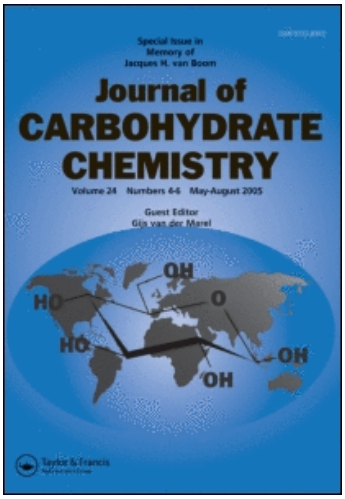

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Isabelle Frappa[a]; Denis Sinou[a]
[a] Laboratoire de Synthèse Asymétrique, associé au CNRS, C.P.E. Lyon, Université Claude Bernard Lyon I, Villeurbanne, France

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REVIEW

TRANSITION METAL CATALYSED FUNCTIONALISATION AT THE ANOMERIC CENTER OF CARBOHYDRATES

Isabelle Frappa and Denis Sinou*

Laboratoire de Synthèse Asymétrique, associé au CNRS, C.P.E. Lyon,
Université Claude Bernard Lyon I, 43, boulevard du 11 Novembre 1918,
69622 Villeurbanne Cédex, France

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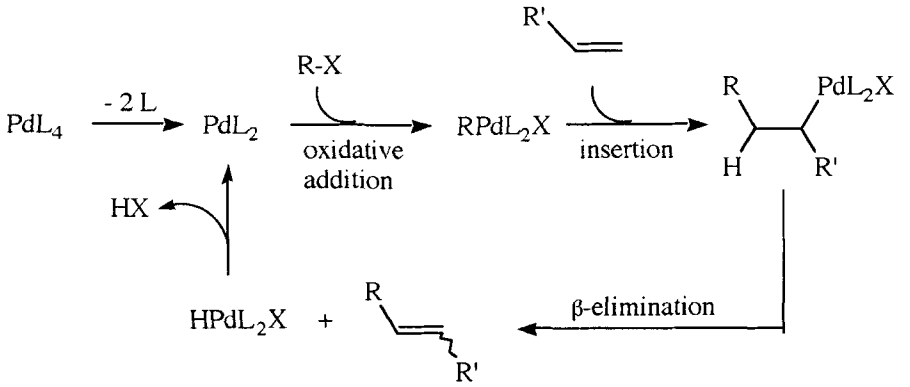
1. INTRODUCTION

There has been an increasing interest during the last thirty years in the development of homogeneous organometallic catalysis in organic chemistry.[1] This is probably due to the high observed stereo- and regioselectivities of these methods and the mildness of the reaction conditions. Even reactions that otherwise would not occur have been reported possible in the presence of a metal catalyst. So the use of organometallic



Scheme 1. Mechanism of the catalytic Heck reaction

catalysis, and particularly that involving transition metals, has produced a number of new and powerful synthetic methods for important classes of compounds, some in optically active form.

Although the use of this methodology in carbohydrate synthesis is relatively recent, extensive development of the applications of this powerful and mild method for the functionalisation of carbohydrates, particularly at the anomeric center, has been realized during the last decade.

This review is divided into four main sections. The first part covers the Heck type coupling reaction at the anomeric center with glycals; the second section covers the use of π-allyl complexes; the third part describes the palladium catalysed vinylic coupling reaction, and finally the fourth part summarizes other methodologies using organometallic catalysis.

2. FUNCTIONALISATION *via* A HECK TYPE COUPLING REACTION

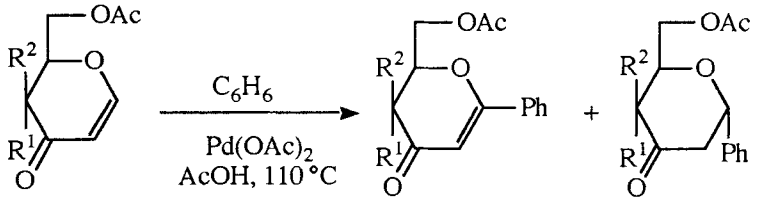
The Heck reaction, reproted in 1968 by R. F. Heck,[2] is the palladium-catalysed arylation or alkenylation of alkenes and has been extensively used in organic synthesis.[3] The usual assumed mechanism of the catalytic Heck reaction has the following steps (Scheme 1): (1) oxidative addition of a haloalkene or arene to a palladium(0) complex to form a σ-alkenyl or σ-arylpalladium complex, (2) association of the alkene to the palladium-complex followed by a *syn*-insertion (or carbopalladation) of the alkene to give a σ-alkyl palladium complex, and (3) *syn*-elimination of β-hydrogen to give an

arylalkene or a conjugated diene, the catalyst being regenerated after reductive elimination of HX in the presence of a base.

The Heck type coupling reaction was used in carbohydrate chemistry mainly by the groups of Czernecki and Daves. In early work, Czernecki coupled various aromatic compounds with peracetylated glycals **1** in the presence of palladium acetate in a **stoichiometric** amount (or eventually as a catalyst, cuprous acetate being used as the reoxidant)[4-6] according to the methodology of Moritani.[7] The reaction was regio- and stereoselective, the formation of the unsaturated α aryl-*C*-glycoside **2** and **3** having being only observed (eq 1). The coupling reaction was generalized to a range of substituted aromatic derivatives such as MeO-C_6H_5, 1,3-diMeO-C_6H_4, 1,4-diMeO-C_6H_4, 1-MeO-4-NO_2-C_6H_4 and 1-MeO-4-F-C_6H_4 and the corresponding aryl-*C*-glycosides were obtained in 40-90 % yields, although regioisomers at the aromatic ring were generally obtained.

The proposed mechanism for the formation of the major product **2** using a **stoichiometric** amount of palladium acetate (Scheme 2) involves a *syn*-addition of ArPdOAc from the α-face of the glycal **1a** leading to a σ-alkyl complex intermediate, followed by an usual *syn*-elimination of HPdOAc. The formation of the by-product **3** was explained by an *anti*-elimination of $Pd(OAc)_2$ after a conformation change.[8]

Later Czernecki applied these palladium-mediated arylation conditions to peracetylated glycal-derived enones (eq 2).[9] Whatever the conditions used, mixtures of *C*-glycosides **5** and **6** were obtained. If the saturated ketone **6** is produced by the protonolysis of the intermediate σ-palladium complex, the formation of the unsaturated ketone **5** could be explained only by a *syn*-elimination of HPdOAc from the epimerised σ-palladium complex.



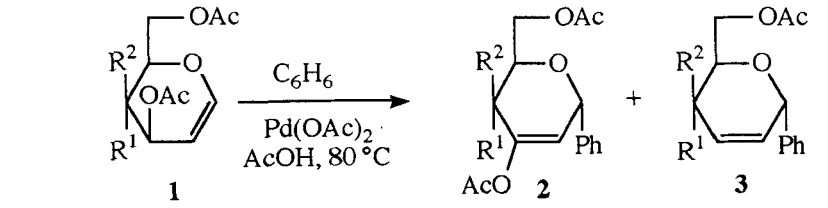
(2)

4 **5** **6**

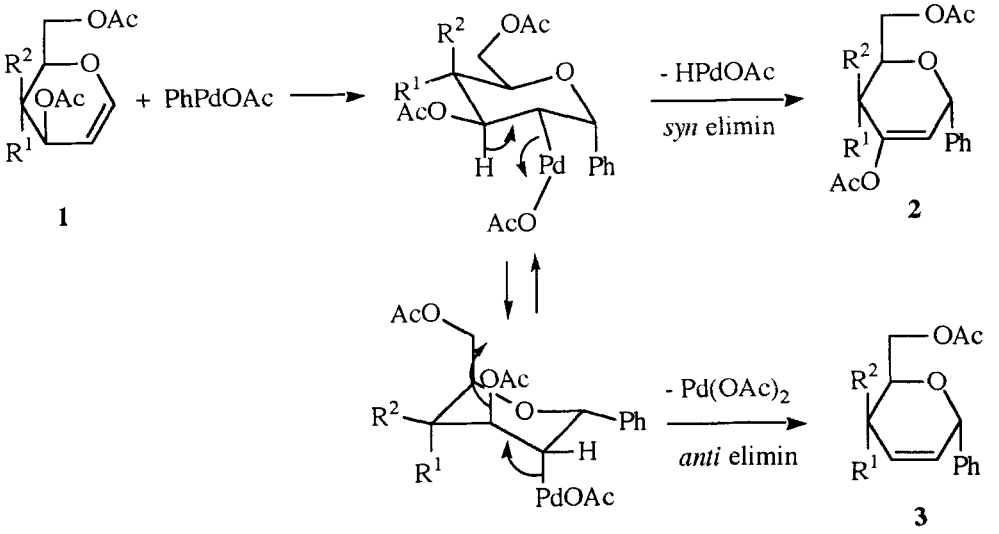
a R^1 = OAc, R^2 = H — 49 % — 21 %

b R^1 = H, R^2 = OAc — 38 % — 32 %

At the same time, Daves explored the use of metallated aromatic rings and especially organomercury reagents in the coupling reaction with glycals catalysed by palladium acetate.[10-12] The overall reaction process of this transformation is the



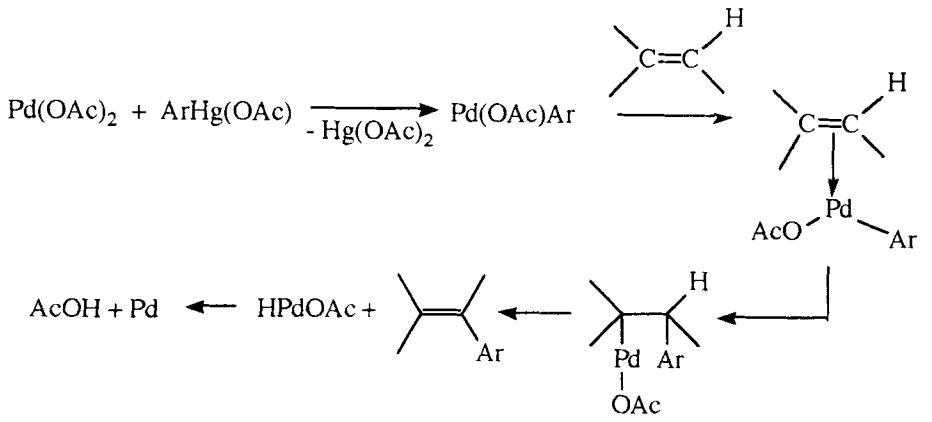
a R^1= OAc, R^2 = H — 54 % — 10 %
b R^1= H, R^2 = OAc — 46 %



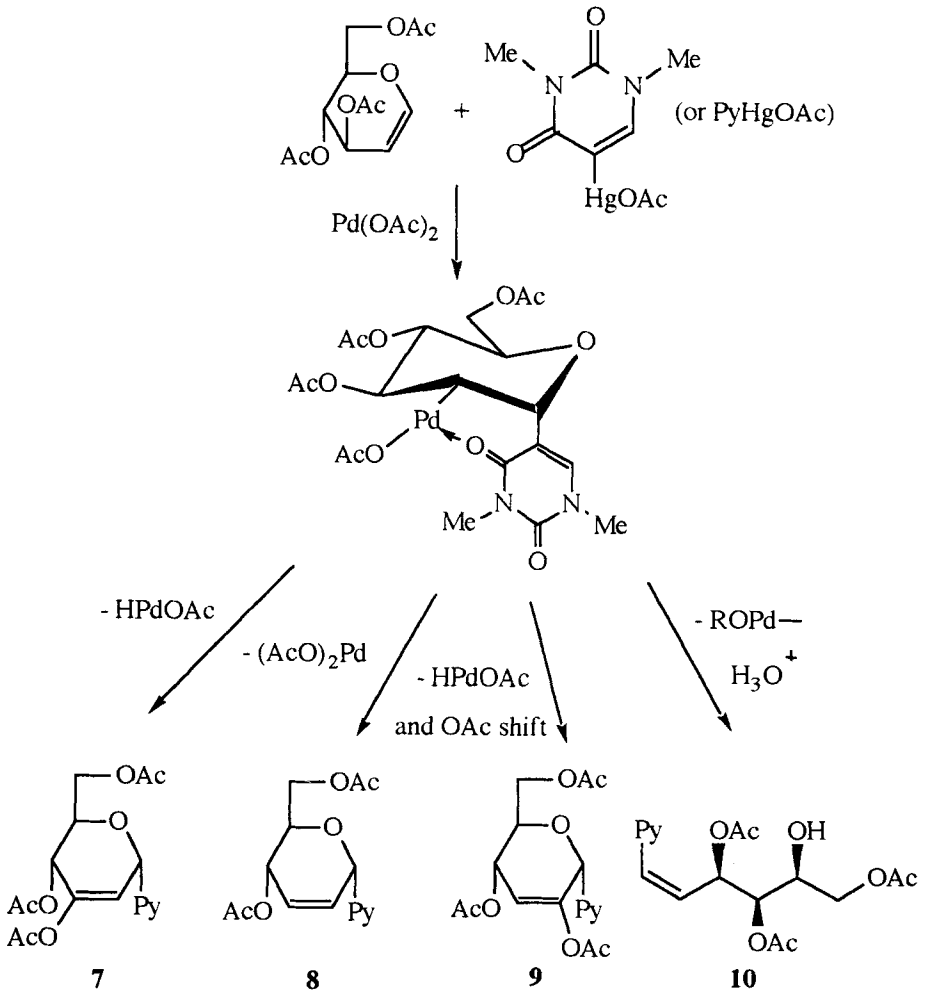
Scheme 2

following one (Scheme 3): (1) transmetallation of palladium acetate by the arylmercury reagent, (2) association of the arylpalladium complex to the double bond (π-complex), (3) *syn*-insertion of the olefin into the palladium aglycon bond with formation of a σ-complex, and (4) palladium elimination to give the arylolefin. It is to be noticed that such a process is stoichiometric in palladium(II).

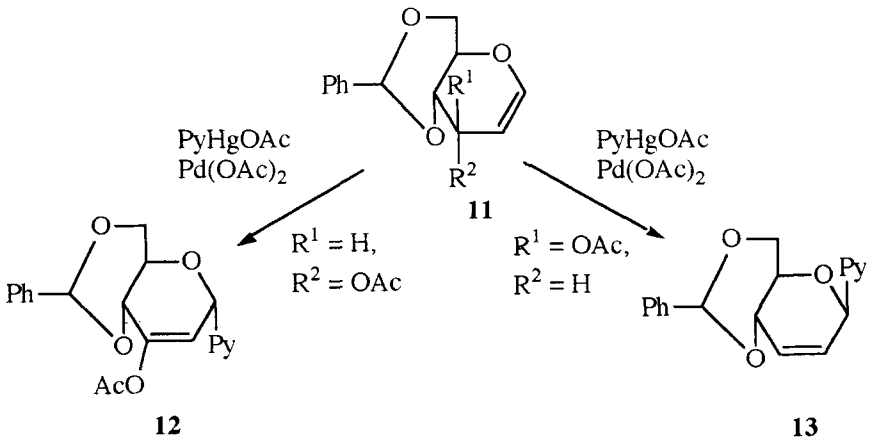
The palladium catalysed reaction of 3,4,6-tri-*O*-acetyl-D-glucal with a pyrimidine-5-ylmercuric salt in the presence of 1 equivalent of $Pd(OAc)_2$ gave a mixture of compounds **7**, **8**, **9** and **10**. The mechanism of the formation of these compounds is summarized in Scheme 4.[13-15] The adduct formation between the pyrimidinylpalladium species and the glycal is regio- and stereospecific. The decomposition of this single σ-bonded palladium adduct, whose structure has been determined by ^1H, ^{13}C, and ^{31}P



Scheme 3. Arylation of alkenes *via trans*-metallation



Scheme 4

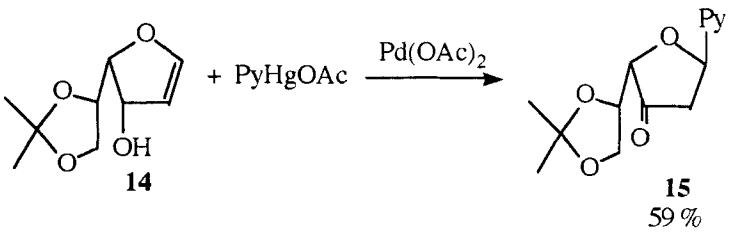


Scheme 5

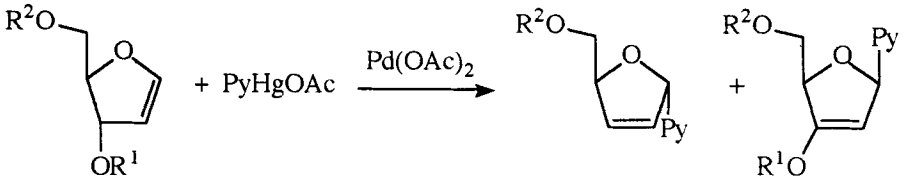
NMR and fast atom bombardment mass spectrometry,[16,17] could occur *via* four different processes involving elimination reactions with apparent steric requirements; i. e., by (1) *syn*-elimination of a hydridopalladium species leading to enol acetate **7**, (2) *anti*-elimination of acetoxy and palladium to form compound **8** (3) *syn*-elimination of a hydridopalladium species followed by a shift of acetate from C-3 to C-2 giving compound **9**, and (4) *anti*-elimination of alkoxide and palladium leading to the cleavage of the ring and the formation of the acyclic compound **10**.

The relative amounts of these different compounds were sensitive to reaction medium composition and depend particularly on the nature of the salts added. Without additive, a mixture of compounds **7**, **8** and **9** was obtained, respectively, in 15%, 31% and 31% yield.[18] Addition of lithium acetate gave higher yields in arylated products, although addition of lithium chloride favoured the formation of the acyclic product **10**. The coupling of pyrimidinylmercuric acetate was extended to other acetylated glycals and the essential role played by the stereochemistry of the C-3 allylic acetoxy group on the regio- and the stereospecific nature of the adduct formation was noticed; in all cases the *syn*-addition of the pyrimidinylpalladium complex occurs to the face of the double bond opposite to that occupied by the allylic acetate at C-3.

This steric requirement for elimination was confirmed using more conformationally rigid benzylidenic glycals **11a** and **11b** (Scheme 5).[18] In this case, due to restricted conformational mobility in the σ-palladium adducts, the formation of a single product was observed by *syn*-elimination of palladium hydride for **12α** or by *anti*-



14 **15** 59 %



16 **17** **18**

Compound	R^1	R^2		Yield (%)
a	H	H	29	45
b	H	Si-*t*-BuPh$_2$	84	
c	H	CH_2OCH_3	75	
d	CH_2OCH_3	H		65
e	CH_2OCH_3	CH_2OCH_3		71
f	$SiPr_3$	$SiPr_3$		51

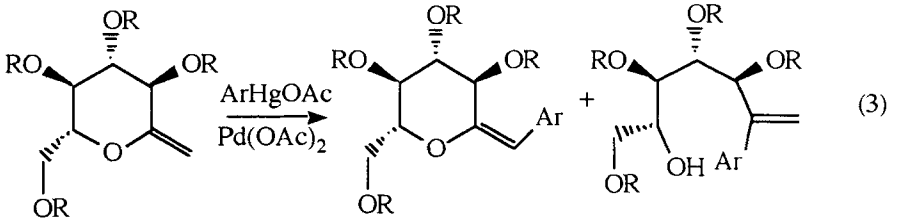
Scheme 6

elimination of palladium acetate for **13** β. This essential role was further confirmed by the reaction of PyHgOAc with 1,5-anhydro-2,3-dideoxy-4,6-di-*O*-(phenylmethylene)-D-*erythro*-hex-1-enitol which gave a mixture of pyrimidinyl α- and β-glycosides **13** in 64 % yield and a ratio of 8/1.[19]

The extension of this methodology to furanoid glycals[20-23] showed that the coupling was also regiospecific and that the stereochemistry of the reaction was again determined by the relative accessibility of the two faces of the double bond to the organopalladium reagent to form the π-complex. However, the reaction seemed to be more sensitive to the steric bulk of the substituent at the allylic C-3 position than to that at the C-5 position of the glycal (Scheme 6). If the attack occurs on the unsubstituted face when all substituents are *cis* as for compound **14**, in the case of *trans* substituents, a bulk substituent at C-3 directed the attack on the β-face of the glycal ring. However, in the case of a small substituent such as -OH, the attack is directed on the α-face by the

substituent on C-4. This was confirmed by coupling of the unsaturated glycal **16a** with PyHgOAc, where a mixture of α and β-*C*-nucleosides was obtained, resulting from organopalladium attack on both faces of the glycal, and of the unsaturated glycals **16b** and **16c** where a single β-*C*-glycoside was obtained.

The use of the exomethylenic sugar **19** in this coupling reaction[24] lead to the formation of two compounds, the acyclic one **20** arising from a β-alkoxypalladium elimination, while compound **21** came from the β-elimination of a hydridopalladium species (eq 3).



(3)

19 **20** **21**

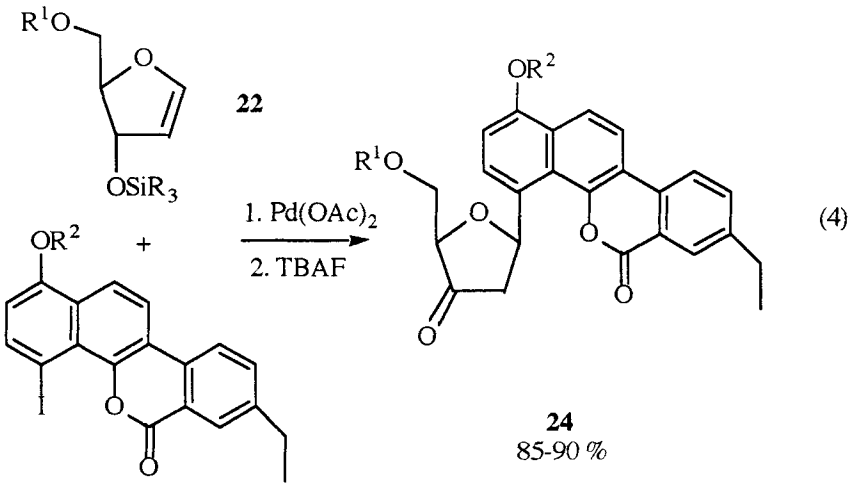
R = Bzl

Aryl tri-*n*-butylstannanes have also been successfully used in the coupling reaction of furanoid glycals with similar yields.[25]

The use of aryl halides in place of arylmercurials or stannanes in the palladium-coupling of glycals allows the reaction to occur using a catalytic amount of palladium acetate. A systematic study concerning the effects of the solvent, added salts and ligands for palladium, as well as catalyst precursor, allows the optimisation of this catalysed palladium-mediated coupling reaction;[26] the best results were obtained using an iodo derivative, palladium acetate as the catalyst, a tertiary amine (2 eq.) and sodium acetate (1 eq.) in dimethylformamide as the solvent. For example coupling of furanoid glycal **22** and 8-ethyl-4-iodo-1-methoxybenzo[d]naphtho[1,2-b] pyran-6-one **23** gave stereo-specifically and in excellent yield, after desilylation, the corresponding 3'-keto-*C*-glycoside **24**. The latter compound is related to the ravidomycin-gilvocarcin class of antibiotics (eq 4). Stannane derivatives of compound **22** were also used in this coupling method with the same stereoselectivity but with lower yields.[27]

The palladium coupling of 3,4,6-tri-*O*-[(1,1-dimethylethyl)dimethylsilyl]-D-glucal with iodo derivative **22** gave lower product yields,[26] although the reaction is stereospecific for the α-*C*-glycoside. The use of conformationally restricted deoxy glucal 1,5-anhydro-2,3-dideoxy-4,6-*O*-(phenylmethylene)-D-*erythro*-hex-1-enitol[19] in this

coupling reaction gave a mixture of α- and β-*C*-anthracyclic glycosides in a ratio 8/1 in agreement with the results using the arylmercury derivative.



(4)

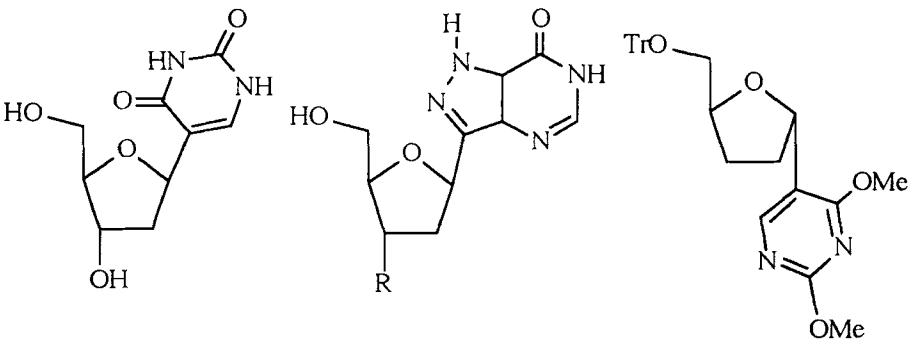
$R^1 = H, CH_2OCH_3$; $R^2 = OCH_3, OCOC(CH_3)_3$

This methodology was applied to the synthesis of 2'-deoxypseudouridine **25**, 2'-deoxyformycin **26a**, 2',3'-dideoxyformycin **26b** [28] as well as some 2',3'-deoxy-*C*-nucleosides **27**[29,30] (Scheme 7), the key step being a palladium-mediated regio- and stereospecific *C*-glycosyl bond forming reaction between a furanoid glycal and the appropriate iodoaglycon derivative. It is to be noticed that water-containing solvent systems are more effective than conventionally used organic reaction solvents for this palladium-mediated coupling reaction.[31]

3. FUNCTIONALISATION *via* π-ALLYL COMPLEXES

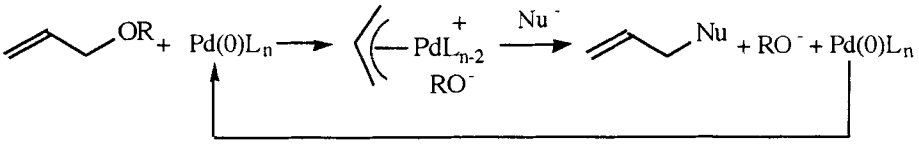
Since the discovery of the reaction of π-allyl palladium complexes with *C*-nucleophiles by Tsuji *et al.*,[32] the organic chemistry of π-allylpalladium complexes has attracted considerable attention and is now a usual tool in synthetic organic chemistry.[3d, 3f, 3i, 33] The mechanism of this reaction is described in Scheme 8. Important characteristics of this reaction are its very high stereoselectivity and very mild experimental conditions.

Dunkerton was the first to apply this methodology in carbohydrate chemistry.[34,35] The treatment of the unsaturated anhydrosugar **28** with the sodium anion of dimethyl formamidomalonate in the presence of a catalytic amount of



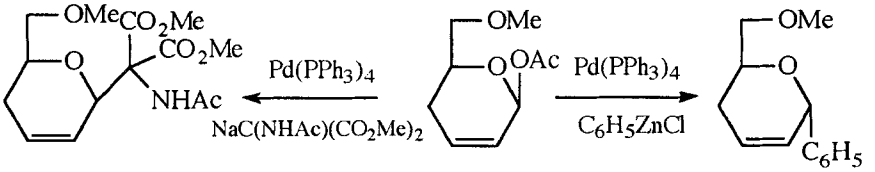
25 **26a** R = H **26b** R = OH **27**

Scheme 7



R = Ac, CO_2R^1, $CONHR^1$, Ph, $PO(OR^1)_2$; L = ligand

Scheme 8. Mechanism of the catalytic alkylation reaction



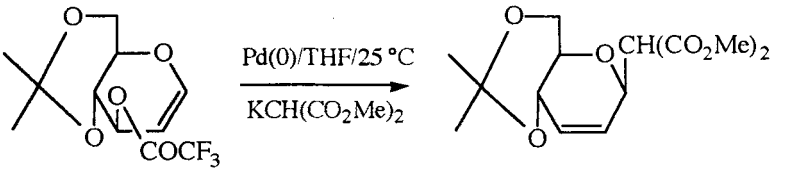
29 **28** **30**

Scheme 9

palladium(0) led regio- and stereospecifically to the formation of the product **29** in 90 % yield; the observed retention of configuration is consistent with an *exo*-attack of the nucleophile on the intermediate π-allyl system (Scheme 9). On the other hand, when a non stabilized carbanion such as phenylzinc chloride was used, the product of net inversion of configuration was exclusively obtained in 94 % yield; the inversion of

configuration is due to a *trans*-metallation of the organometallic reagent to palladium followed by reductive elimination. However, the introduction of a substituent at C-4 drastically decreased the yield.

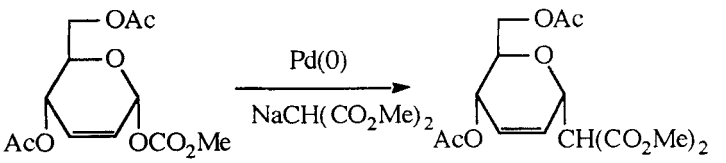
Although tri-*O*-acetyl-D-glucal is unreactive under usual conditions of alkylation, Rajanbabu[36] has found that the use of trifluoroacetate as the leaving group at C-3 allowed the alkylation reaction to take place under very mild conditions; for example compound **31** gave regio- and stereospecifically the β-*C*-glycoside **32** in 56 % yield (eq 5).



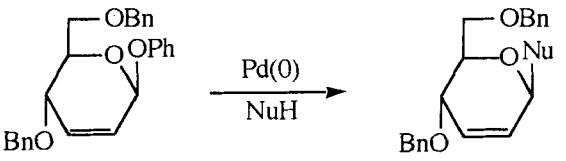
31 **32** (5)

During the same period, this reaction was extensively studied by Sinou and coworkers.[37,38] They found that phenyl 4,6-di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranoside **33** reacted with various 1,3-dicarbonyl compounds in the presence of a catalytic amount of palladium(0) to give regiospecifically the expected unsaturated *C*-glycoside **34** in quite good yield (Schemes 10 and 11). However if the reaction is stereospecific in the case of the β-anomer with global retention of configuration at the anomeric center, the reaction is only highly stereoselective for the α-anomer depending on the nature of the nucleophile. It was shown in further work[39] that this partial inversion of configuration was due to a retro-Michael reaction. This hypothesis was supported by the use of methyl and allyl dimethyl malonate as the nucleophiles; in this case the retro-Michael reaction did not occur due to lack of an acidic hydrogen and the reaction was stereospecific with the formation of the α-anomer only.

More recently, Engelbrecht *et al.*[40] used 2,3-unsaturated α and β glycosyl carbonates **35** as π-allyl precursors (eq 6). The reaction with various carbon nucleophiles such as dimethyl malonate, or better the sodium anion, in the presence of a palladium catalyst afforded the unsaturated *C*-glycoside with net retention of configuration and in quite good yield.

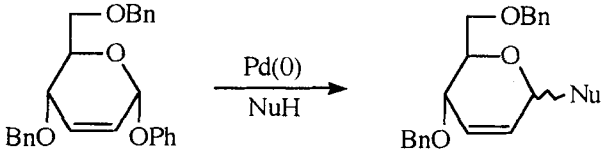


35 α **36** (81 %) (6)



33 β NuH	**34** β Yield (%)
$CH_2(CO_2Et)_2$	82
$CH_2(COMe)_2$	84
$CH_2(NO_2)(CO_2Et)$	72
$CH(NO_2)(CO_2Et)_2$	92

Scheme 10



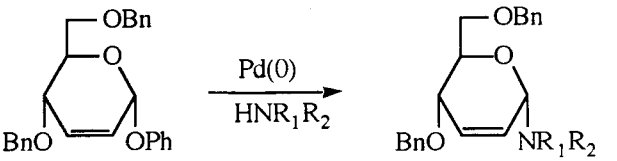
33 α **34**

NuH	Yield (%)	α/β
$CH_2(CO_2Et)_2$	60	75/25
$CH_2(COMe)_2$	67	75/25
$CH_2(NO_2)(CO_2Et)$	90	100/0
$CH(NO_2)(CO_2Et)_2$	93	100/0
$CH(CH_3)(CO_2Et)_2$	88	100/0
$CH(CH_2\text{-}CH{=}CH_2)(CO_2Et)_2$	92	100/0

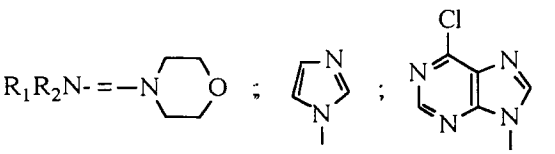
Scheme 11

Amines were also successfully used as nucleophiles in the presence of 2,3-unsaturated phenyl glycosides as π-allyl precursors. Various 2,3-unsaturated *N*-glycosyl derivatives **37** were obtained in quite good yields and with a very high degree of stereoselectivity (Scheme 12).[41] This method was applied to the preparation of nucleoside **39** in 40 % yield starting from the unsaturated furanoside **38** (eq 7).[42]

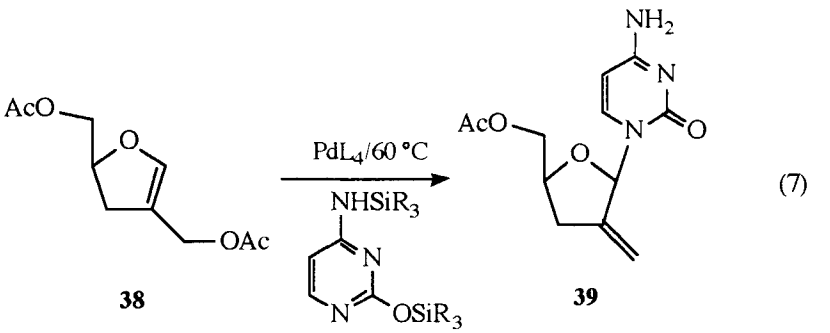
The palladium-catalysed coupling of *p-t*-butylphenyl-α-*O*-Δ^2-glycopyranoside **40** with various substituted arylmagnesium bromides was recently shown to provide stereospecifically the corresponding *C*-α-aryl-Δ^2-glycopyranosides **41**α, while nickel-mediated reaction allowed the preparation of the *C*-β-aryl anomers **41**β (Scheme 13).[43]



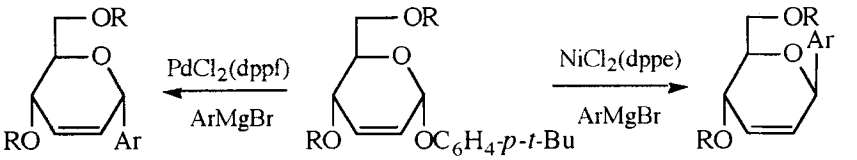
33 α **37**



Scheme 12



38 **39**

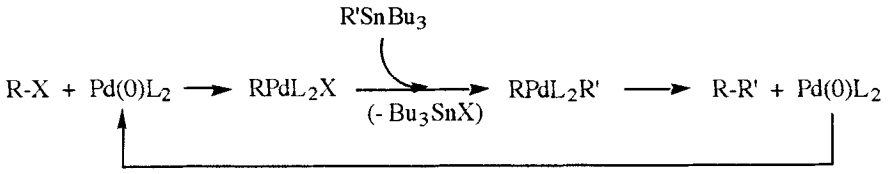


41 α **40 α** **41 β**

yield 70-95 % yield 70-85 %

R = Bn, Si-*t*-BuMe$_2$; Ar = C_6H_5, 2-MeOC_6H_4, 4-MeOC_6H_4, 3,4-$(CH_2O_2)C_6H_3$, 2-MeC_6H_4, 4-MeC_6H_4, 4-ClC_6H_4, $C_6H_5CH_2$

Scheme 13



R = aryl, alkenyl; R' = aryl, alkenyl, alkyl, etc; X = Br, I, OSO_2CF_3; L = ligand

Scheme 14: Mechanism of the Stille coupling reaction

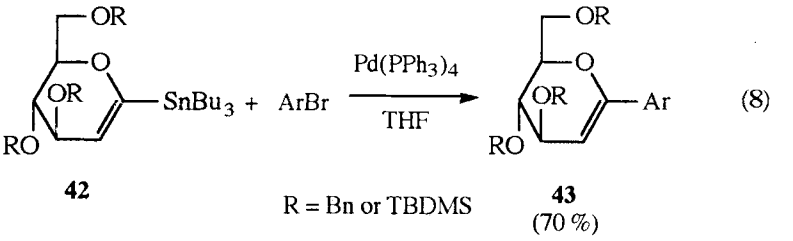
Keinan *et al.* [44] showed that highly chemoselective reductive cleavage of allylic acetates of 1,2-unsaturated monosaccharides could be achieved using diphenylsilane as the reducing reagent in the presence of a catalytic amount of a palladium(0) catalyst and zinc chloride; the reaction occured probably via a π-allyl intermediate with inversion of configuration at the carbon.

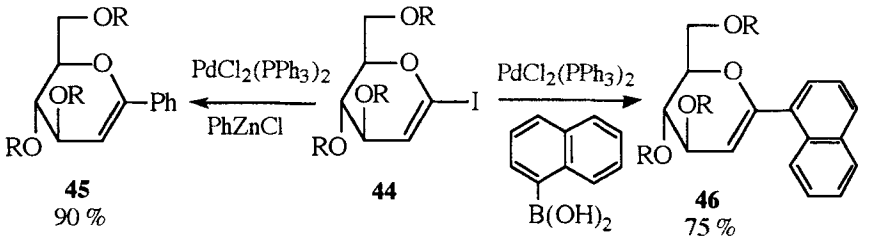
4. FUNCTIONALISATION *via* A PALLADIUM-CATALYSED VINYLIC SUBSTITUTION

The palladium-catalysed vinylic substitution, also called the Stille reaction[45] which is a palladium-catalysed cross-coupling between an organotin compound (or another organometallic compound) and an aryl or alkenyl halide is widely used in organic synthesis.[3d-e,46] The mechanism of this reaction shown in Scheme 14, is as follows: (1) oxidative addition of a haloalkene or arene to a palldium(0) complex to form a σ-alkenyl or σ-arylpalladium intermediate, (2) transmetallation with an organotin compound (or another organometallic compound) to give a new palladium complex, and (3) carbon-carbon bond formation by reductive elimination.

The coupling reaction of various aromatic substrates with benzyl or silyl protected 1-tri-*n*-butylstannyl D-glucal **42** (eq 8) was studied at the same time by the groups of Friesen[47-49] and Beau[50,51] leading to the formation of the *C*-glycoside **43**. After finding the best conditions for this reaction (THF as the solvent at reflux, tetrakistriphenylphosphinepalladium as the catalyst), the coupling was extended to a large variety of other substituted aromatic bromides (*p*-NO_2, *p*-CN, *p*-Cl, *p*-CO_2Me, *p*-OMe, *o*-Me, *o*-CH_2OAc, *o*-CH_2OH, *o*-OBn, α–naphtyle) as well as to *p*-nitrobenzoyl chloride, demonstrating the compatibility of this reaction with many functional groups and especially with unprotected hydroxyl groups.

A complementary approach reversing the polarity in this coupling reaction involved the use of metallated aromatics with the 1-iodo-D-glucal **44**;[52] arylzinc chloride or



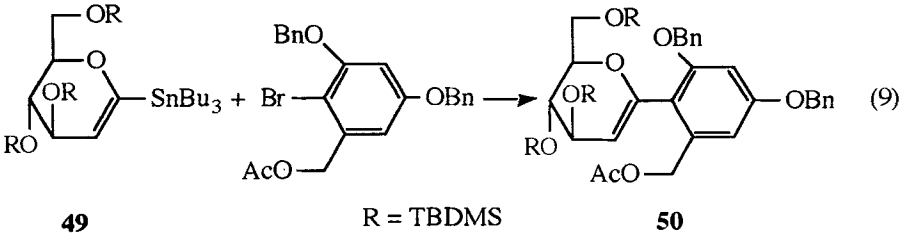


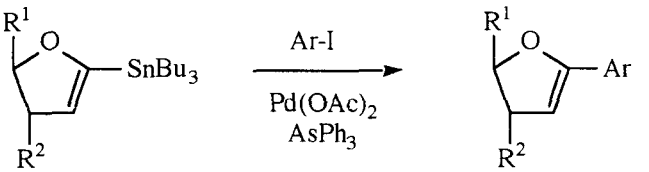
Scheme 15

arylboron compounds were successfully used in this case to give for example compounds **45** and **46** in quite good yields under milder reaction conditions (Scheme 15).

This reaction was recently used in the furanose series by Daves *et al.*[53] to give the corresponding 1-substituted furanoid glycals **48** (Scheme 16) in good to excellent yields by coupling of stannylated furanoïd glycals and iodoaglycon derivatives.

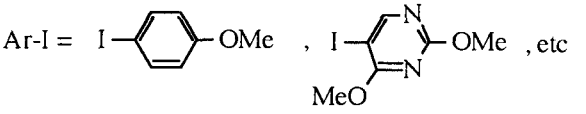
This palladium coupling strategy was applied to the synthesis of some naturally occurring aryl *C*-glycosides by Beau[54,55] and Friesen,[56,57] particularly for the preparation of a key intermediate **50** to the papulacandins (eq 9). The same workers also used this strategy for the construction of models of some di- and tri-*C*-glycosidic antitumor antibiotics (hedamycin, kidamycin, pluramycin).





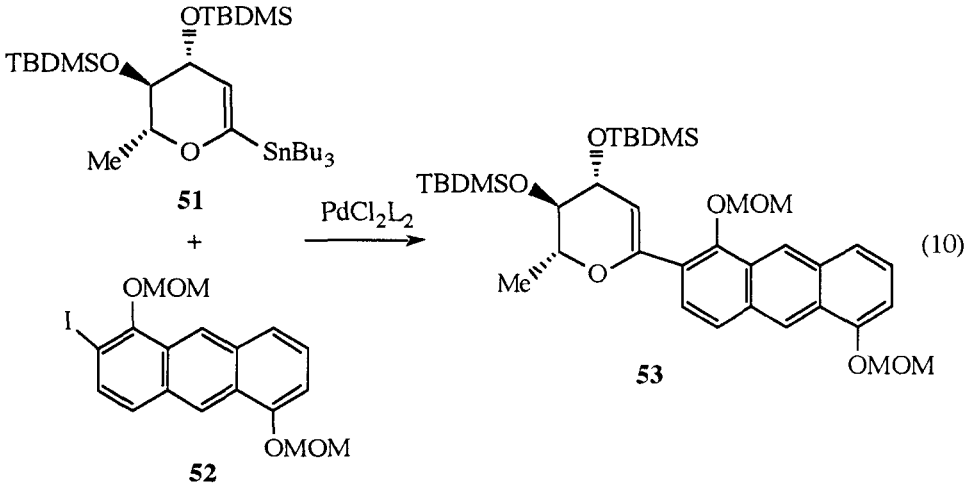
47 **48**

$R^1 = CH_2OCPh_3, CH_2OH, CH_2OTBDMS$; $R^2 = H, OH$

Ar-I = 

Scheme 16

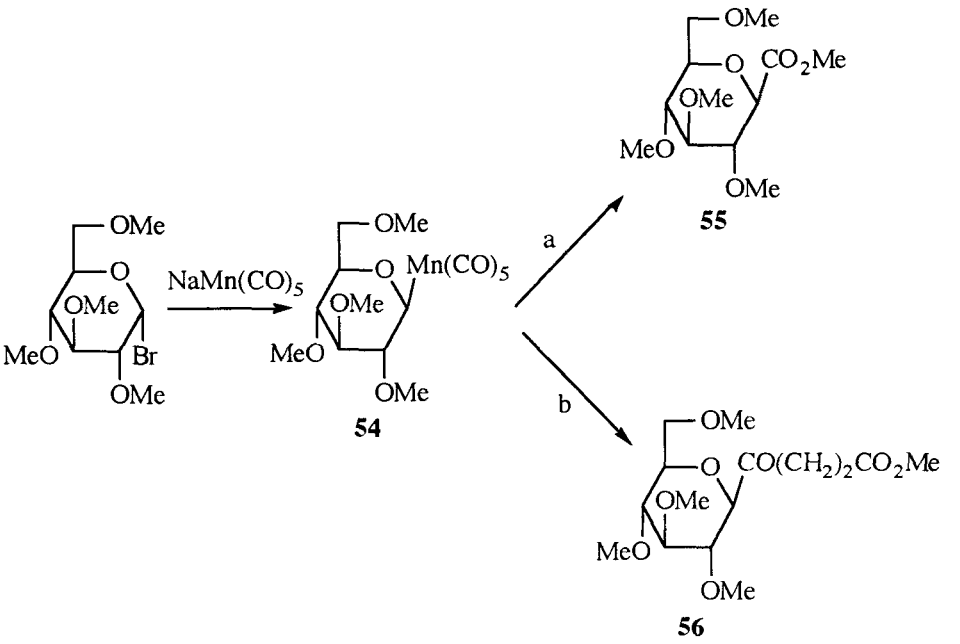
Tius *et al.*[58,59] used this palladium coupling reaction between the rhamnal derivative **51** and the iodo-anthracene **52** as a key step in the synthesis of Vineomycine B2 methyl ester (eq 10); nickel also has been used in this case.



(10)

5. OTHER METHODOLOGIES

Reaction of various glycosyl bromides with a quantitative amount of sodium cobalt tetracarbonyl,[60] or better sodium pentacarbonyl manganate,[61] gave stereospecifically glycosyl-cobalt or manganese carbonyl complexes in good yields. The resulting organometallic complexes are versatile intermediates for carbon-carbon

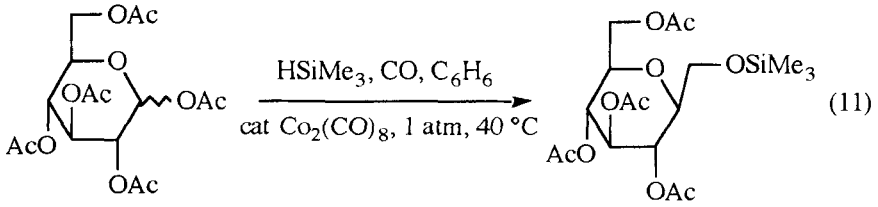


a: CO, MeOH; b: CH_2=$CHCO_2Me$, 6 Kbar, then hν, CH_3CN

Scheme 17

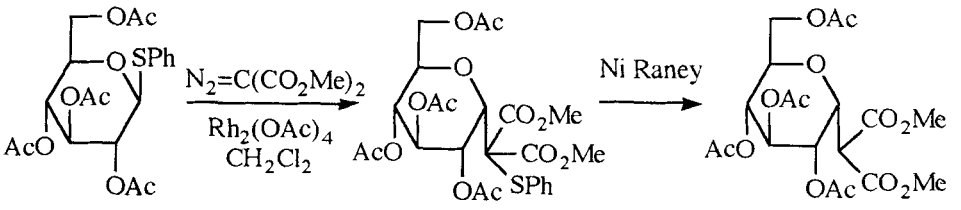
formation at the anomeric center; for example glycosyl complex **54** (Scheme 17) leads to the ester **55** or the *C*-glycoside **56**.

The $Co_2(CO)_8$-catalysed reaction of glycopyranosyl and furanosyl acetates with $HSiMe_3$ and CO[62,63] (eq 11) proceeded catalytically and stereoselectively under mild reaction conditions to afford *C*-glycosides.



(11)

Various oxyglycals were obtained from different carbohydrates, both in the furanose and the pyranose series, having a free anomeric hydroxyl, after mesylation and treatment with a catalytic amount of palladium(0).[64] The unsaturated carbohydrates



57 **58**

Scheme 18

were formed by palladium oxidative addition into the anomeric center followed by subsequent β-hydride elimination.

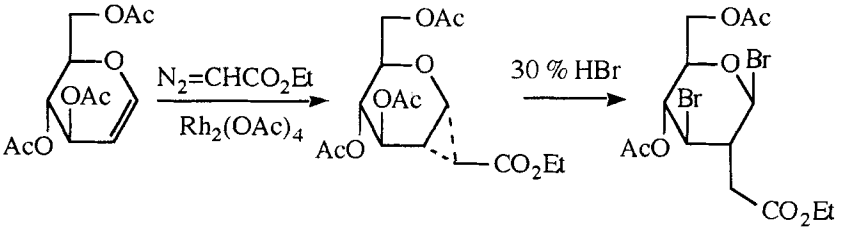
Katemani *et al.*[65] developed a new stereoselective carbon-carbon bond-forming reaction at the anomeric center by means of a carbenoid displacement reaction with phenyl thioglycosides catalysed by rhodium(II) acetate (Scheme 18). This reaction was carried out under neutral conditions and allowed the introduction of various functionalities.

Acetylated glycals reacted with alcohols[66] or with some β-dicarbonyl compounds[67] in the presence of $PdCl_2$ or $PdCl_2(CH_3CN)_2$ to give the corresponding unsaturated *O*- or *C*-glycopyranosides, the catalyst acting probably as a Lewis acid. A very similar methodology was the stereoselective α-*O*-glycosylation of thioglycosyl donors, such as 2,3-dideoxyhex-1-thio-2-enopyranosides, achieved using $PdCl_2(CH_3CN)_2$ and AgOTf in a stoichiometric manner.[68,69]

Palladium(0)-catalysed alkylation of various allylic carbonates with carbohydrates having a free anomeric hydroxyl group was found to be an efficient method for glycosidation of allylic aglycons.[70-72] This methodology has been reported for the preparation of various unsaturated 1,4-disaccharides by alkylation of ethyl α-*O*-Δ^2-glycosides, having a leaving group at C-4, with various carbohydrates having a free anomeric hydroxyl group.[73]

Ester-substituted 1,2-*C*- methylene carbohydrates were obtained by cyclopropanation of the corresponding unsaturated sugars with ethyl diazoacetate and rhodium(II) acetate as the catalyst (Scheme 19);[74] these cyclopropanes offered access to numerous new carbohydrate derivatives.

A 1996 report describes a Pd(0)-catalysed [3 + 2]-cycloaddition reaction between 2-nitro-2,3-unsaturated carbohydrates and various precursors of trimethylenemethyl 1,3-dipole gave chiral bicyclic compounds.[75]



Scheme 19

6. CONCLUSION

This survey of the literature concerning the use of transition metals for the functionalisation at the anomeric center of carbohydrates shows that it provides a very mild and efficient methodology for the formation of a carbon-carbon or carbon-heteroatom bond at the anomeric center. Due to the high regio- and stereoselectivity of this method, as well as its chemiocompatibility, it seems reasonable to think that the use of organometallic catalysis will increase and become a common and powerful tool in the field of synthetic carbohydrate chemistry.

7. ACKNOWLEDGEMENT

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