Brief Communications

Unusual selective allylation of norbornadiene in the presence of palladium nanoclusters*

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The reaction of norbornadiene (NBD) with allyl acetate in the presence of the nanocluster $Pd_{147}phen_{32}O_{60}(OCOBu^t)_{30}$ (Pd-147; phen is 1,10-phenanthroline) and PPh_3 in acetonitrile is nonselective and is accompanied by the decomposition of the cluster, affording the same allylation products of NBD as the reaction with $Pd_3(OAc)_6$ or $Pd(dba)_2$ (dba is dibenzylideneacetone) combined with PPh_3. In contrast, in the ionic liquid $[bmim][BF_4]$ (bmim is 1-butyl-3-methylimidazolinium), the Pd-147 is not decomposed and the reaction occurs selectively to give methylidene(vinyl)norbornene as the sole product. The data obtained suggest that in an ionic liquid, the reaction under study is catalyzed by the nanocluster Pd-147 rather than by the products of its decomposition.

Key words: norbornadiene, allyl acetate, allylation, palladium, complexes, nanoclusters, catalysis.

The problem that usually arises when studying reactions catalyzed by transition metal nanoclusters is the nature of the actual catalyst: this can be the cluster itself or its mononuclear or polynuclear complexes formed in the catalytic system under treatment with the reactants and medium. A convincing answer is very infrequent. For instance, the giant palladium cluster with the idealized formula $Pd_{561}phen_{60}(OAc)_{180}$ (phen is 1,10-phenanthroline) and its analogs (hereafter, Pd-561)[1,2] catalyze a wide range of reactions (oxidative esterification of alkenes and alkylarenes, reduction with formic acid of compounds containing the C=C, C≡N, and N=O multiple bonds, acetal formation from aldehydes and ketones, redox disproportionation of benzyl alcohol, *etc.*).[2,3] There is convincing evidence that oxidative esterification of alkenes is actually catalyzed by the giant cluster Pd-561 rather than by possible products of its decomposition (mono- and binuclear palladium(II) complexes).[4] However, palladium nanoclusters are known[5,6] to easily undergo decomposition into mononuclear Pd^{II} complexes in the presence

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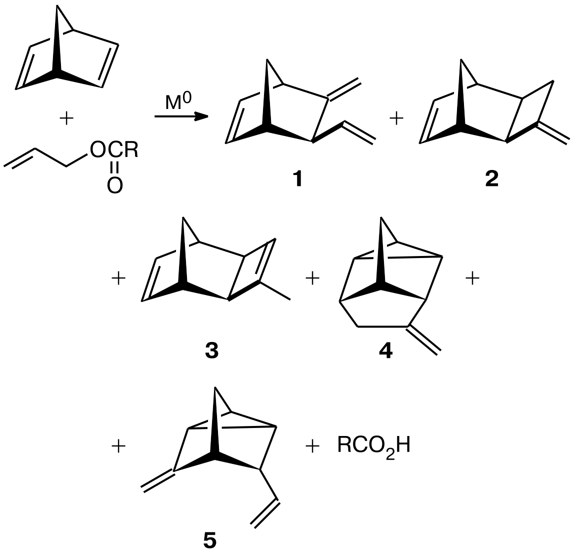
of such reagents as NO, *N*-nitrosomethylurea, phen, *ortho*-benzoquinone, and tetracyanoethene.

In the present work, we studied the allylation of norbornadiene with allyl acetate in the presence of the nanocluster $Pd_{147}phen_{32}O_{60}(OCOBu^t)_{30}$ (Pd-147)[7] and with the trinuclear palladium(II) complex $Pd_3(OAc)_6$ and the mononuclear palladium(0) complex $Pd(dba)_2$ (dba is dibenzylideneacetone) in combination with triphenylphosphine. The goal of this study was to elucidate whether the cluster nature of the catalyst is retained during the reaction. For comparison, the reaction was carried out in two different solvents, namely, acetonitrile and the ionic liquid [bmim][BF_4] (bmim is 1-butyl-3-methylimidazolinium).

Results and Discussion

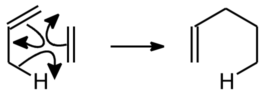
The reactions of norbornadiene (NBD) and norbornene (NB) with allyl carboxylates in the presence of metal complex catalysts afford a broad spectrum of unsaturated polycyclic compounds. For instance, the following products can be obtained from NBD:[8—10]



(1)

M^0 is the catalytically active complex of a Group VIII metal

Formally, reaction (1) is an example of the hydroallylation of olefins, which usually follows the intramolecular concerted mechanism[11] (2) involving the insertion of olefin into the metal—allyl bond with subsequent β-elimination.[12]



(2)

The only example of intermolecular addition of the allyl fragment is provided by NBD and NB. Nickel(0) complexes with trialkyl phosphite efficiently catalyze reaction (1).[8,13,14] Recently, NB[15] and NBD[16] were allylated in the presence of triphenylphosphine palladium complexes. An important advantage of Pd catalysts is that they are less sensitive to moisture and oxygen. However, palladium complexes are less active than the nickel—phosphite catalytic system and variation in the reaction conditions (solvent, temperature, and metal-to-ligand ratio) only slightly affect the reaction selectivity.[16]

Palladium complexes are catalytically active in reaction (1) only in the presence of PPh_3 (molar ratio $PPh_3 : Pd = 2 : 1$).[15,16] For this reason, we added two moles of PPh_3 per mole of Pd whenever palladium complexes were used (Table 1). The reaction was carried out under nitrogen at 60—70 °C for 6 h.

The reaction in acetonitrile is preceded by an induction period (20—40 min), during which the solution turns light yellow. For each of the three Pd catalysts, compounds **1**, **2** and **4** were obtained; the ratio between the reaction products is virtually insensitive to the nature of the starting palladium complex, although the reaction proceeds more slowly with the cluster Pd-147 (see Table 1, entries *1—3*).

The ^{31}P NMR spectra of catalytic solutions, which were recorded in acetonitrile-d_3 one hour after entries *1—3* were started, contain identical signals (Fig. 1). With model experiments, the signals at δ 29.9 and 27.3 were assigned to triphenylphosphine oxide and the complex $Pd(OAc)_2(PPh_3)_2$, respectively. The signals at δ 37.6 (d), 27.3, and 18.3 also appear after the induction period, and their intensities remain unchanged throughout the ex-

Table 1. Products of NBD allylation in the presence of various palladium compounds (solvent (1 mL), catalyst (0.05 mmol of Pd), NBD (1 mmol), allyl acetate (1 mmol), reaction time 6 h)

Entry	Catalyst	Solvent	*T*/°C	Conversion (%)	Reaction products (%)			
					1	**2**	**3**	**4**
1	$Pd_3(OAc)_6 + 2\ PPh_3$	MeCN	70	42	48	20	—	32
2	$Pd(dba)_2 + 2\ PPh_3$	MeCN	70	48	52	19	—	29
3	Pd-147 + 2 PPh_3	MeCN	70	30	46	20	—	34
4	$Pd_3(OAc)_6 + 2\ PPh_3$	[bmim][BF_4]	70	26	38	31	24	7
5	$Pd_3(OAc)_6 + 2\ PPh_3$	[bmim][BF_4]	60	15	70	17	—	13
6	Pd-147 + 2 PPh_3	[bmim][BF_4]	70	10	100	—	—	—

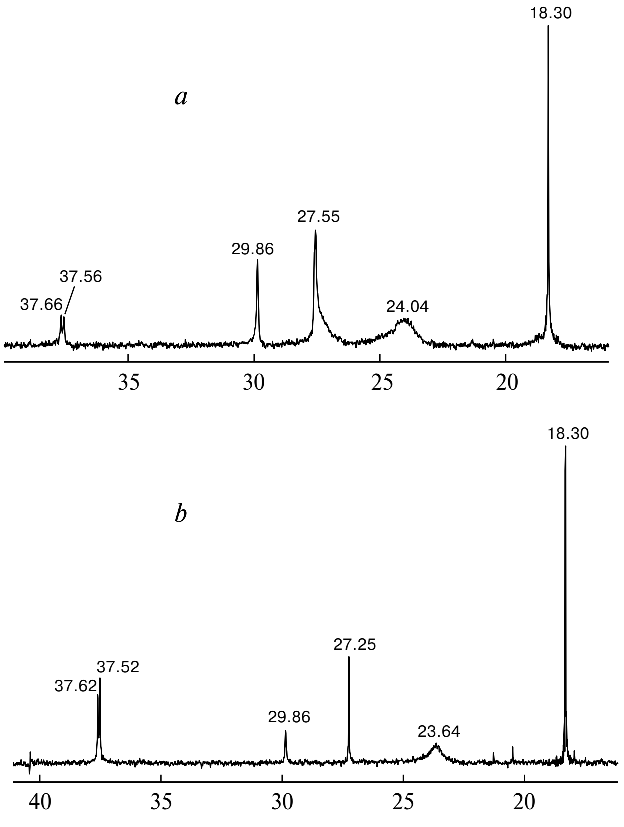


Fig. 1. ^{31}P NMR spectra of the catalytic solutions based on (*a*) Pd-147 + 2 PPh_3 (5 mol. %) and (*b*) $Pd(OAc)_2$ + 2 PPh_3 (5 mol.%); allyl acetate—NBD (1 : 1), 40 °C, reaction time 1 h, acetonitrile-d_3 as a solvent. Singlets at δ 29.9 and 27.3—27.6 correspond to Ph_3PO and $Pd(OAc)_2(PPh_3)_2$, respectively.

periment. Apparently, they can be assigned to mononuclear Pd complexes with phosphine and NBD. The identical composition of the catalytic solutions and the close ratios between the reaction products clearly indicate that the cluster Pd-147 decomposes to form *in situ* mononuclear Pd complexes of the same nature as with the use of $Pd_3(OAc)_6$ and $Pd(dba)_2$.

When passing from acetonitrile to the ionic liquid [bmim][BF_4], the reaction rate decreases and the reaction selectivity changes. With the system $Pd_3(OAc)_6$ + + 2 PPh_3, the composition and ratio of the organic products in the ionic liquid are essentially the same as in acetonitrile (see Table 1, entries *4*, *5*). In entry *4*, compound **3** was also detected; apparently, its formation is due to isomerization of the double methylidene bond in compound **2** into an endocyclic one. A decrease in the reaction temperature favors the formation of compound **1** (entry *5*).

In contrast to acetonitrile, the dark brown (nearly black) color of the solutions in the ionic liquid, which is associated with the nanocluster, does not change either upon the addition of PPh_3 or throughout the reaction time at 70 °C (6 h). However, the reaction selectivity changes dramatically (see Table 1, entries *6*, *3*): the sole detected product was methylidene(vinyl)norbornene **1**. It was shown with special experiments that in the presence of palladium complexes with phosphine, as in the case of the nickel—phosphite catalytic system, neither **2**(**3**) → **1** nor **1** → **2**(**3**) isomerization occurs for the products of NBD allylation.[17]

Hence, unlike solutions in acetonitrile, in the ionic liquid [bmim][BF_4], the cluster Pd-147 and mononuclear Pd complexes behave fairly differently, thus differently affecting the selectivity of reaction (1). Most probably, this is due to stabilization of the cluster catalyst by [bmim][BF_4].

Experimental

Acetonitrile (special purity grade) was distilled over P_2O_5; $Pd(OAc)_2$ [18] and $Pd(dba)_2$ [19] (dba is dibenzylideneacetone) were prepared from $PdCl_2$ according to known procedures. The ionic liquid, 1-butyl-3-methylimidazolinium tetrafluoroborate [bmim][BF_4], was prepared as described in Ref. 20.

Synthesis of the cluster Pd-147. Palladium(II) trimethylacetate (0.772 g, 2.5 mmol) and *o*-phenanthroline (0.2253 g, 1.25 mmol) in 60 mL of ethanol were placed in a flask fitted with a magnetic stirring bar and connected to a gas volumeter. The mixture was stirred at ~20 °C. Then the reaction vessel was evacuated, filled with hydrogen, and saturated with H_2 from the volumometer while vigorously stirring the mixture. After 90 mL of H_2 was absorbed (1.5 mol per Pd atom), stirring was stopped, the hydrogen was pumped out, and the flask was filled with air. The solution was diluted with diethyl ether (240 mL). The black precipitate that formed was separated by centrifuging at 3000 rpm, washed with ether (3×50 mL), and dried *in vacuo*. The yield of the nanocluster Pd-147 was 0.34 g (64%).

Reaction of NBD with allyl acetate was carried out in a temperature-controlled glass flask fitted with a magnetic stirring bar, a reflux condenser, and a sampler. Acetonitrile or [bmim][BF_4] (1 mL) as a solvent, NBD (1 mmol), allyl acetate (1 mmol), a palladium compound (0.05 mmol), and PPh_3 (10 mmol) were placed in the flask, and then the flask was purged with nitrogen. The reaction mixture was heated to a required temperature and stirred under N_2 for 6 h.

Accumulation of the reaction products was monitored by GLC (Khrom-5 chromatograph, flame ionization detector, SPB-20 and β-DEX Supelco capillary columns). The reaction products were identified by the GC-MS (689 ON Agilent Technologies gas chromatograph, mass selective detector) and ^1H NMR spectroscopy (Bruker DPX-300 spectrometer, 300.13 MHz). $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX-300 spectrometer (121.5 MHz) using 80% H_3PO_4 as the external standard.

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