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Unexpected regioselective formation of internal η^3-allylpalladium chloride complexes from terminal alkenes and palladium chloride in 1,2-dichloroethane

Abdelkhalek Riahi, Jacques Muzart *

Unité Mixte de Recherche 'Réactions Sélectives et Applications' CNRS-Université de Reims Champagne-Ardenne, B.P. 1039, F-51687 Reims Cédex 2, France

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Abstract

The reaction of terminal alkenes with $PdCl_2$ in refluxing 1,2-dichloroethane afforded dichlorobis[(2,3,4-η)-alken-2-yl]dipalladium with yields up to 70% rather than the expected dichlorobis[(1,2,3-η)-alken-1-yl]dipalladium.

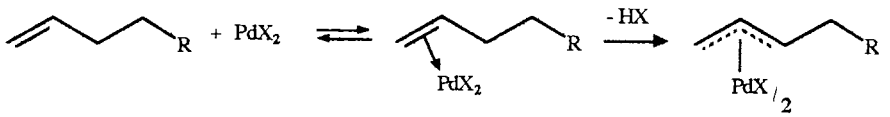
Keywords: Regioselective formation; Chloride complexes; Allylpalladium

1. Introduction

η^3-Allylpalladium complexes are commonly prepared from alkenes [1–6]. This reaction involves the η^2-complexation of the olefin to a Pd(II) salt and then the removal of an allylic hydrogen (Scheme 1) [1,2,6].

A particularly effective procedure for the synthesis of η^3-allylpalladium complexes from linear alkenes was reported by Trost and Metzner some years ago; it consists in the use of palladium trifluoroacetate in acetone, THF or ethyl acetate [4]. This gives a rapid reaction leading to the desired η^3-allylpalladium trifluoroacetate complexes in most cases [4,5]. An older procedure involves the use of a mixture of palladium chloride, cupric chloride, sodium chloride, acetic acid and acetic anhydride at 60–90°C [3]. The role of cupric chloride is manifold and not fully understood [3]. This method has been sometimes modified by using 1,4-benzoquinone instead of cupric chloride [6].

Previously, we have described the oxidation of alcohols using 1,2-dichloroethane (DCE), sodium carbonate and catalytic amounts of both palladium chloride and Adogen 464[1] [7,8]. The catalytic cycle we have proposed involves the insertion of a reduced palladium species into a C–Cl bond of DCE followed by a β-elimination reaction, which leads to ethylene and to the regeneration of Pd(II) [7]. Further work has strengthened our proposition; the elimination of ethylene from a transient complex—$ClCH_2CH_2$-PdCl(dppe)—has been proposed [9] while the formation of Pd–Cl bonds from Pd species and DCE has been reported [10,11]. Furthermore, DCE has also been used by other research groups to regenerate Pd(II) [10,12,13].



Scheme 1.

* Corresponding author. Fax: +33-3-26913166.
E-mail address: jacques.muzart@univ-reims.fr (J. Muzart)

[1] Adogen 464 is a registered trademark of Ashland for methyltrialkyl(C_8–C_{10})ammonium chloride.

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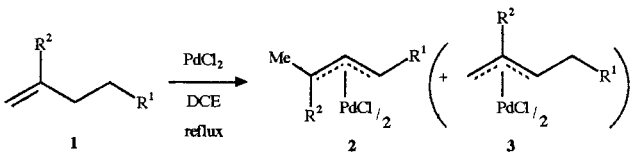
These observations have led us to investigate the reaction of terminal alkenes with palladium chloride in DCE. We expected (i) the formation of η^3-allylpalladium complexes, and (ii) that the presence of DCE would preclude the side reaction which is the reduction of Pd(II) into inactive Pd(0).

When a 2:1 mixture of 1-eicosene (**1a**) and $PdCl_2$ was heated in DCE, an η^3-allylpalladium complex was effectively obtained. Surprisingly, this was the dichlorobis[(2,3,4-η)-eicosen-2-yl]dipalladium (**2a**) instead of the expected dichlorobis[(1,2,3-η)-eicosen-1-yl]dipalladium (**3a**)[2] (Eq. (1), Table 1, run 1). ^{1}H-NMR literature data [3–5] allowed us to establish the structure of **2a**. The signals of the two hydrogens in the anti positions are located between 3.6 and 3.8 ppm and the signal of the central hydrogen is a doublet of doublets centered at 5.10 ppm.



(1)

with **a**: $R^1 = n\text{-}C_{16}H_{33}$, $R^2 = H$; **b**: $R^1 = n\text{-}C_4H_9$, $R^2 = H$; **c**: $R^1 = n\text{-}C_3H_7$, $R^2 = Me$.

Similarly, 1-octene (**1b**) afforded **2b** in a fair yield (run 2). In contrast, the use of the disubstituted olefin **1c** led to an unselective reaction which, furthermore, was more sluggish (run 3). A mixture of two complexes (**2c** and **3c**) was thus obtained; they were separated by chromatography. The ^{1}H-NMR spectra of the more polar complex (**3c**) was in agreement with a literature report [4]. The structure of **2c** was established by comparison of the ^{1}H-NMR characteristics of its allyl unit with those of analogous complexes [3]: singlets at 1.20 and 1.38 ppm for the two methyl groups, a doublet at 4.94 ppm for the central hydrogen and a signal at 3.95 ppm for the other hydrogen.

Table 1
Synthesis of η^3-allylpalladium complexes from terminal alkenes and $PdCl_2$ in DCE [a]

Run	Alkene	Reaction time/h	Complex: yield/%
1	**1a**	22	**2a**: 60
2	**1b**	22	**2b**: 70
3	**1c**	48	**2c**: 62, **3c**: 10
4 [b]	**1b**	22	**2b**: 72
5 [c]	**1a**	26	**2a**: 67
6 [c]	**1b**	22	**2b**: 75

[a] For conditions, see Section 2.
[b] Reaction carried out in the presence of Na_2CO_3 (2 equiv.).
[c] Reaction carried out in the presence of propylene oxide (2 equiv.).

[2] We have already prepared **3a** from $Pd(OCOCF_3)_2$ and **1a**, the complexation being followed by cation exchange using tetra-*n*-butylammonium chloride [5].

Since hydrochloric acid is liberated in the course of the process, we suspected that it could play a role in the regioselectivity of the reaction [14,15]. However, the addition of sodium carbonate in a run carried out with **1b** did not modify the result (run 4). Since Na_2CO_3 is insoluble in DCE, the reaction was repeated using propylene oxide as the proton trap (runs 5 and 6). In fact, the same regioisomer was again isolated. It is interesting to note that the yields were slightly improved in the presence of proton traps.

The palladium-catalyzed isomerization of alkenes under various conditions has already been described [6,16–19]. In a recent report, it has been exemplified that 1-hexene was (i) isomerized effectively into 2-hexene, and (ii) much more reactive towards isomerization than the other hexene isomers [18]. Furthermore, it has been shown that 2-pentene afforded the internal η^3-allylpalladium complex rather than the terminal one [3]. Consequently, we imagined that our conditions mediated firstly a fast isomerization of 1-alkenes into 2-alkenes which then would lead to the internal η^3-allylpalladium complexes. This led us to examine the nature of the non-polar material recovered in run 1. ^{1}H-NMR spectroscopy shows that this material contains ca. 70% of **1a** and 30% of a mixture of internal alkenes (broad signal centered at 5.40 ppm). The presence of various internal alkenes was confirmed by ^{13}C-NMR spectroscopy (new signals at 17–20 ppm and 123–132 ppm).

In conclusion, the regioselective formation of internal η^3-allylpalladium complexes from terminal alkenes and $PdCl_2$ at reflux in 1,2-dichloroethane seems to be due to the isomerization of the initial alkene under these particular experimental conditions.

2. Experimental

^{1}H- and ^{13}C-NMR spectra were obtained on a Bruker AC 250 spectrometer using TMS as internal standard. IR spectra were recorded on Spectra file Plus Midac. Mass spectra were recorded on a Jeol D 300 at 'UFR Pharmacie' of Reims.

2.1. Typical procedure

In a round-bottomed flask containing $PdCl_2$ (1 mmol) was added DCE (5 ml) and a solution of the alkene (2 mmol) in DCE (5 ml). The stirred mixture was refluxed under an air atmosphere for the time

indicated in Table 1. The mixture was filtered over a short pad of silica gel. After evaporation of the solvent, the residue was chromatographed on preparative TLC (eluant: ethyl acetate + petroleum ether). The yellow powder obtained was recrystallized in dichloromethane + petroleum ether.

2.1.1. Dichlorobis[(2,3,4-η)-eicosen-2-yl]dipalladium ***2a***

M.p. 63–64°C; ^{1}H-NMR ($CDCl_3$) δ: 0.88 (t, $J = 7.3$, CH_2CH_3), 1.16–1.80 (m, $(CH_2)_{15}$ and $CHCH_3$), 3.60–3.80 (m, $CHCHCH$), 5.10 (t, $J = 11.1$, $CHCHCH$); ^{13}C-NMR ($CDCl_3$) δ: 13.9 (CH_2CH_3), 22.6 ($CHCH_3$), 28.4, 28.6, 28.9, 29.0, 29.2, 29.3, 29.4, 29.5, 29.6, 31.1, 31.4, 31.6, 31.7, 31.9 and 32.1 (CH_2), 82.0 ($CHCHCH$), 109.8 ($CHCHCH$); IR (KBr) cm^{-1}: 2957, 2928, 1458, 1374; MS (EI) m/z (%): 842 (M^+, 8), 278 (100), 181 (12), 152 (20), 124 (50).

2.1.2. Dichlorobis[(2,3,4-η)-octen-2-yl]dipalladium ***2b***

M.p. 107–108°C; ^{1}H-NMR ($CDCl_3$) δ: 0.80–1.0 (m, CH_2CH_3), 1.20–1.80 (m, 6 H, $(CH_2)_3$), 1.26 (d, $J = 6.5$, $CHCH_3$), 3.60–3.80 (m, $CHCHCH$), 5.13 (dd, $J = 11.6$ and 10.7, $CHCHCH$); ^{13}C-NMR ($CDCl_3$) δ: 13.9 (CH_2CH_3), 25.0 ($CHCH_3$), 29.7, 31.1 and 31.7 (CH_2), 81.7 ($CHCH_3$), 86.5 ($CHCH_2$), 109.0 ($CHCHCH$); IR (KBr) cm^{-1}: 2959, 2930, 1458, 1374; MS (EI) m/z (%): 506 (M^+, 16), 358 (28), 322 (18), 181 (44), 110 (100).

2.1.3. Dichlorobis[(2,3,4-η)-2-methylhepten-2-yl]dipalladium ***2c***

M.p. 82–83°C; ^{1}H-NMR ($CDCl_3$) δ: 0.9–1.0 (m, CH_2CH_3), 1.20 (s, CCH_3), 1.38 (s, CCH_3), 1.45–1.90 (m, $(CH_2)_2$), 3.95 (ddd, $J = 11.8$, 4.6 and 4.2, $CHCH_2$), 4.94 (d, $J = 11.8$, $CHCHCH_2$); ^{13}C-NMR ($CDCl_3$) δ: 13.7 (CH_2CH_3), 22.3 (CH_2), 22.4 and 26.9 ($C(CH_3)_2$), 34.4 ($CHCH_2$), 78.5 ($CHCH_2$), 107.3 ($CHCHCH_2$), 112.3 ($C(CH_3)_2$); IR (KBr) cm^{-1}: 2957, 2895, 1458, 1064; MS (EI) m/z (%): 506 (M^+, 28), 470 (16), 358 (84), 322 (46), 215 (13), 149 (20), 110 (100).

2.1.4. Dichlorobis[(1,2,3-η)-2-methylhepten-1-yl]dipalladium ***3c***

M.p. 96–97°C; ^{1}H-NMR ($CDCl_3$) δ: 0.9 (t, $J = 6.2$, CH_2CH_3), 1.20–1.80 (m, $(CH_2)_3$), 2.07 (s, CCH_3), 2.67 (wide s, $HCHCCH_3$), 3.60 (dd, $J = 6.9$ and 6.5, $CHCH_2$), 3.70 (wide s, $HCHCCH_3$); ^{13}C-NMR ($CDCl_3$) δ: 13.9 (CH_2CH_3), 18.2 (CCH_3), 22.5, 29.2 and 30.5 (CH_2), 60.0 (CH_2CCH_3), 82.7 ($CHCH_2$), 123.8 (CH_2CCH_3); IR (KBr) cm^{-1}: 2959, 2916, 1454; MS (EI) m/z (%): 506 (M^+, 31), 470 (8), 358 (67), 322 (48), 215 (18), 149 (25), 110 (100).

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