Thermolysis of [(η^3-allyl)PdMe(PPh$_3$)]: An Unexpected Evolution of Ethane Gas as a Main Product

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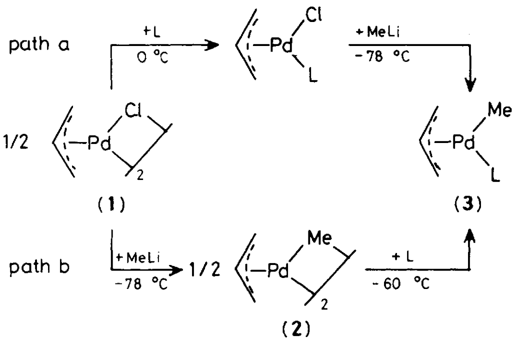
The novel title complex thermally decomposes with preferential evolution of ethane rather than but-1-ene, the allylic alkylation product, indicating that the binuclear methyl-bridged intermediate formed by phosphine dissociation predominantly participates in this thermolysis.

η^3-Allyl complexes, especially those carrying both allylic and other organic groups on a central palladium atom, have frequently been proposed as catalytic intermediates in organic syntheses.[1] Such complexes of the type [(η^3-allyl)Pd(Ar)L] (Ar = aryl; L = tertiary phosphines and arsines) have been synthesized as models of palladium-catalysed allylic coupling utilizing carbon nucleophiles, and their thermolytic behaviour and the role of alkene co-ordination in reductive elimination have been investigated.[2] For instance, thermolysis of [(η^3-2-MeC$_3$H$_4$)Pd(C$_6$Cl$_5$)(PPh$_3$)] in *o*-dichlorobenzene in the presence of added triphenylphosphine resulted in complete reductive elimination of the organic groups to give a quantitative yield of allylpolychlorobenzene.[2b] The reaction with maleic anhydride in chloroform at room temperature also gave the coupling product in good yield.[2b] Now we report a novel intermolecular coupling reaction, which was observed in thermolysis of the first isolated methyl complexes of η^3-allylpalladium(II).

Complexes (**3a**—**e**)† were synthesized by the following two paths: (a) the bridge-splitting reaction of (**1**) with tertiary phosphines, followed by methylation with MeLi, and (b) the reaction of (**1**) with MeLi to afford a methyl-bridged intermediate (**2**) and the subsequent bridge-splitting reaction with tertiary phosphines, in tetrahydrofuran at low temperature under nitrogen (Scheme 1). The isolated complexes are liquids or crystalline or amorphous solids, and are moderately stable in air at room temperature for 1—3 days, except (**3a**) and (**3d**).



a L = PCy$_3$
b L = PPh$_3$
c L = PPh$_2$Me
d L = PPhMe$_2$
e L = PBu$_3$

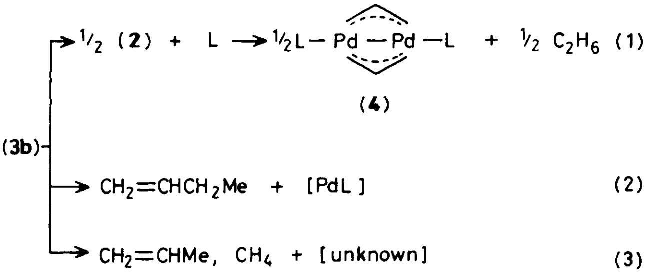
Scheme 1

The thermolytic behaviour of all the complexes was examined in the solid state and in solution with or without other additives, and the results for (**3b**) are summarized in Table 1.

Table 1 shows that ethane rather than but-1-ene, the allylic alkylation product, is the major organic product on thermolysis of (**3b**) in the solid state. The preferential evolution of ethane was also observed on thermolysis in diphenylmethane. These observations are in marked contrast to those for the aryl analogues, as well as those for (1,3-dimethyl-η^3-allyl)methylnickel–ligand complexes,[3] and suggest that thermolysis primarily takes place intermolecularly *via* the binuclear methyl-bridged intermediate (**2**) formed by phosphine dissociation [equation (1) in Scheme 2]. To confirm this hypothesis, we prepared a toluene solution of (**2**) below −78 °C and examined the gases evolved on warming the solution to 0 °C. The relative amounts of the gases liberated [methane : ethane : propene : but-1-ene : others = 12.6 : 74.5 : 7.0 : 3.4 : 2.1; total mole per Pd = 0.63] showed a close resemblance to those for Entry 2 in Table 1, indicating that the above hypothesis may be plausible.

When a [^{2}H$_6$]benzene solution of (**3b**) was heated in a degassed sealed tube (50 °C, 10 min), the formation of (**4**) with concomitant evolution of ethane was observed by the appearance of four new ^{1}H n.m.r. signals [δ 0.76 (s, C$_2$H$_6$), 1.96 (d, *J* 12 Hz, μ-allyl), 2.56 (d, *J* 8 Hz, μ-allyl), 4.15 (m, μ-allyl)]. The formation of (**4**) was recognized more clearly in the ^{31}P{H} n.m.r. spectrum of the solution under similar conditions (50 °C, 3 h) [δ 30.3 (s) p.p.m.].‡

But-1-ene was liberated only as a minor product. It can be formed by reductive elimination, directly from (**3b**) [equation (2) in Scheme 2] or through (**2**). The other minor products, propene§ and methane, probably originate from (**3b**) and (**4**),



L = PPh$_3$

Scheme 2

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† All complexes were fully characterized by elemental analyses and i.r., ^{1}H n.m.r., and mass spectroscopy. Due to thermal instability, (**3a**) and (**3d**) did not give satisfactory elemental analyses, but the mass spectrum of (**3d**) showed the presence of the molecular ion peak.

‡ These data were compared with those for an independently synthesized authentic sample of (**4**) [^{1}H n.m.r. (C$_6$D$_6$) δ 2.01 (d, *J* 12.7 Hz), 2.69 (br.), 4.24 (m); ^{31}P{H} n.m.r. (C$_6$D$_6$) δ 30.5 (s) p.p.m.].

§ The fragment peak for (M^+ − Me, propene) stronger than that for (M^+ − but-1-ene) was also observed in the mass spectra of (**3a**), (**3c**), and (**3d**).

Table 1. Gases evolved on thermolysis of (**3b**).[a]

Entry[b]	Temp./ °C	Time/ min	Additive[c]/ mmol l^{-1}	Total mole per Pd	Evolved gas ratio			
					Methane	Ethane	Propene	But-1-ene
1	100	40	none	0.42	3.2	77.5	3.3	16.1
2	50	60	none	0.36	4.2	79.7	12.9	3.2
3	70	10	PPh_3 (0.3)	1.01	17.0	25.0	4.8	53.2
4	25	60	ma (0.1)	0.49	2.0	0.8	4.8	92.4

[a] Thermolysis in an evacuated tube. [b] In solid (Entry 1); in Ph_2CH_2 (0.1 mmol l^{-1}) [Entries 2—4]. [c] ma = maleic anhydride.

and (**3b**), respectively [equation (3) in Scheme 2]. Hydrogen abstraction can occur from the phosphine ligand or the solvent. For thermolysis in solution, the amount of propene evolved was more than that of but-1-ene but the reverse was found for that in the solid state, indicating that in the solid state the thermolysis process *via* equation (1) is somewhat suppressed compared with that in solution.

The addition of Pd(0)-stabilizing ligands like phosphines and alkenes is known to be effective in preventing the deposition of Pd(0) species and these additives allow clear and complete reductive elimination of η^3-allylpalladium complexes.[2] In the present case, the addition of three equivalents of triphenylphosphine per complex caused an increased evolution of but-1-ene (up to ~50%), but a significant amount of ethane (25%) was still liberated. This means that phosphine dissociation from (**3b**) to form (**2**) is appreciably suppressed so that the two decomposition pathways (1) and (2) become comparably important. The addition of maleic anhydride resulted in the preferential formation of but-1-ene, although the yield of but-1-ene still remained less than half a mole per mole Pd under the conditions shown in Table 1.

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