EurJIC
European Journal of Inorganic Chemistry
ChemPubSoc Europe
FULL PAPER

DOI:10.1002/ejic.201500447

A Kumada Coupling Catalyst, $[Ni\{(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3\text{-}P,P'\}Cl_2]$, Bearing a Ligand for Direct Immobilization Onto Siliceous Mesoporous Molecular Sieves

Ioannis Stamatopoulos,[a] Dimitrios Giannitsios,[a] Vassilis Psycharis,[b] Catherine P. Raptopoulou,[b] Hynek Balcar,[c] Arnošt Zukal,[c] Jan Svoboda,*[d] Panayotis Kyritsis,*[a] and Jiří Vohlídal*[d]

Keywords: Homogeneous catalysis / Heterogeneous catalysis / Cross coupling / Nickel / P-N-P ligands

The ligand-exchange reaction between $[Ni(PPh_3)_2Cl_2]$ and $(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3$ afforded the novel Ni^{II} complex $[Ni\{(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3\text{-}P,P'\}Cl_2]$ (**1**) in which the square-planar NiP_2Cl_2 coordination sphere contains a four-membered Ni–P–N–P ring. Comparison of the structure of **1** and related Ni^{II} square-planar or Ni^0 tetrahedral complexes containing similar P–N–P ligands shows that the magnitude of the P–Ni–P angle is controlled by the presence of the Ni–P–N–P ring, irrespective of the geometry of the nickel coordination sphere. Direct anchoring of **1** onto SBA-15 molecular sieves through the trimethoxysilyl end-group of the ligand afforded heterogeneous catalyst **1**/SBA-15. Both **1** and **1**/SBA-15 catalyze Kumada cross-coupling reactions, exhibiting similar activity and a slightly higher product selectivity than the $[Ni\{Ph_2P(CH_2)_3PPh_2\text{-}P,P'\}Cl_2]$ and $[Ni\{(Ph_2P)_2N\text{-}(S)\text{-}CHMePh\text{-}P,P'\}X_2]$ (X = Cl, Br) complexes described in the literature. The Grignard reagent employed is likely to induce leaching of the catalyst, which retains its activity in solution.

Introduction

The bis(phosphanyl)amine type of ligands, $(R_2P)_2N(R')$, hereinafter referred to as (P,P), is a well-explored family of chelating ligands.[1] The R groups bonded to the P atoms, as well as the R′ group bonded to the N atom of the P–N–P backbone, can be varied, thus conveying different structural and electronic properties to both the ligands and their metal-coordinated complexes. Certain (P,P) ligands have been used to synthesize Cr(P,P)-type complexes, which are catalytically active in olefin oligomerization reactions.[2–6] In addition, $[Ni(P,P)Br_2]$ complexes have been investigated as catalysts for the polymerization[7] or oligomerization[8] of ethene. Furthermore, two $[Ni(P,P)Cl_2]$ complexes, namely $[Ni\{(Ph_2P)_2N(p\text{-}C_6H_4OMe)\text{-}P,P'\}Cl_2]$[9] and $[Ni[(Ph_2P)_2N\text{-}(S)\text{-}CHMePh\text{-}P,P']Cl_2]$,[10] have been shown to catalyze the vinyl-type polymerization of norbornene.

In an effort to further extend the catalytic scope of this family of Ni^{II} complexes, the catalytic activities of $[Ni\{(Ph_2P)_2N\text{-}(S)\text{-}CHMePh\text{-}P,P'\}X_2]$ (X = Cl, Br) have recently been explored in Kumada and Suzuki–Miyaura C–C coupling reactions.[11] These reactions have been extensively investigated during the last four decades[12–17] and a large variety of coordination compounds containing various metal ions, for example, Cr^{III}, Fe^{III}, Co^{II}, Mn^{II}, $Ru^{0,I,II,III}$, Ni^{II} and Pd^{II}, have been shown to afford complexes that are catalytically active in the above reactions.[18–23]

Homogeneous catalytic systems have been extensively employed in these types of reactions, exhibiting, in most cases, higher activity and product selectivity compared with heterogeneous catalysts. On the other hand, the use of the latter allows a simple and efficient separation of the products from the reaction mixture, as well as the possibility of catalyst recycling. Various heterogeneous catalysts have been investigated for Kumada coupling reactions, including Ni on active charcoal,[24–26] Ni^{II} complexes covalently immobilized on a Merrifield resin,[27,28] Ni^{II} acetate immobilized on a cross-linked polystyrene,[29] and Ni^{II}/magnesium/lanthanum mixed oxides.[30]

---

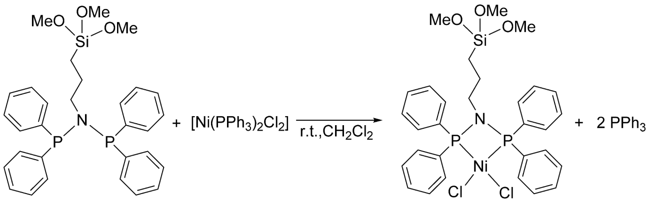
[a] Inorganic Chemistry Laboratory, Department of Chemistry, National and Kapodistrian University of Athens,
Panepistimiopolis, Zografou, 15771 Athens, Greece
E-mail: kyritsis@chem.uoa.gr
http://users.uoa.gr/~kyritsis/home.html
[b] Institute of Advanced Materials, Physicochemical Processes, Nanotechnology and Microsystems, Department of Materials Science, N.C.S.R. "Demokritos",
Aghia Paraskevi, 15310 Attiki, Greece
[c] J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic,
v.v.i, Dolejškova 3, 18223 Prague 8, Czech Republic
[d] Charles University in Prague, Faculty of Science, Department of Physical and Macromolecular Chemistry,
Albertov 2030, 12843 Prague 2, Czech Republic
E-mail: jan.svoboda@natur.cuni.cz
vohlidal@natur.cuni.cz
http://www.natur.cuni.cz/chemistry/fyzchem/freedom
https://www.natur.cuni.cz/chemistry/fyzchem/vohlidal/kontakt

We report herein the preparation of the novel Ni^{II} complex $[Ni\{(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3\text{-}P,P'\}Cl_2]$ (**1**), which can be directly anchored onto siliceous mesoporous molecular sieves through the R′ = $(CH_2)_3Si(OCH_3)_3$ group. Following its structural and spectroscopic characterization, complex **1** was immobilized onto SBA-15 mesoporous molecular sieves to afford the heterogeneous catalyst **1**/SBA-15. The structural properties of **1** have been compared with those of previously reported $[Ni(P,P)X_2]$ (X = Cl, Br, CO) complexes, and the catalytic activities and selectivities of **1** and **1**/SBA-15 in Kumada coupling reactions have been assessed and compared with those of other Ni^{II} catalysts. The catalytic performance of **1**/SBA-15 after recycling has also been explored.

Results and Discussion

Synthesis and Structure of 1

The ligand-exchange reaction shown in Scheme 1 afforded complex **1** in nearly quantitative yield. Crystals of **1** suitable for X-ray crystallography studies were obtained by the layering method using CH_2Cl_2/*n*-hexane (1:3, v/v) as the solvent.



Scheme 1. Synthesis of complex **1**.

The main crystallographic and structural data for **1** are listed in Table 1 and Table 2. The structure of **1** contains discrete molecules (Figure 1) exhibiting a distorted square-planar NiP_2Cl_2 core. Ni^{II} is coordinated to the (P,P) chelate, forming a four-membered Ni–P–N–P ring. The NiP_2Cl_2 core is almost planar, showing a rather small (0.021 Å) mean deviation from the best plane defined by the Ni, P1, P2, Cl1, and Cl2 atoms, with the P2 atom exhibiting the largest deviation (0.193 Å). The four-membered Ni–P1–N–P2 ring is essentially planar, with the mean deviation from the best plane defined by these four atoms being only 0.008 Å.

Table 1. Crystallographic data for complex **1**.

Formula	$C_{30}H_{35}Cl_2NO_3P_2SiNi$
M_r	677.23
Space group	$P2_1/c$
a [Å]	17.1970(4)
b [Å]	8.53010(10)
c [Å]	21.8353(4)
β [°]	90.364(1)
V [Å^3]	3203.0(1)
Z	4
T [°C]	–113
Radiation	Cu-K_α
$\rho_{calcd.}$ [g cm^{-3}]	1.404
μ [mm^{-1}]	3.968
Reflections with $I > 2\sigma(I)$	4153
R_1[a]	0.0554
wR_2[a]	0.1468

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0718P)^2 + 2.87P]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$.

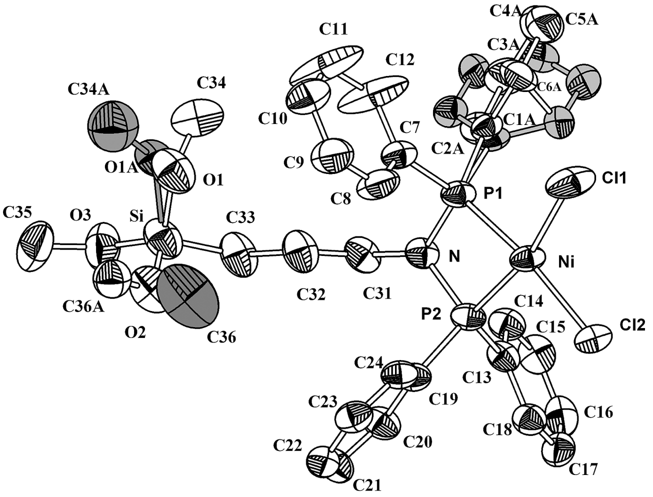


Figure 1. Molecular structure and atom numbering of **1** (ORTEP diagram, 50% thermal ellipsoids). Hydrogen atoms have been omitted for clarity. The atoms at disordered sites are shown in gray.

Structures of Complexes Bearing a Four-Membered Ni–P–N–P Ring

A search of the Cambridge Structural Database (CSD) [31] found six structurally characterized $[Ni(P,P)Cl_2]$ complexes containing $(Ph_2P)_2N(R')$ ligands with different R′ groups bonded to the N atom of the P–N–P backbone. Selected bond lengths and bond angles of these complexes are also listed in Table 2. For a comprehensive appraisal of the relevant literature, it should be added that the complex containing a ligand with three Ph and one $NH(CH)(CH_3)_2$ moiety as R groups and $CH(CH_3)_2$ as the R′ group has also been structurally characterized.[32] Inspection of the data in Table 2 shows that, to a large extent, the main structural characteristics are well conserved within this family of complexes. The endocyclic P–Ni–P angle of **1** (73.39°) seems to be controlled by the formation of the four-membered Ni–P–N–P ring as the range of this angle is rather narrow (73.39–73.99°; Table 2). In a series of structurally characterized analogous $[Ni(P,P)Br_2]$ complexes, this range is only slightly wider (73.00–74.62°).[11] On the other hand, the Cl–Ni–Cl angle of **1** (97.60°) is slightly smaller than the range of values observed for the related complexes listed in Table 2 (98.49–99.77°). The corresponding $[Ni(P,P)Br_2]$ complexes show a somewhat larger range of Br–Ni–Br angles (95.68–101.29°).[11]

The P–N–P angle in **1** (97.47°) is significantly smaller than the angles observed for crystallographically characterized (P,P) ligands such as $(Ph_2P)_2N[(S)\text{-}CHMePh]$ (119.73°)[33] and $(Ph_2P)_2N[C_6H_4Si(OEt)_3]$ (113.66°),[34] ap-

Table 2. Selected bond lengths and angles for the $[Ni(P,P)Cl_2]$ complexes.

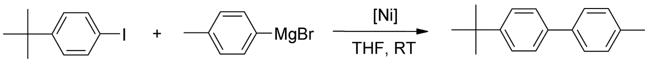
CSD code	R′	Bond lengths Å							Bond angles [°]							
		Ni–Cl1	Ni–Cl2	Ni–P1	Ni–P2	N–P1	N–P2	N–C	Cl1–Ni–Cl2	Cl1–Ni–P1	Cl2–Ni–P2	P1–Ni–P2	Ni–P1–N	Ni–P2–N	P1–N–P2
1	$(CH_2)_3Si(OCH_3)_3$	2.196	2.188	2.126	2.131	1.694	1.690	1.474	97.60	94.13	95.07	73.39	94.60	94.53	97.47
HAFQAI[10]	$CH(CH_3)Ph$	2.206	2.217	2.135	2.129	1.705	1.706	1.501	98.49	93.89	94.55	73.39	94.92	95.05	96.64
MEDTAR[9]	$C_6H_4OCH_3$-*p*	2.192	2.190	2.115	2.123	1.711	1.712	1.425	99.14	92.01	94.96	73.99	94.98	94.64	96.32
YAFCIT[35]	CH_2Ph	2.203	2.199	2.135	2.124	1.706	1.702	1.488	98.30	94.29	93.79	73.64	94.10	94.60	97.02
YAFCOZ[36]	$(CH_2)_2CH_3$	2.198	2.196	2.127	2.124	1.695	1.697	1.481	99.22	91.96	96.11	73.41	94.75	94.80	97.03
BIRNUN[37]	$CH_2C_6H_4CH_3$-*p*	2.191	2.215	2.126	2.135	1.693	1.697	1.485	98.68	91.25	96.31	73.69	94.40	93.94	97.85
MIMNON[38]	$(CH_2)_3SCH_3$	2.190	2.199	2.128	2.116	1.696	1.686	1.480	99.77	94.62	92.00	73.69	93.99	94.68	97.60

parently due to the formation of the four-membered Ni–P–N–P ring in **1**. It should be noted that for the rest of the crystallographically characterized $[Ni(P,P)X_2]$ (X = Cl, Br) complexes, the P–N–P angle spans a rather wide range (95.73–100.98°; Table 2 and ref.[11]). These differences can be attributed to the stereochemical effects of the respective R and R′ groups in the P–N–P backbone and the resulting packing effects in the corresponding crystals.

A search in the CSD[31] did not show any other square-planar $[Ni(P,P)X_2]$ (X = Cl, Br, I) complexes in which a $(CH_2)_3Si(OR)_3$ group is bonded to the N atom. The only related compound to have been reported is the tetrahedral Ni^0 complex $[Ni\{(Ph_2P)_2N(CH_2)_3Si(OCH_3CH_2)_3\text{-}P,P'\}(CO)_2]$.[34] It is of interest that the P–Ni–P angle of this complex (73.68°) is close to that observed for **1** (73.39°), which indicates that the presence of the four-membered Ni–P–N–P ring controls the magnitude of the P–Ni–P angle irrespective of the geometry of the nickel coordination sphere (square planar or tetrahedral). On the other hand, the P–N–P angle in the tetrahedral complex (102.13°) is larger than the corresponding angle in the square-planar complex **1** by 4.7°.

Catalytic Activity of 1 and 1/SBA-15 in Kumada Coupling Reactions

^{31}P MAS NMR analyses of **1** (δ =42.8 ppm) and **1**/SBA-15 (δ =41.8 ppm) showed that immobilization onto SBA-15 did not affect the coordination environment of the Ni^{II} site. Earlier studies showed that Ni^{II} complexes containing a four-membered Ni–P–N–P ring are active in the Kumada coupling reaction but inactive in the Suzuki–Miyaura C–C coupling reaction.[11] Therefore the catalytic activities of **1** and **1**/SBA-15 were tested only in the Kumada reaction (Scheme 2) and compared with the activities of the widely exploited $[Ni\{Ph_2P(CH_2)_3PPh_2\text{-}P,P'\}Cl_2]$ complex[11,39–41] and the recently studied $[Ni\{(Ph_2P)_2N\text{-}(S)\text{-}CHMePh\text{-}P,P'\}X_2]$ (X = Cl, Br) complexes.[11] It should be emphasized here that other Ni^{II} complexes have also been studied as Kumada coupling catalysts[42–48a] as they provide a promising alternative to much more expensive Pd^{II}-based catalysts.[20–22]



Scheme 2. Kumada coupling reaction investigated in this work.

Conversion curves for the cross-coupling of an iodoarene and an aryl Grignard catalyzed by **1** and **1**/SBA-15 are shown in Figure 2 and the corresponding data are presented in Table 3. As can be seen, the final product yield was essentially reached in 15 min for all the reaction systems investigated. Any increase in yield observed afterwards was very small. Therefore the data shown in Table 3 correspond to the reaction time of 1 h.

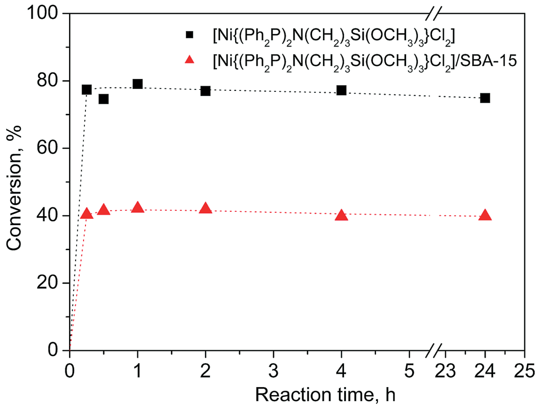


Figure 2. Conversion curves for the cross-coupling of 1-iodo-4-*tert*-butylbenzene (1.0 mmol) and *p*-tolylMgBr (1.2 mmol) catalyzed by **1** and **1**/SBA-15 (10 µmol of Ni) in thf (3 mL; Table 3, entries 4 and 5) with mesitylene (0.5 mmol) as internal standard at room temperature.

The main product of the studied Kumada cross-coupling, 4-*tert*-butyl-4′-methylbiphenyl (MT), was always accompanied by two homocoupling side-products, namely 4,4′-dimethylbiphenyl (MM) and 4,4′-di-*tert*-butylbiphenyl (TT). All these compounds, as well as mesitylene (internal standard), were well resolved in GC chromatograms and clearly identified by GC–MS.

As can be seen (Table 3, entry 5a), under the same reaction conditions A, the heterogeneous catalyst **1**/SBA-15 gave a lower substrate conversion (42%) than **1** (79%), but a significantly increased product selectivity (from 81 to 91%). When the concentrations of both substrates as well as **1**/SBA-15 were increased three-fold (conditions B), the conversion rose to 64% without loss in product selectivity (90%; entry 6a). The observed difference in catalytic activity of **1** and **1**/SBA-15 can thus be mainly ascribed to the limitations of diffusion in each porous system.

The catalytic activity of **1**/SBA-15 after recycling was also tested. The reaction mixture from the previous test (reaction time of 1 h) was centrifuged, its liquid part removed

Table 3. Results of catalytic tests of **1** and **1**/SBA-15 in the Kumada coupling of iodoarene and Grignard reagent at room temperature.[a]

Entry	Catalyst	Reaction conditions[a]	Overall conversion [%]	S_{MT}[b] [%]	S_{MM}[b] [%]	S_{TT}[b] [%]
1[c]	[Ni(dppp)Cl_2]	A	86	72	25	3
2[c]	[Ni{$(Ph_2P)_2N$-(*S*)-CHMePh-*P*,*P′*}Br_2]	A	63	66	31	3
3[c]	[Ni[$(Ph_2P)_2N$-(*S*)-CHMePh-*P*,*P′*]Cl_2]	A	68	70	28	2
4	**1**	A	79	81	17	3
5a	**1**/SBA-15	A	42	91	7	2
5b	**1**/SBA-15	A	44	85	13	2
5c	**1**/SBA-15	A	45	84	14	3
5d	**1**/SBA-15	A	44	83	14	3
5e	**1**/SBA-15	A	35	84	14	3
5f	**1**/SBA-15	A	23	84	13	3
6a	**1**/SBA-15	B	64	90	9	1
6b	**1**/SBA-15	B	78	86	12	2
6c	**1**/SBA-15	B	75	85	13	2
6d	**1**/SBA-15	B	68	84	14	2
7a	**1**/SBA-15	A	40	92	6	2
7b	**1**/SBA-15	A	50	85	13	2
7c	**1**/SBA-15	A	45	81	17	3

[a] Reagents and conditions: 1-iodo-4-*tert*-butylbenzene (1.0 mmol), *p*-tolylMgBr (1.2 mmol), Ni complex (10 µmol), mesitylene (0.5 mmol) as internal standard in A) thf (3 mL) or B) thf (0.8 mL). [b] Selectivity with respect to the (by)product DM, MM, or TT. [c] Reaction time 15 min, data taken from.[11]

and analyzed, and the remaining solid catalyst was redispersed in a new portion of the reactant solution and again allowed to react for 1 h. The whole process was repeated five times (Table 3, entries 5a–5f). The recycled **1**/SBA-15 catalyst apparently showed an increased product yield in the second run. However, this is most likely caused by retention of a fraction of the products inside the pores of the recycled catalyst. This fraction then contributes to the yield of the consecutive catalytic experiment. The product selectivity of recycled **1**/SBA-15 somewhat decreased, but still remained higher than that achieved with **1** alone.

The amount of catalyst leaching from **1**/SBA-15 was determined for reactions carried out in more concentrated mixtures (Table 3, entries 6a–6d). The Ni content was determined in fresh **1**/SBA-15 and the liquid phases isolated at the end of each catalytic cycle. The amount of Ni released in the first to fourth cycle was found to be 47, 47, 35, and 21 µg, respectively, which represents around 13, 13, 10, and 6% (about 40% in total) of the amount of Ni used. Despite that, no significant decrease in the activity and product selectivity of **1**/SBA-15 was observed (Table 3).

To obtain a better insight into this behavior, a "hot filtration" experiment was carried out under reaction conditions A. The reaction mixture was centrifuged 5 min after starting the reaction and the supernatant transferred to a new test tube. GC analyses showed substrate conversion of 40% (Table 3, entry 7a) with no increase in the conversion during the next 60 min. The addition of a new portion of reactants increased the overall conversion to 50% (related to the total amount of reactants added, Table 3, entry 7b). This result proves that the leached Ni^{II} species remained catalytically active. Thus, the apparent lack of activity in the isolated supernatant should be ascribed to the decomposition of the Grignard reagent during centrifugation. A new portion of substrate added to the centrifuged **1**/SBA-15 also reacted, giving a conversion of 45% (Table 3, entry 7c). Thus, it can be concluded that both the leached and the remaining anchored Ni^{II} species retain their activity. This shows that a catalytically competent first coordination sphere is retained in both types of Ni^{II} species.

To probe the integrity of **1**/SBA-15 in the presence of the Grignard reagent, the ^{31}P and ^{1}H NMR spectra of a mixture of **1** and *p*-tolyl-MgBr (mole ratio 1:10) were recorded. The presence of *p*-tolyl-MgBr led to a shift of the ^{31}P signal from 42.8 to 49.8 ppm arising from [Ni{$(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3$-*P*,*P′*}$Br_2$].[48b] Therefore this chemical shift indicates the substitution of Cl^- in **1** by Br^- released from the Grignard reagent, affording NiP_2Br_2-containing species. The catalytic activity of such species in Kumada coupling reactions has been recently documented for [Ni{$(Ph_2P)_2N$-(*S*)-CHMePh-*P*,*P′*}Br_2], which contains a similar first coordination sphere.[11] The ^{1}H NMR spectrum shows a shift of the signal of the linker OCH_3 groups from 3.32 to 3.23 ppm, which may be due to a solvent effect because the Grignard reagent was added as a thf solution. Alternatively, this observation may be considered as indirect evidence for the Grignard reagent causing leaching of **1** when added to **1**/SBA-15.

It is worth comparing the catalyst efficiencies of **1** and **1**/SBA-15 with those of similar catalysts described in the literature, in particular, with those of [Ni{$Ph_2P(CH_2)_3PPh_2$-*P*,*P′*}Cl_2] and [Ni{$(Ph_2P)_2N$-(*S*)-CHMePh-*P*,*P′*}X_2] (X = Cl, Br; Table 3, entries 1–3). As can be seen, under similar reaction conditions, both **1** and **1**/SBA-15 showed comparable activity (conversion) but significantly higher product selectivity compared with those of the published catalysts.

In complex **1** described herein, the Ni^{II}-coordinated ligand contains a linker group through which the complex can be directly anchored onto a siliceous support, thus affording a heterogeneous catalyst. This strategy allowed a thorough characterization of the metal complex prior to its immobilization onto the support. This approach is the opposite of the widely used strategy in which the catalyst support is first modified, for example, by a diphosphane ligand containing a linker capped with anchoring $Si(OR)_3$ groups (R = CH_3 or CH_2CH_3), and then treated with a metal-ion source.[34,49–52] A similar methodology has been recently followed for the immobilization of a Pd^{II}–edta complex onto organo-functionalized SBA-15, which is active in Sonogashira- and Suzuki-type of reactions.[53]

Conclusions

The synthetic protocol affording novel complex **1** is quite simple and very efficient, as well allowing its anchoring onto siliceous supports. The structural data for **1** has provided a deeper insight into the factors controlling the structures of square-planar and tetrahedral complexes of the $[Ni(P,P)X_2]$ type (X = Cl, Br, CO). Complex **1** exhibits comparable catalytic activity and significantly higher product selectivity compared with those of widely used catalysts, such as $[Ni\{Ph_2P(CH_2)_3PPh_2\text{-}P,P'\}Cl_2]$, or the recently investigated $[Ni\{(Ph_2P)_2N\text{-}(S)\text{-}CHMePh\text{-}P,P'\}X_2]$ (X = Cl, Br). However, **1**/SBA-15 exhibits significant leaching, but "hot filtration" experiments revealed that the leached Ni^{II} species retain their catalytic activity. Other experiments indicated that the Grignard reagent may contribute to catalyst leaching. Efforts are currently underway in our laboratories to immobilize **1** onto other solid supports and to test it in other catalytic reactions.

Experimental Section

Materials and Methods: Complex **1** was synthesized under inert conditions (argon atmosphere). The solvents were dried and distilled according to literature procedures.[54] All chemical reagents employed in this work were purchased from Aldrich. The $(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3$ ligand was synthesized by the reaction between Ph_2PCl and $NH_2(CH_2)Si(OCH_3)_3$, according to a published method.[51]

Siliceous mesoporous molecular sieves SBA-15 (S_{BET} = 829 $m^2 g^{-1}$, V = 1.18 $cm^3 g^{-1}$, d = 6.6 nm) was prepared as described elsewhere.[55,56]

The Kumada coupling reactions were carried out under argon by using Schlenk techniques and specific conditions are presented in Table 3. The resulting reaction mixtures were analyzed by GC-FID (Shimadzu 6000) to obtain yields of products and side-products from the catalytic reactions. Mesitylene was used as an internal standard. The Ni contents of both solid and liquid samples were determined by the ICP-OES method using a ThermoScientific iCAP 6500 radial spectrometer. Solid samples were dissolved in a $HF/HClO_4$ mixture and transferred to a 2% w/w aqueous solution of HNO_3.

FTIR spectra were recorded with a Shimadzu IR Affinity-1 spectrometer using KBr pellets. ^1H and ^{31}P NMR spectra were recorded with a Varian V 300 MHz spectrometer at 25 °C. Solid-state NMR spectra were recorded at 11.7 T with a Bruker Avance III HD 500 WB NMR spectrometer in 3.2 mm ZrO_2 rotors at a magic angle spinning (MAS) frequency of 20 kHz. The single-pulse ^{31}P MAS NMR spectrum was recorded at a $B_1(^{31}P)$ field nutation frequency of 89.3 kHz with a repetition delay of 10 s. The number of transients of signal accumulation was 5120 (total experimental time was 14 h). The SPINAL 64 decoupling was applied during the periods of detection. The ^{31}P NMR scale was calibrated with $CaHPO_4$ (–0.6 ppm). The frictional heating of the spinning samples was compensated by active cooling, and temperature calibrations were performed with $Pb(NO_3)_2$.[57]

UV/Vis spectra were recorded with a Perkin–Elmer Lambda 950 spectrometer in quartz cuvettes.

$[Ni\{(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3\text{-}P,P'\}Cl_2]$ (1): A concentrated CH_2Cl_2 solution (0.9 M) of $(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3$ (0.2 mL, 0.18 mmol) was diluted with CH_2Cl_2 (15 mL) and, after 5 min, $[NiCl_2(PPh_3)_2]$ (0.12 g, 0.18 mmol) was added to afford an orange solution that was stirred at room temperature for 1 h. This solution was concentrated to 5 mL and subsequent addition of *n*-hexane (15 mL) afforded an orange powder that was filtered and dried under vacuum (isolated yield 0.12 g, 99%). UV/Vis (CH_2Cl_2): λ = 470 nm, ε = 2150 $L mol^{-1} cm^{-1}$. IR (KBr): $\tilde{\nu}$ = 1625, 1581, 1476, 1430, 1306, 1278, 1181, 1092, 1025, 917, 865, 743, 692, 535, 515 cm^{-1}. ^1H NMR (300.0 MHz, $CDCl_3$): δ = 0.14 (J = 7.8 Hz, 2 H, Si-CH_2), 1.16 (2 H, CH_2), 2.81 (2 H, N-CH_2), 3.32 (9 H, Si-OCH_3), 7.55–7.99 ppm (20 H, Ar-H) ppm. $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, referenced to an external 85% w/w aq. soln. of H_3PO_4): δ = 42.8 ppm; the corresponding peak for the free $(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3$ ligand was observed at δ = 62.2 ppm.

Immobilization of 1 onto SBA-15 Mesoporous Sieves (1/SBA-15): SBA-15 molecular sieves (580 mg), predried in vacuo at 300 °C for 3 h, was placed in a Schlenk tube under Ar. CH_2Cl_2 (10 mL) and complex **1** (30.6 mg, 0.045 mmol, 2.7 mg of Ni) were added and the resulting orange mixture was stirred for 1 h. Subsequently the solid material was separated by filtration, washed twice with CH_2Cl_2 (10 mL), and dried in vacuo. ^{31}P MAS NMR of **1**/SBA-15 (room temp.): δ = 41.8 ppm. The Ni content in **1**/SBA-15 was determined to be 0.45 wt.-% based on the Ni content in the supernatant, as quantified by UV/Vis spectroscopy.

X-ray Crystal Structure Determination: A crystal of **1** (0.03 × 0.29 × 0.804 mm) was taken from the mother liquor and immediately cooled to –113 °C. Diffraction measurements were performed with a Rigaku R-AXIS SPIDER Image Plate diffractometer using graphite-monochromated Cu-K_α radiation. Data collection (ω scans) and processing (cell refinement, data reduction, and numerical absorption correction) were performed by using the CrystalClear program package.[58] The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares methods on F^2 with SHELXL-97.[59] All hydrogen atoms were introduced by using difference maps and refined isotropically. All non-hydrogen atoms were refined anisotropically. One of the phenyl rings shows disorder in two positions with occupancies of 0.617(4) and 0.383(4). Two of the methyl groups of the ligand are also in disordered positions. In one case, both oxygen and carbon atoms of the OCH_3 group are disordered with occupancies of 0.625(7) and 0.375(7), and in the other case only the carbon atom is disordered with occupancies of 0.81(1) and 0.19(1). The hydrogen atoms were located with difference maps and refined by using both models, isotropic and riding on corresponding carbon atoms. The hydrogen atoms bonded to disordered atoms were not included in the refinment. Important crystallographic and refinement data are listed in Table 1. Further experimental crystallographic details for **1**: $2\theta_{max}$ = 130°; number of reflections collected/unique/used, 27946/5254 [R(int) = 0.0635]/5254; 503 parameters refined; Δ/σ =

0.001; $(\Delta\rho)_{max}/(\Delta\rho)_{min}$ = 0.770/–0.641 e Å^{-3}; R/R_w (for all data), 0.0676/0.1625.

CCDC-1024721 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

Financial support by the Special Account of the University of Athens (grant number 7575), the Ministry of Education of Greece and the Czech Science Foundation (project number P108/12/1143) is gratefully acknowledged. This research was co-financed by the European Union (EU) (European Social Fund - ESF) and Greek National Funds through the Operational Program “Education and Lifelong Learning” of the National Strategic Reference Framework (NSRF) – Research Funding Program “Heracleitus II”: Investing in knowledge society through the European Social Fund. Dr. Jiří Brus is gratefully thanked for recording solid-state NMR spectra. P. K. participated in the activities of the CM0802 Cost Action (PhoSciNet) and thanks the European Union Cost Office as well as other PhoSciNet members (Prof. E. Hey-Hawkins, Prof. M. Peruzzini, Dr. I. D. Kostas) for helpful discussions. The authors would also like to thank the referees of this manuscript for their constructive comments.

---

[1] T. Appleby, J. D. Woollins, *Coord. Chem. Rev.* **2002**, *235*, 121–140.

[2] E. Killian, K. Blann, A. Bollmann, J. T. Dixon, S. Kuhlmann, M. C. Maumela, H. Maumela, D. H. Morgan, P. Nongodlwana, M. J. Overett, M. Pretorius, K. Hofener, P. Wasserscheid, *J. Mol. Catal. A* **2007**, *270*, 214–218.

[3] L. E. Bowen, M. F. Haddow, A. G. Orpen, D. F. Wass, *Dalton Trans.* **2007**, 1160–1168.

[4] L. E. Bowen, M. Charernsuk, T. W. Hey, C. L. McMullin, A. G. Orpen, D. F. Wass, *Dalton Trans.* **2010**, *39*, 560–567.

[5] L. H. Do, J. A. Labinger, J. E. Bercaw, *ACS Catal.* **2013**, *3*, 2582–2585.

[6] S. Sa, S. M. Lee, S. Y. Kim, *J. Mol. Catal. A* **2013**, *378*, 17–21.

[7] N. A. Cooley, S. M. Green, D. F. Wass, K. Heslop, A. G. Orpen, P. G. Pringle, *Organometallics* **2001**, *20*, 4769–4771.

[8] K. M. Song, H. Y. Gao, F. S. Liu, J. Pan, L. H. Guo, S. B. Zai, Q. Wu, *Eur. J. Inorg. Chem.* **2009**, 3016–3024.

[9] Z. G. Sun, F. M. Zhu, Q. Wu, S. A. Lin, *Appl. Organomet. Chem.* **2006**, *20*, 175–180.

[10] G. C. Vougioukalakis, I. Stamatopoulos, N. Petzetakis, C. P. Raptopoulou, V. Psycharis, A. Terzis, P. Kyritsis, M. Pitsikalis, N. Hadjichristidis, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 5241–5250.

[11] I. Stamatopoulos, M. Plaček, V. Psycharis, A. Terzis, J. Svoboda, P. Kyritsis, J. Vohlídal, *Inorg. Chim. Acta* **2012**, *387*, 390–395.

[12] K. Tamao, K. Sumitani, M. Kumada, *J. Am. Chem. Soc.* **1972**, *94*, 4374–4376.

[13] K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, *16*, 4467–4470.

[14] E. Negishi, S. Baba, *J. Chem. Soc., Chem. Commun.* **1976**, 596b–597b.

[15] D. Milstein, J. K. Stille, *J. Am. Chem. Soc.* **1979**, *101*, 4992–4998.

[16] N. Miyaura, K. Yamada, A. Suzuki, *Tetrahedron Lett.* **1979**, *20*, 3437–3440.

[17] A. Suzuki, *Angew. Chem. Int. Ed.* **2011**, *50*, 6722–6737; *Angew. Chem.* **2011**, *123*, 6854.

[18] W. Shi, C. Liu, A. W. Lei, *Chem. Soc. Rev.* **2011**, *40*, 2761–2776.

[19] C. C. Johansson, T. J. Colacot, *Angew. Chem. Int. Ed.* **2010**, *49*, 676–707; *Angew. Chem.* **2011**, *123*, 702.

[20] W. A. Herrmann, K. Ofele, D. Von Preysing, S. K. Schneider, *J. Organomet. Chem.* **2003**, *687*, 229–248.

[21] E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem. Int. Ed.* **2007**, *46*, 2768–2813; *Angew. Chem.* **2007**, *119*, 2824.

[22] R. Corberan, E. Mas-Marza, E. Peris, *Eur. J. Inorg. Chem.* **2009**, 1700–1716.

[23] V. B. Phapale, D. J. Cardenas, *Chem. Soc. Rev.* **2009**, *38*, 1598–1607.

[24] H. Lipshutz, T. Tomioka, P. A. Blomgren, J. A. Sclafani, *Inorg. Chim. Acta* **1999**, *296*, 164–169.

[25] B. H. Lipshutz, S. Tasler, W. Chrisman, B. Spliethoff, B. Tesche, *J. Org. Chem.* **2003**, *68*, 1177–1189.

[26] S. Tasler, B. H. Lipshutz, *J. Org. Chem.* **2003**, *68*, 1190–1199.

[27] P. Styring, C. Grindon, C. M. Fisher, *Catal. Lett.* **2001**, *77*, 219–225.

[28] N. T. S. Phan, D. H. Brown, H. Adams, S. E. Spey, P. Styring, *Dalton Trans.* **2004**, 1348–1357.

[29] J. M. Richardson, C. W. Jones, *J. Mol. Catal. A* **2009**, *297*, 125–134.

[30] A. Kiss, Z. Hell, M. Balint, *Org. Biomol. Chem.* **2010**, *8*, 331–335.

[31] F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 380–388.

[32] B. R. Aluri, N. Peulecke, S. Peitz, A. Spannenberg, B. H. Muller, S. Schulz, H. J. Drexler, D. Heller, M. H. Al-Hazmi, F. M. Mosa, A. Wohl, W. Muller, U. Rosenthal, *Dalton Trans.* **2010**, *39*, 7911–7920.

[33] F. Robert, Y. Gimbert, M. T. Averbuch-Pouchot, A. E. Greene, *Z. Kristallogr. New Cryst. Struct.* **2000**, *215*, 233–236.

[34] T. Posset, F. Rominger, J. Blümel, *Chem. Mater.* **2005**, *17*, 586–595.

[35] B. S. Yin, T. B. Li, M. S. Yang, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2011**, *67*, M1571.

[36] B. S. Yin, T. B. Li, M. S. Yang, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2011**, *67*, M1572.

[37] L.-C. Song, J.-P. Li, Z.-J. Xie, H.-B. Song, *Inorg. Chem.* **2013**, *52*, 11618–11626.

[38] A. Ghisolfi, C. Fliedel, V. Rosa, R. Pattacini, A. Thibon, K. Y. Monakhov, P. Braunstein, *Chem. Asian J.* **2013**, *8*, 1795–1805.

[39] F. Indolese, *Tetrahedron Lett.* **1997**, *38*, 3513–3516.

[40] R. D. McCullough, S. P. Williams, S. Tristramnagle, M. Jayaraman, P. C. Ewbank, L. Miller, *Synth. Met.* **1995**, *69*, 279–282.

[41] D. Bondarev, J. Zednik, I. Sloufova, A. Sharf, M. Prochazka, J. Pfleger, J. Vohlídal, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 3073–3081.

[42] Y. Zhou, Z. Xi, W. Chen, D. Wang, *Organometallics* **2008**, *27*, 5911–5920.

[43] A. Rudolph, M. Lautens, *Angew. Chem. Int. Ed.* **2009**, *48*, 2656–2670; *Angew. Chem.* **2009**, *121*, 2694.

[44] S. Gu, W. Chen, *Organometallics* **2009**, *28*, 909–914.

[45] R. Ghosh, A. Sarkar, *J. Org. Chem.* **2010**, *75*, 8283–8286.

[46] J. Sanford, C. Dent, J. D. Masuda, A. B. Xia, *Polyhedron* **2011**, *30*, 1091–1094.

[47] P. Ren, O. Vechorkin, K. von Allmen, R. Scopelliti, X. Hu, *J. Am. Chem. Soc.* **2011**, *133*, 7084–7095.

[48] a) Y. Sun, X. Li, H. Sun, *Inorg. Chim. Acta* **2014**, *415*, 95–97; b) I. Stamatopoulos, P. Kyritsis, *unpublished results.*

[49] J. Blümel, *Coord. Chem. Rev.* **2008**, *252*, 2410–2423.

[50] T. Posset, J. Guenther, J. Pope, T. Oeser, J. Blümel, *Chem. Commun.* **2011**, *47*, 2059–2061.

[51] P. Braunstein, H. P. Kormann, W. Meyer-Zaika, R. Pugin, G. Schmid, *Chem. Eur. J.* **2000**, *6*, 4637–4646.

[52] J. C. Pope, T. Posset, N. Bhuvanesh, J. Blümel, *Organometallics* **2014**, *33*, 6750–6753.

[53] P. Sharma, A. P. Singh, *Catal. Sci. Technol.* **2014**, *4*, 2978–2989.

[54] W. L. F. Armarego, C. L. L. Chai (Eds.), *Purification of Laboratory Chemicals*, Butterworth–Heinemann, Oxford, UK, **2003**.
[55] D. Bek, N. Žilková, J. Dědeček, J. Sedláček, H. Balcar, *Top. Catal.* **2010**, *53*, 200–209.
[56] V. Meynen, P. Cool, E. F. Vansant, *Microporous Mesoporous Mater.* **2009**, *125*, 170–223.
[57] J. Brus, *Solid State Nucl. Magn. Reson.* **2000**, *16*, 151–160.
[58] *CrystalClear*, Rigaku/MSC Inc., The Woodlands, TX, **2005**.
[59] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.* **2008**, *64*, 112–122.

Received: April 23, 2015