

Nickel vs. palladium catalysts for coupling reactions of allyl alcohol with soft nucleophiles: activities and deactivation processes

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Abstract

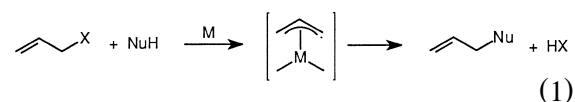
The performance of nickel–phosphine and palladium–phosphine catalytic systems for model coupling reactions of allyl alcohol (**1**) with soft nucleophiles such as diethylamine (**2**), some active methylene compounds (**4**) or **1** itself in the formation of diallylether (**7**) are reported. It is shown that for a number of reactions, particularly the amination of **1**, nickel catalysts are much more active than comparable palladium systems. However, Ni-catalytic species are more sensitive than the corresponding Pd ones, so that catalyst poisoning prevents some reactions to go to completion. The detection of allylbenzene (**8**) as a by-product in the etherification and amination reactions of **1** together with a ^{31}P NMR study has allowed to highlight a degradation pathway involving the cleavage of a phosphorus–carbon bond in a Ni-dppb intermediate. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Allyl alcohol; Nucleophilic substitution; Nickel; Phosphine; Catalyst poisoning

1. Introduction

Transition metal catalysed nucleophilic substitution of allylic substrates provides a useful tool in organic synthesis for the creation of carbon–carbon or carbon–heteroatom bonds (Eq. (1)) [1–7]. Much studies have defined the scope and limitations of this so-called Tsuji–Trost reaction, such as the variety of nucleophiles and leaving groups, and have also highlighted the efficiency of palladium and nickel catalysts [1–7]. The reaction pathway proceeds via a (π -allyl)metal intermediate, whose forma-

tion depends in part on the nature of the leaving group and which may affect the overall catalytic rate.



X = OCOR, OPh, SO₂R
OH

M = Pd⁰, Ni⁰

Accordingly, allylic alcohols show much lower propensity for nucleophilic substitution than the corresponding carbonates, carboxylates or aryl ether derivatives, most probably because of the poor leaving ability of hydroxide anion

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compared to the above groups [1–7]. On the other side, allylic alcohols are cheap, widely available starting materials so that the design of effective catalysts for their direct conversion [8–12] into more added value compounds remains a major objective in catalytic allylation.¹ Particularly relevant in this regard is the coupling of allylic alcohols with secondary amines [13–15] or stabilised carbon nucleophiles [16–20]. These reactions have been reported to take place in the presence of preformed or in situ generated zerovalent palladium- and nickel-phosphine catalysts, but required severe conditions (low substrate/catalyst ratio and/or long reaction time) for satisfactory yields. Coupling of allyl alcohol into diallyl ether is another potentially valuable application which is known to proceed in the presence of analogous zerovalent Pd and Ni catalysts, but with moderate success [14,21–23].

Recently, we reported that the use of preformed Ni(0)–{P₂} catalysts, in which P₂ is a chelating diphosphine or bis(aminophosphine) such as dppb or dppmae, enables the reaction of soft nucleophiles with allylic carboxylates, carbonates and phenates to proceed under mild conditions with high turnover frequencies [24,25].² Most interestingly, this type of complexes also catalyses the rearrangement of dialkyl allylmalonate derivatives [26], a recently discovered case of nucleophilic substitution in which the dialkyl malonate anion acts as a leaving group through C–C bond cleavage [27]. In this special reaction, preformed zerovalent nickel catalysts proved to be significantly more active than comparable palladium catalysts, thus suggesting the ability of the former to activate allylic substrates having a poor leaving group. This paper reports on the catalytic performance

of such nickel complexes to promote various coupling reactions of allyl alcohol, chosen as a model substrate. Classical palladium systems have also been (re)investigated for comparison purposes.

2. Experimental

Bis(1,5-cyclooctadiene)nickel, nickel(II) acetylacetonate, palladium(II) acetate, palladium(II) acetylacetonate and phosphines (dppb, dppp, dppe, PBu₃) were purchased from Strem Chemicals. Allyl alcohol, diethylamine, methyl acetoacetate, dimethyl malonate, acetylacetone, acetonitrile and DMF were purchased from Aldrich Chemical in ≥ 99% purity and used without further purification. Toluene and THF were distilled from sodium benzophenone ketyl. All the catalytic reactions were performed under nitrogen using standard Schlenk techniques. All the solvents and liquid reagents were degassed by two freeze–thaw cycles before use.

Gas liquid chromatography analyses were carried out on a Chrompack apparatus equipped with a CP Sil 5-CB column (25 m × 0.32 mm). ³¹P{¹H} NMR spectra (121.5 MHz) were recorded at room temperature on a Bruker AC-300 spectrometer. Chemical shifts (δ) are reported in ppm relative to external 85% aqueous H₃PO₄ (δ = 0).

2.1. General procedure for coupling reactions of allyl alcohol catalysed by Ni(dppb)₂

In a typical experiment (Table 1, run 1), Ni(COD)₂ (36 mg, 0.13 mmol) in a 50 ml glass reactor equipped with a Teflon cap was added to a degassed solution of dppb (111 mg, 0.26 mmol) in toluene (5 ml). After 15 min of magnetic stirring, allyl alcohol (**1**) (1.51 g, 26 mmol), diethylamine (**2**) (2.85 g, 39 mmol) and heptane (1.00 g, 10 mmol, GLC internal standard) were added. The solution was stirred at 80°C and the reaction was monitored by quantitative GLC analysis of aliquot samples. After total comple-

¹ Beside direct formation of π -allylmetal complexes from allylic alcohols which are reported in Refs. [13–20], the stoichiometric activation of allylic hydroxyl by a Lewis or Bronsted acid has also been described.

² dppb, 1,4-bis(diphenylphosphino)butane; dppmae, 1,2-bis(*N*-methyl-*N*-diphenylphosphino-amino)ethane.

Table 1

Catalysed exchange reactions of allyl alcohol (**1**) with diethylamine (**2**)^a

Run	Catalyst precursor (<i>n</i>) ^b	Solvent	Time (h)	Conv. 1 ^c (mol%)	TOF ^d (h ⁻¹)
1	Ni(COD) ₂ + dppb (2)	PhMe	15	83	50
2	Ni(COD) ₂ + dppb (2)	DMF	15	94	80
3	Ni(COD) ₂ + dppb (2)	MeCN	15	96	110
4	Pd(OAc) ₂ + PPh ₃ (5)	PhMe	5	1	0.4
5	Pd(OAc) ₂ + PPh ₃ (5)	MeCN	15	8	1.5
6	Pd(acac) ₂ + PPh ₃ (1)	none	15	5	0.5
7	Pd(OAc) ₂ + dppb (3)	PhMe	15	46	9

^aThe reactions were carried out at 80°C under nitrogen atmosphere in 5 ml of solvent with 0.13 mmol of Ni or Pd; [Ni or Pd]/[**1**]/[**2**] = 1/200/300.^bMolar ratio of ligand to metal.^cConversion of **1** into *N,N*-diethylallylamine (**3**) (quantitative GC monitoring); Allylbenzene was detected in trace amounts (< 0.1 mol%) in runs 1–3.^dInitial activity (5–10% conversion) expressed in mol of **1** transformed/mol catalyst/h.

tion, *N,N*-diethylallylamine (**3**) was isolated from the reaction mixture by distillation. Etherification and coupling reactions of **1** with active methylene compounds **4a–c** (neutral reagents NuH) using preformed zerovalent nickel–phosphine catalysts were carried out in a similar manner.

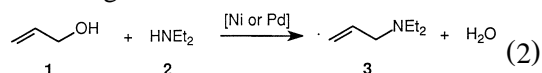
In situ palladium catalysts were prepared by mixing the palladium salt (Pd(OAc)₂ or Pd(acac)₂) with a degassed solution (toluene, acetonitrile) of the phosphine ligand. The resulting yellow solution was stirred for 15 min at room temperature before use.

All the allylation products described in this paper are known. Unambiguous identification was made by comparison of GLC retention times with authentic samples, GC-MS, and ¹H, ¹³C NMR data of isolated products.

3. Results

We first investigated allylic amination and we chose the coupling of allyl alcohol (**1**) with diethylamine (**2**) into *N,N*-diethyl-allylamine (**3**) as a model reaction (Eq. (2)). The results are reported in Table 1. The Ni(dppb)₂ catalyst was

generated from Ni(COD)₂ (COD = cycloocta-1,5-diene) and 2 mol equivalents of the diphosphine. The allylation reaction performed with 0.5 mol% of this catalyst (with respect to **1**) at 80°C toluene as solvent afforded amine **3** with excellent selectivity (> 99.9%, small amounts of allylbenzene account for the balance, vide infra) and an initial activity of 50 h⁻¹ (turnover frequency, TOF^o) (entry 1). However, the activity progressively decreased after 2 h, so that the conversion into **3** was limited to 83% after 15 h (Fig. 1). Using DMF as the solvent resulted in a slightly higher TOF^o, but the decrease in activity was still observed and the yield of **3** reached 94% over the same reaction time (entry 2). A further improvement in TOF^o was gained by carrying out the reaction in acetonitrile, which led to the almost quantitative conversion of **1** into **3** (entry 3). Comparatively, palladium-based catalytic systems were found to be much less efficient in terms of activity. As a matter of fact, the combination of palladium(II) acetate with 5 mol equivalents of triphenylphosphine (in order to generate Pd(0)–PPh₃ complexes [28]), as well as the Atkins's system Pd(acac)₂/PPh₃ [13], led to low TOF^o and poor final yields, whatever the solvent used (entries 4–6).^{3, 4} The performance of Pd catalysts were improved by using dppb in place of PPh₃ (entry 7), but still remained lower than those obtained with nickel systems (Fig. 1).



We next examined the coupling of allyl alcohol with active methylene compounds (Eq. (3)).

³ Several in situ combinations PPh₃/Pd(OAc)₂ with P/Pd ratios of 1, 3 and 5, respectively were investigated using toluene as solvent. The best results in terms of catalytic activity were obtained for a P/Pd ratio of 5.

⁴ All our attempts to reproduce Atkins' results in amination of allyl alcohol were unsuccessful, even by varying reaction conditions. Masuyama et al. [11] also reported recently their inability to perform allylic amination with Pd(0)–PPh₃ catalytic systems.

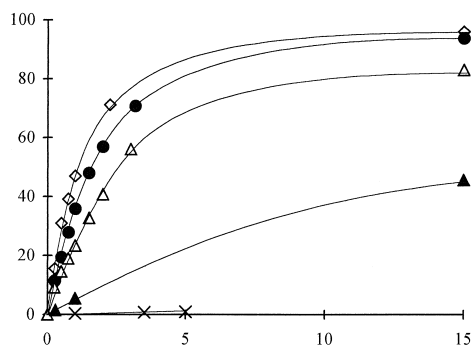
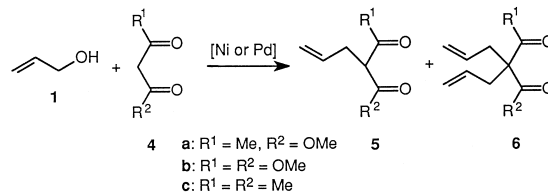


Fig. 1. Conversion (mol%) of allyl alcohol (**1**) vs. time (h) during catalytic coupling with diethylamine (**2**). [Ni or Pd]/[**1**]/[**2**] = 1/200/300; $T = 80^{\circ}\text{C}$; 5 ml of solvent for 0.13 mmol of Ni or Pd. \diamond , Ni-dppb/MeCN; \bullet , Ni-dppb/DMF; \triangle , Ni-dppb/PhMe; \blacktriangle , Pd-dppb/PhMe; \times , Pd-PPh₃/PhMe.

For this purpose, methyl acetoacetate (**4a**), dimethyl malonate (**4b**) and acetylacetone (**4c**) were reacted with **1** in the presence of 2 mol% of a metal catalyst and the results are reported in Table 2. In all cases, the reaction was totally selective for allylation products but a mixture of

monoallylation (**5a–c**) and diallylation (**6a–c**) products was obtained. The latter arise from subsequent reaction of the primary products.



(3)

The best results in terms of activity were observed for the reaction of **4a** with **1** (Table 2, entries 8–12). Namely, the Ni(dppb)₂ catalytic system in toluene as solvent at 80°C showed an initial activity much higher than 300 h^{-1} and the reaction was completed within 10 min, affording **5a:6a** in a 74:26 molar ratio (entry 8). At 50°C , a total conversion was obtained in 50 min with the same **5a:6a** ratio. Contrary to the

Table 2

Catalytic alkylation of active methylene compounds (**4a–c**) using allyl alcohol (**1**)^a

Run	4a–c	Catalyst precursor (<i>n</i>) ^b	Time ^c (h)	Conv. 1 ^d (mol%)	Sel. 5/6 ^e (mol%)	TOF ^{of} (h ^{−1})
8	4a	Ni(COD) ₂ + dppb (2)	0.15	100	85/15	> 300
9 ^g	4a	Ni(COD) ₂ + dppb (2)	0.8	100	85/15	100
10 ^h	4a	Ni(COD) ₂ + dppb (2)	16	90	87/13	40
11	4a	Pd(OAc) ₂ + PPh ₃ (5)	5	90	89/11	50
12	4a	Pd(OAc) ₂ + dppb (3)	1.5	90	84/16	100
13	4b	Ni(COD) ₂ + dppb (2)	4	75	95/5	17
			12	100	94/6	
14	4b	Pd(OAc) ₂ + dppb (3)	2	75	95/5	60
			3	90	95/5	
15	4c	Ni(COD) ₂ + dppb (2)	3.75	75	91/9	35
			12	100	87/13	
16 ⁱ	4c	Ni(COD) ₂ + dppb (2)	2	30	94/6	115
			17	30	94/6	
17	4c	Pd(OAc) ₂ + dppb (3)	0.5	75	86/14	125
			1.5	100	82/18	

^aUnless otherwise stated, the reactions were carried out at 80°C under nitrogen atmosphere in 12.5 ml of toluene with 0.13 mmol of Ni or Pd; [Ni or Pd]/[**1**]/[**4**] = 1/50/75.

^bMolar ratio of ligand to metal.

^cThe reaction times were not necessarily optimized.

^dConversion of **1** into mono- and diallylation products **5** and **6a–c** (quantitative GC monitoring); No by-product was detected.

^eMolar selectivity.

^fInitial activity (5–10% conversion) expressed in mol of **1** transformed/mol catalyst per h.

^gReaction performed at 50°C .

^hDMF as solvent.

ⁱ[Ni]/[**1**]/[**4**] = 1/170/200; 0.13 mmol of Ni in 5 ml of toluene.

allylation of diethylamine, the use of DMF as the solvent was detrimental (entry 10), and the coupling of **1** with active methylene nucleophiles was generally best conducted in toluene. The performances of palladium-based catalysts were strongly affected by the nature of the phosphorus ligand, and demonstrated once again the superiority of the dppb-modified system over PPh_3 (entries 11 and 12) but the best activity was about the tenth of that of the $\text{Ni}(\text{dppb})_2$ catalyst. An opposite trend was found for the allylation of **4b** and **4c**, i.e., palladium catalysts proved to be more efficient than comparable nickel systems. In the case of dimethyl malonate (**4b**), the Pd-dppb catalyst was about twice faster than Ni-dppb, judging by the completion times (entries 13 and 14). This difference is even more marked with acetylacetone (**4c**), for which there is ca. one order of magnitude between the two catalytic systems (entries 15

and 17). However, it has to be mentioned that the presence of **4c** most likely induced the degradation of the Ni-dppb catalyst, as the colour of the solution slightly shifted in the reaction course from orange–yellow (typical colour of $\text{Ni}(\text{dppb})_2$) to light green (Ni(II) species, vide infra). This degradation had little influence on the final yield in **5c:6c** when a low substrate:catalyst ratio was used (entry 15), but it stopped definitely the reaction before completion at higher ratio (entry 16).

When no external nucleophile is opposed to allyl alcohol, the formation of diallyl ether (**7**) may be observed (Eq. (4)) [14,21–23]. We evaluated the capability of various catalysts to promote this reaction and the results are reported in Table 3. Several experiments aimed at comparing in situ generated and preformed zerovalent Ni systems were first conducted. Thus, Furukawa's system [14], formed by the in situ

Table 3
Catalysed etherification of allyl alcohol (**1**) into diallylether (**7**)^a

Run	Catalyst precursor (<i>n</i>) ^b	Time (h)	Conv. 1 ^c (mol%)	Sel. 7 (mol%)	Yield 8 ^d (%/Ni)	TOF ^{oe} (h ^{−1})
18	$\text{Ni}(\text{acac})_2 + \text{PBu}_3 + \text{NaBH}_4$ (1:3:1)	1	26	100 ^f	—	35
		15	56	100 ^f	—	
19	$\text{Ni}(\text{COD})_2 + \text{PBu}_3$ (3)	1	45	100	—	80
		15	73	100	—	
20	$\text{Ni}(\text{acac})_2 + \text{dppb} + \text{NaBH}_4$ (1:1.5:1)	1	26	99.4 ^f	12	35
		15	50	99.0 ^f	38	
21	$\text{Ni}(\text{COD})_2 + \text{dppb}$ (2)	1	46	98.8	40	90
		15	52	97.3	100	
22 ^g	$\text{Ni}(\text{COD})_2 + \text{dppb}$ (2)	1	13	96.0	36	25
		15	22	93.8	96	
23	$\text{Ni}(\text{COD})_2 + \text{dppb}$ (4)	1	60	99.0	40	120
		15	66	96.1	180	
24	$\text{Ni}(\text{COD})_2 + \text{PPh}_3$ (4)	1	ca. 1 ^h	0 ^h	—	< 1
		15	ca. 1 ^h	0 ^h	—	
25	$\text{Pd}(\text{OAc})_2 + \text{PPh}_3$ (5)	1	51	100	—	70
		15	92	100	—	
26	$\text{Pd}(\text{OAc})_2 + \text{dppb}$ (3)	1	29	100	—	25
		15	93	100	—	

^aUnless otherwise stated, the reactions were carried out at 80°C under nitrogen atmosphere in 5 ml of toluene with 0.13 mmol of Ni or Pd; $[\text{Ni or Pd}]/[\text{1}] = 70\text{--}77.3$.

^bMolar ratio of ligand to metal.

^cConversion of **1** into diallylether (**7**) and allylbenzene (**8**) (quantitative GC monitoring).

^dYield of allylbenzene with respect to Ni.

^eInitial activity (5–10% conversion) expressed in mol of **1** transformed/mol catalyst per h.

^fMinute amounts of 3-allyl-2,4-pentanedione were detected by GC.

^gTHF as solvent.

^hAcroleine and propene account for the conversion.

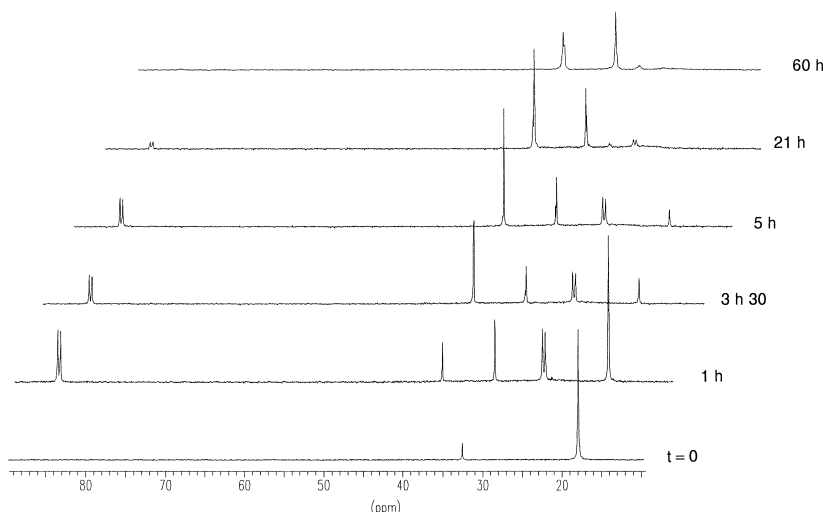


Fig. 3. $^{31}\text{P}\{^1\text{H}\}$ NMR monitoring (121 MHz) of etherification of **1** into **7** catalysed by $\text{Ni}(\text{dppb})_2$. Reaction conducted with 0.13 mmol of $\text{Ni}(\text{COD})_2$, 0.26 mmol of dppb and 9.1 mmol of **1** in 5 ml of THF at 80°C .

ppm, but two new singlets emerged at $\delta = 39.3$ and 32.8 ppm. These signals were the main ones observed after 60 h. On the other side, GC analysis of the samples analysed by ^{31}P NMR spectroscopy showed that allylbenzene (**8**) is produced concomitantly with the appearance of the two doublets.⁶

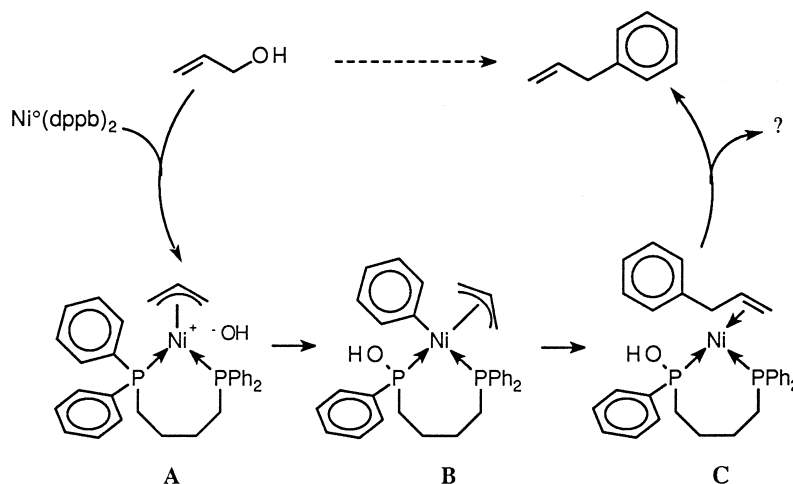
4. Discussion and mechanistic considerations

The above results strongly suggest that the species at the origin of the doublets in the ^{31}P NMR spectra arises from the degradation of dppb in a catalytic intermediate, and accounts for the catalyst decay observed in the course of some etherification reactions (Fig. 3). Unfortunately, our efforts to isolate this complex were unsuccessful. A tentative structure together with a likely mechanism for its formation are out-

lined in Scheme 1.⁷ We propose that the π -allyl- $\text{Ni}(\text{dppb})$ complex (intermediate **A**, singlet at $\delta = 32.3$ ppm) resulting from the oxidative addition of **1** onto $\text{Ni}(\text{dppb})_2$ would undergo an exchange of an aryl group of a diphenylphosphino moiety with an hydroxy group at nickel (intermediate **B**). Such a process of cleavage of aryl–phosphorus bond, involving transfer of the aryl group to the metal and reverse migration of the organic group from metal to phosphorus, has been demonstrated for the formation of diaryl(allyl)phosphine from π -allyl- $\text{Pd}(\text{II})$ [31,32]. At this stage, **8** would be produced via intramolecular nucleophilic attack of the migrating phenyl group at nickel to π -allyl (intermediate **C**) and subsequent decooordination. In this hypothesis, the two doublets observed in the ^{31}P NMR spectra can be explained by the

⁶ The formation of allylbenzene could also be observed upon reacting $\text{Ni}(\text{dppb})_2$ with diallylether at 80°C in THF, though the reaction proceeded more slowly than with allyl alcohol (Yield of **8** with respect to Ni: 7% in 6.5 h; 63% in 63 h; compare with entry 22, Table 3). The ^{31}P NMR spectrum of the reaction medium after 60 h exhibited singlets at $\delta = -14.9$ ppm (broad, dppb), 17.9 (minor, $\text{Ni}(\text{dppb})_2$), 27.6 and 33.6 (major signals).

⁷ The formation of a nickel species bearing dppb-monoxide ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{PPh}_2$) as a chelating ligand was examined as an alternative possibility. For this purpose, dppb-monoxide was synthesized from dppb [29], and reacted with different nickel complexes such as $\text{Ni}(\text{COD})_2$, $\text{Ni}(\text{dppb})_2$ and the $\text{Ni}(\text{dppb})_2$ / **1** (1:1) combination. ^{31}P NMR analysis of the above combinations showed only singlets ($\delta \sim 30$ – 35 ppm), without any couple of doublets as expected from such chelated complex [30], thus turning down this hypothesis.



Scheme 1. Plausible degradation pathway of Ni-dppb catalyst accounting for the side formation of allylbenzene.

presence of two strongly inequivalent phosphorus atoms in intermediate **B** or **C**, or other related species.⁷ Also, singlets at $\delta \sim 39$ ppm, whose integration at the end of the reaction accounts for about the half of phosphorus atoms initially introduced, may be regarded as the final stage of degradation of one diphenylphosphino moiety of dppb.

The formation of **8** was also noticed during the allylic amination of **1** by diethylamine catalyzed by Ni(0)-dppb systems in various solvents (Table 1, entries 1–3), but the amounts were significantly lower than those observed for the etherification process (maximal amount of **8**: 0.1% vs. **1**, i.e., 20% vs. Ni). So, it is likely that the presence of the amine delays the degradation pathway of Ni-dppb intermediates outlined in Scheme 1, thus resulting in longer catalyst life and better final yields.

On the contrary, when active methylene compounds (**4a–c**) were reacted with allyl alcohol, no traces of allylbenzene (**8**) (nor diallylether (**7**)) could be detected, so that the catalyst decay observed during alkylation of **1** with **4c** with Ni(0)-dppb systems, especially at high substrate/catalyst ratios (Table 2), implies another route. The pale green colour of the final solution indicates the presence of Ni(II) species, most probably Ni(acac)₂ produced through slow

protolysis of Ni(dppb)₂ by **4c** (Eq. (5)). In fact, acetylacetonate is the most acidic compound among those tested (pK_a in water at 25°C **4c**: 9; **4b**: 11; **4a**: 13; **1**: 16).



5. Conclusion

In conclusion, preformed zerovalent nickel-dppb complexes are intrinsically active catalysts for a number of coupling reactions of allyl alcohol with soft nucleophiles such as diethylamine, some active methylene compounds or even **1** itself in the etherification process. Initial activities observed with this type of catalysts are most often higher than those of comparable palladium systems; this may be due either to the better ability of the nickel catalytic species to activate allylic substrates having a poor leaving group and/or to the fact that preformed zerovalent Ni-dppb complexes act as better catalyst precursors than palladium-phosphine. However, Ni(0)-dppb species suffer from poor stability during the reaction course, so that their overall performance are not totally satisfactory.

Two degradation pathways of nickel intermediates have been highlighted, which could help in the next future for the design of active and more stable nickel-based catalysts.

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