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Intramolecular carbon–carbon coupling reactions of a $\kappa^2(P,P)$-bis(diphenylphosphino)methanide ligand with unsaturated carbene moieties in indenyl–ruthenium(II) complexes

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Dedicated to Professor J. Barluenga on the occasion of his 60th birthday

Abstract

Treatment of disubstituted indenyl–ruthenium(II) vinylidene complexes $[Ru\{=C=C(Me)R\}(\eta^5\text{-}C_9H_7)(dppm)][CF_3SO_3]$ (R = ^{t}Bu (**4a**), Ph (**4b**); dppm = bis(diphenylphosphino)methane) with NaOMe results in the deprotonation of the coordinated dppm ligand to give a $\kappa^2(P,P)\text{-}(Ph_2P)_2CH$ ligand. Subsequent intramolecular nucleophilic attack of the methanide group on the electrophilic vinylidene α-carbon gives the alkenyl metallacycles (*Z*)-$[Ru\{\kappa^3(C,P,P)\text{-}C=C(Me)R(Ph_2PCHPPh_2)\}(\eta^5\text{-}C_9H_7)]$ (R = ^{t}Bu (**6a**), Ph (**6b**)). The related metallacycle species $[Ru\{\kappa^3(C,P,P)\text{-}C(OMe)=C(H)C(H)R(Ph_2PCHPPh_2)\}(\eta^5\text{-}C_9H_7)]$ (R = H (**11a**), Ph (**11b**)) have also been prepared. They have been obtained through an analogous carbon–carbon coupling process involving the bisdiphenylphosphino)methanide anion, generated by the treatment of the α,β-unsaturated methoxy–carbene derivatives $[Ru\{=C(OMe)C(H)=C(H)R\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ (R = H (**9a**), Ph (**9b**)) and Li^{t}Bu, and the C_γ atom of the unsaturated carbene ligand. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Vinylidene complexes; α,β-Unsaturated carbene complexes; Alkenyl complexes; Indenyl; Ruthenium; C–C-couplings

1. Introduction

A great deal of attention has been devoted to the chemistry of transition-metal vinylidene complexes $[M]=C=R_2$ during the last two decades [1]. The interest in these species arises not only from the structural properties and the versatile reactivity modes but also because they play an important role in a large number of catalytic processes involving selective transformations of terminal alkynes [2], as well as in ring-opening metathesis polymerization (ROMP) of olefins [3]. The rapid development of this chemistry is based mainly on their relatively facile accessibility since several synthetic methodologies are now available [1]. The chemical behavior, in accordance with theoretical calculations [4], is governed mainly by the marked electrophilic character of the C_α atom. Thus, a large variety of neutral and anionic nucleophiles can be regioselectively added at this carbon atom affording among other species alkenyl $[M]\text{–}C(Nu)=CR_2$, acyl $[M]\text{–}C(=O)\text{–}CHR_2$, and Fischer type carbene derivatives $[M]=C(X)\text{–}CHR_2$ ($X = OR'$, NR'_2) [1].

In the course of our investigations dealing with the synthesis and reactivity of indenyl ($\eta^5\text{-}C_9H_7$) complexes of Group 8 metals [5], we have reported the preparation of a wide series of ruthenium(II) vinylidene derivatives of the type $[Ru\{=C=C(H)R\}(\eta^5\text{-}C_9H_7)L_2][PF_6]$ ($L = PPh_3$; L_2 = 1,2-bis(diphenylphosphino)ethane (dppe), bis(diphenylphosphino)methane (dppm)) [4c,6] and $[Ru\{=C=C(Me)R\}(\eta^5\text{-}C_9H_7)L_2][CF_3SO_3]$ ($R \neq H$) [4c, 6a]. A large variety of analogous functionalized vinylidene derivatives $[Ru\{=C=C(H)CRR'(Nu)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ have been synthesized also while studying the chemical behavior of allenylidene complexes $[Ru(=C=C=CRR')(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ towards nucleophiles [6,7]. In accordance with the expected electrophilic

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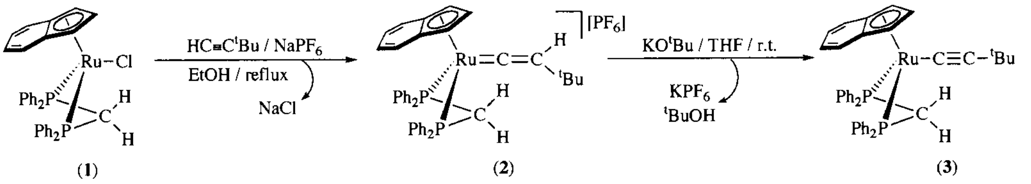
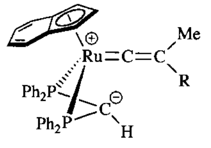


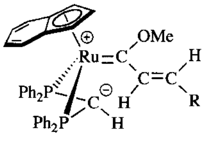
Scheme 1.

nature of the C_α atom of these vinylidene species, and selecting properly both the substituents on the vinylidene chain and the ancillary ligands, alcohols and amines can be added at this position leading to the formation of alkoxy- and amino-carbene derivatives $[Ru\{=C(X)\text{-}C(H)RR'\}(\eta^5\text{-}C_9H_7)L_2]^+$ ($X = OR'$, NH_2) [4c]. In contrast, the nucleophilic addition of PPh_3 to alkenyl–vinylidene complexes $[Ru\{=C=C(H)R\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R = 1-cyclohexenyl, 1-cycloheptenyl) follows a different path since phosphonio–alkenyl complexes $[Ru\{C(H)=C(PPh_3)R\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ are obtained [6a]. Furthermore, we have also reported that the vinylidene ligand in monosubstituted species $[Ru\{=C=C(H)R\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ is labile being replaced easily by acetonitrile to afford the corresponding terminal alkyne and $[Ru(N\equiv CMe)(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ [6c,7g].

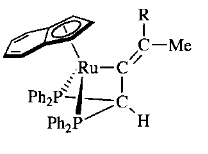
Continuing with our reactivity studies on the nucleophilic additions on vinylidene indenyl–ruthenium(II) complexes and related unsaturated carbene complexes, in this paper we report: (i) The formation of transient species **A** and **B** which are generated in situ via deprotonation of the coordinated dppm ligand in vinylidene complexes $[Ru\{=C=C(Me)R\}(\eta^5\text{-}C_9H_7)(dppm)][CF_3SO_3]$ ($R = {}^tBu$, Ph) and methoxy–carbene complexes $[Ru\{=C(OMe)\text{-}C(H)=C(H)R\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ (R = H, Ph) [7a], respectively. (ii) The synthesis of alkenyl metallacyclic derivatives (*Z*)-**C** and related metallacycles **D** resulting from the intramolecular C–C coupling of the nucleophilic methanide site in **A** or **B** with the vinylidene and the unsaturated carbene chain, respectively. (iii) The thermal isomerization of the alkenyl (*Z*)-**C** derivatives which leads to the corresponding stereoisomers (*E*)-**C**. The synthesis of the vinylidene precursor $[Ru\{=C=C(Me){}^tBu\}(\eta^5\text{-}C_9H_7)(dppm)][CF_3SO_3]$ is also described.



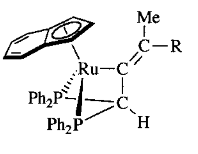
(A)



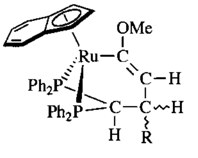
(B)



[(*Z*)-C]



[(*E*)-C]



(D)

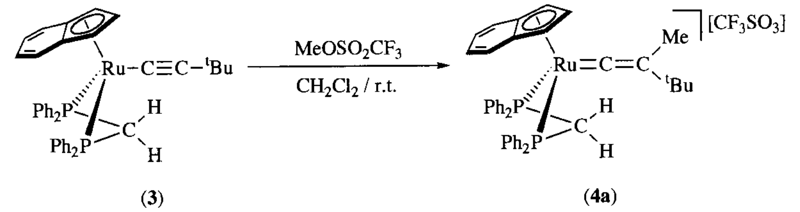
2. Results and discussion

2.1. Preparation of the precursor vinylidene complexes *$[Ru\{=C=C(R){}^tBu\}(\eta^5\text{-}C_9H_7)(dppm)]^+$ (R = H (**2**), Me (**4a**))*

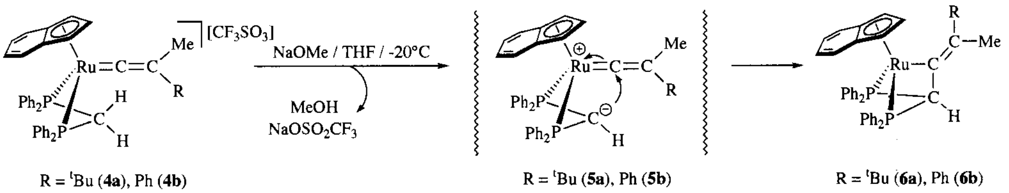
Following the standard synthetic procedure used for the preparation of analogous monosubstituted indenyl–ruthenium(II) vinylidene derivatives $[Ru\{=C=C(H)R\}\text{-}(\eta^5\text{-}C_9H_7)L_2][PF_6]$ ($L = PPh_3$; L_2 = dppe, dppm) [4c,6], the novel vinylidene complex $[Ru\{=C=C(H){}^tBu\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ (**2**) has been obtained as an air stable orange solid (70% yield) by treatment of $[RuCl(\eta^5\text{-}C_9H_7)(dppm)]$ (**1**) [8] with an excess of 3,3-dimethyl-1-butyne and $NaPF_6$ in refluxing ethanol (Scheme 1). The unequivocal characterization of **2** was achieved by means of standard spectroscopic techniques (IR and $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$-NMR) as well as elemental analyses (see Section 4 for details). In particular, the presence of the vinylidene moiety was identified, as usual, on the basis of: (i) (^1H-NMR) the triplet resonance ($^4J_{HP} = 2.4$ Hz) at 3.28 ppm of the Ru=C=CH proton; and (ii) ($^{13}C\{^1H\}$-NMR) the typical low-field resonance of the carbenic C_α which appears as a triplet at 350.85 ppm ($^2J_{CP} = 15.2$ Hz).

The proposed structure for **2** was also assessed by studying its reactivity. Thus, the acidic vinylidene proton can be abstracted easily by treatment of a THF solution with KO^tBu to afford the neutral σ-alkynyl complex $[Ru(C\equiv C{}^tBu)(\eta^5\text{-}C_9H_7)(dppm)]$ (**3**) (80% yield) (Scheme 1). Spectroscopic data (see Section 4) of **3** are similar to those reported for related indenyl–ruthenium(II) σ-alkynyl derivatives $[Ru(C\equiv CR)(\eta^5\text{-}C_9H_7)L_2]$ ($L = PPh_3$; L_2 = dppe, dppm) [4c,6,7,9]. Significantly, the IR spectrum exhibits the expected $\nu(C\equiv C)$ absorption band at 2097 cm^{-1}, and the $^{13}C\{^1H\}$-NMR spectrum shows characteristic resonances for the Ru–C_α and C_β carbon atoms at 88.30 (t, $^2J_{CP} = 24.2$ Hz) and 118.54 (s) ppm, respectively.

The addition of electrophiles at the β-position of σ-alkynyl complexes [M]–C≡C–R has been described as a versatile entry into vinylidene derivatives for a wide variety of systems [1]. Accordingly, complex **3** reacts with one equivalent of methyl trifluoromethanesulfonate, in dichloromethane at room temperature (r.t.), to yield the disubstituted vinylidene derivative $[Ru\{=C=C(Me){}^tBu\}(\eta^5\text{-}C_9H_7)(dppm)][CF_3SO_3]$ (**4a**) (85% yield) (Scheme 2). Analytical and spectroscopic



Scheme 2.



Scheme 3.

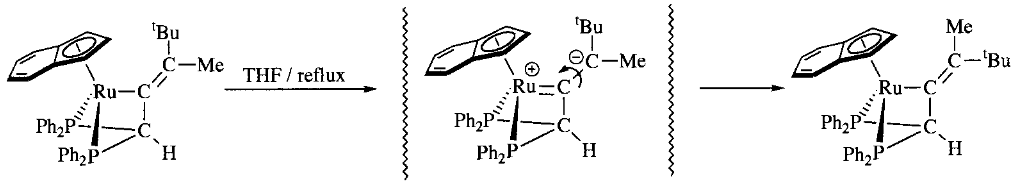
data support the proposed formulation (see Section 4). In particular, the most remarkable features in the $^{13}C\{^1H\}$-NMR spectrum are: (i) a triplet resonance ($^2J_{CP}$ = 14.8 Hz) for the Ru=C_α carbon nucleus (354.90 ppm); and (ii) singlet signals for the C_β (124.37 ppm) and methyl (4.53 ppm) carbon nuclei.

2.2. Synthesis of metallacyclic derivatives $[Ru\{\kappa^3(C,P,P,)\text{-}C{=}C(Me)R(Ph_2PCHPPh_2)\}\eta^5\text{-}C_9H_7)]$ ($R = {}^tBu$ (**4a**), Ph (**4b**))

Vinylidene complexes $[Ru\{{=}C{=}C(Me)R\}(\eta^5\text{-}C_9H_7)(dppm)][CF_3SO_3]$ (R = ᵗBu (**4a**), Ph (**4b**) [4c]) react with NaOMe, in tetrahydrofuran at −20°C, to furnish yellow solutions from which the alkenyl metallacycles (*Z*)-$[Ru\{\kappa^3(C,P,P,)\text{-}C{=}C(Me)R(Ph_2PCHPPh_2)\}\text{-}(\eta^5\text{-}C_9H_7)]$ (R = ᵗBu (**6a**), Ph (**6b**)) have been isolated in 64 and 58% yield, respectively (Scheme 3).

These novel metallacyclic derivatives have been obtained as air stable yellow solids. They have been characterized by microanalysis, and infrared and NMR ($^{31}P\{^1H\}$, ^1H, $^{13}C\{^1H\}$) spectroscopy in which all data are fully consistent with the presence of a 1-ruthena-2,4-diphosphabicyclo[1.1.1]pentane ring in the molecular skeleton (details are given in Section 4). Thus, the $^{31}P\{^1H\}$-NMR spectra exhibit a singlet line (−1.40 (**6a**) and 0.83 (**6b**) ppm) in accordance with the chemical equivalence of the two phosphorus atoms, and the ^1H-NMR spectra display, in addition to the expected indenyl and aromatic proton resonances, two triplet signals for the methyl and $(Ph_2P)_2CH$ protons in the ranges 1.56–1.93 ppm (approximately $^5J_{HP}$ = 7.5 Hz) and 5.95–6.10 ppm (approximately $^2J_{HP}$ = 3.7 Hz), respectively. $^{13}C\{^1H\}$-NMR spectra are very informative since they show the disappearance of the typical low-field vinylidene α-carbon resonance of **4a**,**b** (aproximately 356 ppm ($^2J_{CP}$ = 15 Hz)) and the appearance of a novel triplet signal at approximately 200 ppm higher fields (**6a**: 142.28 ppm ($^2J_{CP}$ = 15.5 Hz); **6b**: 151.17 ppm ($^2J_{CP}$ = 6.2 Hz)). These chemical shifts, which are similar to those found in alkenyl derivatives $[Ru\{C(R){=}C(H)R'\}(\eta^5\text{-}C_9H_7)(dppm)]$ [10], confirm clearly that a nucleophilic addition at the α-carbon of the vinylidene group has occurred giving rise to a loss of the sp character of this carbon. Triplet resonances for the $=C_\beta$ ($^3J_{CP}$ = 9.7–15.8 Hz) and $(Ph_2P)_2CH$ (J_{CP} = 22.0–24.3 Hz) atoms are also observed at approximately 135 and 70 ppm, respectively. It is worth mentioning that the proposed *Z* stereochemistry for the carbon–carbon double bond in these complexes (methyl group *trans* to ruthenium) has been assigned on the basis of NOE experiments. Thus, irradiation of the $(Ph_2P)_2CH$ proton signal results, in both cases, in the intensity enhancement of the methyl group resonance.

The formation of complexes **6a**,**b** seems to be the result of an initial deprotonation of one of the methylenic protons on the coordinated dppm ligand of **4a**,**b** to afford zwitterionic intermediates **5a**,**b** which evolve through a favorable intramolecular addition of the methanide carbon atom at the electrophilic α-position of the vinylidene group (Scheme 3). We note that no products arising from the nucleophilic attack of the methoxide anion at the Ru=C_α of **4a**,**b** were detected by NMR spectroscopy. This unusual reactivity has precedents in the literature. Thus, we have reported the preparation of similar cyclopentadienyl iron(II) derivatives (*E*)-$[Fe\{\kappa^3(C,P,P,)\text{-}C{=}C(Me)R(Ph_2PCHPPh_2)\}(\eta^5\text{-}C_5H_5)]$ (R = ᵗBu, Ph) which were obtained through the same reaction pathway starting from vinylidenes $[Fe\{{=}C{=}C(Me)R\}(\eta^5\text{-}C_5H_5)(dppm)][CF_3SO_3]$ [11]. The existence of a metallacyclic moiety in complexes **6a**,**b** is also confirmed on the basis of the analogy of their NMR data with those of the iron derivatives for which a X-ray crystal structure has been



Scheme 4.

determined. More recently, the related allenyl-metallacycle [Ru{κ^3($C,P,P,$)-C=CPh$_2$(Ph$_2$PCHPPh$_2$)}(η^5-C$_9$H$_7$) has been prepared also in our group via dppm deprotonation and subsequent intramolecular C–C coupling on the diphenylallenylidene complex [Ru(=C=C=CPh$_2$)(η^5-C$_9$H$_7$)(dppm)][PF$_6$] [7b].

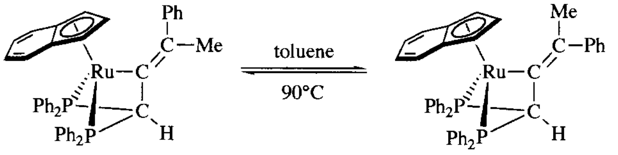
Although complex **6a** is stable in solution at r.t., it rearranges slowly in refluxing THF to generate the thermodynamically more stable *E* isomer **8a** (95% isolated yield) (Scheme 4) [12]. A plausible mechanism for this isomerization, which seems to be promoted by the steric requirements of the close indenyl and ^{t}Bu bulky groups, is shown in Scheme 4 [13]. Analytical and spectroscopic data for complex **8a** (IR and ^{31}P{^{1}H}, ^{1}H and ^{13}C{^{1}H}-NMR) are in accordance with the proposed structure being comparable to those found for **6a** (see Section 4). We note, in particular, the presence of triplet signals in the ^{1}H and ^{13}C{^{1}H}-NMR spectra at 6.29 ($^2J_{HP} = 3.8$ Hz) and 71.68 ($J_{CP} = 22.6$ Hz) ppm, respectively attributed to the (Ph$_2$P)*CH* unit.

In contrast to **6a**, alkenyl complex **6b** does not isomerize into the corresponding *E* stereoisomer **8b** in refluxing THF (Scheme 5). Only a partial isomerization, to yield a non-separable mixture of complexes **6b** and **8b** in a approximately 3:2 ratio, was observed when a toluene solution of **6b** was heated at 90°C for 6 h. These species seem to be in equilibrium in solution since the same molecular ratio was obtained when larger reaction times or higher temperatures were used. Apparently, the steric hindrance between the indenyl ligand and the C$_\beta$ substituents decrease strongly when the ^{t}Bu unit is replaced by the smaller phenyl group preventing therefore the total isomerization of the carbon–carbon double bond. IR and NMR data of complex **8b** are collected in Section 4 supporting the proposed formulation.

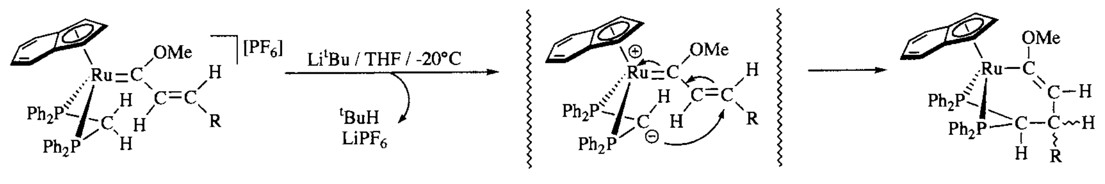
2.3. *Synthesis of metallacyclic complexes [Ru{κ^3(C,P,P)-C(OMe)=C(H)C(H)R(Ph$_2$PCHPPh$_2$)}-(η^5-C$_9$H$_7$) (R = H (**11a**), Ph (**11b**))*

Since the deprotonation of the coordinated dppm ligand in vinylidene and allenylidene [7b] indenyl–ruthenium(II) complexes has been found to occur easily yielding rare coupling products, we became interested in extending this unusual reactivity to other functionalized indenyl–ruthenium(II) carbene derivatives. In particular, we explored the behavior of the readily available α,β-unsaturated methoxy–carbene derivatives [Ru{=C(OMe)C(H)=C(H)R}(η^5-C$_9$H$_7$)(dppm)][PF$_6$] (R = H (**9a**), Ph (**9b**)) [7a] towards deprotonating reagents since the presence of two electrophilic centers in the unsaturated hydrocarbon chain (C$_\alpha$ and C$_\gamma$) offers two different possibilities of C–C coupling [14]. We have found that by treating a THF solution of complexes **9a**,**b** with a slight excess of Li^{t}Bu at −20°C the unprecedented metallacycles [Ru{κ^3(C,P,P)-C(OMe)=C-(H)C(H)R(Ph$_2$PCHPPh$_2$)}(η^5-C$_9$H$_7$)] (R = H (**11a**), Ph (**11b**)) are formed (63–68% yield) through the regioselective nucleophilic attack of the bis(diphenylphosphino)methanide anion at the C$_\gamma$ atom of the carbenic moiety in the zwitterionic intermediates **10** (Scheme 6). This result seems to indicate the presence of a remarkable lower electron density on the γ-position of the alkenyl–carbene chain when compared to the carbenic Ru=C$_\alpha$ carbon atom [15].

Complexes **11** have been isolated as yellow air-stable solids and their structures elucidated by NMR spectroscopy (details are given in the Section 4). Thus, while the ^{31}P{^{1}H}-NMR spectrum of **11a** shows a singlet resonance at 29.38 ppm indicating the chemical equivalence of both phosphorus nuclei, an AB system is observed for complex **11b** (31.38 and 35.92 ppm ($^2J_{PP} = 85.7$ Hz)) due to the presence of a stereogenic carbon atom on the metallacycle. These ^{31}P chemical shifts, which are approximately 30 ppm deshielded when compared to those found for complexes **6** and **8**, strongly support the formation of a larger ring [16]. ^{1}H and ^{13}C{^{1}H}-NMR spectra give also evidence of the



Scheme 5.



R = H (**9a**), Ph (**9b**) R = H (**10a**), Ph (**10b**) R = H (**11a**), Ph (**11b**)

Scheme 6.

formation of a six-membered metallacycle. Remarkable features are: (i) (^{1}H-NMR) characteristic $(Ph_2P)_2CH$ resonances (3.9 ppm) which appear as a triplet of triplets ($^2J_{HP} = 12.1$ Hz, $J_{HH} = 6.9$ Hz) for **11a** or as a multiplet for **11b**; and (ii) ($^{13}C\{^1H\}$-NMR) typical signals for the Ru–C_α (**11a**: 182.61 ppm (t, $^2J_{CP} = 21.7$ Hz); **11b**: 183.00 ppm (dd, $^2J_{CP} = 20.8$, $^2J_{CP'} = 19.5$ Hz)), =C_βH (**11a**: 96.49 ppm (s); **11b**: 98.20 ppm (dd, $^3J_{CP} = 6.3$, $^3J_{CP'} = 3.0$ Hz)) and $(Ph_2P)CH$ (**11a**: 55.53 ppm (t, $J_{CP} = 21.3$ Hz); **11b**: 61.55 ppm (dd, $J_{CP} = 20.7$, $J_{CP'} = 17.1$ Hz)) carbon atoms. We note also the presence of singlet resonances for the CH_2 (**11a**: 28.73 ppm) and *C*HPh (**11b**: 42.45 ppm) carbons the former being assigned using DEPT experiments.

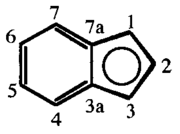
3. Conclusions

In summary, in this paper we have demonstrated that indenyl–ruthenium(II) vinylidene and α,β-unsaturated Fischer type carbene derivatives containing a coordinated dppm ligand are excellent substrates for the high yield preparation of original metallacyclic structures formed via intramolecular carbon–carbon coupling reactions. The synthetic approach involves the in situ formation of a coordinated $\kappa^2(P,P)$-bis(diphenylphosphino)methanide moiety through the deprotonation of the dppm ligand in the precursor complexes. Its subsequent regioselective nucleophilic attack at one electrophilic site of the unsaturated hydrocarbon chain gives rise the metallacycle species. Further studies concerning the reactivity of these metallacycles are currently in progress.

4. Experimental

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The compounds $[RuCl(\eta^5\text{-}C_9H_7)(dppm)]$ (**1**) [8], $[Ru\{=C=C(Me)Ph\}(\eta^5\text{-}C_9H_7)(dppm)][CF_3SO_3]$ (**4b**) [4c] and $[Ru\{=C(OMe)\text{-}C(H)=C(H)R\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ (R = H (**9a**), Ph (**9b**)) [7a] were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin–Elmer 1720-XFT spectrometer. Conductivities were measured at r.t., in approximately 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. The C and H analyses were carried out with a Perkin–Elmer 240-B microanalyzer (uncompleted combustions were systematically observed for all the complexes reported). Mass spectra (FAB) were recorded using a VG Autospec spectrometer, operating in the positive ion mode; 3-nitrobenzyl alcohol was used as the matrix. NMR spectra were recorded on a Bruker AC300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P) or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the complexes. Abbreviations used: br, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; dt, doublet of triplets; tt, triplet of triplets; m, multiplet.

The numbering for the indenyl skeleton is as follows:



4.1. Synthesis of $[Ru\{=C=C(H)^tBu\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ (2)

A mixture of complex $[RuCl(\eta^5\text{-}C_9H_7)(dppm)]$ (**1**) (0.636 g, 1 mmol), $NaPF_6$ (0.336 g, 2 mmol) and 3,3-dimethyl-1-butyne (0.615 ml, 5 mmol) in ethanol (30 ml) was heated under reflux for 15 min. The resulting orange solution was evaporated to dryness and the solid residue dissolved in dichloromethane (5 ml) and filtered. Addition of 100 ml of diethyl ether precipitated an orange solid which was washed with diethyl ether (3 × 20 ml) and vacuum-dried. Yield: 70% (0.579 g); conductivity: 119 Ω^{-1} cm^2 mol^{-1}; Anal. Calc. for $RuC_{40}H_{39}F_6P_3$ (827.73): C, 58.04; H, 4.71. Found: C, 57.83; H, 4.71%; IR (KBr, cm^{-1}): 838 $\nu(PF_6^-)$, 1618 ν(=C=C); $^{31}P\{^1H\}$-NMR ($CDCl_3$) 5.82 (s) ppm; ^{1}H-NMR ($CDCl_3$) 0.51 (s, 9H, $C(CH_3)_3$), 3.28 (t, 1H, $^4J_{HP} = 2.4$ Hz, =CH), 4.48 (dt, 1H, $J_{HH} = 14.7$ Hz,

$^2J_{HP} = 12.6$ Hz, PCH_aH$_b$P), 4.90 (dt, 1H, $J_{HH} = 14.7$, $^2J_{HP} = 10.2$ Hz, PCH$_a$$H_b$P), 5.82 (t, 1H, $J_{HH} = 2.7$ Hz, H-2), 6.10 (d, 2H, $J_{HH} = 2.7$ Hz, H-1,3), 7.04–7.56 (m, 24H, H-4,7, H-5,6 and Ph) ppm; ^{13}C{^{1}H}-NMR (CDCl$_3$) 31.50 (s, C(CH$_3$)$_3$), 31.80 (s, C(CH$_3$)$_3$), 45.26 (t, $J_{CP} = 27.7$ Hz, PCH$_2$P), 78.57 (s, C-1,3), 95.11 (s, C-2), 110.93 (s, C-**3a**,**7a**), 123.00 and 127.97 (s, C-4,7 and C-5,6), 125.88 (s, C$_\beta$), 129.19–131.97 (m, Ph), 350.85 (t, $^2J_{CP} = 15.2$ Hz, Ru=C$_\alpha$) ppm. Δδ (C-**3a**,**7a**) = −19.77 ppm.

4.2. Synthesis of [Ru(C≡C^{t}Bu)(η^5-C$_9$H$_7$)(dppm)] (**3**)

A solution of complex [Ru{=C=C(H)^{t}Bu}(η^5-C$_9$H$_7$)(dppm)][PF$_6$] (**2**) (0.828 g, 1 mmol) in THF (15 ml) was treated with KO^{t}Bu (0.123 g, 1.1 mmol) and the mixture stirred at r.t. for 30 min. The solution was then evaporated to dryness and the solid residue extracted with diethyl ether (approximately 100 ml) and filtered. Evaporation of the solvent affords **3** as a yellow solid. Yield: 80% (0.545 g); Anal. Calc. for RuC$_{40}$H$_{38}$P$_2$ (681.76): C, 70.48; H, 5.58. Found: C, 69.95; H, 5.50%; IR (KBr, cm^{-1}): 2097 ν(C≡C); ^{31}P{^{1}H}-NMR (CDCl$_3$) 20.01 (s) ppm; ^{1}H-NMR (CDCl$_3$) 0.43 (s, 9H, C(CH$_3$)$_3$), 4.17 (dt, 1H, $J_{HH} = 13.5$, $^2J_{HP} = 12.0$ Hz, PCH_aH$_b$P), 4.57 (dt, 1H, $J_{HH} = 13.5$, $^2J_{HP} = 9.3$ Hz, PCH$_a$$H_b$P), 5.21 (t, 1H, $J_{HH} = 2.5$ Hz, H-2), 5.29 (d, 2H, $J_{HH} = 2.5$ Hz, H-1,3), 6.94 (m, 2H, H-4,7 or H-5,6), 7.18–7.42 (m, 22H, H-4,7 or H-5,6 and Ph) ppm; ^{13}C{^{1}H}-NMR (CDCl$_3$) 28.84 (s, C(CH$_3$)$_3$), 32.08 (s, C(CH$_3$)$_3$), 49.89 (t, $J_{CP} = 23.7$ Hz, PCH$_2$P), 67.09 (s, C-1,3), 88.30 (t, $^2J_{CP} = 24.2$ Hz, Ru–C$_\alpha$), 88.58 (s, C-2), 106.18 (s, C-**3a**,**7a**), 118.54 (s, C$_\beta$), 122.40 and 124.50 (s, C-4,7 and C-5,6), 127.06–139.14 (m, Ph) ppm. Δδ (C-**3a**,**7a**) = −24.52 ppm.

4.3. Synthesis of [Ru{=C=C(Me)^{t}Bu}(η^5-C$_9$H$_7$)(dppm)][CF$_3$SO$_3$] (**4a**)

A solution of the σ-alkynyl complex [Ru(C≡C^{t}Bu)(η^5-C$_9$H$_7$)(dppm)] (**3**) (0.682 g, 1 mmol) in dichloromethane (15 ml) was treated dropwise, at r.t., with MeOSO$_2$CF$_3$ (0.11 ml, 1 mmol) and stirred for 1 h. The resulting solution was then concentrated to approximately 5 ml. Addition of 100 ml of diethyl ether precipitated an orange solid which was washed with diethyl ether (3 × 20 ml) and vacuum-dried. Yield: 85% (0.718 g); conductivity: 129 Ω^{-1} cm^2 mol^{-1}; Anal. Calc. for RuC$_{42}$H$_{40}$F$_3$O$_3$P$_2$S (844.85): C, 59.71; H, 4.77. Found: C, 59.50; H, 4.85%; IR (KBr, cm^{-1}): 1149, 1223 and 1265 ν(CF$_3$SO$_3^-$), 1618 ν(=C=C); ^{31}P{^{1}H}-NMR (CDCl$_3$) 6.05 (s) ppm; ^{1}H-NMR (CDCl$_3$) 0.51 (s, 9H, C(CH$_3$)$_3$), 0.72 (s, 3H, CH$_3$), 4.42 (dt, 1H, $J_{HH} = 14.0$, $^2J_{HP} = 12.3$ Hz, PCH_aH$_b$P), 4.85 (dt, 1H, $J_{HH} = 14.0$, $^2J_{HP} = 10.3$ Hz, PCH$_a$$H_b$P), 5.93 (t, 1H, $J_{HH} = 2.6$ Hz, H-2), 6.07 (d, 2H, $J_{HH} = 2.6$ Hz, H-1,3), 6.88–7.70 (m, 24H, H-4,7, H-5,6 and Ph) ppm; ^{13}C{^{1}H}-NMR (CDCl$_3$) 4.53 (s, CH$_3$), 29.13 (s, C(CH$_3$)$_3$), 32.70 (s, C(CH$_3$)$_3$), 44.13 (t, $J_{CP} = 27.6$ Hz, PCH$_2$P), 78.37 (s, C-1,3), 93.36 (s, C-2), 110.61 (s, C-**3a**,**7a**), 124.37 (s, C$_\beta$), 124.51 and 127.68 (s, C-4,7 and C-5,6), 128.00–134.27 (m, Ph), 354.90 (t, $^2J_{CP} = 14.8$ Hz, Ru=C$_\alpha$) ppm. Δδ (C-**3a**,**7a**) = −20.09 ppm.

4.4. Synthesis of (Z)-[Ru{κ^3(C,P,P)-C=C(Me)R(Ph$_2$PCHPPh$_2$)}(η^5-C$_9$H$_7$)] (R = ^{t}Bu (**6a**), Ph (**6b**))

A solution of the corresponding vinylidene complex [Ru{=C=C(Me)R}(η^5-C$_9$H$_7$)(dppm)][CF$_3$SO$_3$] (R = ^{t}Bu (**4a**), Ph (**4b**)) (1 mmol) in THF (20 ml) was treated at −20°C with an excess of NaOMe (prepared in situ from MeOH (10 ml) and NaH (0.048 g, 2 mmol)). The reaction mixture stirred at r.t. for 1 h and then evaporated to dryness. The resulting solid residue was extracted with diethyl ether (50 ml) and filtered. Evaporation of the diethyl ether gave complexes **6** as yellow solids. (**6a**): Yield: 64% (0.445 g); Anal. Calc. for RuC$_{41}$H$_{40}$P$_2$ (695.78): C, 70.77; H, 5.79. Found: C, 71.43; H, 5.39%; IR (KBr, cm^{-1}): 1584 ν(C=C); ^{31}P{^{1}H}-NMR (C$_6$D$_6$) −1.40 (s) ppm; ^{1}H-NMR (C$_6$D$_6$) 1.18 (s, 9H, C(CH$_3$)$_3$), 1.56 (t, 3H, $^5J_{HP} = 7.4$ Hz, CH$_3$), 5.42 (d, 2H, $J_{HH} = 2.4$ Hz, H-1,3), 5.44 (t, 1H, $J_{HH} = 2.4$ Hz, H-2), 5.95 (t, 1H, $^2J_{HP} = 3.9$ Hz, PCHP), 6.64–7.73 (m, 20H, Ph), 6.85 and 7.46 (m, 2H each one, H-4,7 and H-5,6) ppm; ^{13}C{^{1}H}-NMR (C$_6$D$_6$) 17.58 (t, $^4J_{CP} = 6.7$ Hz, CH$_3$), 30.87 (t, $^5J_{CP} = 3.5$ Hz, C(CH$_3$)$_3$), 36.31 (t, $^4J_{CP} = 4.4$ Hz, C(CH$_3$)$_3$), 66.92 (t, $^2J_{CP} = 3.8$ Hz, C-1,3), 68.65 (t, $J_{CP} = 24.3$ Hz, PCHP), 91.43 (s, C-2), 102.17 (s, C-**3a**,**7a**), 122.13 and 126.81 (s, C-4,7 and C-5,6), 127.34–133.82 (m, Ph), 134.95 (t, $^3J_{CP} = 9.7$ Hz, =C), 142.28 (t, $^2J_{CP} = 15.5$ Hz, Ru–C$_\alpha$) ppm. Δδ (C-**3a**,**7a**) = −28.53 ppm. (**6b**): Yield: 58% (0.415 g); Anal. Calc. for RuC$_{43}$H$_{36}$P$_2$ (715.77): C, 72.16; H, 5.03. Found: C, 73.97; H, 5.20%; IR (KBr, cm^{-1}): 1594 ν(C=C); ^{31}P{^{1}H}-NMR (C$_6$D$_6$) 0.83 (s) ppm; ^{1}H-NMR (C$_6$D$_6$) 1.93 (t, 3H, $^5J_{HP} = 7.6$ Hz, CH$_3$), 4.35 (t, 1H, $J_{HH} = 2.4$ Hz, H-2), 5.30 (d, 2H, $J_{HH} = 2.4$ Hz, H-1,3), 6.10 (t, 1H, $^2J_{HP} = 3.6$ Hz, PCHP), 6.70–8.10 (m, 29H, H-4,7, H-5,6 and Ph) ppm; ^{13}C{^{1}H}-NMR (C$_6$D$_6$) 22.19 (t, $^4J_{CP} = 6.7$ Hz, CH$_3$), 68.48 (t, $^2J_{CP} = 4.4$ Hz, C-1,3), 71.35 (t, $J_{CP} = 22.0$ Hz, PCHP), 88.09 (t, $^2J_{CP} = 1.7$ Hz, C-2), 102.91 (s, C-**3a**,**7a**), 122.07 and 126.69 (s, C-4,7 and C-5,6), 127.48–137.93 (m, Ph), 135.11 (t, $^3J_{CP} = 15.8$ Hz, =C), 151.17 (t, $^2J_{CP} = 6.2$ Hz, Ru–C$_\alpha$) ppm. Δδ (C-**3a**,**7a**) = −27.79 ppm.

4.5. Synthesis of (E)-[Ru{κ^3(C,P,P)-C=C(Me)^{t}Bu(Ph$_2$PCHPPh$_2$)}(η^5-C$_9$H$_7$)] (**8a**)

A solution of **6a** (0.696 g, 1 mmol) in THF (15 ml) was heated under reflux for 24 h and then evaporated to dryness. The resulting yellow solid was washed with hexanes (2 × 5 ml) and dried in vacuo. Yield: 95% (0.661 g); Anal. Calc. for $RuC_{41}H_{40}P_2$ (695.78): C, 70.77; H, 5.79. Found: C, 71.60; H, 5.42%; IR (KBr, cm^{-1}): 1588 ν(C=C); $^{31}P\{^1H\}$-NMR (C_6D_6) 0.22 (s) ppm; ^1H-NMR (C_6D_6) 0.71 (s, 9H, $C(CH_3)_3$), 2.27 (t, 3H, $^5J_{HP} = 7.7$ Hz, CH_3), 5.56 (d, 2H, $J_{HH} = 2.3$ Hz, H-1,3), 5.60 (t, 1H, $J_{HH} = 2.3$ Hz, H-2), 6.29 (t, 1H, $^2J_{HP} = 3.8$ Hz, PCHP), 6.60–7.73 (m, 24H, H-4,7, H-5,6 and Ph) ppm; $^{13}C\{^1H\}$-NMR (C_6D_6) 27.64 (t, $^4J_{CP} = 5.8$ Hz, CH_3), 31.02 (t, $^5J_{CP} = 3.0$ Hz, $C(CH_3)_3$), 39.01 (t, $^4J_{CP} = 5.5$ Hz, $C(CH_3)_3$), 65.30 (t, $^2J_{CP} = 3.3$ Hz, C-1,3), 71.68 (t, $J_{CP} = 22.6$ Hz, PCHP), 80.58 (t, $^2J_{CP} = 1.8$ Hz, C-2), 99.28 (s, C-**3a**,**7a**), 121.45 and 124.80 (s, C-4,7 and C-5,6), 126.95–132.07 (m, Ph), 133.67 (t, $^3J_{CP} = 5.7$ Hz, =C), 140.68 (t, $^2J_{CP} = 15.4$ Hz, Ru–C_α) ppm. $\Delta\delta$ (C-**3a**,**7a**) = −31.42 ppm.

4.6. Spectroscopic characterization of (E)-[Ru{κ^3(C,P,P)-C=C(Me)Ph(Ph$_2$PCHPPh$_2$)}-(η^5-C$_9$H$_7$)] (**8b**)

A solution of **6b** (0.716 g, 1 mmol) in toluene (15 ml) was heated at 90°C for 6 h and then evaporated to dryness. The resulting yellow solid was washed with hexanes (2 × 5 ml) and dried in vacuo to yield a non separable mixture containing complexes **6b** and **8b** in approximately ratio 3:2 (0.690 g). IR and NMR data for **8b** are as follows: IR (KBr, cm^{-1}): 1592 ν(C=C); $^{31}P\{^1H\}$-NMR (C_6D_6) 1.93 (s) ppm; ^1H-NMR (C_6D_6) 2.64 (t, 3H, $^5J_{HP} = 8.4$ Hz, CH_3), 5.82 (d, 2H, $J_{HH} = 2.2$ Hz, H-1,3), 5.97 (t, 1H, $J_{HH} = 2.2$ Hz, H-2), 6.07 (t, 1H, $^2J_{HP} = 3.8$ Hz, PCHP), 6.50–8.00 (m, 29H, H-4,7, H-5,6 and Ph) ppm; $^{13}C\{^1H\}$-NMR (C_6D_6) 28.47 (t, $^4J_{CP} = 5.6$ Hz, CH_3), 66.49 (t, $^2J_{CP} = 3.6$ Hz, C-1,3), 72.27 (t, $J_{CP} = 22.0$ Hz, PCHP), 84.97 (s, C-2), 102.81 (s, C-**3a**,**7a**), 122.10 and 126.41 (s, C-4,7 and C-5,6), 125.49–137.50 (m, Ph and =C), 146.21 (t, $^2J_{CP} = 7.1$ Hz, Ru–C_α) ppm. $\Delta\delta$ (C-**3a**,**7a**) = −27.89 ppm.

4.7. Synthesis of [Ru{κ^3(C,P,P,)-C(OMe)=C(H)C(H)R(Ph$_2$PCHPPh$_2$)}(η^5-C$_9$H$_7$)] (R = H (**11a**), Ph (**11b**))

A solution of the corresponding alkenyl–methoxy–carbene complex [Ru{=C(OMe)C(H)=C(H)R}(η^5-C_9H_7)(dppm)][PF_6] (R = H (**9a**), Ph (**9b**)) (1 mmol) in THF (20 ml) was treated at −20°C with a slight excess of Li^{t}Bu (1.7 M in pentane) (0.7 ml, 1.2 mmol). The reaction mixture was stirred at r.t. for 1 h and then evaporated to dryness. The resulting solid residue was extracted with diethyl ether (50 ml) and filtered. Evaporation of the diethyl ether gave complexes **11** as yellow solids. (**11a**): Yield: 63% (0.422 g); Anal. Calc. for $RuC_{38}H_{34}OP_2$ (669.70): C, 68.15; H, 5.11. Found: C, 68.60; H, 5.20%; IR (KBr, cm^{-1}): 1577 ν(C=C); $^{31}P\{^1H\}$-NMR (C_6D_6) 29.38 (s) ppm; ^1H-NMR (C_6D_6) 1.94 (d, 2H, $J_{HH} = 6.9$ Hz, CH_2), 3.40 (s, 3H, OCH_3), 3.94 (tt, 1H, $^2J_{HP} = 12.1$, $J_{HH} = 6.9$ Hz, PCHP), 5.46 (m, 4H, H-1,3, H-2 and =CH), 6.65–7.53 (m, 24H, H-4,7, H-5,6 and Ph) ppm; $^{13}C\{^1H\}$-NMR (C_6D_6) 28.73 (s, CH_2), 55.53 (t, $J_{CP} = 21.3$ Hz, PCHP), 56.81 (s, OCH_3), 70.31 (s, C-1,3), 90.91 (s, C-2), 96.49 (s, =CH), 109.65 (s, C-**3a**,**7a**), 122.68 and 126.12 (s, C-4,7 and C-5,6), 128.10–138.97 (m, Ph), 182.61 (t, $^2J_{CP} = 21.7$ Hz, Ru–C_α) ppm. $\Delta\delta$ (C-**3a**,**7a**) = −21.05 ppm. (**11b**): Yield: 68% (0.507 g); Anal. Calc. for $RuC_{44}H_{38}OP_2$ (745.80): C, 70.86; H, 5.13. Found: C, 71.09; H, 5.29%; IR (KBr, cm^{-1}): 1553 ν(C=C); $^{31}P\{^1H\}$-NMR (C_6D_6) 31.38 (d, $^2J_{PP} = 85.7$ Hz), 35.92 (d, $^2J_{PP} = 85.7$ Hz) ppm; ^1H-NMR (C_6D_6) 3.65 (s, 3H, OCH_3), 3.93 (m, 1H, PCHP′), 4.79 (d, 1H, $J_{HH} = 2.8$ Hz, =CH), 5.50 (br, 2H, H-1 and H-3), 5.64 (m, 1H, CH), 5.83 (br, 1H, H-2), 6.73–7.75 (m, 29H, H-4,7, H-5,6 and Ph) ppm; $^{13}C\{^1H\}$-NMR (C_6D_6) 42.45 (s, CH), 55.08 (s, OCH_3), 61.55 (dd, $J_{CP} = 20.7$, $J_{CP} = 17.1$ Hz, PCHP′), 68.15 (d, $^2J_{CP} = 3.2$ Hz, C-1 or C-3), 68.79 (d, $^2J_{CP} = 4.1$ Hz, C-1 or C-3), 88.32 (s, C-2), 98.20 (dd, $^3J_{CP} = 6.3$, $^3J_{CP'} = 3.0$ Hz, =CH), 108.02 (s, C-**3a**,**7a**), 120.65–144.26 (m, C-4, C-5, C-6, C-7 and Ph), 183.00 (dd, $^2J_{CP} = 20.8$, $^2J_{CP'} = 19.5$ Hz, Ru–C_α) ppm. $\Delta\delta$ (C-**3a**,**7a**) = −22.68 ppm; MS (FAB): m/z 747 [$M^+ + 1$], 715 [$M^+ - OCH_3$].

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[13] Although the zwitterionic resonance form **7a** (see Scheme 4) seems to play a key role in the **6a**/**8a** isomerization, we note that all attempts to promote selective electrophilic additions (using HBF_4 or $MeOSO_2CF_3$) on the β-carbon of complexes **6**, in order to generate cationic carbenic species, were unsuccessful obtaining instead complicated mixtures of uncharacterized products.

[14] Fischer type alkenyl-carbene complexes $[M]{=}C(OR^1)C(R^2){=}CR^3R^4$ have shown a wide and versatile reactivity playing a burgeoning role in modern organic synthesis. For reviews see: (a) K.H. Dötz, in: A. de Meijere, H.T. Dieck, (Eds.), Organometallics in Organic Synthesis 1: Aspects of a Modern Interdisciplinary Field, Springer-Verlag, Berlin, 1987. (b) W.D. Wulff, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, vol. 5, Pergamon, New York, 1991, p. 1065. (c) L.S. Hegedus, Pure Appl. Chem. 62 (1990) 691. (d) M.J. Winter, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 5, Pergamon, Oxford, 1995, p. 155. (e) M.P. Doyle, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon, Oxford, 1995, p. 389. (f) W.D. Wulff, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon, Oxford, 1995, p. 469. (g) L.S. Hegedus, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, Pergamon, vol. 12, Oxford, 1995, p. 549. (h) J. Barluenga, Pure Appl. Chem. 68 (1996) 543. (i) F. Zaragoza Dörwald, Metal Carbenes in Organic Synthesis, Wiley-VCH, Weinheim, 1999.

[15] The thermodynamic stability of a six-membered ring towards a four-membered ring could be also responsible of the observed regioselectivity.

[16] P.E. Garrou, Chem. Rev. 81 (1981) 229.