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Preliminary Communication

Novel secondary allenylidene ruthenium complexes and preparation of *trans*-[(dppm)$_2$(H)Ru–C≡C–CH(OMe)R] derivatives *

Nadine Pirio, Daniel Touchard and Pierre H. Dixneuf

Laboratoire de Chimie de Coordination Organique (URA CNRS 415), campus de Beaulieu, Université de Rennes 1, 35042 Rennes (France)

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Abstract

cis-[(dppm)$_2$Cl$_2$Ru], **1** (dppm = $Ph_2PCH_2PPh_2$) reacts with H–C≡C–CH(OH)R and $NaPF_6$ to give *secondary* allenylidene complexes *trans*-[(dppm)$_2$ClRu=C=C=CHR][PF_6], **3** [R = Ph (**a**), *p*-Ph–Cl (**b**), *p*-PhOMe (**c**), or *trans*-CH=CHPh (**d**)]. Complex **3a** treated with $NaBH_4$ gives *trans*-[(dppm)$_2$ClRu–C≡C–CH_2Ph], **6a** and the reaction of **3a–c** with MeONa in MeOH affords *trans*-[(dppm)$_2$(H)Ru–C≡C–CH(OMe)R], **7a–c**.

1. Introduction

Allenylidene metal complexes have potential as precursors of new carbene derivatives [1] or metal-containing polymers [2,3]. They constitute a possible step toward allenes, *via* transfer of the allenylidene moiety to an organic molecule, and the influence of the allenylidene on the metal reactivity has not yet been shown. The most straightforward route to allenylidene metal complexes consists in the dehydration of propargylic alcohol derivatives promoted by ruthenium(II) complexes (eqn. (1)).

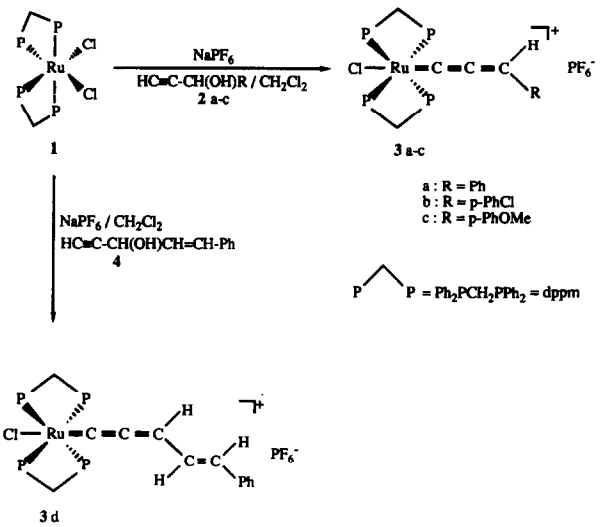
$$[M{-}X] + HC{\equiv}C{-}C(OH)R_2 \xrightarrow[H_2O]{} [M{=}C{=}C{=}CR_2]X \quad (1)$$

The first example was reported by Selegue [4] with [M–X] sequal to [$RuCl(PPh_3)_2C_5H_5$], but the allenylidene was stable only for R = Ph. Other examples have recently been reported from [$RuCl_2(PR_3)$(arene)] [5], [$N(CH_2CH_2PPh_2)_3RuCl_2$] [6], [$RuCl_2$(dppm)$_2$] [7]. They only involve *tertiary* propargylic alcohols, for substitution at carbon Cγ stabilizes the allenylidene metal moiety as does the electron-richness of the metal [5]. However, only one *primary* allenylidene ruthenium intermediate [Ru^+=C=C=CH_2] has even been postulated [8] and *secondary* allenylidene ruthenium(II) derivative [Ru^+=C=C=CHR] are likely to be the key intermediate in the polyenylidene ruthenium complex preparation [5] and in the catalytic coupling of propargylic alcohol compounds with allylic alcohols [9].

We now report (i) the formation of the first characterized secondary allenylidene metal derivatives *trans*-[(dppm)$_2$ClRu=C=C=CHR][PF_6] (dppm = $Ph_2PCH_2PPh_2$) *via* activation of HC≡C–CHOHR with *cis*-[$RuCl_2$(dppm)$_2$] and (ii) show that the :C=C=CHR significantly modifies the reactivity of the *trans* Ru–Cl bond, with respect to the :C=C=CR_2, and allows access to new hydridoruthenium complexes.

2. Discussion

As the organometallic moiety (dppm)$_2$(Cl)Ru^+ was shown to stabilize the Cγ disubstituted allenylidene complexes towards weak nucleophiles such as alcohols [7], its precursor **1** was allowed to react with HC≡C–C*H*(OH)R, **2a–c**, in dichloromethane in the presence of $NaPF_6$ and the red *secondary* allenylidene complexes **3a–c** were isolated in 75–85% yield (Scheme 1).



Scheme 1.

Correspondence to: Professor P.H. Dixneuf.

* Dedicated to Professor M.F. Lappert on the occasion of his 65th birthday.

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TABLE 1. Selected NMR data for allenylidene compounds [a]

Compound	$\delta(^{31}P)$, ppm PPh_2	$\delta(^{13}C)$, ppm Ru=*C* (quint.) ($^2J_{PC}$, $^3J_{CH}$, Hz)	Ru=C=*C* ($^3J_{PC}$, Hz)	Ru=C=C=*C* ($^1J_{CH}$, Hz) =C*H*($^5J_{PH}$, Hz)
3a	−14.91	323.10 (14.4, 6.6)	217.28 (2.5)	150.86 (165.1) 8.49 (2.7)
3b	−15.17	323.24 (14.4, 6.6)	220.24 (2.7)	148.84 (165.5) 8.47 (2.8)
3c	−13.71	308.38 (14.3, 6.3)	200.78 (2.9)	149.92 (163.2) 8.03 (2.6)
3d	−14.59	315.17 (14.3, 6.9)	220.36 (2.7)	149.85 (164.2) 8.06 (2.3)

[a] All spectra in CD_2Cl_2 at 297 K.

Analogously, 1-(2-phenylethyl)prop-3-yn-1-ol, **4**, led to the 3-alkenyl allenylidene complex **3d** (77%). The *trans* complexes **3** were characterized by NMR spectroscopy: equivalent ^{31}P nuclei, a low field =C*H*R signal in the ^1H NMR spectrum ($\delta \sim 8.5$ ppm), a quintuplet for the Ru=C signal in the ^{13}C NMR spectrum ($\delta \leq 310$ ppm; $^2J_{PC}$: ~ 14 Hz) and $^1J_{HC\gamma} = 165$ Hz) (Table 1). The absorption among from the C=C=C structure is at $\nu = 1938$ cm^{-1} (**3a**), much lower than with the *tertiary* complex *trans*-[(dppm)$_2$ClRu(=C=C=CPh$_2$)][PF$_6$]**5** (ν = 1964 cm^{-1}).

The possibility of nucleophilic addition to the allenylidene at C(α) or C(γ) was studied with hydride. Complex **3a** reacts with sodium borohydride in THF to give the alkynyl derivative **6a**[ν(C≡C) = 2103 cm^{-1}; 35%], arising from the selective addition of the hydride at the Cγ carbon atoms only (Scheme 2, Table 2). The high field signal ($\delta = -5.47$ ppm) of the ^{31}P nuclei in NMR spectrum is characteristic of a *trans* Cl–Ru–C≡C–R arrangement in related complexes [10].

In contrast, the addition to complex **3** of MeONa in methanol led to an unexpected development. Complexes **7a–c** were obtained and characterized by NMR

TABLE 2. Selected NMR data for acetylide compounds [a]

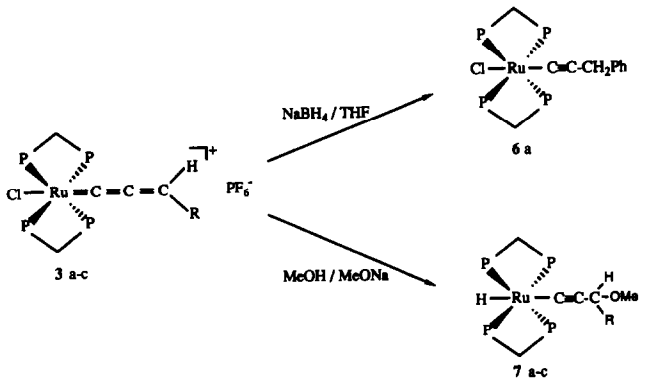
Compound	$\delta(^{31}P)$, ppm PPh_2	$\delta(^1H)$, ppm *H*–Ru ($^2J_{PH}$, Hz)	$\delta(^{13}C)$, ppm Ru–*C*≡C ($^2J_{PC}$, Hz)	Ru–C≡*C*
6a	−5.47	–	101.44 (15.6)	105.94
7a	3.08	−7.19 (20)	123.64 (13.4)	109.89
7b	3.04	−7.16 (19.9)	124.96 (13.4)	109.23
7c	3.00	−7.21 (19.9)	123.12 (13.4)	110.14

[a] All spectra in CD_2Cl_2 at 297 K.

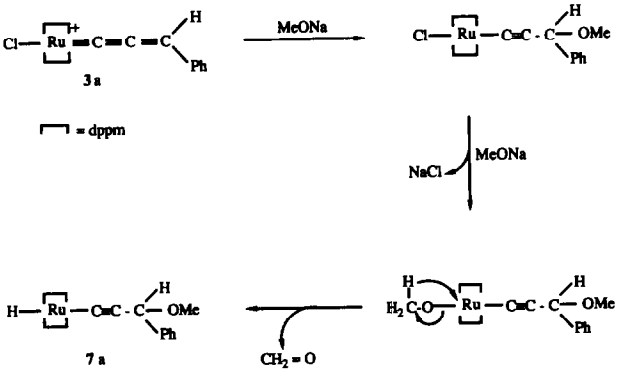
spectroscopy (Table 2). Their spectra are consistent with the addition of the methoxide to the Cγ carbon atom and the conversion of the *trans* Ru–Cl bond into a Ru–H bond. The reaction of **3a** with CD_3ONa in CD_3OD led to the sole formation of *trans*-[(dppm)$_2$(D)Ru–C≡C–CH(OCD$_3$)Ph], **8** isolated in 30% yield [δ(ppm) = 3.15 (PPh_2), = 4.75(s, ≡C–C*H*-(OCD$_3$), correct elemental analysis). The formation of the Ru–H bond likely takes place after the nucleophilic addition of MeO$^-$ at Cγ and results from substitution of the chloride by the methoxide, followed by formaldehyde elimination (Scheme 3).

This formation of an Ru–H bond *trans* to the allenylidene would not be observed under similar conditions with Cγ disubstituted complexes such as *trans*-[(dppm)$_2$ClRu=C=C=CPh$_2$][PF$_6$]**5**, for which addition of the methoxide at Cγ only took place, giving *trans*-[(dppm)$_2$ClRu–C≡C–C(OMe)Ph$_2$]**9**. It is likely that, in the intermediates *trans*-[(dppm)$_2$ClRu–C≡C–C(OMe)-(R)Ph] the C≡C–CH(OMe)Ph group favours *trans*-chloride substitution.

The isolation of complex **3** show that non-heteroatom-stabilized *secondary* allenylidene ruthenium complexes are stable, and their transformations suggest that *secondary* allenylidene ligands are able to introduce subtle modifications in the reactivity of ruthenium complexes.



Scheme 2.



Scheme 3.

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