Co-dimerisation of 1,3-Dienes and Acrylic Esters catalysed by Cationic Allylpalladium Complexes: the Role of Phosphines

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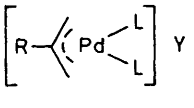
Basic phosphines, especially tributylphosphine, when added in 1:1 ratio to cationic allylpalladium complexes, allow the selective co-dimerisation of 1,3-dienes and acrylic esters to linear, unsaturated esters, presumably owing to the inducement of an η^3–η^1 shift of the allyl ligands by the phosphines.

Transition metal-catalysed co-dimerisation reactions of 1,3-dienes with alkenes have attracted considerable interest recently as useful linear products are obtained instead of the expected Diels–Alder adducts.[1] The co-dimerisation of buta-1,3-diene and ethylene has been studied in detail and proceeds through the intermediacy of η^3-but-2-enyl complexes which are capable of reacting with ethylene co-ordinated to the same metal centre.[2] Other 1,3-diene–alkene pairs were also examined but fewer mechanistic studies were undertaken. For example, the co-dimerisation of buta-1,3-diene with acrylic esters to heptadienoates occurs with iron,[3] cobalt,[4] and palladium[5] catalysts. Interestingly, nickel catalysts give undecatrienyl derivatives which arise from the co-condensation of two C_4 units with the acrylic esters.[6] In all cases, the rate of the reaction as well as product selectivity is strongly dependent on the ligands present in the co-ordination sphere of the transition metal ion. It seems reasonable that in these cases, η^3-but-2-enyl complexes derived from buta-1,3-diene are also formed before C–C coupling with acrylic esters occurs. This is very likely in the case of palladium since the catalytic precursors claimed by Hattori and Tatsuoka are preferentially the dimers $[(\eta^3\text{-}RC_3H_4)PdCl]_2$ (R = H, Me). These precursors are activated by the addition of one equivalent of a P^{III} compound, especially PBu_3. Although not stated by these authors, this procedure should lead to cationic allylpalladium complexes.



(1a) R = Me; L_2 = cod; Y = BF_4
(1b) R = Me; L_2 = 1.5 hexamethylphosphoramide; Y = BF_4
(1c) R = Me; L = PBu_3; Y = BF_4
(1d) R = Me; L = PPh_3; Y = PF_6
(1e) R = Me; L = $CH_2{=}CHCO_2Me$; Y = BF_4

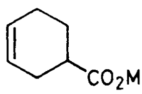
We recently devised a convenient synthesis of cationic allylpalladium complexes of the general structure $[(\eta^3\text{-}RC_3H_4)\text{-}PdL_2]Y$ (**1**) (R = H, 2-Me, or 2-Ph; Y = PF_6, BF_4, or ClO_4) where L represents a donor solvent, a chelating diolefin, or a phosphorus(III) ligand.[7] Our interest in the catalytic applications of these compounds[8] prompted us to investigate their ability to catalyse the co-dimerisation of 1,3-dienes and acrylates.

As shown in Table 1 methyl cyclohex-3-enecarboxylate (**2**) is the sole product when the catalysts are complexes (**1a**—**d**). It is also the only product when the catalyst results from the reaction of 2-methylallyloxytris(dimethylamino)phosphonium hexafluorophosphate with $Pd_2(dba)_3$ (dba = dibenzylidene acetone).[7] The same yield of (**2**) is obtained when (**1a**—**d**) are omitted. The complex (**1e**), despite its η^2-methyl acrylate lig-

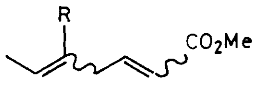
Table 1. Reaction of 1,3-dienes with methyl acrylates in the presence of cationic allylpalladium compounds.

Catalyst	1,3-Diene (mmol)	Methyl acrylate (mmol)	Reaction t/°C	Reaction Time/h	Diene conversion, %	Product selectivity, % Diels–Alder product	Product selectivity, % Linear co-dimer
(**1a**)[a]	240[b]	300	80	5	9	(**2**), 100	0
(**1b**)[a]	200[b]	300	75	6	traces	(**2**), 100	0
(**1c**)[a]	213[b]	300	75	6	traces	(**2**), 100	0
(**1d**)[a]	240[b]	300	75	6	traces	(**2**), 100	0
(**1e**)[a]	240[b]	300	80	5	traces	(**2**), 100	0
(**1a**) + PBu_3[c]	220[b]	325	80	5	87	(**2**), 10	(**3**), 83
(**1a**) + $P(C_6H_{11})_3$[c]	210[b]	300	80	5	23	(**2**), 40	(**3**), 52
(**1a**) + (**1c**)[d]	230[b]	325	80	5	92	(**2**), 7	(**3**), 82
(**1a**) + PBu_3[c]	290[f]	320	80	20	100	19	(**4**), 78
(**1a**) + PBu_3[c]	250[b]	300[e]	80	20	27	30	68
(**1a**) + PBu_3[c]	80[g]	110	80	5	57	55	45

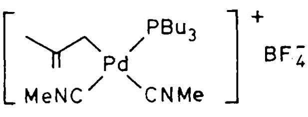
[a] 0.5 mmol. [b] Buta-1,3-diene. [c] 0.5 mmol of each reactant. [d] 0.25 mmol of each reactant. [e] Methyl methacrylate. [f] Isoprene. [g] 2,3-Dimethylbuta-1,3-diene.



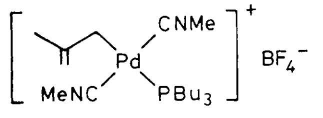
(**2**)



(**3**) *E*, *E*; R = H
(**4**) *E*, *E*; R = Me



(**5a**)



(**5b**)

ands,† is also unable to orientate the co-dimerisation reaction towards methyl heptadienoate. Furthermore, heating (**1e**) in dichloroethane leads only to decomposition without formation of the expected coupling products of the 2-methallyl ligand with methyl acrylate.

The addition of one equivalent of tributylphosphine to complexes (**1a**) or (**1e**) allows the conversion of 1,3-dienes and acrylic esters into linear heptadienoate derivatives (Table 1). The new selectivity pattern cannot be accounted for by an isomerisation process involving the Diels–Alder adducts. In fact, reaction of (**2**) with a 1 : 1 mixture of (**1a**) and PBu_3 leads to positional isomers of (**2**) only. In the case of buta-1,3-diene and methyl acrylate, only one heptadienoate, methyl *E*,*E*-hepta-2,5-dienoate (**3**) is obtained. Substitution of PBu_3 by $P(C_6H_{11})_3$ provides a catalyst with a lower activity but still a good selectivity for this linear co-dimer. Conversely, addition of one equivalent of PPh_3 or $P(OPh)_3$ to (**1a**) does not catalyse formation of (**3**). The co-dimerisation reaction is also observed for the isoprene–methyl acrylate and buta-1,3-diene–methyl methacrylate pairs. However, the conversion in both pairs is lower, presumably owing to the steric hindrance arising from the methyl groups. Noteworthy is the formation of only methyl 5-methyl-*E*,*E*-hepta-2,5-dienoate (**4**) from the reaction of isoprene and methyl acrylate. Finally, similar results are achieved when equimolar amounts of (**1a**) and (**1c**) are used together for the co-dimerisation reaction.

The reaction of (**1a**) with one equivalent of PBu_3 or PPh_3 has been studied by i.r. and n.m.r. spectroscopy. I.r. monitoring of the 1600—1400 cm^{-1} region indicates partial displacement of the cyclo-octa-1,5-diene (cod) ligand. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ N.m.r. spectra (CD_3CN) confirm these observations. For the reaction with PPh_3, only (**1a**) and (**1d**) are detected in practically equal amounts (n.m.r. integration). Conversely, the $^{31}P\{^1H\}$ n.m.r. spectrum of the reaction mixture resulting from the addition of PBu_3 reveals the presence of two PBu_3-containing complexes. The ^1H n.m.r. spectrum indicates complete displacement of cod and the presence of signals assigned to two 2-methylallyl ligands. The peaks corresponding to δ 1.80 (s, 3H), 2.92 (three lines owing to virtual coupling with phosphorus), and 4.06 (s, 2H), are easily assigned to the *trihapto*-2-methylallyl ligand of (**1c**). The peaks corresponding to δ 1.92 (s, 3H), 3.47 (d, J_{PH} 9 Hz, 2H), 4.57 (s, 1H), and 4.65 (s, 1H) are attributed to the *monohapto*-2-methylallyl ligand of complexes (**5a**) or (**5b**) where only one tributylphosphine is co-ordinated to the palladium centre. Attempts to isolate complex (**5**) failed since precipitation from the reaction mixture with Et_2O leads to a mixture of products from which only (**1c**) can be recovered. One would expect that a similar η^3-2-Me-$C_3H_4 \rightarrow \eta^1$-2-Me-$C_3H_4$ shift would also take place in the case of methyl acrylate. The same process occurs with tricyclohexylphosphine in acetonitrile, although to a lesser extent. Thus, the co-dimerisation of 1,3-dienes and acrylic esters occurs with subtle modifications of the co-ordination sphere of the palladium(II) centre. The dramatic influence of the nature of the phosphine ligand is reflected in its capability to shift the η^3-allyl ligand to the η^1-allyl form.

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† $^{13}C\{^1H\}$ N.m.r. spectrum in CH_2Cl_2: δ 52.1 (C–O), 122.3 and 124.9 (C=C), and 167 p.p.m. (C=O), assuming δ 54.0 p.p.m. for CH_2Cl_2.

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