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The versatility of molecular ruthenium catalyst RuCl(COD)(C_5Me_5)

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Abstract

This review reports the contribution of the catalyst precursor RuCl(COD)C_5Me_5, and of the Rennes team, for the selective transformation of alkynes to generate high value chemicals with atom economy reactions. Ruthenium activation processes are discussed. Are successively presented (i) the cross-oxidative coupling of alkyne and allyl alcohol to generate γ,δ-unsaturated aldehydes, (ii) the head-to-head dimerisation of alkynes in the presence of carboxylic acids, via a mixed Fischer–Schrock type biscarbene–ruthenium complex, to give functional dienes, and that of propargyl alcohols, via cyclobutadienyl–ruthenium intermediate, to produce cyclobutene derivatives, (iii) the addition of diazoalkanes to alkynes leading to functional dienes via double carbene addition and (iv) the reaction of diazoalkanes to enynes leading to new bicyclo[3.1.0]hexane compounds. Most of the above catalytic reactions involve carbene–ruthenium catalytic species of type Cp*(Cl)Ru(biscarbene) or Cp*(Cl)Ru=CHR.

Keywords: Ruthenium catalysts; RuCl(COD)C_5Me_5 in catalysis; Alkynes; Biscarbene–ruthenium; Alkylidene–ruthenium; Diazoalkanes; Atom economy reactions

1. Introduction

During the last decade molecular ruthenium complexes have promoted a large variety of improved catalytic reactions and the creation of novel catalytic combinations of simple molecules to generate high-value chemicals. In the field of alkene metathesis alkylidene–ruthenium complexes have offered high catalytic activity associated to high tolerance toward a variety of functional groups [1,2]. This evidence has led to design several novel, efficient 16 electron alkylidene–ruthenium catalyst precursors of general formula $RuX_2(=CHR)(L^1)(L^2)$ [3–5] but also ionic, 18 electron complexes of type allenylidene $[RuX(=C=C=CR_2)(PR_3)(arene)]^+Y^-$ [6] or indenylidene–ruthenium [7,8]. In parallel ruthenium catalysed enantioselective hydrogenation has tremendously contributed to the field, not only with the introduction of chiral binap–ruthenium catalysts [9] but especially by showing that optically active RuX_2(diamine)(diphosphine) catalysts can transfer both proton and hydride to ketone without its coordination to the ruthenium atom [10]. The catalytic activation of inert C–H bonds has now been promoted by ruthenium catalysts and offer the possibility of insertion of a variety of molecules for the functionalisation of aromatic compounds and alkenes [11]. Ruthenium catalysts are also well known to promote the selective anti-Markovnikov additions to alkynes via vinylidene–ruthenium intermediates [12–14] and to control the regioselective oxidative couplings of unsaturated substrates to generate unprecedented C–C bond formation reactions [15,16] including carbonylation reactions [17].

In this field of catalysed C–C bond formation $RuX(L_2)C_5R_5$ complexes constitute a very useful family of versatile catalyst precursors as they promote combinations of molecules often with atom economy [18–20]. The versatility arises from the modulation of both electron-richness and steric hindrance brought by the C_5R_5 ligand and from the lability of the L_2 or $(L)_2$ and X ligands. Weakly bonded L_2 ligands offer 14 electron intermediates, suitable for oxidative

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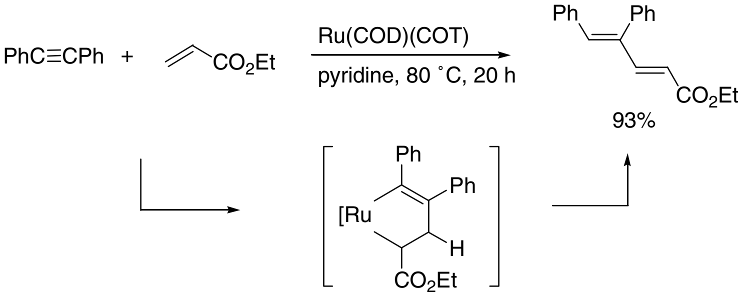
couplings of unsaturated molecules [18–20], whereas strongly bonded L_2 ligands with labile X^- group offer ionic 16 electron intermediates suitable for generation of vinylidene species from terminal alkynes [13,21,22].

The objective of this review is to present selected recent RuCl(COD)C_5Me_5 activation processes leading to catalytic applications performed by the Rennes team. Successively, will be presented

(i) cross-oxidative couplings of C≡C and C=C bonds for the synthesis of unsaturated aldehyde derivatives,
(ii) oxidative couplings of alkynes for the synthesis of functional dienes and cyclobutenes,
(iii) in situ generated ruthenium carbene from diazoalkane for the double addition of carbene to alkynes and for the transformation of enynes into bicyclo[3.1.0]hexane derivatives.

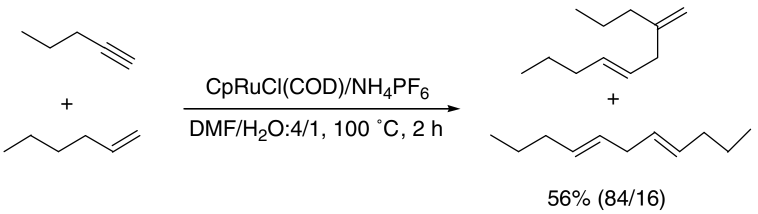
2. Oxidative coupling of C=C and C≡C bonds: catalytic synthesis of γ, δ-unsaturated aldehydes

The first examples of cross-coupling of a double and a triple carbon–carbon bonds via oxidative coupling have been achieved with a ruthenium(0) catalyst precursor Ru(COD)(COT) or a ruthenium(II) catalyst precursor $RuH_2(PPh_3)_4$ and led to functional cyclobutene derivatives and 1,3-dienes [23] (Eq. (1))



(1)

Trost has shown that ruthenium(II) complexes such as RuCl(COD)C_5H_5 in the presence of NH_4PF_6 or $[Ru(NCMe)_3C_5H_5]PF_6$ could also lead to oxidative coupling of non activated alkene and alkyne (Eq. (2)) [24] and to that of functional derivatives (Eq. (3)) [25] to generate 1,4-dienes, for which the branched isomer is the major derivative



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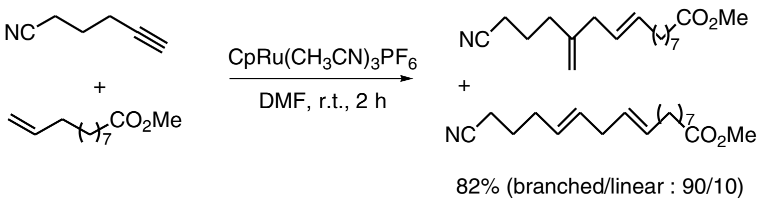
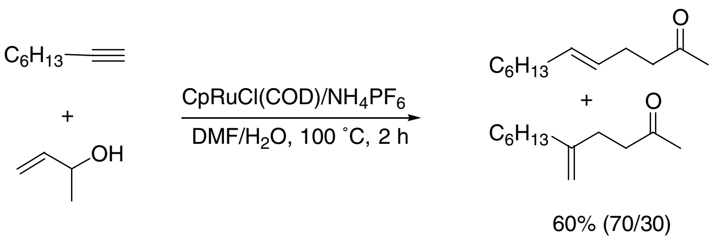


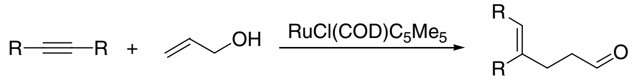
(3)

An interesting extension of this reaction deals with the synthesis of γ,δ-unsaturated ketones by oxidative coupling of alkynes and substituted allylic alcohols in the presence of RuCl(COD)Cp/NH_4PF_6 catalytic systems (Eq. (4)) [26]. In that case the linear isomer is the major product



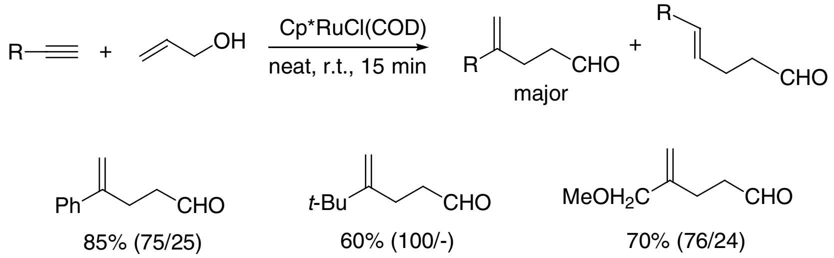
(4)

It is noteworthy that the above reaction with the simple allyl alcohol is not efficient to generate the corresponding aldehydes. However, we have been able to generate the γ,δ-unsaturated aldehydes from allyl alcohol simply by using the more electron-rich and hindered catalyst precursor RuCl(COD)C_5Me_5 [27] (Eq. (5))



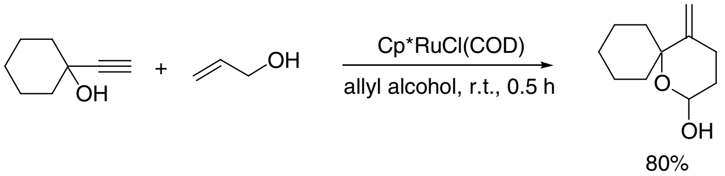
(5)

The reaction can be performed without solvent in neat allyl alcohol or even in water in mixture water/allyl alcohol: 8/1. With terminal alkyne two isomers are produced, this time the branched isomer being the major product [27] (Eq. (6)). The increase in the branched/linear ratio observed with RuCl(COD)C_5Me_5 can be explained by the preferred formation of the oxidative coupling product leading to the weaker interaction of the alkyne substituent with the C_5Me_5 ligand. The catalytic cycle can be explained by Scheme 1



(6)

The reaction of propargylic alcohols with allyl alcohol in the presence of RuCl(COD)C_5Me_5 is by contrast highly regioselective and only the hemiacetals of 5-methylenetetrahydropyrans can be produced [19,28] (Eq. (7)). The reaction can be applied to molecules containing two or three identical propargyl alcohol moieties [19] (Eq. (8))



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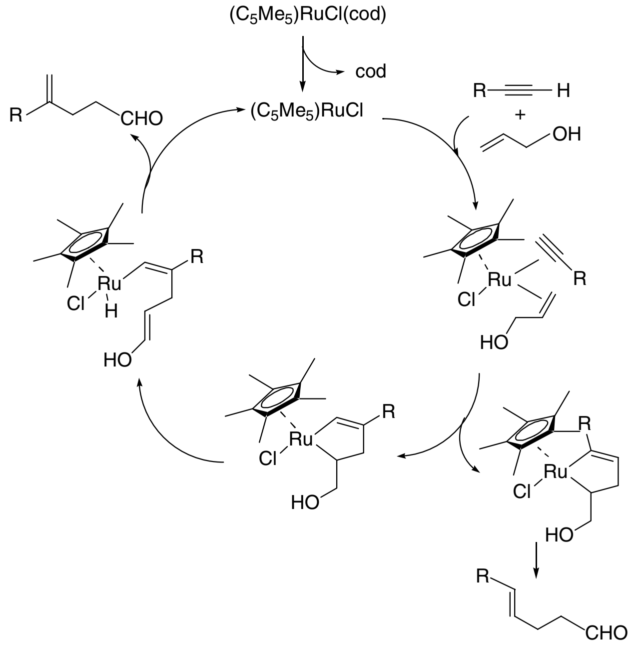
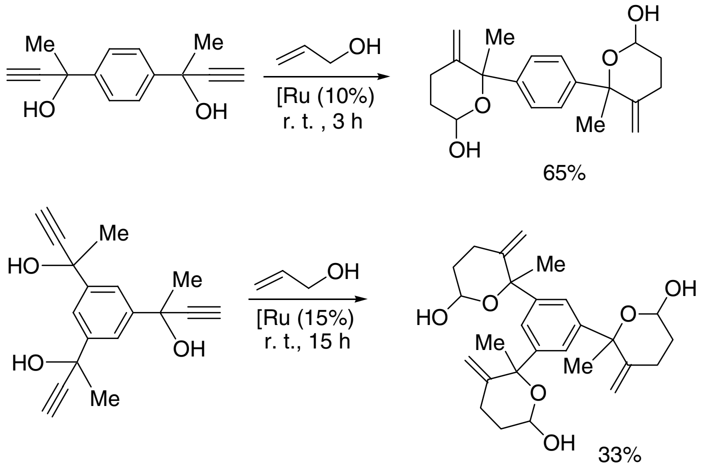


Scheme 1.

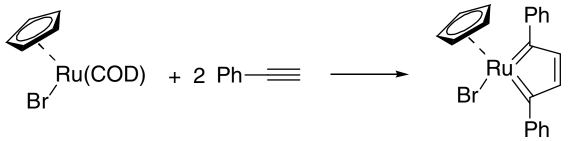


(8)

The above results show the versatility of $RuCl(COD)C_5R_5$ catalysts. The simple replacement of C_5H_5 by C_5Me_5 makes possible the coupling of alkynes with simple allyl alcohol and favours the formation of the branched product.

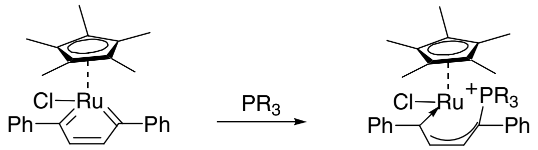
3. Oxidative coupling of C≡C bonds: catalytic synthesis of functional 1,3-dienes

The first evidence for the stoichiometric oxidative coupling of phenylacetylene at the ruthenium site was shown to lead to a head-to-head coupling and the formation of a biscarbene ruthenium complex as represented in Eq. (9) [29]. The biscarbene X-ray structure revealed a C(2)=C(3) double bond



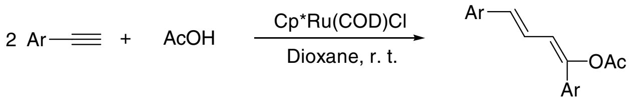
(9)

Since this discovery, a variety of related biscarbene ruthenium complexes were obtained from alkynes and their stoichiometric reactivity was explored by Dinjus [30] and Kirchner and coworkers [31]. Especially, the addition of two electron ligand takes place at one carbene carbon to form an allyl carbene derivative [31] (Eq. (10))



(10)

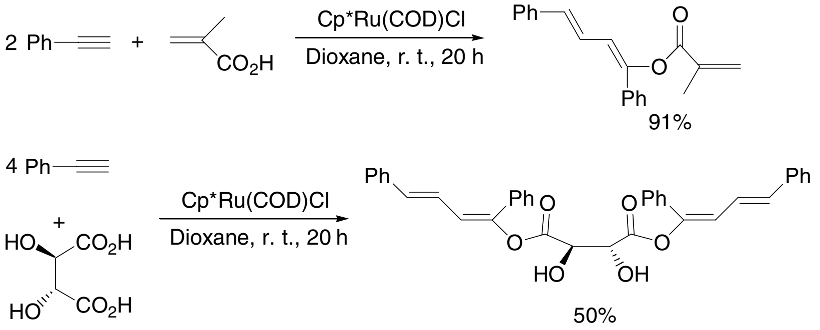
Only recently these biscarbenes were involved into a catalytic process [20] by successive addition of an electrophile (proton) and a nucleophile (carboxylate). Thus the reaction of two equivalents of terminal alkynes and one of carboxylic acid in the presence of 5 mol% of $RuCl(COD)C_5Me_5$ led to the formation of functional dienes (Eq. (11)) [20,32]. The reaction takes place under mild conditions (r.t., 2–40 h) in dioxane



Ar : p-MeOC$_6$H$_4$	42 h	85%
C_6H_5	20 h	90%
p-CNC$_6$H$_4$	15 min	81%

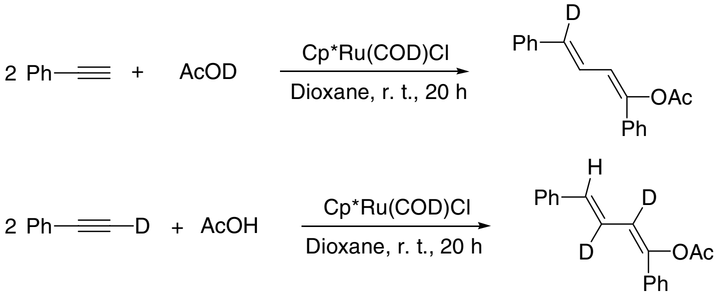
(11)

This catalytic reaction actually performs in one step the combination of three molecules into only one with formation of C–H, C–C and C–O bonds with high regio- and stereoselectivity. It is revealed that the reaction is much faster with alkynes containing electron withdrawing groups (Eq. (11)) and can be applied with a variety of carboxylic acids without protection of functional groups (Eq. (12)) [32]



(12)

The mechanism of the reaction was established on the basis of labelled experiments and computational studies. The use of deuteriated acids and alkynes shows that the HC(2)–CH(3) hydrogen atoms arise from the alkyne, and thus a vinylidene intermediate can be eliminated, and that the acid proton adds regioselectively at carbene carbon(1) [32] (Eq. (13)). In addition the biscarbene complex (Eq. (14)) has been isolated and was shown to catalyse the reaction



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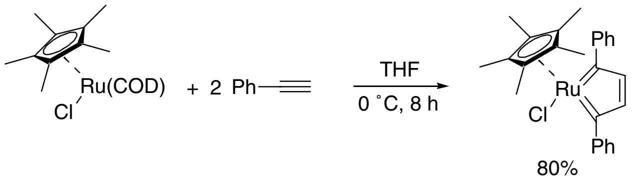
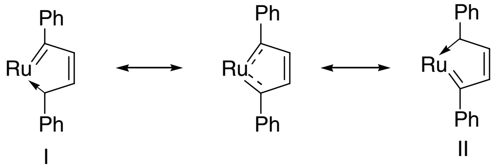


(14)

Initial computational studies performed by Calhorda and coworkers [33] on the biscarbene ruthenium complex suggest that the complex is consistent with a ruthenium(IV) derivative. Thus the catalyst intermediate can be representated as resulting from the two canonical forms I and II (Eq. (15)). Consequently, this biscarbene ruthenium(IV) complex is expected to behave as a mixed Fischer and Schrock type biscarbene

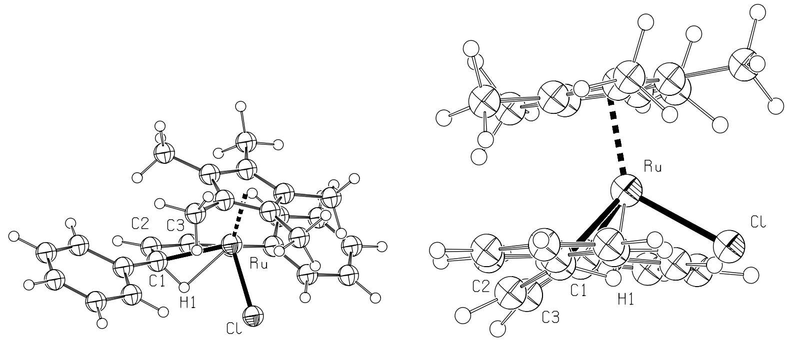


(15)

Eisenstein and Clot have studied the addition of carboxylic acid to this biscarbene complex using QM/MM (ONIOM) method. They do not observe protonation at the metal but at one carbene carbon. The most stable isomer has its C_1–H and Ru–Cl bonds in *cis* position and is 15.2 kcal mol^{-1} more stable than the *trans* isomer (Fig. 1) [32].

The remarkable features of this intermediate are that (i) the $C_2{=}C_3$ double bond is not coordinated to the ruthenium but contributes to the stabilisation of the remaining carbene ligand and (ii) the resulting 16 electron intermediate is stabilised by a weak C_1–H…Ru agostic bond. Consequently, the intermediate is not the expected carbene allyl ruthenium complex, but an alkyl carbene derivative. A realistic mechanism of the catalytic reaction is represented in Scheme 2 [32].

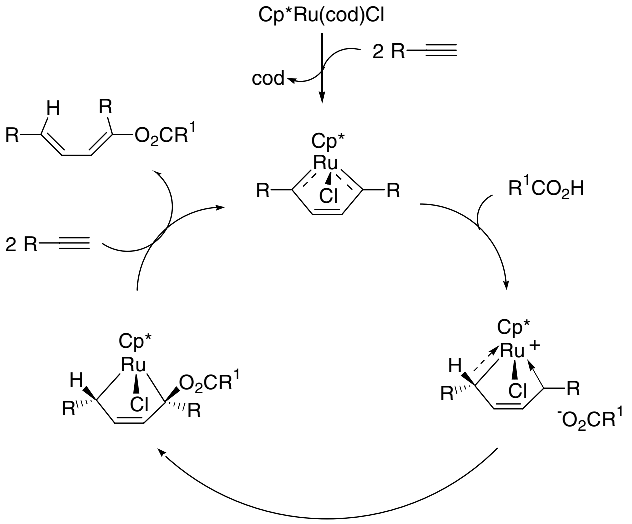
The above new catalytic reaction has potential for the access to a large variety of functional dienes or unsaturated ketones [32], but also to conjugated polymers.



Ru-C1 = 2.315 Å
Ru-C4 = 1.981 Å
C1-H1 = 1.120 Å
H...Cl = 2.407 Å

C1-C2 = 1.412 Å
C2-C3 = 1.388 Å
C3-C4 = 1.412 Å

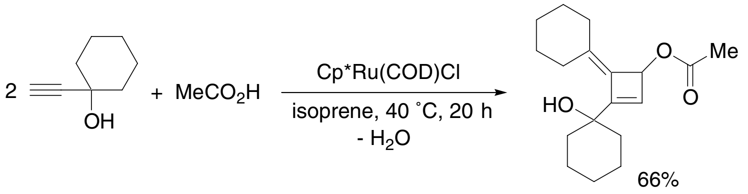
Fig. 1. Two views of the optimised (B3PW91) structure of the *cis* $Cp^*Ru(C_4Ph_2H_2)(Cl)(H)^+$ isomer, distances in Angstrom.



Scheme 2.

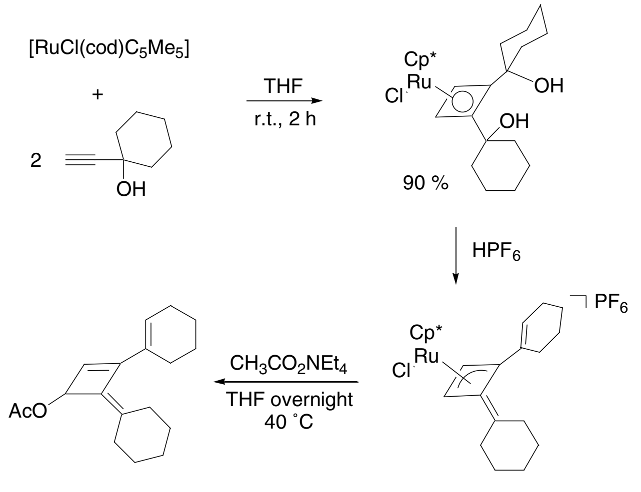
4. Oxidative coupling of propargylic alcohols: catalytic synthesis of cyclobutenes

When the previous reaction was studied with propargylic alcohols it led to the formation of new functional cyclobutenes [34]. Thus the reaction of two equivalents of propargylic alcohol, one of carboxylic acid in the presence of 5 mol% of the same catalyst $RuCl(COD)C_5Me_5$ in various solvents at 40–60 °C led to the formation of a 4-membered cycle (Eq. (16))



(16)

The reaction formally results from the 2 + 2 addition of the C≡C bond with addition of the carboxylic acid and elimination of water. It corresponds to another example of atom economy reaction leading to the formation of a complex molecule in one step from simple substrates. The mechanism of the reaction has been established on the basis of stoichiometric reactions. Thus, RuCl(COD)Cp* reacts with propargylic alcohol to give a cyclobutadienyl ruthenium complex resulting from head-to-head coupling. The protonation of the later with strong acid (HPF_6, HBF_4) lead to dehydration and to the allyl derivative of which the X-ray structure has been established. The later reacts with one equivalent of ammonium acetate to give the acetate addition on the less substituted allyl carbon (Eq. (17)) [34]



(17)

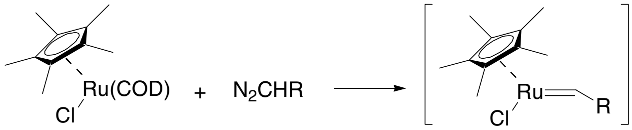
5. In situ generated ruthenium carbenes from RuCl(COD)Cp* and diazoalkanes

Ruthenium carbene intermediates have already been in situ generated by addition of diazoalkane to a ruthenium complex. Thus, Noels has achieved the polymerisation of cyclic olefins, such as norbornadiene derivatives, catalysed by in situ generated alkylidene–ruthenium species, arising from $[RuCl_2(p\text{-cymene})]_2$ and $N_2CHSiMe_3$ as a carbene source [35].

A variety of ruthenium catalysts, notably chiral catalysts [36,37] have been developed to lead to efficient asymmetric cyclopropanation of alkenes. Nishiyama has shown that, in the case of Ru–Pybox system, ruthenium carbene species derived from diazo compounds, could be characterised [37].

The reaction of the complex $RuCl_2(PPh_3)_3$ with a number of diazoalkanes has allowed the synthesis of the alkylidene–ruthenium complexes $RuCl_2(=CHR)(PR_3)_2$. Thus, Grubbs has shown that the related complex $RuCl_2(=CHPh)(PCy_3)_2$ was an efficient catalyst for alkene metathesis [1,3].

The reactivity of the complex RuCl(COD)Cp* in the presence of diazo compounds has been explored. It has the potential to generate on release of the COD ligand a coordinatively unsaturated alkylidene–ruthenium, protected by a bulky C_5Me_5 ligand and having a vacant site in *cis* position (Eq. (18))



(18)

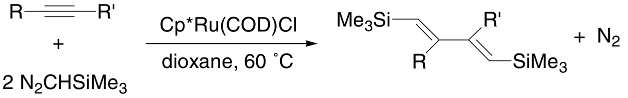
5.1. Double carbene addition to alkynes: catalytic synthesis of functional conjugated dienes

Catalytic additions of diazo compounds to alkynes deals essentially with the use of the $Rh_2(OAc)_4$ catalyst and afford either cyclopropene intermediates [38] or reactive vinylcarbenoid species [39].

The stoichiometric addition of two molecules of diazo compounds to a coordinated alkyne has been shown by O'Connor. Thus the reaction of a cobalt alkyne complex has allowed to isolate a complex with a diene ligand [40].

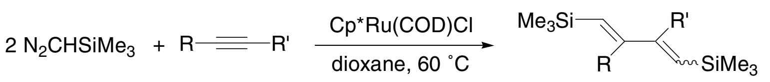
To our knowledge, no example of ruthenium-catalysed double addition of diazo compounds to alkynes has been reported. However, ruthenium-carbene species, derived from olefin metathesis, are well-known to react with alkynes. Thus Mori has carried out a 1,3-diene synthesis by reaction of alkyne and ethylene using an alkylidene–ruthenium alkene metathesis catalyst [41].

The Cp*RuCl moiety being able to accomodate two *cis* carbene ligands, we have investigated the possibility of coupling alkenylcarbene–ruthenium, in situ generated from diazoalkane derivative and $RuCl(COD)C_5Me_5$ with alkyne. A second addition of carbene species arising from diazoalkane takes place and produces dienes. A novel selective synthesis of new substituted 1,4-bistrimethylsilylbuta-1,3-dienes was performed by a catalytic double addition of trimethylsilyldiazomethane to alkynes, catalysed by RuCl(COD)Cp* (Eq. (19)) [42]. The stereoselective formation of these functional conjugated dienes results from the selective creation of two carbon–carbon double bonds



(19)

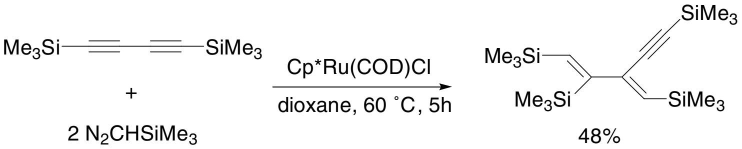
With terminal alkynes, two isomers are obtained, the major one showing a *Z* stereoselectivity for the trisubstituted double bond and a *E* stereoselectivity for the disubstituted double bond. The extension of this reaction to various disubstituted alkynes has led to the formation of tetrasubstituted dienes with only one isomer having both substituents in the *cis* position on each double bond (Eq. (20)) [42]



R	R'	
Ph	H	72% (*E*/*Z*: 70/30)
Ph	Me	56% (*E*/*Z*: 100/-)
CH_2OH	Me	95% (*E*/*Z*: 100/-)

(20)

The reaction of 1,4-bis(trimethylsilyl)diyne has allowed the synthesis of a tetrasilylated dienyne (Eq. (21))

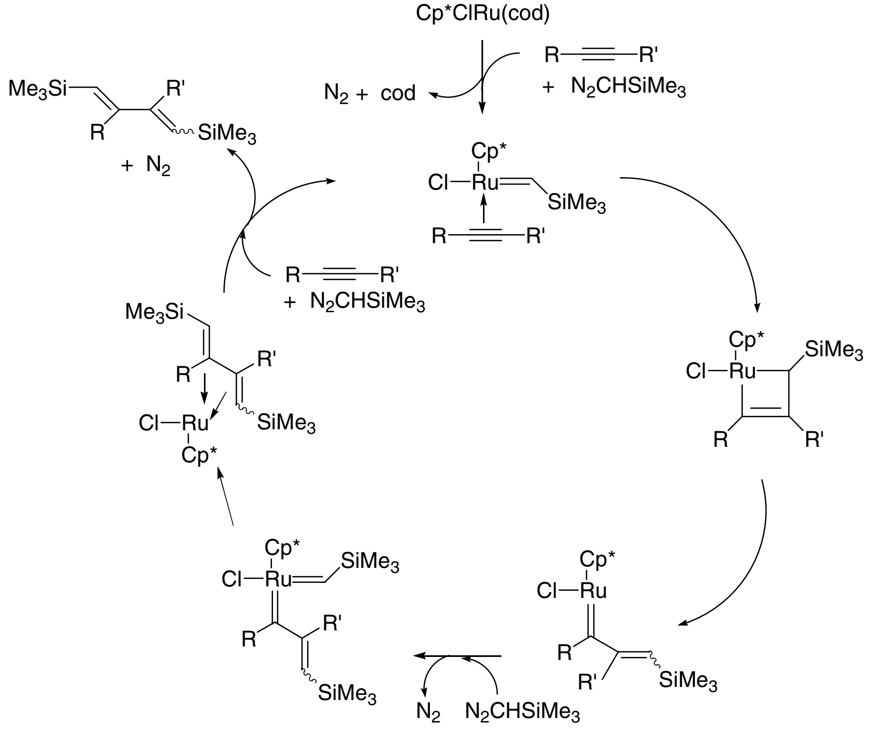


(21)

A possible mechanism for this selective formation of 1,4-bistrimethylsilylbutadiene derivatives is shown in Scheme 3.

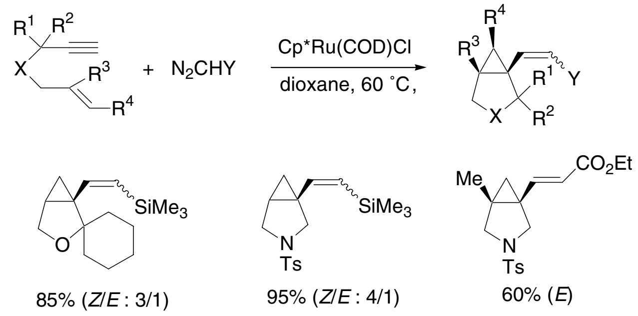
5.2. Diazoalkane addition to enynes: catalytic synthesis of alkenylbicyclo[3.1.0]hexane derivatives

The previous reaction has been applied to enynes and has led to the discovery of a new catalytic reaction. This one-step reaction of enynes with diazoalkane, catalysed by $RuCl(COD)C_5Me_5$ involves the selective formation of three C–C bonds including a cyclopropanation step and directly leads to alkenylbicyclo[3.1.0]hexane derivatives [43].



Scheme 3.

The reaction performed with enynes that contain oxygen selectively afforded the bicyclic products after 20–48 h at 60 °C in dioxane. The enynes that contain a TsN bridge are more reactive and have led to the corresponding bicycles in good yields after 1–2 h. The configuration of the double bond depends on the nature of the diazo compound and the nature of the substituents of the enyne (Eq. (22)) [43]

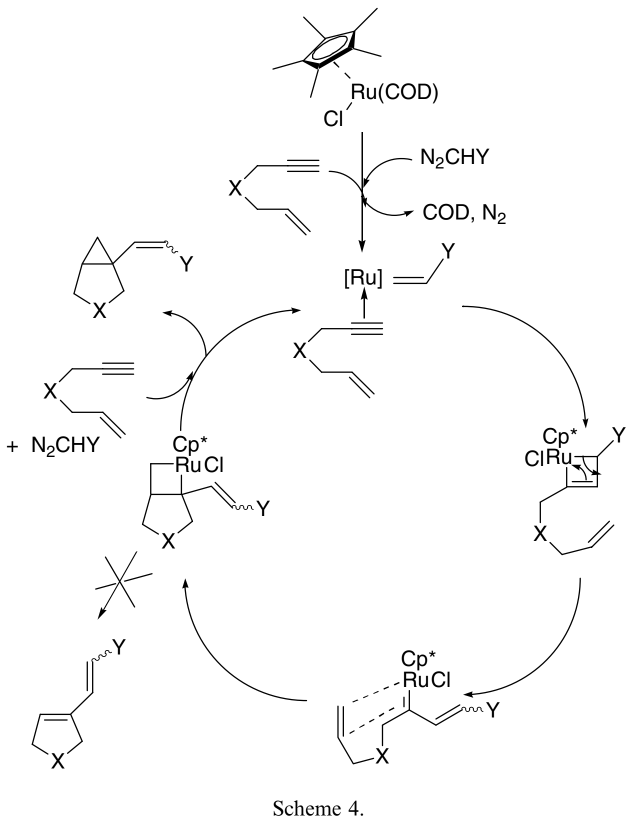


(22)

Thus the presence of a double C=C bond in the catalytic intermediate inhibits the double addition to the triple bond. The mechanism of the reaction can be explained according to Scheme 4. The novelty of this catalytic reaction is related to the last step: a promoted reductive elimination rather than the classical formation of the enyne metathesis product.

This reaction appears to be the first catalytic version of the stoichiometric Hoye–Harvey reaction [44,45]. Indeed, the stoichiometric reaction of enynes with metal–carbene complexes [$(OC)_5M{=}C(OR)R'$] derivatives of chromium [44] and molybdenum [45] have been shown to lead to the synthesis of bicyclic derivatives with a cyclopropane moiety.

More recently, the stoichiometric formation of alkenylbicyclo[3.1.0]hexane derivatives was observed by Mori and coworkers [46] with [$RuCl_2(=CHPh)(PCy_3)$(heterocyclic carbene)] and enyne as a side reaction of the catalytic enyne metathesis.



Scheme 4.

6. Conclusion

The above reactions illustrate new selective transformations of alkynes catalysed by the RuCl(COD)C_5Me_5 precursor, most of them taking place with atom economy. The activation processes usually involve the oxidative coupling of cross C≡C and C=C bonds or that of two C≡C bonds. It is striking that several catalytic species are actually carbene–ruthenium species such as RuCl(biscarbene)C_5Me_5 arising from the dimerisation of alkynes and RuCl(=CHR)C_5Me_5 or RuCl(=C(R)–C(R)=CHR)C_5Me_5 arising from the initial interaction of RuCl(COD)C_5Me_5 with diazoalkane and insertion of alkyne into alkylidene–ruthenium species. Whereas a variety of stoichiometric transformations of metal–carbene complexes to generate complex organic molecules are well-known, the involvement of carbene–metal species in catalytic reactions is more scarce except for alkene metathesis and cyclopropanation. The above catalytic transformations thus constitute a contribution to the increasing field of carbene metal species in catalysis.

Acknowledgements

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