

C–H Allylic Bond Cleavage to generate an Active Hydridopalladium Species for the Alkoxycarbonylation of Alkenes. X-Ray Crystal Structure of $[(\text{Ph}_3\text{PCH}_2\text{CH}=\text{CHPh})_4(\text{PdCl}_6)(\text{SnCl}_6)]$

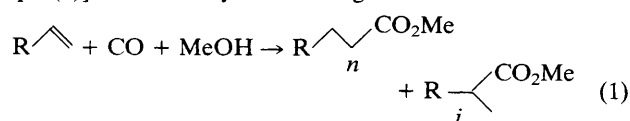
**Thomas Chenal,^a Ruth Naignre,^a Isabelle Ciprés,^a Philippe Kalck,*^a Jean-Claude Daran^b
and Jacqueline Vaissermann^b**

a Laboratoire de Chimie des Procédés, Ecole Nationale Supérieure de Chimie, 118, route de Narbonne, 31077 Toulouse Cédex, France

^b Laboratoire de Chimie des Métaux de Transition, 4 Place Jussieu, 75252 Paris Cédex 05, France

On the basis of a reactivity study using various alkenes and of the X-ray crystal structure analysis of the title compound isolated from the alkoxycarbonylation reaction, the formation of an active $\text{Pd(H)(SnCl}_3\text{)}$ species, generated from the $[\text{PdCl}_2(\text{PPh}_3)_2]\text{SnCl}_2\text{-PPh}_3$ system, is proposed.

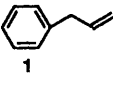
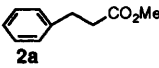
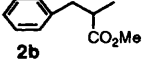
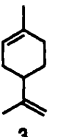
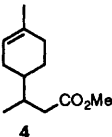
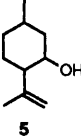
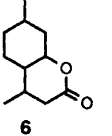
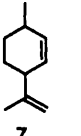
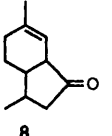
The transition-metal catalysed synthesis of esters by direct addition of carbon monoxide and an alcohol to an alkene [eqn. (1)] has recently been recognised to involve a metal



hydride species.¹ Previous results by Knifton² have revealed that terminal alkenes can be transformed selectively into the corresponding linear ester under a high pressure (20 MPa) provided that SnCl₂ was added to the catalyst precursor [PdCl₂(PPh₃)₂]. It has been proposed but not proved that the hydrogen of the active Pd-H species involved arises from the alcohol.^{1,2}

Recently, we have studied the catalytic methoxycarbonyla-

Table 1 Isomeric distribution of products obtained by alkoxy-carbonylation^a

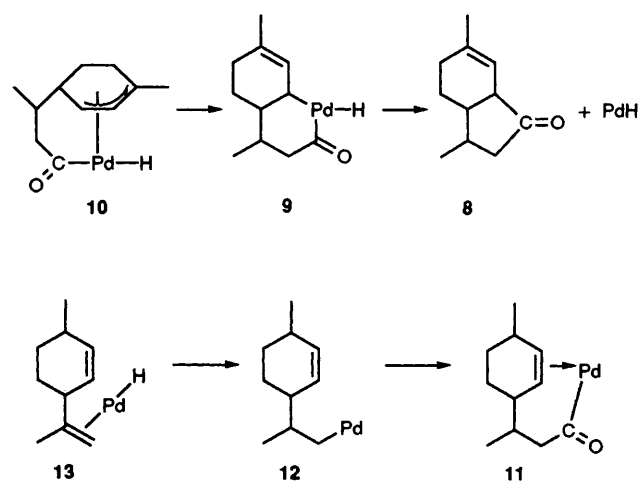
Compound	Product	Turnover frequency h ⁻¹	<i>n</i> : <i>n</i> + <i>i</i> (%)
	 	17	90
		4	100
		6	100
		3.6	100

^a Run conditions: [PdCl₂(PPh₃)₂] = 1 mmol, [PPh₃] = 2 mmol, [SnCl₂] = 2.5 mmol, alkene = 100 mmol, methanol (for 1 and 3) = 200 mmol, solvent = 25 ml toluene, CO pressure = 4 MPa, *T* = 100 °C, *t* = 6 h (1) or 16 h (3, 5 and 7), yields: 2 (100%), 4 (67%), 6 (93%), 8 (58%).

tion of 3-phenylpropene **1**³ and several representative alkenes of natural origin,⁴ not only to prepare novel esters but also to gain a deeper insight into the mechanism of the reaction. Milder conditions than those previously published² have been employed (100 °C, 4 MPa) using the catalytic system [PdCl₂(PPh₃)₂]-2.5 SnCl₂-2PPh₃. The results are shown in Table 1; 3-phenylpropene **1** is fully converted into the two corresponding linear (**2a**) and branched (**2b**) esters, limonene **3** is selectively transformed into the less constrained ester **4**, isopulegol **5** into lactone **6** or *trans*-isolimone **7** into cyclopentanone **8**, regardless of the presence or not of methanol for the two last substrates.

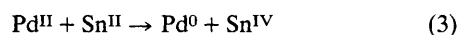
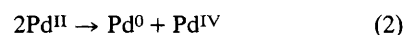
Very recently, El Ali and Alper⁵ have shown that [Pd⁰.diphos] species catalyse the cyclocarbonylation of allylic alcohols or alkynols; the first step is suggested to be an oxidative addition of the alcohol to afford a H-Pd-OR complex. With the substrates **3**, **5** and **7**, we have checked that [Pd(PPh₃)₄], with or without SnCl₂, does not induce any carbonylation at all. Thus, the generation of a hydride species from methanol can apparently be ruled out; it must arise directly from the C-H allylic cleavage of these substrates. Particularly relevant in this demonstration is the carbonylation of **7** to afford **8**. The formation of **8** obviously involves the two species **9** and **10**. The formation of **10** can be envisaged to involve the species **11**-**13** which, however, have not been detected in the reaction mixture. Such a mechanism prevails for the carbonylation of isopulegol.

The hydrogen source for the formation of the active Pd-H species seems to be the olefin, as evidenced by the isolation of the title compound from the reaction with 3-phenylpropene. Red crystals were obtained at room temp. upon decantation of

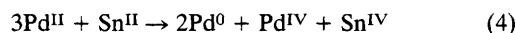


the red reaction mixture from black palladium, after the catalytic reaction.

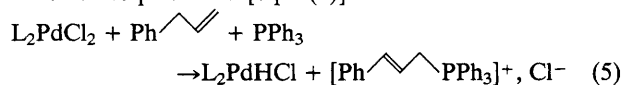
The X-ray crystal structure determination[†] revealed that palladium(IV) and tin(IV) hexachloride anions are associated with four triphenyl(3-phenylpropenyl)phosphonium cations as shown in Fig. 1. Thus, the molecule can be represented as [(Ph₃PCH₂CH=CHPh)₄(PdCl₆)(SnCl₆)]. We were puzzled by this structure which shows palladium(IV) metal centres whereas in fact it was palladium(II) which was introduced under a reducing atmosphere. Black palladium was produced by a disproportionation reaction [eqn. (2)] and tin(II) was oxidised into tin(IV) by palladium(II) [eqn. (3)].



A combination of eqns. (2) and (3) gives eqn. (4), which



affords the same stoichiometry of Sn^{IV} : Pd^{IV} = 1 : 1 as in the crystal. Moreover, the phosphonium cations do not contain a phenylpropyl group but a 3-phenyl-prop-2-enyl group and thus require the substrate **1** to lose a hydrogen atom which is transferred to palladium [eqn. (5)].



Combination of eqns. (4) and (5) takes into account the formation of the title compound with simultaneous production

[†] Crystal data: C₁₀₈H₉₆P₄PdSnCl₁₂, *M* = 2168.4, triclinic, space group *P* $\bar{1}$, *a* = 10.797(2), *b* = 14.739(2), *c* = 17.084(2) Å, α = 91.33(1), β = 99.75(1), γ = 108.33(1)°, *D*_c = 1.42 g cm⁻³, *Z* = 1, crystal size 0.18 × 0.20 × 0.34 mm, μ(Mo-Kα) = 8.47 cm⁻¹. Data were collected at 20 °C on a Nonius CAD4 diffractometer. Empirical absorption correction using DIFABS (min. 0.88, max. 1.12) was applied. Anomalous dispersion terms were applied. The structure was solved by a combination of direct method (SHELXS) and standard Patterson-Fourier techniques and refined by least-squares analysis using anisotropic thermal parameters for all non-hydrogen atoms. H atoms were located on a difference Fourier map and their coordinates were refined with an overall U(iso) thermal parameter. Of the 7033 observed reflections, 4746 with *I* > 3σ(*I*) were used to solve and refine the structure to *R* = 0.033 and *R*_w = 0.035 (unit weights, 724 least-squares parameters). The programs used were CRYSTALS and ORTEP-2.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge crystallographic Data Centre. See Notice to Authors, Issue No. 1.

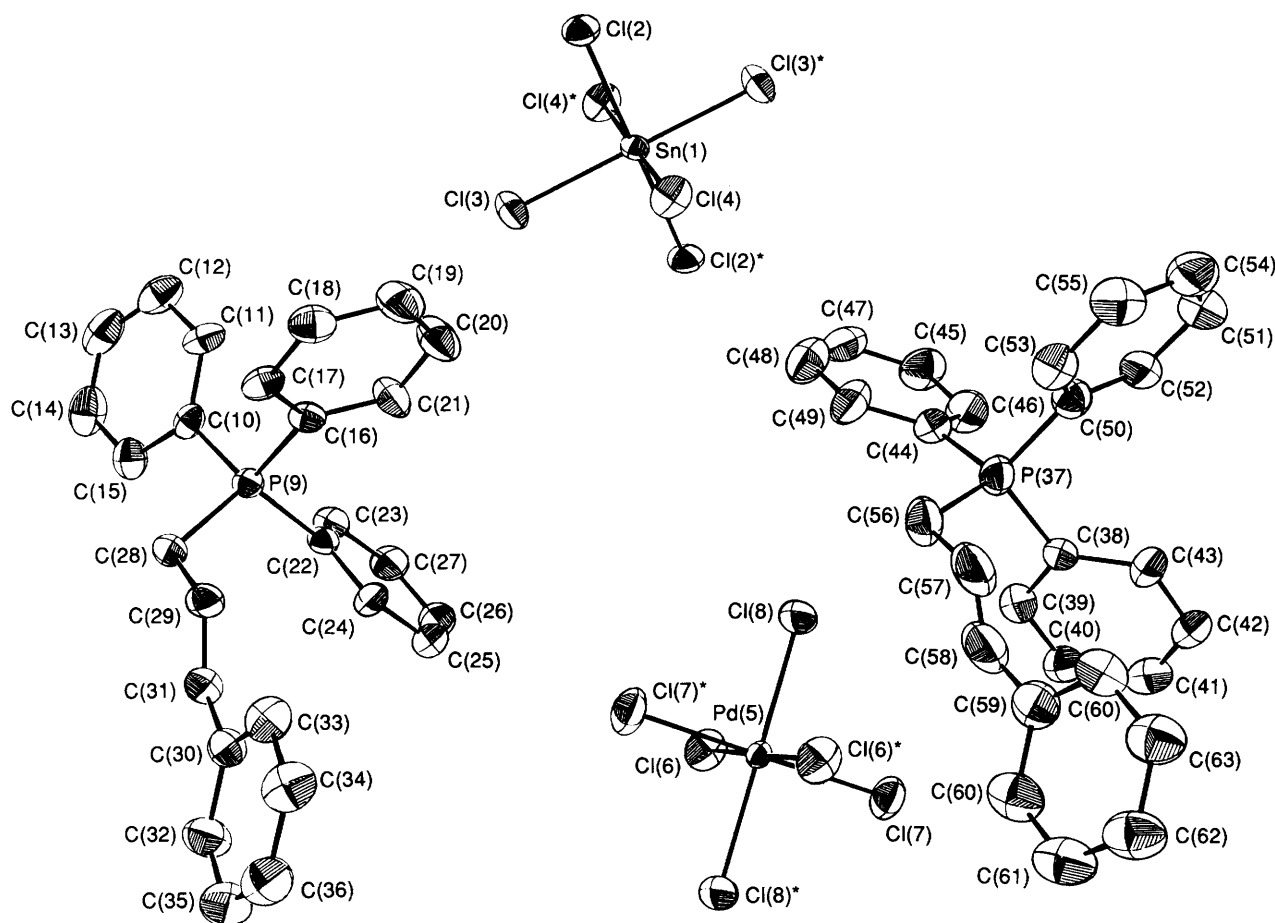
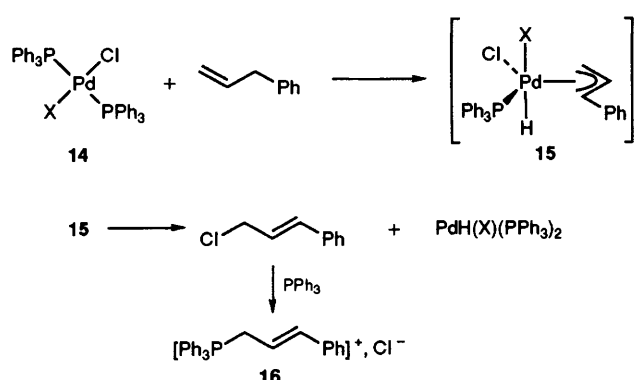


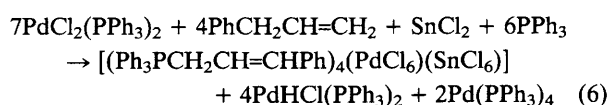
Fig. 1 Perspective ORTEP drawing of $[(\text{Ph}_3\text{PCH}_2\text{CH}=\text{CHPh})_4(\text{PdCl}_6)(\text{SnCl}_6)]$ showing 50% thermal ellipsoids for non-hydrogen atoms. For more clarity, only two phosphonium groups have been represented as well as the complete coordination spheres for palladium and tin atoms (chlorine atoms with stars). Bond lengths (Å) of interest are: Sn(1)–Cl(2), 2.432(1); Sn(1)–Cl(3), 2.412(1) and Sn(1)–Cl(4), 2.404(1); Pd(5)–Cl(6), 2.433(2); Pd(5)–Cl(7), 2.404 and Pd(5)–Cl(8), 2.421(2); P(9)–C(10), 1.784(5); P(9)–C(28), 1.809(5); C(29)–C(31), 1.292(7). The Sn^{IV} and Pd^{IV} atoms are in octahedral environments and the P atom in a tetrahedral one.



Scheme 1 Proposed pathway for the generation of the palladium hydride species; X = Cl, SnCl_3

of the Pd–H species under interest and a palladium(0) complex such as $\text{Pd}(\text{PPh}_3)_4$ [eqn. (6)].[‡]

[‡] Starting from 0.350 g of $[\text{PdCl}_2(\text{PPh}_3)_2]$, 0.155 g of $[(\text{Ph}_3\text{PCH}_2\text{CH}=\text{CHPh})_4(\text{PdCl}_6)(\text{SnCl}_6)]$ were expected from eqn. (6) and 0.120 g obtained; ^{31}P NMR spectra of the supernatant solution show mainly the presence of $[\text{PdCl}_2(\text{PPh}_3)_2]$ (δ 23.05) and free PPh_3 .



Eqn. (6) is certainly an oversimplification of what occurs in the system since yellow crystals of $[\text{PdCl}_2(\text{PPh}_3)_2]$ were also found. Similarly, in the presence of SnCl_2 (Sn: Pd = 2.5) the complex $[\text{PdHCl}(\text{PPh}_3)_2]$ affords certainly $[\text{PdH}(\text{SnCl}_3)(\text{PPh}_3)_2]$, which was previously proposed by Knifton,² and not yet identified. Under an atmosphere of CO, Hidai has identified the complex $[\text{Pd}(\text{CO})(\text{PPh}_3)_3]$ starting from $[\text{Pd}(\text{PPh}_3)_4]$.⁶ As indicated above, this palladium(0) complex is inactive for the methoxycarbonylation of **3** and **7**. Palladium(IV) and tin(IV) were engaged also ($\text{Na}_2\text{PdCl}_6 + \text{SnCl}_4 + 2\text{PPh}_3$) for **3**; the reaction is characterized by a complete loss of selectivity since 26% of the ester is obtained in addition to several isomerized terpenes.

A large number of allyl palladium complexes are described in the literature.⁷ On this basis we propose that the four substrates considered here generate an allyl species such as **15** by hydride abstraction (Scheme 1). This intermediate generates the phosphonium salt, presumably after elimination of 1-phenyl-3-chloro-propene, followed by reaction with PPh_3 . Thus, the active species $[\text{PdHX}(\text{PPh}_3)_2]$ is formed in this case because a significant fraction of palladium introduced is sacrificed giving *inter alia* the palladium(IV) complex analysed here.

We are indebted to Comptoir Lyon-Alemand-Louyot for a generous gift of palladium salt. T. C., I. C. and R. N. thank the Ministère de la Recherche et de la Technologie for a research grant.

Received, 29th October 1992; Com. 2/05769G

References

- 1 G. Cavinato and L. Toniolo, *J. Organomet. Chem.*, 1990, **398**, 187.
 - 2 J. F. Knifton, *J. Org. Chem.*, 1976, **41**, 285.
 - 3 I. Ciprès, J. Jenck and Ph. Kalck, *J. Mol. Cat.*, 1990, **58**, 387.
 - 4 Th. Chenal, I. Ciprès, J. Jenck, Ph. Kalck and Y. Pérès, *J. Mol. Cat.*, 1993, **78**, 351.
 - 5 B. El Ali and H. Alper, *J. Org. Chem.*, 1991, **56**, 5357.
 - 6 M. Hidai, M. Kokura and Y. Uchida, *J. Organomet. Chem.*, 1973, **52**, 431.
 - 7 P. M. Maitlis, P. Espinet and J. H. Russell, *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 6, p. 385.
-