www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 593–594 (2000) 485–488

Journal of Organometallic Chemistry

Communication

Ruthenium-assisted synthesis of *gem*-deuterated alkenes from monosubstituted propargyl alcohols and D_2O

Claudio Bianchini *, Isaac de los Rios, Carlos Lopez, Maurizio Peruzzini [1], Antonio Romerosa

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, ISSECC, CNR, Via J. Nardi 39, I-50132 Firenze, Italy

Received 8 April 1999; accepted 1 June 1999

Professor Fausto Calderazzo in recognition of his outstanding contributions to organometallic chemistry.

Abstract

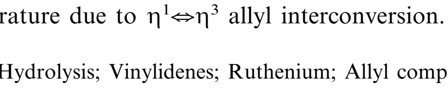
The cyclohexenylvinylidene complex *fac,cis*-[(PNP)RuCl$_2${$\overline{C{=}CH(C{=}CHCH_2CH_2CH_2CH_2)}$}] (**2**) is synthesized by reaction of *mer,trans*-[(PNP)RuCl$_2$(PPh$_3$)] (**1**) with 1-ethynylcyclohexanol [PNP=$CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$]. Complex **2** reacts with water yielding *fac,cis*-[(PNP)RuCl$_2$(CO)] and methylenecyclohexane. The regioselective incorporation of deuterium from D_2O into the methylene group of methylenecyclohexane is consistent with the intermediacy of an η^1-allyl ruthenium complex along the metal-assisted hydrolysis of the vinylidene C–C bond. The hydrolysis of the alkenylvinylidenes *fac,cis*-[(PNP)RuCl$_2${C=CHCR=CH$_2$}] (R = Me, Ph) proceeds similarly but the regioselectivity of deuterium incorporation depends on the temperature due to $\eta^1 \Leftrightarrow \eta^3$ allyl interconversion. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Hydrolysis; Vinylidenes; Ruthenium; Allyl compounds; Reaction mechanisms

1. Introduction

It has been reported that the ruthenium(II) complex *mer,trans*-[(PNP)RuCl$_2$(PPh$_3$)] (**1**) assists the hydrolysis of terminal alkynes to give CO and the hydrocarbon resulting from the homologation of the alkyne substituent (eq. 1) [PNP=$CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$] [1]. A similar reaction has recently been found to involve disubstituted propargyl alcohols [2]. In this case, however, alkenes are formed (eq. 2).

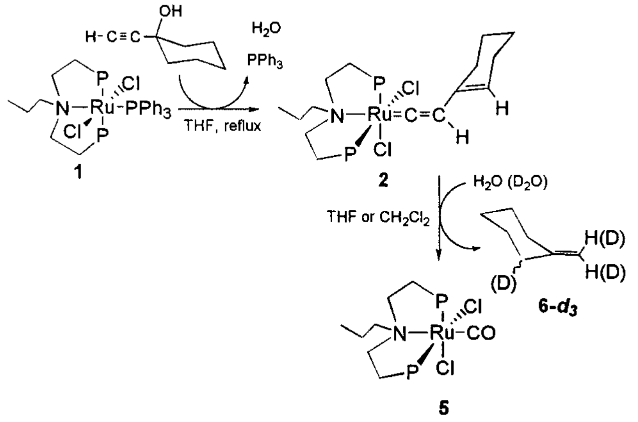
$$\equiv\!\!-R \;+\; H_2O \xrightarrow{[M]} CO \;+\; RCH_3 \qquad (1)$$



$$\equiv\!\!-CR_2\!-\!OH \xrightarrow{[M]} CO \;+\; R_2C{=}CH_2 \qquad (2)$$

[M] = [(PNP)RuCl$_2$]

Irrespective of the alkyne substituent, the cleavage of the C≡C triple bond proceeds via Ru-cumulene complexes that react with H_2O to give hydroxycarbene intermediates. Simple 1-alkynes generate Ru-vinylidene complexes by formal 1,2-hydrogen shift (eq. 3) [1,3],



Scheme 1.

---

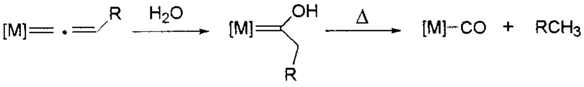
* Corresponding author.

E-mail addresses: bianchin@fi.cnr.it (C. Bianchini), peruz@fi.cnr.it (M. Peruzzini)

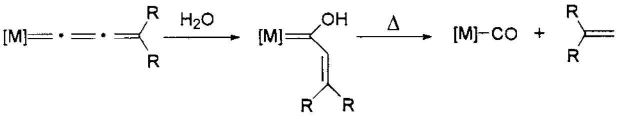
[1] Also corresponding author.

PII: S0022-328X(99)00324-1

while propargyl alcohols are dehydrated to Ru-allenylidene complexes (eq. 4) [2,4].

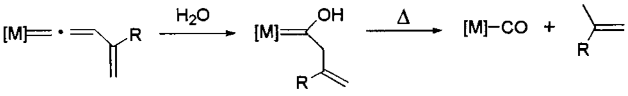


(3)



(4)

In the case of propargyl alcohols bearing a hydrogen on the C_δ position, it is anticipated that ruthenium-alkenylvinylidene intermediates are formed yielding CO and alkenes upon reaction with water (eq. 5) [2].



(5)

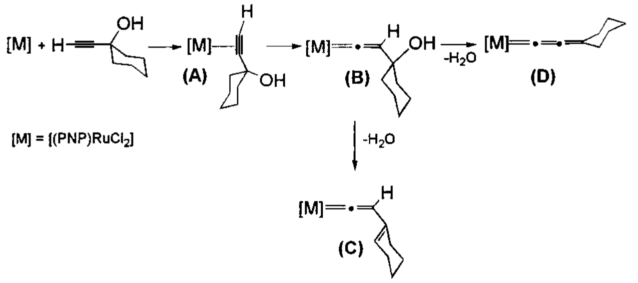
In this work, we show that the reaction sequence outlined in eq. 5 does occur with a mechanism involving the intermediacy, inter alia, of ruthenium-η^1-allyl species. Moreover, it is shown that the use of D_2O in the hydrolysis reaction leads to the selective formation of *gem*-deuterated alkenes. The example detailed here involves 1-ethynyl-cyclohexanol and describes its selective conversion to methylenecyclohexane that is indeed a difficult alkene to prepare [5] with interesting applications in organic synthesis (Scheme 1) [6].

Reaction of 1-ethynylcyclohexanol with **1** in refluxing THF under nitrogen yields quantitatively the cyclohexenylvinylidene complex *fac,cis*-[(PNP)RuCl$_2$-{C=CH(C=CHCH$_2$CH$_2$CH$_2$CH$_2$)}] (**2**) (Scheme 1). Analogous metal-promoted transformations of propargyl alcohols are well-known and proceed via a stepwise mechanism in which key events are the formation of π-acetylene complexes (**A**), their tautomerization to hydroxyvinylidene intermediates (**B**) [7] and the dehydration of these latter to give alkenylvinylidene products (**C**) (Scheme 2) [2,4,8].

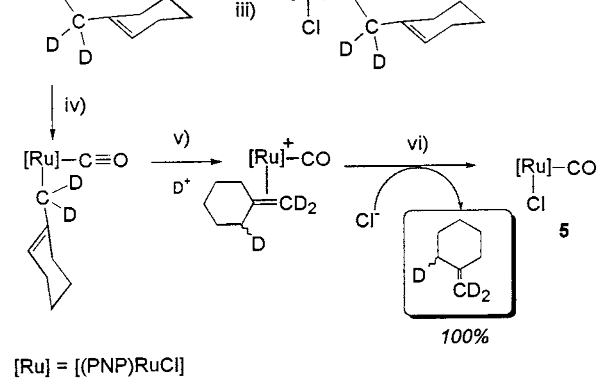
No intermediate species was detected by NMR spectroscopy during the transformation of **1** into **2** in the temperature range from 20 to 50°C. Likewise, no trace of ruthenium allenylidene compound (**D**) was seen confirming that the deydration of γ-hydroxyvinylidene metal complexes can selectively involve δ-hydrogen atoms [2,8].

The cyclohexenylvinylidene complex **2** undergoes rapid hydrolysis in either THF or $CHCl_3$ already at room temperature yielding the carbonyl complex *fac,cis*-[(PNP)RuCl$_2$(CO)] (**5**) [1] and one equivalent of methylenecyclohexane, $CH_2{=}CCH_2CH_2CH_2CH_2CH_2$ (**6**) (Scheme 1). No trace of the isomeric alkene 1-methyl-1-cyclohexene was formed even when the hydrolysis reaction was carried out at 50°C (in situ NMR experiments; GC analysis). Substitution of D_2O for H_2O gives exclusively methylenecyclohexane-d_3 in which two deuterium atoms are bound to the exocyclic methylene carbon atom and one deuterium atom is bound to the carbon atom in the 2 position of the cyclohexenyl group (Scheme 1). Identification of **6** and **6**-d_3 was made using NMR and GC-MS spectroscopy on pure samples obtained by column chromatography.

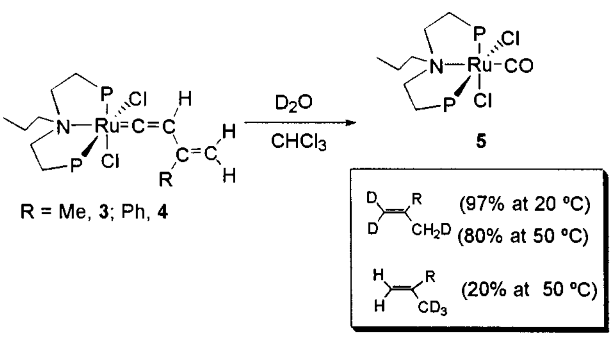
The regioselective incorporation of deuterium in methylenecyclohexane-d_3 together with previous mechanistic studies [1] allows us to rationalize the present hydrolytic C–C bond cleavage as well as the chemoselective formation of the exocyclic alkene instead of the thermodynamically stable 1-methyl-1-cyclohexene isomer. The proposed mechanism (Scheme 3) involves several steps, the majority of which have previously been proved for analogous systems: (i) deuteration of the vinylidene proton by D_2O to give **2**-d_1 [1]; (ii) addition of D_2O across the vinylidene C=C bond to generate a transient hydroxycarbene species [1,9]; (iii)



Scheme 2.



Scheme 3.



Scheme 4.

intramolecular elimination of DCl to form a coordinatively and electronically unsaturated acyl complex [1,10]; (iv) formal migration of the methylcyclohexenyl group (CO deinsertion) to give a (carbonyl)(η^1-allyl) complex; (v) electrophilic attack by D^+ at the γ-carbon atom of the η^1-allyl ligand to give an alkene adduct [11]; (vi) alkene displacement by chloride ion.

In keeping with this mechanistic picture, the known alkenylvinylidene complexes *fac,cis*-[(PNP)RuCl$_2${C=CHCR=CH$_2$}] (R = Me, **3**; Ph, **4**), [2] dissolved in $CHCl_3$, react with D_2O at 20°C yielding almost exclusively CD_2=C(R)CH$_2$D (> 97%) (Scheme 4). At 50°C, the *gem*-deuterated alkene is still the major product but a 20% amount of the isotopomer CH_2=C(R)CD$_3$ is formed which is consistent with a low energy barrier to η^1-CD$_2$–C(R)=CH$_2$⇔η^3-CD$_2$–C(R)–CH$_2$⇔η^1-CH$_2$–C(R)=CD$_2$ interconversion at ruthenium [12].

2. Experimental

2.1. Synthesis of 2

To a THF solution (20 ml) of **1** (0.92 g, 1.00 mmol) was added a 2-fold amount of 1-ethynylcyclohexanol (0.215 g, 2.00 mmol) and the resulting solution was refluxed for 150 min under N_2. After half the solvent was removed under vacuum, 30 ml of petroleum ether (b.p. 40 – 70°C) was added. The orange precipitate of *fac,cis*-[(PNP)RuCl$_2$$\{\overline{C=CH(C=CHCH_2CH_2CH_2C}H_2)\}$] (**2**) was filtered off, washed with light petroleum ether and dried under a stream of nitrogen. Yield 82%. Selected spectroscopic data: IR (Nujol mull, KBr plates), ($\nu_{C=C}$) 1632 (w) and 1611 cm^{-1} (m). ^{1}H-NMR (200.13 MHz, CD_2Cl_2, TMS reference, 294 K), 5.39 (t, $^3J_{HH}$ 5.4 Hz, 1H, C=C$H_{cyclohexenyl}$); 5.03 (t, $^4J_{HP}$ 3.3 Hz, 1H, Ru=C=CH). ^{31}P{^{1}H}-NMR (81.01 MHz, CD_2Cl_2, H_3PO_4 85% reference, 294 K), 47.8 (s). ^{13}C{^{1}H}-NMR (50.32 MHz, CD_2Cl_2, TMS reference, 294 K), 358.9 (t, $^2J_{CP}$ 17.3 Hz, Ru=C=CH); 118.2 (s, confirmed by a DEPT-135 experiment, C=CH$_{cyclohexenyl}$); 116.6 (s, confirmed by a DEPT-135 experiment, Ru=C=CH); 29.8, 26.5, 23.8, 23.3 (all s, confirmed by a DEPT-135 experiment, $CH_{2cyclohexenyl}$); C=CH$_{cyclohexenyl}$ not observed.

2.2. Reaction of 2 with H_2O

In a typical experiment, a 10-fold excess of water (48 µl, 2.66 mmol) was syringed under nitrogen into a well stirred solution of **2** (0.200 g, 0.26 mmol) in THF (10 ml). The solution was stirred overnight at room temperature. The volatiles were removed in vacuo at room temperature to leave a brown residue. A portion of the residue was analyzed by ^{31}P{^{1}H}-NMR spectroscopy which confirmed the formation of **5** as the only ruthenium-phosphine complex. To the rest of the residue was added diethyl ether (3 × 3 ml) which was dried over sodium sulfate and evaporated to dryness at atmospheric pressure. The residue was dissolved in $CDCl_3$ and characterised by ^{1}H-, ^{13}C{^{1}H}-NMR and GC-MS spectroscopy (see Section 2.3). The yield of **6** calculated by integration of the ^{1}H-NMR resonances with respect to ferrocene as internal standard was higher than 90%. Column chromatography on silica-gel of the diethyl ether solution (diethyl ether as eluant), afforded pure **6**. Replacing H_2O with D_2O in the above experiment gave **6**-d_3 in yield exceeding 90% after similar work-up (^{1}H- and ^{2}H-NMR and GC-MS analysis, see Section 2.3).

2.3. Chemico-physical properties of 6 and 6-d_3

Spectral data for **6**: ^{1}H-NMR (299.45 MHz, $CDCl_3$, TMS reference, 293 K), 4.57 (qu, $^4J_{HH}$ 0.9 Hz, 2H, C=CH_2); 2.12 (m, 4H, $CH_{2(\beta)}$), 1.27 (m, 6H, $CH_{2(\gamma)}$=$CH_{2(\delta)}$). ^{13}C{^{1}H}-NMR (50.32 MHz, $CDCl_3$, TMS reference, 293 K), 150.7 (s, C_α); 107.0 (s, confirmed by a DEPT-135 experiment, C=CH_2); 35.5 (s, confirmed by a DEPT-135 experiment, C_β); 28.2, 26.6 (all s, confirmed by a DEPT-135 experiment, C_γ and C_δ). [M^+ = 96(40), M – CH_3^+ = 81(100)]. Spectral data for **6**-d_3: ^{2}H-NMR (76.77 MHz, $CHCl_3$, TMS reference, 293 K), 4.6 (br s, 2D, C=CD_2); 2.2 (m, transforms in a singlet in the ^{2}H{^{1}H}-NMR spectrum, 1D, $CHD_{(\beta)}$).

2.4. Reaction of 3 (or 4) with H_2O

The hydrolysis reactions of **3** and **4** were followed in a 5-mm NMR tube by adding two equivalents of H_2O to a $CDCl_3$ or THF-d_8 solution of the alkenylvinylidene complex at either 20 or 50°C. Irrespective of the temperature, ^{1}H-, ^{31}P{^{1}H}-NMR and GC-MS spectra confirmed the formation of **5** and the generation of one equivalent of alkene [CH_2=C(Me)R (R = Me, Ph)]. Spectral data for methylpropene, CH_2=CMe$_2$: ^{1}H-NMR (200.13 MHz, $CDCl_3$, TMS reference, 293 K), 4.75 (sept, $^4J_{HH}$ 1.2 Hz, 2H, C=CH_2); 1.83 (t, 6H, CH_3)

[$M^+ = 56(42)$, $M - CH_3^+ = 41(100)$, $M - CH_2CH_3^+ = 27(22)$]. Spectral data for α-methylstyrene, CH_2=CMePh: ^{1}H-NMR (200.13 MHz, $CDCl_3$, TMS reference, 293 K), 7.5–7.2 (m, 5H, Ph), 5.48 (dq, $^2J_{HH}$ 1.6 Hz, $^4J_{HH}$ 0.8 Hz, 1H, alkene proton *trans* to Ph); 5.17 (qu, $^2J_{HH}$ ca. $^4J_{HH}$ ca. 1.6 Hz, 1H, alkene proton *cis* to Ph), 2.18 (dd, 3H, Me). [$M^+ = 118(100)$, $M - CH_3^+ = 103(46)$]. When H_2O was substituted for D_2O, the *gem*-deuterated alkenes CD_2=C(R)CH_2D were the largely major products (> 97%) at 20°C. At 50°C, the isotopomers CH_2=C(R)CD_3 were formed in ca. 20% yield [(19%, R = Ph; 23%, R = Me) as determined by ^{1}H-NMR integration of the CH_2 resonance of CH_2=C(R)CD_3 with respect to ferrocene as internal standard].

Acknowledgements

This work was supported by the bilateral program 'Azione Integrata' between the University of Florence (Italy) and Almeria (Spain), by the international cooperation agreement CNR (Italy)/RAS (Russia) and by the EC contract INTAS 96-1176.

References

[1] C. Bianchini, J.A. Casares, M. Peruzzini, A. Romerosa, F. Zanobini, J. Am. Chem. Soc. 118 (1996) 4585.

[2] C. Bianchini, M. Peruzzini, F. Zanobini, I. de los Rios, C. Lopez, A. Romerosa, Chem. Commun. (1999) 443.

[3] (a) C. Bianchini, P. Innocenti, M. Peruzzini, A. Romerosa, F. Zanobini, Organometallics 15 (1996) 272. (b) M.I. Bruce, Chem. Rev. 91 (1991) 197.

[4] M.I. Bruce, Chem. Rev. 98 (1998) 2797.

[5] Beilstein Handbuch der Organischen Chemie, Springer Verlag, Berlin, Germany. Beilstein Registry Number: 773760.

[6] (a) D. Arnold, J. Am. Chem. Soc. 70 (1948) 2590. (b) B. Hazdra, J. Am. Chem. Soc. 81 (1959) 228. (c) M.J. Burk, R.H. Crabtree, D.V. McGraith, Anal. Chem. 58 (1986) 977.

[7] E. Bustelo, M. Jímenez-Tenorio, M.C. Puerta, P. Valerga, Organometallics 18 (1999) 950.

[8] V. Cadierno, M.P. Gamasa, J. Gimeno, J. Borge, S. García-Granda, Organometallics 16 (1997) 3178.

[9] C. Bianchini, A. Marchi, L. Marvelli, M. Peruzzini, A. Romerosa, R. Rossi, Organometallics 15 (1996) 3804.

[10] J. O'Connor, K. Hiibner, Chem. Commun. (1995) 1209.

[11] (a) J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987 (Chapter 8). M. Rosenblum, J. Watkins, J. Am. Chem. Soc. 112 (1990) 6316.

[12] K. Vrieze, in: L.M. Jackman, F.A. Cotton (Eds.), Dynamic Nuclear Magnetic Resonance Spectroscopy, Academic Press, New York, 1975, p. 441.