazomethane catalyzed by bis-(oxazoline)palladium(II) complexes were investigated. Virtual no asymmetric induction was obtained in these reactions which led to the conclusion—especially in light of the excellent asymmetric environment bis(oxazolines) metal complexes offer in general—that partial or complete ligand dissociation must have been occurred during the course of the reaction.

C. CYCLOPROPANATION OF ALKENYLBORONIC ESTERS

Alkenylboronic esters proved to be good substrates for the palladium catalyzed cyclopropanation by diazomethane (**Table 3**).[16],[17] Since the substrates can be obtained by hydroboration of alkynes and the resulting cyclopropylboronic ester can be further modified, this strategy offers an especially versatile entry to functionalized cyclopropanes. Besides oxidation to cyclopropanols, functionalization in Suzuki coupling reactions are possible as discussed in **Sect. III.2.2**.

TABLE 3. Cyclopropanation of vinyl boranes with dizomethane

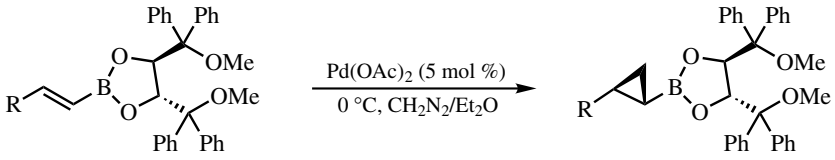


R^1	R^2	R^3	Yield (%)
H	H	H	92
n-Bu	H	H	88
H	*n*-Bu	H	67
$Cl(CH_2)_3$	H	H	90
H	H	CH_3	72
CH_3OCO	H	H	63
$PhSCH_2$	H	H	62
Me_3Si	H	H	83
CH_3	CH_3	H	0[a]
CH_3	H	CH_3	0[b]
PhS	H	H	0[c]

[a]Starting material was recovered unchanged.
[b]40/60 mixture of starting material and product.
[c]only unidentified products were obtained which obtained neither the starting material nor the product.

Moreover, alkenylboronic esters can be modified by chiral auxiliaries,[18]–[20] and especially the TADDOL auxiliary has been demonstrated to be an effective chiral inductor for the cyclopropanation reactions discussed here (**Table 4**).[19],[20] In order to keep the catalyst concentration low its pretreatment by ultrasonication to guarantee a fine distribution was found to be advantageous.

TABLE 4. Cyclopropanation of vinyl boranes modified with the TADDOL auxiliary with diazomethane

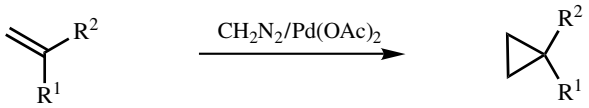


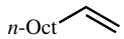
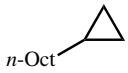
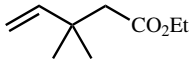
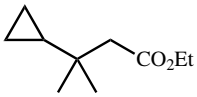
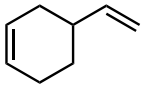
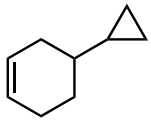
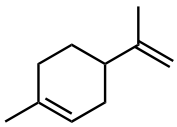
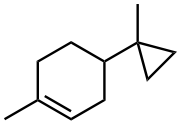
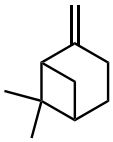
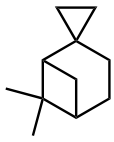
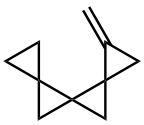
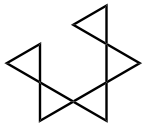
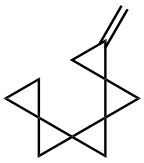
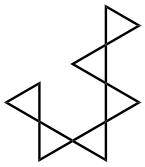
R	de (%)	Yield (%)
n-Bu	78	98
t-Bu	74	95
n-Pentyl	86	99
$TPSO(CH_2)_3$	90	89
Ph	72	93
$TBSOCH_2$	40	90
$HOCH_2$	60	98

D. CYCLOPROPANATION OF NON FUNCTIONALIZED ALKENES

Non functionalized alkenes undergo cyclopropanation with diazomethane/Pd(II) if they are strained[21]–[23] or terminal substituted.[24] Consequently, carbene transfer to alkenyl substituted cyclohexenes occurs highly regioselective,[24] contrasting the reactivity of such derivatives towards cyclopropanation using diiodomethane/zinc or metal carbenoids (**Table 5**).

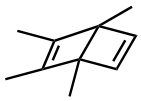
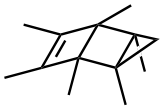
TABLE 5. Cyclopropanation of unfunctionalized alkenes with diazomethane



Alkene	Product	Yield (%)	Reference
		89	[24]
		90	[22]
		77	[24]
		82	[24]
		63	[24]
		91[a]	[23]
		93[a]	[23]
		67	[21]

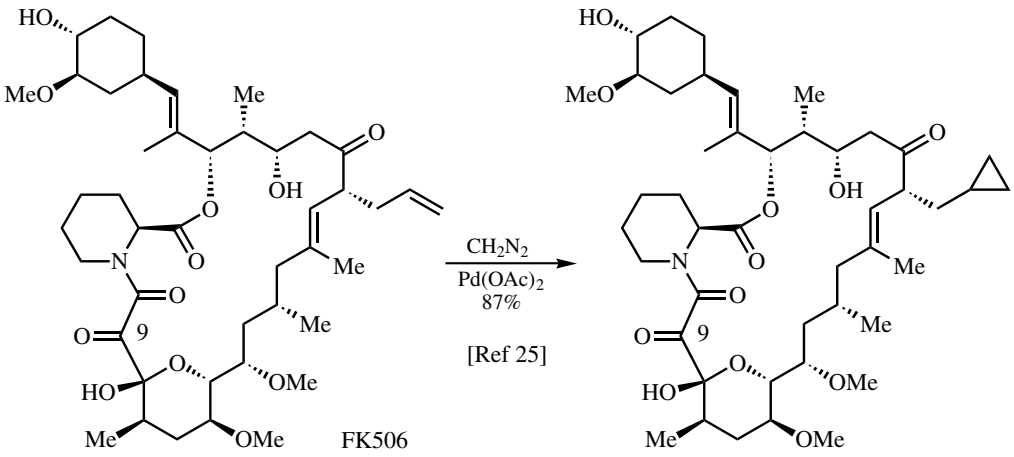
(*Continued*)

TABLE 5. (*Continued*)

Alkene	Product	Yield (%)	Reference
		63	[21]
		89	[21]

[a] mixture of diastereomers.

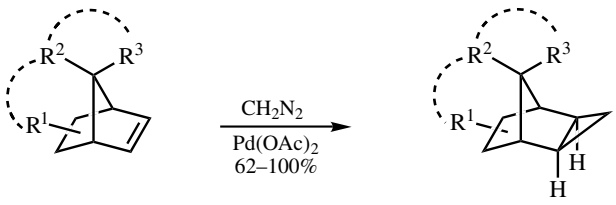
Accordingly, the regioselective cyclopropanation of FK506 can be understood despite of the two other C—C double bonds present and, most notably, the carbonyl function at C-9 which reacts with diazomethane in the absence of palladium(II) acetate to the corresponding oxirane (**Scheme 6**).[25]



Scheme 6

A very large number of norbornene derivatives has been cyclopropanated in good yields giving the *exo* distereomer in all cases (**Scheme 7**).[5],[6],[21],[23],[26]–[29]

Besides strained cyclopentenes, cyclobutenes such as dewar benezene derivatives (see **Table 5**) also undergo cyclopropanation with respectable yields. In contrast, cyclopropenes react with diazomethane in a complex manner to form mixtures of monomeric



Scheme 7

products as a result of ring opening and insertion accompanied by considerable amounts of oligomeric products.[5]

Interesting results are obtained for the cyclopropanation of conjugated dienes and polyenes (**Table 6**). Not surprisingly, aryl substituted alkenes react selectively at the olefinic double bond, but also in non aromatic polyenes differentiation of the double

TABLE 6. Cyclopropanation of polyenes with diazomethane

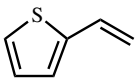
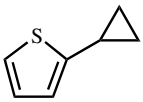
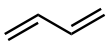
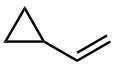
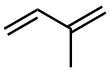
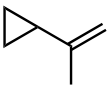
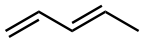
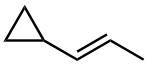
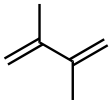
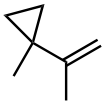
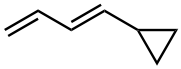
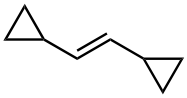
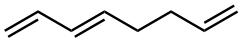
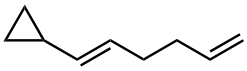
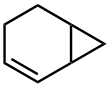
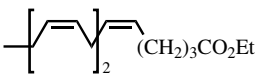
Alkene	Product	Yield (%)	Comment	Reference
		90		[30]
		98		[5]
		67	along with 29% of biscyclopropyl product	[26]
		70	along with 12% of regioisomer and 9% of biscyclopropyl product	[26]
		90		[6]
		65	along with 15% of biscyclopropyl product	[26]
		91		[6]
		49	along with 6% of terminal regioisomer and 8% of α,ω-biscyclopropyl product	[6]
		75	along with 15% of monocyclopropyl product	[26]
		53	along with 13% of biscyclopropyl product	[26]
		90		[5]

TABLE 7. Cyclopropanation of allenes with diazomethane

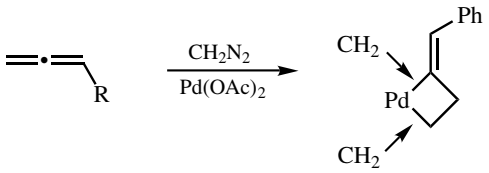
26 **27** **28**

R	Yield of **27** (%)	Yield of **28** (%)
Bu	67	25
CH_2CH_2OH	2	60
CH_2CH_2OAc	34	56
CH_2CH_2OTs	78	—
CH_2CH_2Br	63	27
Ph	49	—

bonds has been successful. For a number of 1,3-butadienes it was demonstrated that monocyclopropanation preferentially takes place at the sterically less hindered double bond. A terminal conjugated double bond is more reactive than a non conjugated one. Although in many cases regioisomers or biscyclopropanated products are obtained, some impressive cases of regioselective cyclopropanations of dienes or even trienes have been reported (**Table 6**). However, 1,3,5-cyclohexatriene and 1,3,5,7-cycloocattetraene failed to give cyclopropanation at all.[5]

Allenes are also successfully cyclopropanated if a large excess of diazomethane is employed, which preferentially takes place at the less substituted double bond. Nevertheless, the bisadducts are formed in many cases as well (**Table 7**).[31]

However, in these reactions complex mixtures of unusual side products resulting from an oligomethylenation have been also isolated. The products can be explained by invoking intermediates like **29**, which undergo methylene insertion into the metal carbon bond (**Scheme 8**).[32]



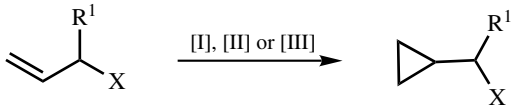
26 **29**

Scheme 8

E. CYCLOPROPANATION OF ALLYLOXY AND RELATED COMPOUNDS

Allyloxy[33],[34] and allylamino[12],[33]–[35] are also good substrates for the title reaction. While mostly terminal alkenes have been used, internal alkenes are activated sufficiently in such cases to undergo cyclopropanation (**Table 8**).

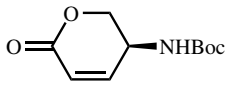
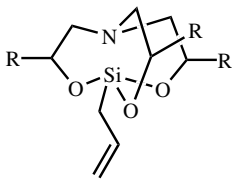
TABLE 8. Cyclopropanation of allylic substrates with diazomethane



[I] = CH_2N_2 (2 equiv), $PdCl_2(PhCN)_2$ (0.2–0.5 mol %), CH_2Cl_2/Et_2O (1:1), 0–10 °C, 30 min; then r.t.

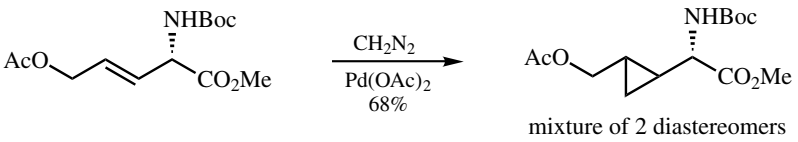
[II] = CH_2N_2 (excess), $Pd(OAc)_2$ (10 mol %), Et_2O, r.t.

[III] = CH_2N_2 (excess), $Pd(OAc)_2$ (1 mol %), Et_2O, –10 to –25 °C

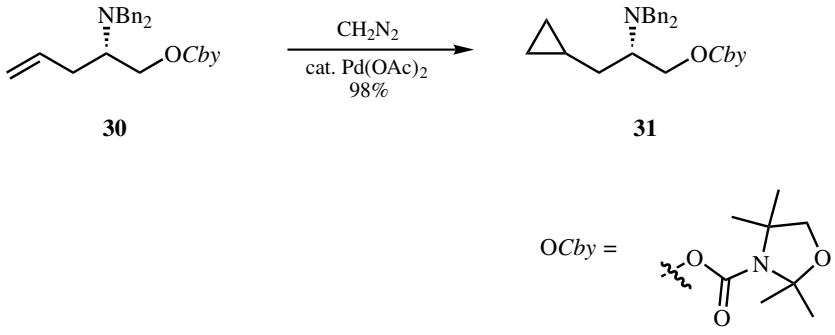
R^1	X	Yield (%)	Method	Reference
H	OH	72	I	[33]
CH_2CHCH_2	OH	31	I	[37]
H	OMe	74	I	[33]
H	OPh	88/97	I/III	[33]/[24]
H	O-(3-BrC_6H_4)	85	I	[33]
H	OAc	80	I	[33]
OEt	OEt	81	I	[33]
CH_2OMs	$OCH_2P(O)(Oi\text{-}Pr)_2$	96	I	[34]
H	NH_2	65	I	[33]
H	NMe_2	68	I	[33]
H	NHPh	62	I	[33]
CO_2Et	NHBoc	80	II	[35] [12]
		46	II	
H	$Si(OEt)_3$	15	III	[38]
	R = H R = Me	82 76	III III	[38]

Especially, vinylglycins (**Scheme 9**, see also **Table 8**) can be used as substrates, opening a synthetic route to conformationally restricted, non-proteinogenic amino acids, which display interesting biological properties.[35],[36]

Also, homoallyl amines are converted to the corresponding cyclopropanes by palladium(II)/diazomethane as was demonstrated with the synthesis of the β-cyclopropylalaninol derivative **31** (**Scheme 10**). [39]



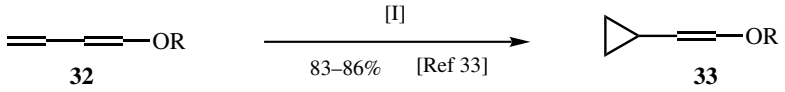
Scheme 9



Scheme 10

In contrast, vinylamines seem to be less useful substrates, i.e. cyclopropanation of β-arylvinylamines with diazomethane occurs only in low yields.[40]

1-oxy-1,3-butadienes **32** are cyclopropanated regioselectively and stereospecifically at the terminal alkene double bond, giving rise to vinylcyclopropanes **33** (**Scheme 11**).[33] Again, use of palladium(II) acetate as the catalyst proved to be superior in comparison with copper(I) chloride, which only resulted in product mixtures.



R = Me, Et, Ac, $SiMe_3$

[I] = CH_2N_2 (1.5 equiv)/$PdCl_2(PhCN)_2$(0.4 mol %)/CH_2Cl_2/Et_2O, 0–10 °C, 30 min; then r.t.

Scheme 11

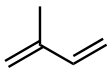
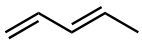
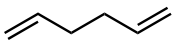
F. CYCLOPROPANATION WITH DIAZOACETATES

Diazoacetates are also known to decompose under the influence of palladium catalysts, however, only with α,β-unsaturated alkenes and strained cycloalkenes good yields of cyclopropanes are obtained (**Table 9**). This was investigated in detail by intermolecular competition experiments between olefins having different coordinating power.[41] With styrene and ethyl diazoacetate as model reaction it was also established that palladium(II) acetate is the most efficient catalyst for such reactions (catalyst (Yield): $Pd(OAc)_2$ (98%), $PdCl_2$ (70%), $PdCl_2 \cdot 2PhCN$ (65%), $Pd(PPh_3)_4$ (57%), Pd on C (0%)).[42]

Doyle et al. reported similar results using $PdCl_2 \cdot 2PhCN$ as a catalyst (**Table 10**) in a comparative study with rhodium(II) and copper(I) catalysts.[41]

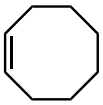
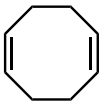
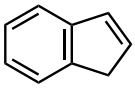
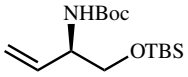
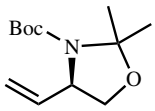
Last but not least, formation of the oxazole **35** has been observed in the reaction of methacrylonitirile (**34**) and diazoacetate catalyzed by palladium(II) acetate (**Scheme 12**).[45]

TABLE 9. Cyclopropanation of alkenes with diazoacetates

R^1	R^2	R^3	R^4	R	Yield (%)	Reference
Ph	H	H	H	Et	76[a]	[43]
Ph	H	H	H	Et	98[b]	[42]
Ph	Me	H	H	Et	42[b]	[42]
4-Me-Ph	H	H	H	Me	81[b]	[42]
4-MeO-Ph	H	H	H	Me	79[b]	[42]
4-Cl-Ph	H	H	H	Me	86[b]	[42]
2-No_2-Ph	H	H	H	Me	73[b,c]	[42]
4-No_2-Ph	H	H	H	Me	77[b,c]	[42]
4-NMe_2-Ph	H	H	H	Me	0[b]	[42]
Ph	Ph	H	H	Me	0[b]	[42]
Ph	H	Ph	H	Me	0[b]	[42]
4-pyridyl	H	H	H	Me	0[b]	[42]
1-imidazoyl	H	H	H	Me	0[b]	[42]
n-Bu	H	H	H	Me	30[b]	[42]
Me	H	H	Me	Me	24[b]	[42]
Me	H	Me	H	Me	21[b]	[42]
Et	H	H	Et	Et	15[b]	[42]
Me	H	H	*n*-Pent	Me	5[b]	[42]
Me	H	*n*-Pent	H	Me	2[b]	[42]
n-Pr	H	H	*n*-Pr	Me	12[b]	[42]
Me	Me	Me	Me	Et	5[b]	[42]
				Et	37, 11[b,d]	[42],[44]
				Et	35, 13[b,d]	[42],[44]
				Et	37[b]	[42],[44]
				Et	60[b]	[42]
				Me Et *n*-Bu	15[b] 21[b] 19[b]	[42]
				Et	18–21[b]	[42],[44]
				Et	40[b]	[42]

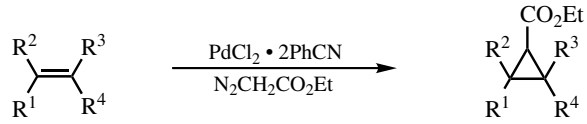
(*Continued*)

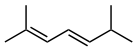
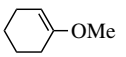
TABLE 9. (*Continued*)

R^1	R^2	R^3	R^4	R	Yield (%)	Reference
				Et	20[b]	[42]
				Et	10[b]	[42],[44]
				Et	87[b]	[42]
				Et	95[b]	[42]
				Et	20[b]	[42]
OAc	H	H	H	Et	5[b]	[42]
OEt	H	H	H	Et	42[b]	[42]
					20[b]	[42]
				Et	88[e]	[13]
				Et	14[e,f]	[13]
CO_2Me	H	H	H	Et	85[a]	[43]
CO_2Me	Me	H	H	Et	30[a]	[43]
CO_2Me	H	H	CO_2Me	Et	trace[b]	[43]
CO_2Me	H	H	H	Et	76[a]	[43]
CO_2Me	H	H	H	Et	64[a]	[43]

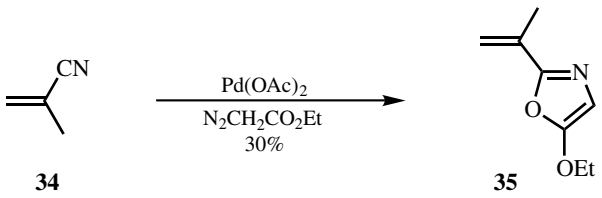
[a] 0.03 mol Alkene, 0.04 mol diazoacetate, 0.4 mmol $Pd(OAc)_2$, benzene, yield based on alkene employed.
[b] 0.03 mol Alkene, 0.002 mol diazoacetate, 0.01 mmol $Pd(OAc)_2$, yield based on diazoacetate employed.
[c] Product was obtained not pure.
[d] Yield for cyclopropanation of disubstituted double bond.
[e] 15 mmol Alkene, 150 mmol diazoacetate, 1.5 mmol $Pd(OAc)_2$, ether, yield based on alkene employed.
[f] 80% of the starting material was recovered.

TABLE 10. Cycopropanation of alkenes with ethyl diazoacetate



R^1	R^2	R^3	Yield (%)
Ph	H	H	52
OEt	H	H	43
O*n*-Bu	H	H	34
t-Bu	H	H	34
$C(Cl)=CH_2$	H	H	<8
$C(Ph)=CH_2$	H	H	5/10[a]
$C(Me)=CH_2$	H	H	16/24[a]
$C(t\text{-Bu})=CH_2$	H	H	4/6[a]
CH=CHOMe (trans)	H	H	16/22[a]
CH=CHCl (trans)	H	H	<8
Me	OMe	H	66
t-Bu	OMe	H	28
Me	$CH=CH_2$	H	8/24[a]
Cl	$CH=CH_2$	H	2/4[a]
OMe	$CH=CH_2$	H	12/12[a]
t-Bu	$CH=CH_2$	H	2/6[a]
			31
			41
			20
			39

[a] Mixture of diastereomers.



34 **35**

Scheme 12

G. CONCLUSION

Palladium(II) compounds are clearly the catalysts of choice for cyclopropanation of alkenes with diazomethane. A broad range of alkenes is amenable for this process, nevertheless, α,β-unsaturated carbonyl compounds and strained alkenes generally give the best results. While no enantioselective process by means of chiral palladium catalysts have

been developed so far, various auxiliary based strategies have been used to synthesize cyclopropane derivatives with good enantioselectivitiy. Although it also has been demonstrated that cyclopropanations with diazoacetates can be catalyzed by palladium(II), rhodium(II) and copper(I) catalysts seem to be superior in such cases.

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