

Allenylpalladium(II) Species: Possible Intermediates in the Tetrakis(triphenylphosphine)palladium(0)-catalysed Formation of Allenes from Prop-2-ynylic Substrates

Cornelis J. Elsevier, Henk Kleijn, Klaas Ruitenbergh, and Peter Vermeer*

Department of Organic Chemistry, State University, Croesestraat 79, 3522 AD Utrecht, The Netherlands

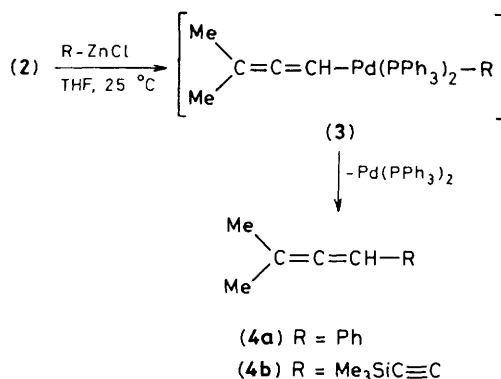
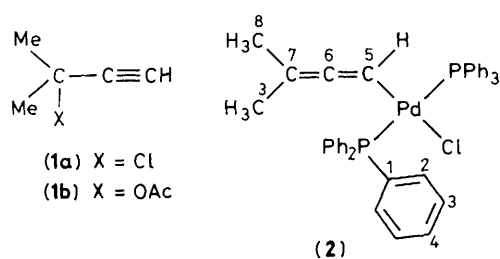
The formation of a 3-methylbuta-1,2-dienylpalladium(II) complex (**2**) from the prop-2-ynylic chloride (**1a**) or the prop-2-ynylic acetate (**1b**) and tetrakis(triphenylphosphine)palladium(0), as well as its conversion into the allenes (**4**), is described.

Palladium(0) complexes are versatile catalysts for the conversion of prop-2-ynylic halides and esters into allenes.¹⁻⁴ The reaction is especially useful for the synthesis of allenes bearing unsaturated groups, *e.g.* aryl, 1-alkenyl, 1,2-alkadienyl, 1-alkynyl, and 1,3-alkadiynyl. The formation of allenes is thought to proceed *via* an allenylpalladium(II) species resulting from the oxidative addition of the prop-2-ynylic substrate to palladium. In order to gain more insight into the actual course of this reaction we have attempted to isolate intermediates and study their reactivity.

For this purpose the prop-2-ynylic chloride (**1a**) was treated with 1.0 equiv. of the complex Pd(PPh₃)₄ using tetra-

hydrofuran (THF) as solvent. A yellow solid was obtained in almost quantitative yield, of low solubility in polar solvents such as acetonitrile, dioxane, and methanol. The compound was crystallized from THF and decomposed at its m.p. of 142 °C; spectroscopic data were consistent with its formulation as the *trans* adduct (**2**). To our knowledge this is the first reported example of an isolated σ -allenylpalladium(II) compound. Corresponding complexes derived from iridium, platinum, and cobalt are known, however.⁵

The i.r. spectrum of (**2**) showed no strong absorption in the allenic region, and it is most likely that the *very* weak absorption at 1910 cm⁻¹ should be attributed to $\nu(\text{C}=\text{C}=\text{C})$



Scheme 1

(*cf.* ref. 5). The ¹H n.m.r. spectrum of (2) (C₆D₆, Me₄Si) {δ 0.97 (6H, dt), 5.00 [1H, m, ³J(P, H) 8.3 Hz], 6.9–7.2 (18H, ArH), and 7.7–8.1 (12H, ArH)} corresponded reasonably with those reported for *trans*-[PtCl(CH=C=CMe₂)-(PPh₃)₂].⁵ Its ¹³C n.m.r. spectrum (CDCl₃, Me₄Si) showed the following signals: δ 194.6 (C-6), 135.1 [C-2, t, ²J(P, C) 5.9 Hz], 131.6 [C-1, t, ¹J(P, C) 22.1 Hz], 130.5 (C-4), 128.1 [C-3, t, ³J(P, C) 4.6 Hz], 91.4 (C-7), 84.3 (C-5), and 19.9 p.p.m. (C-8). The single resonance observed in the ³¹P n.m.r. spectrum (CDCl₃, Na₃PO₄, 24 °C), δ 15.7 p.p.m., confirms the *trans*-configuration for the complex. Ebulliometric molecular weight determination showed that the compound is monomeric in THF (found: *M* = 770; calc.: 735).

An alternative route to (2) was provided by the reaction of the prop-2-ynyl acetate (1b) with Pd(PPh₃)₄ and ZnCl₂. In the absence of ZnCl₂ no reaction occurred. Other workers have found that allyl acetate does not undergo substitution by the complex Pd(PPh₃)₄.⁶

In the catalytic preparation of allenes, adducts like (2) have been assumed as the initial intermediates (*cf.* refs. 2–4). This assumption is quite reasonable in view of the following results. Treatment of (2) with phenyl- and (trimethylsilyl)ethynyl-zinc chloride in THF produced, in quantitative yield, allenes (4) (see Scheme 1). Compounds (4) are also obtained in the catalytic reaction. The formation of (4) from (2) will proceed through the palladium(II) complexes (3) (*cf.* ref. 7) but, unfortunately, attempts to detect (3) spectroscopically failed. An impure allene (4b) was obtained after reaction of (2) with (trimethylsilyl)ethynyl-lithium in THF. Also in the catalytic reaction organolithium compounds gave disappointing results.⁴ The nature of the metal in the reagent used for the conversion of (2) into (4) is apparently important.

The support given to two of us (C. J. E. and K. R.) by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.) is gratefully acknowledged.

Received 14th June 1983; Com. 789

References

- 1 T. Jeffery-Luong and G. Linstrumelle, *Tetrahedron Lett.*, 1980, **21**, 5019.
- 2 K. Ruitenbergh, H. Kleijn, C. J. Elsevier, J. Meijer, and P. Vermeer, *Tetrahedron Lett.*, 1981, **22**, 1451.
- 3 H. Kleijn, J. Meijer, G. C. Overbeek, and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, 1982, **101**, 97; C. J. Elsevier, P. M. Stehouwer, H. Westmijze, and P. Vermeer, *J. Org. Chem.*, 1983, **48**, 1103.
- 4 K. Ruitenbergh, H. Kleijn, H. Westmijze, J. Meijer, and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, 1982, **101**, 405.
- 5 J. P. Collman, J. N. Cawse, and J. W. Kang, *Inorg. Chem.*, 1969, **8**, 2574; B. E. Mann, B. L. Shaw, and N. I. Tucker, *J. Chem. Soc. A*, 1971, 2667.
- 6 T. Yamamoto, O. Saito, and A. Yamamoto, *J. Am. Chem. Soc.*, 1981, **103**, 5600.
- 7 M. K. Loar and J. K. Stille, *J. Am. Chem. Soc.*, 1981, **103**, 4174.