ELSEVIER

Journal of Molecular Catalysis A: Chemical 182–183 (2002) 309–317

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Silica immobilised palladium phosphine complexes as recyclable, regioselective catalysts for the allylic alkylation

Albertus J. Sandee, Dragana Dimitrijevic, Richard J. van Haaren, Joost N.H. Reek*, Paul C.J. Kamer, Piet W.N.M. van Leeuwen[1]

Institute of Molecular Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Received 10 January 2001; accepted 10 July 2001

Abstract

The covalent immobilisation of palladium phosphine complexes on silica is demonstrated to be a viable method for the recovery of allylic alkylation catalysts. Both bidentate and monodentate phosphine ligands form stable palladium catalysts that could be recycled without catalyst deterioration and metal leaching. The regioselectivity of the immobilised catalyst for the alkylated products showed the same trend as the homogeneous analogues; in the alkylation of 3-methyl-but-2-enyl trifluoroacetate with sodium diethyl 2-methylmalonate we observed an increase in selectivity for the branched product from 11.6 to 58.3% on increasing the P–Pd–P bite angle from 93 to 108°. The morphology of the silica support did not have impact on the catalyst performance as amorphous silica and MCM-41 supported Pd(**1**) gave a similar product distribution in the alkylation of 3-methyl-but-2-enyl trifluoroacetate with sodium diethyl 2-methylmalonate (42% linear (*E*) alkylated product and 58% branched alkylated product). We observed that a pre-modification of the silica surface using dichlorodimethylsilane was crucial for the recycling properties of the catalyst system. Using non-modified silica both the conversion (from 24 to 19%) and the regioselectivity (from 43 to 19% for the branched alkylation product) dropped in four consecutive catalyst runs using Pd(**1**)′. The modified systems yielded high conversions (68–64%) and increased regioselectivies for the branched alkylation product (58–57%) in four consecutive catalytic runs.

Keywords: Allylic alkylation; Bite angle; Immobilisation; Recycling; Palladium

1. Introduction

Palladium catalysed C–C bond formation reactions are powerful tools in organic synthesis, providing mild and selective methods to a great variety of valuable chemicals from basic precursors. An intriguing example of such a reaction is the allylic substitution reaction. After the discovery by Tsuji, further development of this reaction by Trost and others led to catalyst systems that can be extensively used in modern organic synthesis [1–7]. For applications in the fine chemical industry it is of great importance that these palladium containing catalysts are completely and conveniently separated from the product and, preferably, reused in numerous catalytic runs thereby increasing the number of turnovers. The vast amount of research devoted to the Trost–Tsuji reaction also stimulated the investigation of several approaches to the immobilisation of alkylation catalysts on organic polymers [8–16]. Despite the advantages (i.e. chemical and mechanical inertness) there is surprisingly

* Corresponding author.
E-mail addresses: reek@anorg.chem.uva.nl (J.N.H. Reek), pwnm@anorg.chem.uva.nl (P.W.N.M. van Leeuwen).
[1] Co-corresponding author.

1381-1169/02/$ – see front matter
PII: S1381-1169(01)00297-7

little reported on the covalent anchoring of this type of catalysts on inorganic supports [17,18]. Sinou et al. investigated the application of a two phase H_2O-nitrile catalyst system, using $Pd(TPPTS)_x$ as the water soluble catalyst. This enabled a straightforward catalyst recovery via phase-separation [19]. The use of this catalyst in a set-up involving a supported aqueous phase catalyst resulted in an important increase in catalyst performance and recovery compared to the two phase system [20]. The activity and recycling of these systems were found to be largely dependent on the miscibility of the two phases and the water content on the silica support, respectively [21,22]. As part of an ongoing research toward sustainable and recyclable catalyst systems [23–27] we studied the covalent immobilisation of palladium catalysts on silica. Here we report that the immobilisation of palladium phosphine complexes to silica, tethered via the phosphine ligand, enables an easy and complete separation of the active catalyst from the products. Moreover, it will be shown that the regioselectivity of the alkylation reaction is influenced by the nature of the phosphine ligand similar to the homogeneous analogues.

2. Experimentals

2.1. General

4,5-Bis(diphenylphosphino)-phenoxazine [28] and bis(2-(diphenylphosphino)ethyl)ammonium chloride [29] were synthesised according to literature procedures. All other chemicals were purchased commercially and used without further purification. The type of silica was silica 60 A (70–200 μm). Hexane, pentane, diethyl ether, THF, toluene and benzene were distilled from sodium. Dichloromethane was distilled from calcium hydride. All reactions were performed using standard Schlenk techniques under Ar. All solutions and solvents not stated above were degassed prior to their use. NMR spectra were recorded on a Bruker AMX 300 or DRX 300 spectrometer. Chemical shifts are in ppm relative to TMS as external standard unless stated otherwise. FTIR spectra were obtained on a Bio-Rad FTS-7 spectrophotometer. Mass spectra (FAB) were recorded on a JEOL JMS SX/SX102A. Elemental Analyses were performed on an Elementar Vario EL apparatus (Foss Electric). GC samples were measured on an Interscience Mega2 apparatus, equipped with a DBI column, length 30 m, inner diameter 0.32 mm, film thickness 3 μm, and an FID detector.

2.1.1. N-(3-trimethoxysilane-n-propyl)–4,5-bis (diphenylphosphino)-phenoxazine (**1**)

A solution of 500 mg (0.907 mmol) 4,5-bis(diphenylphosphino)-phenoxazine in 5 ml of dimethylformamide was added to a suspension of 44 mg (1.833 mmol) NaH in 5 ml of dimethylformamide. The orange mixture was stirred for 90 min at 70 °C. An amount of 362 mg (1.819 mmol) (3-chloropropyl)trimethoxysilane was added at room temperature. The mixture was stirred for 18 h at 70 °C. The brown-yellow suspension was filtered and the solvent was removed under reduced pressure. The product was washed with several portions of pentane until a white powder was obtained. The solvent was removed in vacuo (1×10^{-5} mbar) at 60 °C for 18 h (yield 77%). Mp 138 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20 (m, 20H; ArH), 6.66 (t, 2H, $^3J = 7.9$ Hz; CP–C<u>H</u>–CH), 6.49 (d, 2H, $^3J = 1.0$ Hz; CH–C<u>H</u>–CH), 5.97 (dd, 2H, $^3J = 1.6, 7.8$ Hz; CH–C<u>H</u>–CC), 3.61 (s, 9H; C<u>H</u>$_3$–O), 3.49 (t, 2H, $^3J = 8$ Hz; N–C<u>H</u>$_2$), 1.80 (m, 2H, $^3J = 8.1$ Hz; CH_2–C<u>H</u>$_2$–CH_2), 0.72 (t, 2H, $^3J = 8.0$ Hz; Si–C<u>H</u>$_2$). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, versus H_3PO_4): δ −18.5. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 146.7 (t, J(P, C) = 10.9 Hz, CO), 136.8 (t, J(P, C) = 12.8 Hz; PC), 133.5 (t, J(P, C) = 10.5 Hz; PC<u>C</u>H), 132.9 (CN), 128 (CH), 127.9 (CH), 124.9 (CH), 124.4 (t, J(P, C) = 8.5 Hz, C), 123.5 (CH), 111.6 (CH), 50.4 (CH_3–O), 46.6 (CH_2–N), 17.7 (CH_2–<u>C</u>H_2–CH_2), 5.8 (CH_2–<u>C</u>H_2–Si). ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$): δ −43. FTIR (KBr, cm^{-1}): 3058 (w), 2940 (w), 2839 (w), 1553 (m), 1461 (s), 1417 (s), 1377 (m), 1226 (m), 1087 (s), 696 (s). Exact mass (FAB): 714.2353 $[M + H]^+$ (calcd. $C_{42}H_{42}NO_2P_2Si$: 714.2358). Anal. calcd. for $C_{42}H_{41}NO_2P_2Si{\cdot}H_2O$: C, 68.93; H 5.92; N, 1.92. Found: C, 69.08; H, 5.70; N, 1.76.

2.1.2. N-(3-triethoxysilane-n-propyl)–N′N′-bis (2-(diphenylphosphino)ethyl)urea (**2**)

416.9 mg (0.943 mmol) bis(2-(diphenylphosphino)-ethyl)ammonium chloride was dissolved in 10 ml of dichloromethane. A volume of 10 ml of 0.1 M NaOH was added and the mixture was stirred vigorously

at room temperature for 10 min. The organic layer was dried on $MgSO_4$ and the water traces were removed by azeotropic distillation with three times 3 ml of toluene. The residue was dissolved in 10 ml of dichloromethane and 243 mg (1.132 mmol) 3-isocyanatopropyltriethoxysilane was added to the solution. The mixture was stirred at room temperature for 18 h. The solvent was removed in vacuo (60 °C at 1×10^{-5} mbar for 18 h). The product is a colorless oil (yield: 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40–7.26 (m, 20H, ArH), 4 (br, t, 1H, NH), 3.81 (q, 6H, ^3J = 7.0 Hz, O–CH$_2$), 3.23 (m, 4H, ^3J = 9.1 Hz, CH$_2$–CH$_2$–P), 3.08 (m, 2H, ^3J = 5.9, 7 Hz, CH$_2$–CH$_2$–N), 2.27 (m, 4H, CH$_2$–P), 1.47 (m, 2H, ^3J = 7.4 Hz, CH$_2$–CH$_2$–CH$_2$), 1.22 (t, 9H, ^3J = 7.1 Hz, CH$_3$–CH$_2$), 0.55 (m, 2H, ^3J = 8.5 Hz, CH$_2$–Si). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, versus H_3PO_4): δ −20.5. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 156.8 (C=O), 137.5 (d, J(P, C) = 12.8 Hz; PC), 132.4 (d, J(P, C) = 18.9 Hz; PCCH), 128.6 (PC–CH–CH–CH), 128.4 (d, J(P, C) = 6.8 Hz; PC–CH–CH), 58.2 (CH$_3$–CH$_2$), 44.7 (d, J(P, C) = 24.9 Hz; CH$_2$–CH$_2$–P), 43.1 (CNH), 27.3 (d, J(P, C) = 15.1 Hz; CH$_2$–P), 23.4 (CH$_2$–CH$_2$–CH$_2$), 18.12 (CH$_3$). FTIR (KBr, cm^{-1}): 3365 (m), 3058 (w), 2976 (s), 2927 (s), 1634 (s), 1526 (s), 1107 (s), 1079 (s), 742 (s), 697 (s). Exact mass (FAB): 689.3043 $[M + 1]^+$ (calcd. $C_{38}H_{51}O_4N_2SiP_2$: 689.3015). Anal. calcd. for $C_{38}H_{50}O_4N_2P_2Si{\cdot}0.5H_2O$: C, 65.40; H, 7.37; N, 4.01. Found: C, 65.21; H, 7.32; N 3.84.

2.1.3. Ligand immobilisation procedure

An amount of 1 g of silica, which was dried at 180 °C for several days, was further dried under reduced pressure at 180 °C for 2 h. After cooling down to room temperature, 100 mg ligand was added to a suspension of the silica in 20 ml of toluene. After the reaction mixture was stirred for 2 h at 65 °C, the silica was filtered and washed with three portions of toluene. The silica was suspended in a mixture of 20 ml of toluene and 2 ml of triethylamine and 0.5 ml of dichlorodimethylsilane were added to the mixture after stirring it for 5 min. The resulting mixture was stirred at room temperature for 1 h and the silica was filtered and carefully washed with one portion of diethyl ether, two portions of methanol and again with two portions of diethyl ether. Finally, the product was dried under reduced pressure and stored under an inert atmosphere.

When MCM-41 was the support, the exterior of the material was pre-modified with dichlorodimethylsilane. To this end, one drop of dichlorodimethylsilane was added to a suspension of 1 g of MCM-41 in 20 ml of diethyl ether and the reaction mixture was stirred at room temperature for 1 h. After the MCM-41 was filtered and washed with diethyl ether the preparation was finished using the method described above.

2.2. Catalysis procedure

The catalytic experiments were performed in 2 ml of THF, using 5×10^{-7} mol of Pd(dba)$_2$, 50 mg of the above described immobilised ligand, 1 mmol of substrate and 0.5 mmol of sodium diethyl 2-methylmalonate at room temperature. A mixture of the palladium precursor and the silica-immobilised ligand were stirred in the THF for 30 min. After washing the catalyst with THF the catalysis was started by the addition of the substrate and the sodium diethyl 2-methylmalonate. The reaction was monitored by taking samples from the reaction mixture that, after aqueous work-up, were analysed by GC using decane as the internal standard. Subsequent catalytic runs were performed after removal of the products and washing of the catalyst with THF.

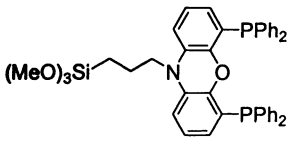
The ICP–AES measurements were performed on a sequential Jarrell Ash upgraded Atomscan model 2400 ICP scanning monochromator with a typical detection limit for palladium of ng/ml. Further specifications of the spectrometer are given elsewhere [31]. Samples taken from the reaction mixture were pre-treated prior to analysis. After evaporation of the solvent the organic residue was completely oxidised by boiling sulphuric acid (96%) and subsequent addition of nitric acid (65%). Demineralised water was carefully added and a clear solution of 50 ml was obtained, which was analysed by ICP–AES.

3. Results and discussion

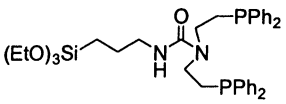
3.1. Ligand immobilisation

Three different trialkoxysilane functionalised phosphine ligands were used in this study: *N*-(3-trimethoxy-

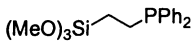
silane-*n*-propyl)–4,5-bis(diphenylphosphino)-phenoxazine (**1**), *N*-(3-triethoxysilane-*n*-propyl)–*N*′,*N*′-bis (2-(diphenylphosphino)ethyl)urea (**2**), and 2-(diphenylphosphino)ethyltrimethoxysilane (**3**) are shown below.



1



2



3

Ligand **1** was synthesised via an *N*-alkylation of 4,5-bis(diphenylphosphino)-phenoxazine [28] using (3-chloropropyl)trimethoxysilane and NaH as a base. Ligand **2** was obtained after a straightforward and clean reaction of 3-isocyanatopropyltriethoxysilane with bis((2-diphenylphosphine)ethyl)amine and ligand **3** was obtained commercially. Ligands were tethered to the support-surface by stirring a toluene suspension of the ligand and silica at 65°C for 2 h. Subsequently, the remaining silanols on the silica were modified to alkylsilyl species by treatment with dichlorodimethylsilane. This "capping" of silanols is done in order to avoid side reactions during catalysis. The efficiency of this modification is clearly visible in the IR spectra, which show that the broad OH band at 3000–3300 cm^{-1} is decreased to a large extent (Fig. 1). The obtained supported ligand systems can be stored for months under an inert atmosphere.

3.2. Catalysis

The palladium phosphine catalysts Pd(**1**), Pd(**2**) and Pd(**3**) were prepared in situ by stirring a mixture of silica immobilised ligand in a solution of $Pd(dba)_2$ in THF. This resulted in a decoloration of the solution within 5 min (from purple to colorless) and at the

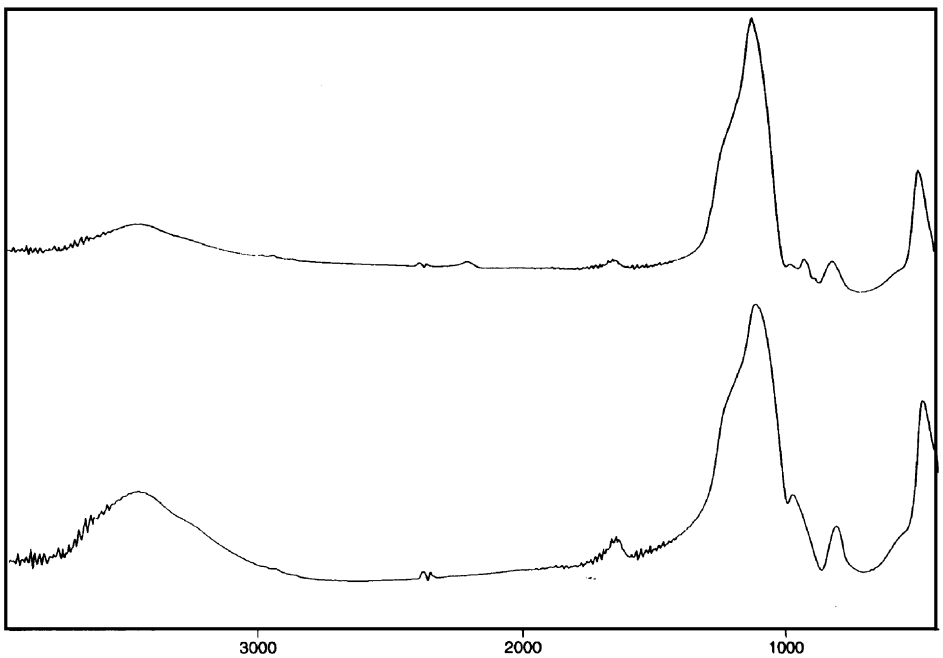
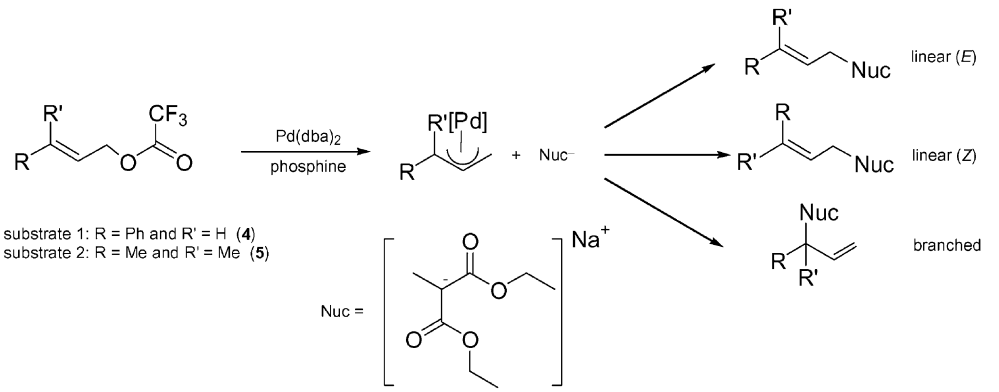


Fig. 1. Infrared spectra of silica (bottom) and silica modified with dimethyldichlorosilane (top).



Scheme 1. Formation of the different regioisomers in the allylic alkylation of **4** and **5** using diethyl 2-methylmalonate as the nucleophile.

same time the silica turned yellow. When no ligand is present on the silica no adsorption of the Pd precursor on the silica surface takes place and the $Pd(dba)_2$ remained in solution. After washing the catalyst containing silica, the systems were used in the allylic alkylation of 3-phenyl-prop-2-enyl trifluoroacetate (**4**) using sodium diethyl 2-methylmalonate as the nucleophile (Scheme 1). In this reaction three alkylated products can be formed, the linear (*E*), the linear (*Z*) and the branched product.

All catalyst systems were very active in this reaction; turnover frequencies (TOFs, determined as average TOFs by means of GC-analysis) ranged from 17×10^3 mol mol^{-1} h^{-1} for Pd(**1**) to 10^4 mol mol^{-1} h^{-1} for Pd(**3**) (Table 1). In all cases the linear (*E*) product is the main product (up to 95%). The amount of branched product formed increases in the order Pd(**2**) < Pd(**3**) < Pd(**1**) (2.5, 3.4, 5.3% respectively). The differences, however, are very small because the linear (*E*) product, in which the conjugation is maintained, is more stable and, thus, the nature of the catalyst influences the product distribution only marginaly. The sterically more hindered substrate 3-methyl-but-2-enyl trifluoroacetate (**5**) was converted somewhat more slowly compared to **4** (Table 2). Also for **5** the reaction rate is dependent on the nature of the phosphine ligand, the xanthene based diphosphine again forming the fastest catalyst. Using substrate **5**, the differences in reaction rate are more pronounced; Pd(**1**) (TOF of 6800 mol mol^{-1} h^{-1}) is nearly three times faster than the other catalysts. Pd(**2**) showed a TOF of 1800 mol mol^{-1} h^{-1} and Pd(**3**) showed a TOF of 2700 mol mol^{-1} h^{-1}. The higher catalyst activity of Pd(**1**) compared to Pd(**2**) is ascribed to the larger P–Pd–P bite angle, which was calculated to be 108° for ligand **1** and 93° for ligand **2** [24]. This bite angle effect was previously observed for the homogeneous catalysed alkylation of **5** using the same nucleophile.

Table 1
Results from the allylic alkylation of **4** with sodium diethyl 2-methylmalonate[a]

Entry	Catalyst	Conversion[b] (%)	TOF[c] ($\times 10^4$)	Linear product[d] (%)	Branched product[d] (%)
1	Pd(**1**)	54	1.7	94.6	5.3
2	Pd(**2**)	28	1.2	97.5	2.5
3	Pd(**3**)	30	1.0	96.6	3.4
4	No Pd[e]	1.7	–	100	0.0

[a] Reactions were run in 2 ml of THF, using 5×10^{-7} mol of $Pd(dba)_2$, 50 mg silica immobilised ligand (containing 1×10^{-5} mol phosphine), 1 mmol of substrate and 0.5 mmol of sodium diethyl 2-methylmalonate at room temperature.

[b] Determined after 1 min.

[c] The average TOF calculated after 1 min in mol mol^{-1} h^{-1}.

[d] Determined by means of GC-analysis.

[e] A blank reaction with all components present in the reaction mixture, including silica, but without the presence of the catalyst.

Table 2
Results from the allylic alkylation of **5** with sodium diethyl 2-methylmalonate[a]

Entry	Catalyst	Conversion[b] (%)	TOF[c] ($\times 10^3$)	Linear product[d] (%)	Branched product[d] (%)
1	Pd(**1**)	68	6.8	41.7	58.3
2	Pd(**2**)	25	1.8	88.4	11.6
3	Pd(**3**)	20	2.7	89.3	10.7
4	Pd(**1**)/MCM-41	68	ND	41.6	58.4

[a] Reactions were run in 2 ml of THF, using 5×10^{-7} mol of $Pd(dba)_2$, 50 mg of silica immobilised ligand (containing 1×10^{-5} mol phosphine), 1 mmol of substrate and 0.5 mmol of sodium diethyl 2-methylmalonate at room temperature.
[b] Determined after 5 min.
[c] The average TOF calculated after 5 min in mol mol^{-1} h^{-1}.
[d] Determined by means of GC-analysis.

Ligands containing a wide bite angle were found to decrease the back-bonding to the substituted site of the allyl moiety, which results in a pronounced effect on the reactivity of the allylic carbon atoms and also on the regioselectivity of this reaction [30]. Using the silica immobilised systems, the differences in regioselectivity for the branched product were also clearly observed. Pd(**1**) produced the branched product with 58.3% selectivity whereas Pd(**2**) and Pd(**3**) formed only 11.6 and 10.7% of the branched product, respectively. As was observed for comparable homogeneously catalysed experiments, the larger bite angle of **1** enhances the electronic preference for nucleophilic attack on the branched position [30]. The current results clearly indicated that the catalyst performance of this type of systems remain largely intact upon immobilisation to a silica support. Ligand **2**, having a non-rigid backbone with a small bite angle, induces a selectivity similar as monophosphine containing Pd(**3**).

Johnson et al. [18] showed that the use of MCM-41 as support has a large impact on the enantioselectivity and regioselectivity in the allylic alkylation reaction. The constrained catalyst environment gave a significant increase in the percentage of branched product in the alkylation of **2**. In contrast, we observed that Pd(**1**) immobilised on MCM-41 gave the same regioselectivity as Pd(**1**) tethered to amorphous silica; 58.4 and 58.3%, respectively (Table 2, entries 4 and 1).

3.3. Recycling of the catalyst

The catalyst recovery was investigated by performing series of four consecutive catalytic runs using both **4** and **5** as the substrate. For **4** both the activity and the high regioselectivity for the linear product remained the same upon recycling catalyst Pd(**1**), Pd(**2**) and, surprisingly, also Pd(**3**) (Table 3). Neither a systematic drop in activity nor a decrease in selectivity was observed in four catalyst runs which indicates that a complete retention of the active catalyst on the silica support was obtained. Colourless product mixtures were separated from the solid catalyst and also no palladium black formation was observed. With AES experiments no significant palladium could be detected in the product phase, indicating that leaching was less then 1% per cycle of the total amount of palladium used. Even Pd(**3**), containing the monophosphine ligand **3**, showed a full recovery of catalytic activity in these recycling experiments.

The recycling experiments were also adopted to the allylic alkylation of **5** (Table 4). Pd(**1**), Pd(**2**) and Pd(**3**) again showed a clean and straightforward catalyst recovery upon reuse of the catalysts in four consecutive catalytic runs. Pd(**1**) remained selective for the branched product up to the fourth catalyst runs (the regioselectivity varied between 56.7 and 58.4% (entries 1–4)). Also Pd(**2**), for which the regioselectivity ranged between 88.4 and 93.2% (entries 5–8) and Pd(**3**) with a regioselectivity ranging between 87.2 and 91.9% (entries 9–12) showed a good catalyst recovery in four consecutive catalytic runs. No systematic drop in catalyst activity was observed for the three catalyst systems, which was substantiated by the absence of significant Pd leaching.

The recycling experiments were also adopted to Pd(**1**) immobilised on MCM-41 (Table 4, entries 13–16). The conversion of the alkylation of **5** remained the same in four consecutive catalytic runs (ranging between 65 and 71%) and also the selectivity

Table 3
Catalyst recycling experiments for the allylic alkylation of **4** with sodium diethyl 2-methylmalonate[a]

Entry	Catalyst (cycle)	Conversion[b] (%)	Linear product[c] (%)	Branched product[c] (%)
1	Pd(**1**) [1]	81	94.3	5.7
2	[2]	79	97.0	3.0
3	[3]	82	96.9	3.1
4	[4]	83	96.6	3.4
5	Pd(**2**) [1]	85	97.6	2.4
6	[2]	79	97.4	2.6
7	[3]	81	97.3	2.7
8	[4]	80	97.5	2.5
9	Pd(**3**) [1]	24	97.0	3.0
10	[2]	24	100.0	0.0
11	[3]	21	99.4	0.6
12	[4]	34	98.9	1.1

[a] Reactions were run in 2 ml of THF, using 5×10^{-7} mol of $Pd(dba)_2$, 50 mg silica immobilised ligand (containing 1×10^{-5} mol phosphine), 1 mmol of substrate and 0.5 mmol of sodium diethyl 2-methylmalonate at room temperature.
[b] Determined after 10 min.
[c] Determined by means of GC-analysis.

Table 4
Catalyst recycling experiments for the allylic alkylation of **5** with sodium diethyl 2-methylmalonate[a]

Entry	Catalyst (cycle)	Conversion[b] (%)	Linear product[c] (%)	Branched product[c] (%)
1	Pd(**1**) [1]	68	41.7	58.3
2	[2]	75	41.6	58.4
3	[3]	65	42.5	57.5
4	[4]	64	43.3	56.7
5	Pd(**2**) [1]	25	88.4	11.6
6	[2]	22	89.9	10.1
7	[3]	19	91.4	8.6
8	[4]	18	93.2	6.8
9	Pd(**3**) [1]	20	89.3	10.7
10	[2]	24	87.2	12.8
11	[3]	25	89.5	10.5
12	[4]	27	91.9	8.1
13	Pd(**1**)/MCM-41 [1]	68	41.6	58.4
14	[2]	71	41.4	58.6
15	[3]	65	41.9	58.1
16	[4]	69	41.2	58.8
17	Pd(**1**)′ [1]	24	56.9	43.1
18	[2]	23	75.7	24.3
19	[3]	19	82.7	17.3
20	[4]	19	83.2	16.8

[a] Reactions were run in 2 ml of THF, using 5×10^{-7} mol of $Pd(dba)_2$, 50 mg of the above described immobilised ligand (containing 1×10^{-5} mol phosphine), 1 mmol of substrate and 0.5 mmol of sodium diethyl 2-methylmalonate at room temperature.
[b] Determined after 5 min.
[c] Determined by means of GC-analysis.

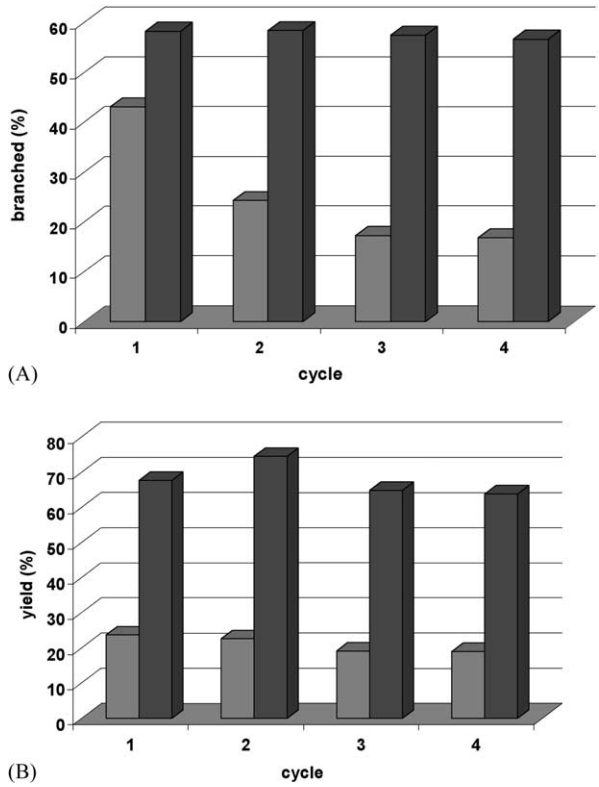


Fig. 2. Four consecutive allylic alkylations of **5** with diethyl 2-methylmalonate using Pd(**1**) on modified (black bars) and non-modified silica (grey bars). Graph A, regioselectivity for branched product; graph B, overall product yield.

for the branched product was virtually unaltered (ranging between 58.1 and 58.8%). Hence, the morphology of the silica support does not have any effect on the stability or recyclability of this type of catalyst.

It is concluded that these silica immobilised palladium phosphine catalysts are all very stable under catalytic conditions and that the palladium phosphine bond, even when monophosphines were used, is strong enough to maintain all the palladium strongly anchored to the support.

The surface of the non-modified silica was found to have a major impact on the catalysis. When Pd(**1**) on non-modified silica (Pd(**1**)′) was used in the alkylation of **5**, both the activity and selectivity of the catalyst decreased dramatically (Fig. 2 and Table 4, entries 17–20). Using Pd(**1**)′ the selectivity for the branched product is already low compared to that of Pd(**1**) in the first run (43.1 and 58.3%, respectively) (entries 17 and 1)). The selectivity decreased further to 16.8% in the forth run (entries 17–20). Moreover, the catalyst activity was observed to be a factor of three lower for Pd(**1**)′. This experiment clearly indicates that the silanols on the silica surface of Pd(**1**)′ strongly interfere with the catalyst. Hence, the modification of the silanols on the silica surface with dichlorodimethylsilane is crucial in the development of this type of selective and stable immobilised alkylation catalysts.

4. Conclusions

The covalent immobilisation of palladium phosphine complexes on silica is a viable approach to obtain recyclable allylic alkylation catalysts. Both bidentate and monodentate phosphine ligands form stable palladium catalysts that can be recycled without catalyst deterioration and metal leaching has not been observed. Catalyst performances were largely retained

upon immobilisation but a pre-modification of the silanols on the silica surface using dichlorodimethylsilane was essential. The xanthene-based diphosphine **(1)**, a ligand with a large natural P–Pd–P bite angle, gave rise to an increased regioselectivity for the branched product. The morphology of the silica support did not have an impact on the catalyst performance, amorphous silica and MCM-41 supported Pd(**1**) gave similar results.

Acknowledgements

We thank J. Elgersma for performing the AES analyses. We are grateful to the Innovation Oriented Research Program (IOP-katalyse) for the financial support of this research.

References

[1] J. Tsuji, Palladium Reagents and Catalysts: Innovations in Organic Synthesis, Wiley, Germany, 1997.
[2] B.M. Trost, T.R. Verhoeven, in: G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Vol. 8, Pergamon, Oxford, UK, 1982, p. 799.
[3] B.M. Trost, D.V. van Vranken, Chem. Rev. 96 (1996) 395.
[4] P.S. Pregosin, R. Salzmann, Coord. Chem. Rev. 155 (1996) 35.
[5] P. Dierkes, R. Ramdeehul, L. Barloy, A. De Lian, J. Fisher, P.C.J. Kamer, P.W.N.M. van Leeuwen, J.A. Osborn, Angew. Chem. Int. Ed. Engl. 37 (1998) 3116.
[6] M.P.T. Sjörgren, S. Hansson, B. Åkermark, A. Vitagliano, Organometallics 13 (1994) 1963.
[7] P.E. Blöchl, A. Togni, Organometallics 15 (1996) 4125.
[8] Y. Uozumi, H. Danjo, T. Hayashi, Tetrahedron Lett. 38 (1997) 3557.
[9] H. Danjo, D. Tanaka, T. Hayashi, Y. Uozumi, Tetrahedron 55 (1999) 14341.
[10] Y. Uozumi, H. Danjo, T. Hayashi, Tetrahedron Lett. 39 (1998) 8303.
[11] K. Hallman, E. Macedo, K. Nordström, C. Moberg, Tetrahedron Asym. 10 (1999) 4037.
[12] C. Saluzzo, R. ter Halle, F. Touchard, F. Fache, E. Schultz, M. Lemaire, J. Organomet. Chem. 603 (2000) 30.
[13] D.E. Bergbreiter, B.L. Case, Y.S. Liu, J.W. Caraway, Macromolecules 31 (1998) 6053.
[14] D. de Groot, E.B. Eggeling, J.C. de Wilde, H. Kooijman, R.J. van Haaren, A.W. van der Made, A.L. Spek, D. Vogt, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Chem. Commun. (1999) 1623.
[15] G.E. Oosterom, R.J. van Haaren, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Chem. Commun. (1999) 1119.
[16] N. Brinkmann, D. Giebel, G. Lohmer, M.T. Reetz, U. Kragl, J. Catal. 183 (1999) 163.
[17] B. Gotov, S. Toma, D.J. Macquarrie, New J. Chem. 24 (2000) 597.
[18] B.F.G. Johnson, S.A. Raynor, D.S. Shephard, T. Maschmeyer, J.M. Thomas, G. Sankar, S. Bromley, R. Oldroyd, L. Gladden, M.D. Mantle, Chem. Commun. (1999) 1167.
[19] E. Blart, J.P. Genet, M. Safi, M. Savignac, D. Sinou, Tetrahedron 50 (1994) 505.
[20] P. Schneider, F. Quignard, A. Choplin, D. Sinou, New J. Chem. 20 (1996) 545.
[21] A. Choplin, S. Dos Santos, F. Quignard, S. Sigismondi, D. Sinou, Catal. Today 42 (1998) 471.
[22] S. dos Santos, Y. Tong, F. Quignard, A. Choplin, D. Sinou, J.P. Dutasta, Organometallics 17 (1998) 78.
[23] A.J. Sandee, V.F. Slagt, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Chem. Commun. (1999) 1633.
[24] A.J. Sandee, L.A. van der Veen, J.N.H. Reek, P.C.J. Kamer, M. Lutz, A.L. Spek, P.W.N.M. van Leeuwen, Angew. Chem. Int. Ed. Engl. 38 (1999) 3231.
[25] N.J. Meehan, A.J. Sandee, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, M. Poliakoff, Chem. Commun. 16 (2000) 1497.
[26] M. Schroeder Goedheijt, B.E. Hanson, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Am. Chem. Soc. 8 (2000) 1650.
[27] A.J. Sandee, D.G.I. Petra, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Chem. Eur. J. 7 (2001) 1202.
[28] L.A. van der Veen, P.H. Keeven, G.C. Schoemaker, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, M. Lutz, A.L. Spek, Organometallics 19 (2000) 872.
[29] R.G. Nuzzo, S.L. Haynie, M.E. Wilson, G.M. Whitesides, J. Org. Chem. 46 (1981) 2861.
[30] R.J. van Haaren, K. Goubitz, J. Fraanje, G.P.F. van Strijdonck, H. Oevering, B. Coussens, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Inorg. Chem. 40 (2001) 3363.
[31] P.W.J.M. Boumans, J.A. Tielrooy, F.J.M.J. Maessen, Spectrochim. Acta 43B (1988) 173.