Isolation of Stable β-Alkoxyethylpalladium Complexes and the First Direct Evidence for *trans* Alkoxypalladation of Ethylene

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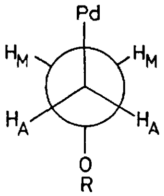
Summary ^{1}H n.m.r. spectra of unusually stable alkoxypalladation adducts of ethylene and *cis*-dideuterioethylene provided the first direct evidence for stereospecific *trans* alkoxypalladation of acyclic olefins.

The stereochemistry of the oxypalladation of acyclic olefins has been a matter of great controversy.[1] We report here the first direct evidence for *trans* alkoxypalladation of acyclic olefins based on the ^{1}H n.m.r. analysis of alkoxypalladation adducts of ethylene possessing unusually high thermal stability.

Treatment of $[(\eta^5\text{-}C_5H_5)Pd(PPh_3)L]ClO_4$ (**1**) (L = $CH_2{=}CH_2$)[2] with sodium methoxide in dichloromethane–methanol at −10 °C afforded orange-red crystals of the first isolable alkoxypalladation adduct of ethylene, $[(\eta^5\text{-}C_5H_5)Pd(PPh_3)(CH_2CH_2OR)]$ (**2**) (R = Me), m.p. 142—144 °C (decomp.); compounds (**2**) (R = Et, Pr^n, Pr^i, or Bu^t) were prepared similarly. These are fairly stable in the solid state, and decompose only very slowly when dissolved in solvents such as benzene and chloroform at room temperature.



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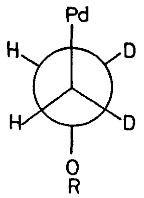
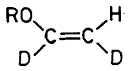


[$^2H_2$]-(2)

The 100 MHz ^{1}H n.m.r. spectra of (**2**) in $CDCl_3$ at 23 °C exhibited AA′MM′X multiplets for the two methylene groups (*e.g.* for R = Me; $PdCH_2$ δ 1·40, J_{gem} 9·3 Hz, J_{vic} 12·3 Hz, J'_{vic} 4·8 Hz,[3] J_{PH} 5·6 Hz, CH_2O δ 3·20, J_{gem} 7·5 Hz), indicating that conformer (**2**) predominated. The appearance of only a doublet of doublets at δ 1·40 (J_{vic} 4·8 Hz,[3] J_{PH} 5·6 Hz) and a doublet at δ 3·20 in the spectrum of [$^2H_2$]-(**2**) (R = Me), prepared from (**1**) (L = *cis*–CHD=CHD, >98% isotopic purity) unambiguously demonstrated that the methoxypalladation had occurred stereospecifically *trans*.

Heating a benzene solution of (**2**) at 80 °C for 2 h gave alkyl vinyl ethers and cyclopentadiene, apparently *via* β-hydride elimination as in the decomposition of [(η^5–C_5H_5)-Pd(PPh_3)(Bu^n)].[3] *Ca.* 90% of the total isomeric deuteriovinyl ethers obtained from [$^2H_2$]-(**2**) (R = Me or Pr^i) was found by ^{1}H n.m.r. spectroscopy to have originated from direct *cis* β-H (or D) elimination with the ratio of (**3a**) : (**3b**) = *ca.* 2 : 1. It is notable that this apparent isotope effect for the β-hydride elimination is similar in magnitude to that[4] for the 1,2-hydride shift of a β-hydroxyethylpalladium complex postulated as an intermediate in the oxidation of ethylene to acetaldehyde. The *ca.* 5% of (**3c**) + (**3d**), and traces of (**3e**) and (**3f**) also obtained may have been formed from an intermediate α-alkoxyethylpalladium analogue of (**2**) after readdition of the palladium hydride or deuteride to the vinyl ethers.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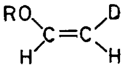
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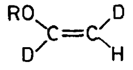
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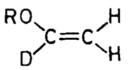
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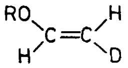
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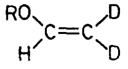
(3f)

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[1] P. M. Henry, *Adv. Organometallic Chem.*, 1975, **13**, 363; H. B. Lee and P. M. Henry, *Canad. J. Chem.*, 1976, **54**, 1726; D. E. James, L. F. Hines, and J. K. Stille, *J. Amer. Chem. Soc.*, 1976, **98**, 1806.

[2] T. Majima and H. Kurosawa, *J. Organometallic Chem.*, in the press.

[3] H. Felkin and G. K. Turner, *J. Organometallic Chem.*, 1977, **129**, 429.

[4] P. M. Henry, *J. Org. Chem.*, 1973, **38**, 2415.