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Article

Group 10 Metal Aminopyridinato Complexes: Synthesis, Structure, and Application as Aryl-Cl Activation and Hydrosilane Polymerization Catalysts

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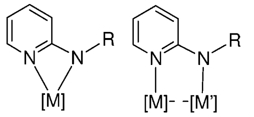
(4-Methyl-pyridin-2-yl)(trimethylsilanyl)amine (ApSi-H) and *tert*-butyl(4-methyl-pyridin-2-yl)amine **(**Ap*t*Bu-H**)** were synthesized via salt metathesis and aryl amination reactions, respectively. Lithiation of these two aminopyridines using *n*-BuLi and the reactions with [(dme)NiCl$_2$] (dme = dimethoxyethane) or [(cod)PdCl$_2$] (cod = cyclooctadiene) in THF at low temperature gave rise—after workup in hexane—to group 10 amido compounds, [(ApSi)$_4$Ni$_2$], [(Ap*t*Bu)$_2$-Pd], [(Ap*t*Bu-H)(Ap*t*Bu)$_2$Ni], [(Ap*t*Bu)$_3$(C$_2$H$_5$O)$_3$Ni$_3$OLi(thf)], and [(Ap*t*Bu)$_2$Ni(*t*Bupy)$_2$] (*t*Bupy = 4-*tert*-butylpyridine). The aminopyridinato complexes were characterized by X-ray crystal structure analysis. The highly strained binding situation of the aminopyridinato ligands suggested that these compounds might be efficiently converted into catalytically active species. The applications of some of the synthesized complexes as Suzuki cross-coupling catalysts (activation of aryl chlorides) are described and [(ApSi)$_4$Ni$_2$] is a rare example of a "phosphine-free" catalyst system. A number of late transition metal complexes were found to successfully catalyze polymerization of MeH$_2$SiSiH$_2$Me toward soluble, linear poly(methylsilane). Remarkable activity was observed for [(ApSi)$_2$Pd].

Introduction

Deprotonated 2-aminopyridines have emerged to an intensively investigated class of amido ligands[1] recently. The interest arises, for instance, from the flexibility of the binding mode ranging from a strained η^2 coordination (Chart 1, left)—predominantly observed in early transition metal and lanthanide complexes—to a bridging binding mode (Chart 1, right) dominating late transition metal chemistry.[2]

Chart 1. Two Important Binding Modes of Deprotonated 2-Aminopyridines[a]



[a] [M] and [M′] = transition metal moiety; R = aryl, silyl, or alkyl substituent.

Since late transition metal amido chemistry is significantly less developed than early transition metal amido chemistry[3,4] (probably due to the mismatch of the "hard" amido ligand with the "soft" late metals[5]), we became interested in the synthesis of strained η^2 bound group 10 metal aminopyridinates.[6] We expect such complexes to show a unique reactivity due to the strained binding mode, and report here on the synthesis and structure of nickel and palladium complexes.

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Aminopyridinato complexes of nickel and palladium[7] (strained η^2 binding mode) are known but rarely described. A large variety of multimetallic nickel complexes stabilized by deprotonated aminopyridines and poly(amino)pyridines involving the bridged binding mode have been described recently.[8]

Besides synthesis and structure we report here on the application of selected strained coordinated Pd and Ni aminopyridinates as aryl-Cl activation (Suzuki reaction) and hydrosilane polymerization catalysts. The palladium-catalyzed cross-coupling reaction between organo boron reagents and, for example, and aryl halides is a powerful synthetic tool. It is one of the most intensively used methods for carbon−carbon bond formations, because this type of reaction shows a very high selectivity and tolerance against functional groups.[9] Besides palladium, research focuses on "alternative" transition metals such as the significantly more redox stable and cheaper nickel.[10,11] Many palladium-based catalyst systems applied successfully for the activation of aryl-Cl compounds require the presence of bulky and electron-rich phosphine[14] (or N-heterocyclic carbene)[12] ligands which were significantly modified in the last years and have given rise to highly active systems in palladium-catalyzed coupling reactions.

Due to their interesting physical properties polysilanes have received considerable attention in recent years.[13] While Wurtz-type coupling of dichloroorganosilanes[14] is still the main route to these materials, several other methods have emerged during the past few years.[15] Among these the group 4 metallocene-catalyzed polymerization of hydrosilanes was mainly established by the groups of Harrod and Tilley.[16] Late transition metal compounds, although well-known for their ability to promote Si−C or Si−O bond formation, were found to be only of limited use as catalysts in the synthesis of polysilanes. Early studies in this direction carried out with phenylsilanes showed that oligomers are formed to some extent and thus demonstrated the principal possibility of silicon−silicon bond formation.[17] However, redistribution of phenyl groups was found to be a major side reaction. A variety of quite different (mostly also hydrosilylation) catalysts are able to promote dimerization of hydrosilanes,[18] and for instance, platinum or cationic nickel complexes can catalyze even polysilane formation.[19] We are engaged in a program that investigates the possibilities for the synthesis

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Table 1. Details of the X-ray Crystal Structure Analyses

param	4	5	6	7	8
cryst system	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	Cc	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	20.122(5)	7.800(1)	22.878(5)	12.225(2)	11.380(3)
b (Å)	11.952(4)	14.659(2)	18.224(4)	12.699(2)	12.902(3)
c (Å)	20.906(5)	8.861(1)	17.034(3)	16.029(2)	13.206(3)
α (deg)				95.20(1)	88.01(2)
β (deg)	113.96(3)	95.11(1)	119.01(3)	90.14(1)	78.76(2)
γ (deg)				108.79(1)	72.87(2)
V (Å^3)	4594(2)	1009.1(2)	6211(2)	2344.0(6)	1816(1)
cryst size (mm^3)	0.5 × 0.4 × 0.2	0.4 × 0.3 × 0.1	0.3 × 0.2 × 0.2	0.1 × 0.1 × 0.1	0.6 × 0.4 × 0.2
ρ_{calcd} (g cm^{-3})	1.207	1.425	1.175	1.271	1.198
μ (mm^{-1}) (Mo Kα)	0.7107	0.7107	0.7107	0.7107	0.7107
T (K)	293(3)	173(2)	173(2)	173(2)	193(2)
θ range (deg)	2.03−24.26	2.62−25.85	1.51−26.23	1.28−25.88	1.65−25.66
no. of reflcns unique	4294	1937	6168	9058	4942
no. of reflcns obsd [$I > 2\sigma(I)$]	3522	1734	4607	4348	4316
no. of params	451	115	338	500	406
wR^2 (all data)	0.0828	0.0699	0.0983	0.1327	0.1027
R value [I > 2s(I)]	0.0370	0.0257	0.0385	0.0559	0.0384

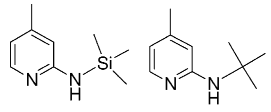
of poly(methylsilane) for some time.[20] This particular polymer is of special interest since it possesses the required stoichiometric ratio (Si/C = 1) for the generation of silicon carbide.[21] First results by Harrod[22] and one of our laboratories[23] demonstrated the feasibility of a metallocene-catalyzed synthesis. However, while the obtained polymers gave excellent ceramic yields of up to 88%, they are extremely insoluble and therefore only of limited technical value.

Results and Discussion

Synthesis of the Ligands. (4-Methyl-pyridin-2-yl)(trimethylsilanyl)amine (**1**) was synthesized as reported.[24] The corresponding (alkylamino)pyridine *tert*-butyl(4-methyl-pyridin-2-yl)amine (**2**) can be synthesized via palladium-catalyzed aryl amination.[25] The reaction of 2-bromo-4-methylpyridine with an excess of *tert*-butylamine and 1.25 equiv of sodium-*tert*-butoxide in the presence of 1−2 mol % Pd catalyst in xylene (120 °C, autogenic pressure, 2 days) leads after workup and purification by distillation to compound **2** (Chart 2) in good yields.

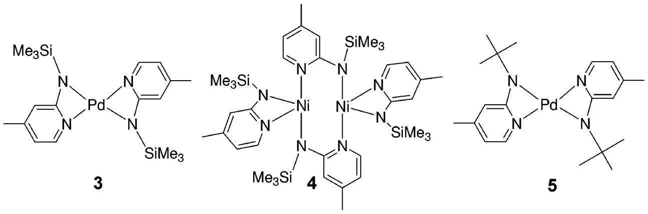
Synthesis and Structure of the Nickel and Palladium Aminopyridinato Complexes. Using the already developed protocol of the synthesis of the palladium complex **3**[6] (Chart 3, left), the lithiation of **1** in diethyl ether followed by an addition of a THF suspension of [(dme)NiCl$_2$] (dme = dimethoxyethane) at low temperature results in the formation of **4** (Chart 3, middle). Complex **4** was isolated—after workup in hexane—in moderate yield as a green crystalline material.

Chart 2. Synthesized Aminopyridines (Yields in Parentheses)



1 (85 %) **2** (80 %)

Chart 3. Homoleptic Nickel and Palladium Aminopyridinates



3 **4** **5**

NMR spectroscopic investigations revealed **4** to be diamagnetic and a dimeric complex in solution due to the observation of a double signal set of the aminopyridinato ligands. Crystals suitable for X-ray analysis were grown from hexane solution.

Details of the X-ray crystal structure analysis are summarized in Table 1. The molecular structure of **4** is shown in Figure 1. In the solid state a dimeric structure, Ni−Ni distance 2.619 Å, was found as well. Two of the four aminopyridinato moieties coordinate in a strained η^2-fashion, and the other two act as bridging ligands. A similar protocol using **2** and [(cod)PdCl$_2$] (cod = cyclooctadiene) as starting materials led to **5** (Chart 3). NMR data are indicative of a mononuclear complex due to the presence of one signal set of deprotonated **2** only. The same structural arrangement was found in the solid state. Details of the X-ray crystal structure analysis are summarized in Table 1. The molecular structure of **5** is shown in Figure 2.

The structure of complex **5** is similar to the structure observed for **3**.[6] In both cases a transoid strained η^2-coordination is observed. The two N−Pd−N angles [115.55(8) and 64.45(8)°] in **5** differ drastically. Attempts to syn-

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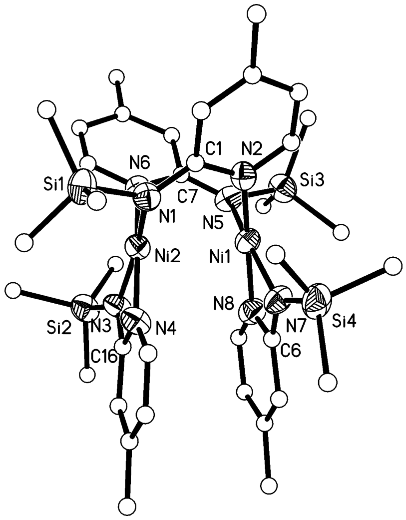


Figure 1. Molecular structure of **4**. Selected bond lengths (Å) and angles (deg): Ni1−Ni2 2.6194(12), Ni1−N2 1.886(5), Ni1−N5 1.917(5), Ni1−N7 1.970(5), Ni1−N8 1.894(5), Ni2−N1 1.911(5), Ni2−N3 1.980(5), Ni2−N4 1.912(5), Ni2−N6 1.885(5); N1−Ni2−Ni1 85.7(2), 85.7(2), N3−Ni2−Ni1 103.47(15), N2−Ni1−N5 92.8(2), N5−Ni1−N8 98.8(2), N3−Ni2−N6 98.0(2), N1−Ni2−N6 84.54(15), N3−Ni2−N4 69.2(2), N1−Ni2−N4 99.5(2).

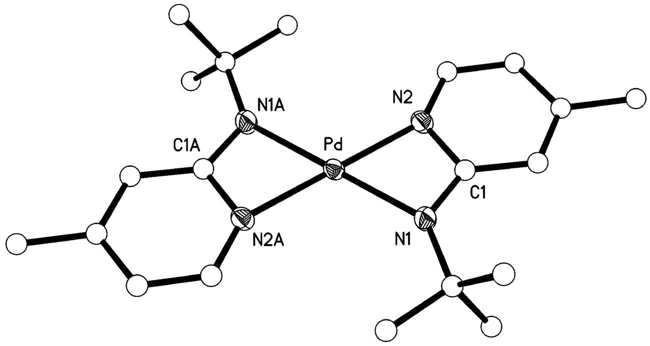
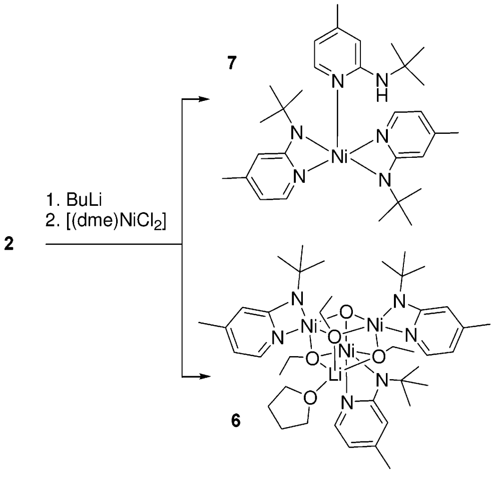


Figure 2. Molecular structure of **5** selected bond lengths (Å) and angles (deg): Pd−N1 2.044(2), Pd−N2 2.048(2); N1A−Pd−N2 115.55(8), N1−Pd−N2 64.45(8), N1−C1−N2 107.6(2).

Scheme 1. Syntheses of **6** and **7**



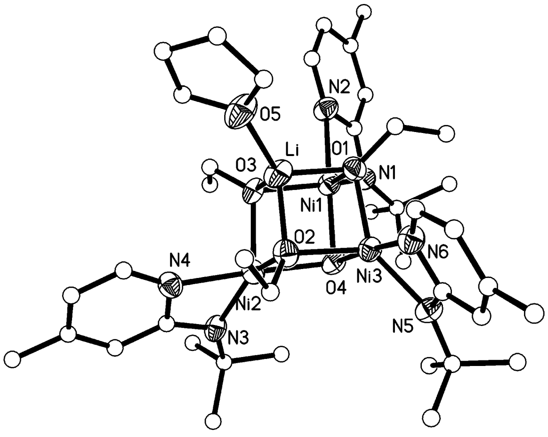


Figure 3. Molecular structure of **6**. Selected bond lengths (Å) and angles (deg): Ni1−N1 2.005(5), Ni1−N2 2.093(6), Ni1−O1 2.018(4), Ni1−O3 2.026(4), Ni1−O4 2.045(5), Ni2−O2 2.013(4), Ni2−O3 2.011(5), Ni2−O4 2.049(6), Ni2−N3 2.011(5), Ni2−N4 2.071(6), Ni3−O1 2.018(5), Ni3−O2 2.028(4), Ni3−O4 2.054(5), Ni3−N5 2.001(5), Ni3−N6 2.077(5), O1−Li 1.908(13), O2−Li 1.918(13), O3−Li 1.897(12); O1−Li−O2 93.2(5), O1−Ni3−O2 86.75(18), Ni1−O4−Ni2 97.7(2), Ni1−O1−Ni3 99.59(19), O3−Ni1−O4 80.9(2), N1−Ni1−N2 65.9(2).

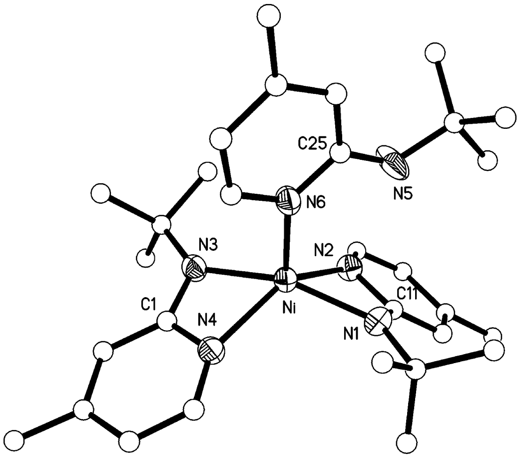


Figure 4. Molecular structure of **7**. Selected bond lengths (Å) and angles (deg): Ni−N1 2.0269(19), Ni−N2 2.1526(18), Ni−N3 2.015(2), Ni−N4 2.13698 (19), Ni−N6 2.0594(19); N1−Ni−N3 157.74(8), N2−Ni−N4 140.02(7), N1−Ni−N4 108.58(8), N2−Ni−N3 107.32(8), N1−Ni−N2 63.63(7), N3−Ni−N4 64.16(8), N1−Ni−N6 102.01(8), N2−Ni−N6 115.29(8), N3−Ni−N6 100.22(8), N4−Ni−N6 104.68(7).

thesize the analogous *tert*-butyl-substituted aminopyridinate of **4** failed. The reaction of deprotonated **2**, lithiation in ethyl ether, with [(dme)NiCl$_2$] afforded **6** and **7** (Scheme 1).

Compounds **6** and **7** were characterized by X-ray analysis. Details of the X-ray crystal structure analysis are summarized in Table 1. The molecular structures of **6** and **7** are shown in Figures 3 and 4.

Both compounds are paramagnetic. The coordination sphere around the Ni center of **7** can be described best as square pyramidal. The Ni center is surrounded by five nitrogen atoms. The base is built by four nitrogen atoms of two strained η^2-bound aminopyridinato ligands, and the top is occupied by the pyridine function of the third, the protonated Ap ligand. Compound **6** is a rare example of a heterometallic oxacubane structure. Such mixed alkaline metal transition metal quarters are known for Zn,[26] Tc,[27] Mo,[28] Cr,[29] and Fe.[30] We propose ether cleavage in the course

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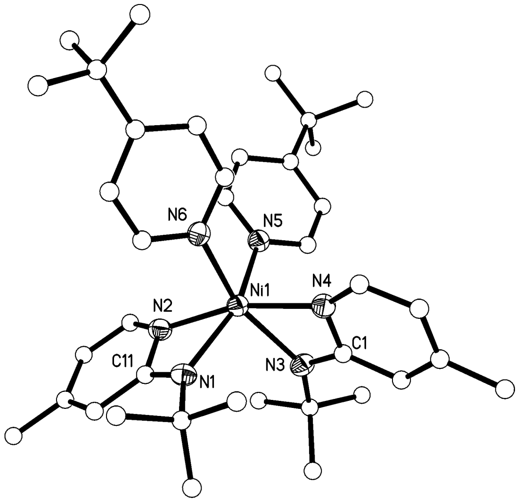
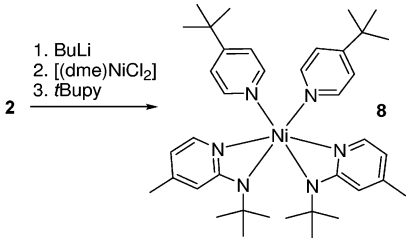


Figure 5. Molecular structure of **8**. Selected bond lengths (Å) and angles (deg): Ni−N1 2.1500(17), Ni−N2 2.068(2), Ni−N3 2.142(2), Ni−N4 2.086(2), Ni−N5 2.1597(19), Ni−N6 2.149(2); N1−Ni−N2 63.14(8), N1−Ni−N3 96.09(8), N1−C11−N2 109.72(18), N3−Ni−N4 63.04(8), N3−C1−N4 109.6(2), N2−Ni−N3 105.49(9), N2−Ni−N6 95.84(9), N6−Ni−N5 88.76(7).

Scheme 2. Synthesis of **8**



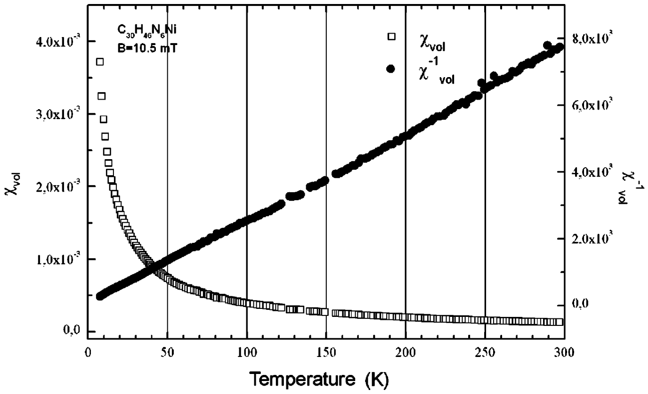


Figure 6. Temperature dependence of the susceptibility of **7**. Plots of χ (left-hand ordinate) and $1/\chi$ vs temperature.

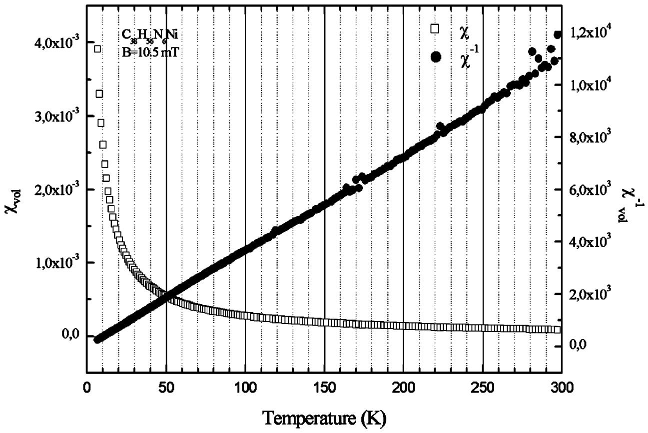


Figure 7. Temperature dependence of the susceptibility of **8**. Plots of χ (left-hand ordinate) and $1/\chi$ vs temperature.

of the synthesis of **6** and **7** and a protonation of some of the lithiated aminopyridinato ligands. Aminopyridinato nickel complexes seem to favor higher coordination numbers than the corresponding palladium complexes since we could not isolate the nickel analogues of **3** and **5**. Thus, additional pyridine ligands should help to stabilize the strained coordination of deprotonated **2** at a Ni(II) center. Reaction of deprotonated **2** and [(dme)NiCl$_2$] in the presence of *tert*-butylpyridine proceeds smoothly to give a light green crystalline and paramagnetic material of **8** (Scheme 2). Details of the X-ray crystal structure analysis of **8** are summarized in Table 1. The molecular structure is shown in Figure 5.

The compound is monomeric in the solid state, and the nickel center is surrounded by six nitrogen atoms in a distorted octahedral environment.

The susceptibility of **7** and **8** in the solid state was measured in a temperature range 5−300 K. Both compounds showed typical paramagnetic behavior which is shown for compound **7** in Figure 6.

The plot of $1/\chi$ versus temperature reveals a strictly linear relationship along with the temperature range. The effective magnetic moment (μ_{eff}) of five-coordinated **7** was determined as 3.4 μ_{B} and significantly higher than the predicted spin-only value for Ni^{2+} (2.83 μ_{B}[31]) but similar to observations made by others for this type of complexes.[32] For compound **8** the value of the magnetic moment (Figure 7) was determined as $\mu_{\mathrm{eff}} = 3.2\ \mu_{\mathrm{B}}$, which is consistent with the experimental range for two unpaired electrons in octahedral geometry (2.9−3.4 μ_{B}).[33]

Suzuki Coupling Investigation. The binuclear strained nickel complex **4** is able to activate aryl chlorides for coupling reactions in the absence of phosphines (Table 2). For initial experiments the couplings of chloropyridine and chlorotoluene with phenyl boronic acid were investigated (Scheme 3).

Benchmark catalyst systems (entries 1−3) had been nearly inactive under screening conditions. Interestingly, **4** was able to activate aryl chlorides in a catalytic fashion without the addition of supporting phosphines. In the course of the reaction the formation of metallic nickel is observed. We propose this to be the main catalyst deactivation step responsible for the incomplete conversions observed.

Cross-coupling between phenyl boronic acid and 3-chloropyridine using **4** as a catalyst was monitored to understand

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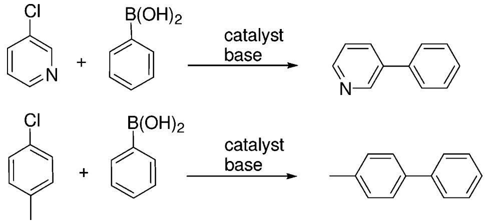
Table 2. Suzuki Coupling Investigation[a]

entry	precatal	coligand	ratio (mol %)	yield[b] (%)	yield[c] (%)	T (°C), solvent
1	[$Pd_2(dba)_3$]	ttbp	1:1	4.3	0	60, thf
2	[$Pd_2(dba)_3$]	rac BINAP	1:1	0	0	60, thf
3	[$Pd_2(dba)_3$]	bdpp	1:2	0	0	60, thf
4	**4**		0.5:0	10.5	1	60, thf
5	**4**		1:0	15	1	60, thf
6	**4**		1.5:0	20	3	60, thf
7	**4**		1:0	45	35	100, dioxane
8	**4**		1.5:0	65	52	100, dioxane

[a] Base: K_3PO_4. Time: 24 h. ttbp = tri-*tert*-butylphoshine, rac BINAP = *rac*-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, and bdpp = 1,3-bis(diphenylphosphanyl)propane. [b] Synthesis of 3-phenylpyridine. [c] Synthesis of 4-methylbiphenyl.

Scheme 3. Model Reactions Used for Initial Cross-Coupling Experiments



the catalytic behavior of **4** [Figure 8, pentagons for the product and circles for the byproduct formation (homocoupling)]. The activation and/or reduction of the catalyst seems to be very fast since no induction period is observed. This reaction step proceeds via homocoupling since homocoupling takes place in the absence of chloropyridine. NMR scale experiments indicate that there is no oxidative addition reaction of **4** with 3-chloropyridine. We observe the coordination of the pyridine including a fast exchange of noncoordinated and coordinated pyridine. The ^{1}H NMR spectra of **4** in the presence of 1, 2, 5, and 10 equiv of 3-chloropyridine are shown in Figure 9.

It can be seen that a paramagnetic compound is formed due to the appearance of very broad low field signals (expanded and highlighted signals). (We propose the formation of five- or six-coordinated complexes such as **7** or **8**.) These signals shift to lower fields with a decreasing metal complex to 3-chloropyridine ratio (spectra 1:1, 1:2, and 1:5) indicating a fast pyridine exchange process. At a 1:10 ratio no more diamagnetic complex is observed and the pyridine excess is responsible for the shift of this signal back to higher field.

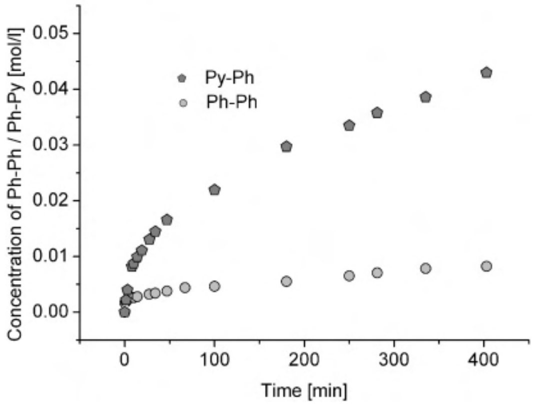


Figure 8. Conversion and byproduct formation in the coupling of chloropyridine with phenyl boronic acid (1.2 equiv): catalyst loading, 1 mol % (compound **4**); base, 1.2% K_3PO_4; solvent, dioxane; temperature, 100 °C; Ph = phenyl, Py = pyridinyl.

Table 3. Reaction of 1,2-Dimethyldisilane with Selected Late Metal Compounds and **3** as Catalysts

catal	t	$10^{-3}M_w$	$10^{-3}M_n$	M_w/M_n	yield: mg (%)
[$(PPh_3)_3RhCl$]	3 d	2.7	1.5	1.8	210 (43)
[$Pd_2(C_3H_6)_2Cl_2$]	4 d	27	19	1.4	160 (33)
[$Pt(PEt_3)_3$]	3 d	8.4	2.8	3.0	230 (47)
3	30 min	3.0	2.2	1.4	410 (84)

Polymerization of Hydrosilanes. In the course of this study we tested several late transition metal complexes as polymerization catalysts, using MeH_2SiSiH_2Me (**9**) as starting material (Table 3). A number of these metal compounds showed remarkable activity in polymerizing **9**, yielding poly(methylsilane) with molecular weights up to 2×10^4 (Table 3). The observed gas evolution which accompanies the reaction first suggested a dehydrocoupling polymerization with loss of hydrogen. On the other hand, GC/MS and ^{29}Si NMR analysis of the reaction revealed that the main byproduct is $MeSiH_3$. Therefore, we assume that the reaction follows a redistribution mechanism. On the basis of a mechanistic rationale presented by Tanaka et al.[34] for the oligomerization reaction of $Me_2HSiSiHMe_2$ with [$Pt(PEt_3)_3$], we propose the catalytic cycle depicted in Scheme 4 for this reaction.

Remarkably, the poly(methylsilanes) we obtained were extremely soluble compared to the material obtained in the early metal catalyzed[21] process. GC-MS analysis of the early stage of the reaction showed that predominantly linear chains are formed, whereas in the zirconocene- and titanocene-mediated reactions branched oligomers were produced almost from the very beginning of the reaction leading to low solubility.[21]

An attempt to raise the temperature was performed in a sealed tube due to the low boiling point of **1**. Interestingly, no polymerization was observed in this case; ^{29}Si NMR showed only $MeSiH_3$. Most likely, removal of the volatile methylsilane seems to be a driving force of polymerization. The resulting polymers show a broad peak from −60 to −80 ppm in ^{29}Si NMR and therefore seem to indicate an atactic microstructure. Speed of reaction varies considerably; most catalysts required reaction times of a few days, whereas the reaction with **3** was finished after only 30 min. The high activity of the late metal amido complex **3** might be due to the rapid generation of the catalytically active species caused by the strained binding mode of the aminopyridinato ligands.

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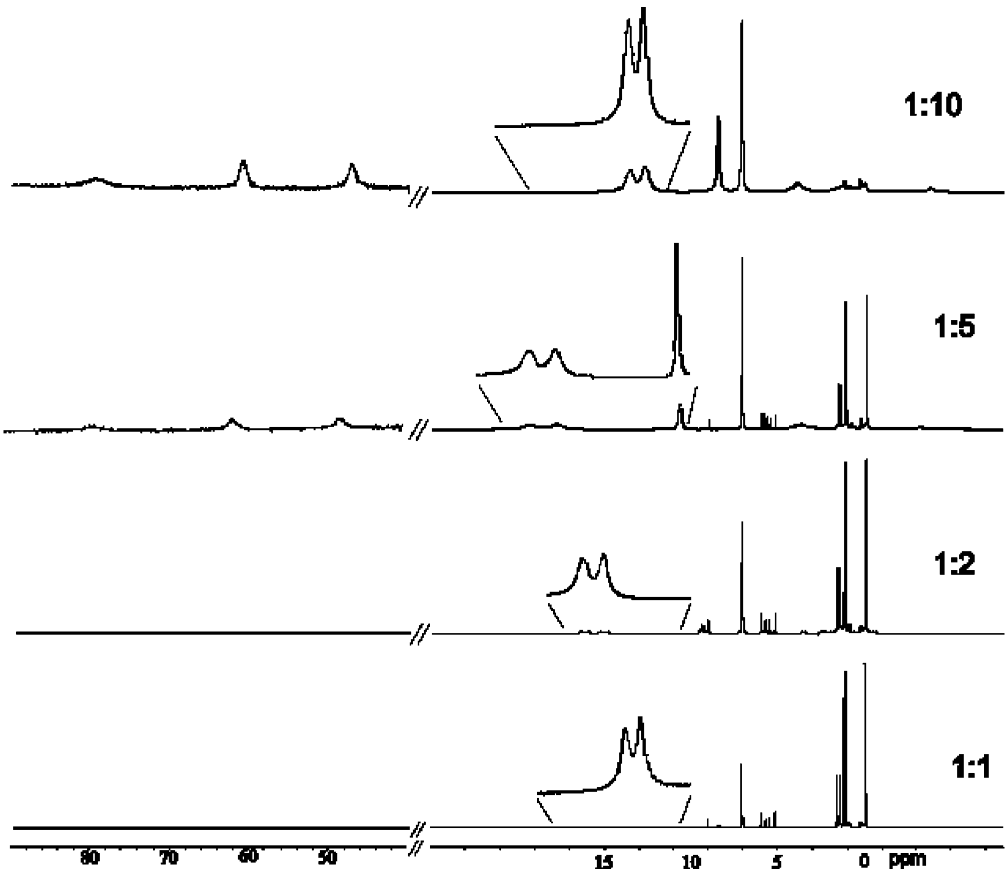
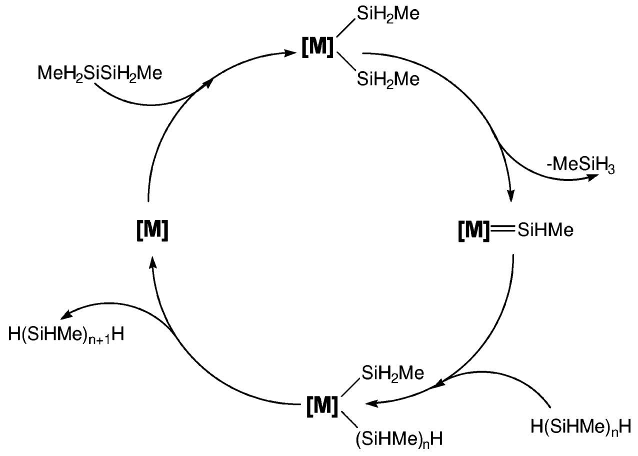


Figure 9. ^{1}HNMR spectra of **4** in the presence of 1, 2, 5, and 10 equiv of 3-chloropyridine/nickel. 3-Chloropyridine coordinates the nickel center of **4**, and a paramagnetic complex analogous to **7** or **8** is formed. Furthermore, a fast exchange with noncoordinated pyridine is observed.

Scheme 4. Proposed Catalytic Cycle for the Polymerization of 1,2-Dimethyldisilane



Conclusions

In conclusion, we found a convenient protocol to synthesize group 10 metal aminopyridinates. These late metal amido complexes are unique in terms of their structure and reactivity due to the strained binding mode of the aminopyridinato ligands. The Pd(II) compound **3** is an active catalyst in the late transition metal catalyzed polymerization of hydrosilanes. Ni(II) complexes such as **4** can catalyze Suzuki coupling of aryl chlorides without the need of stabilizing phosphine ligands. The catalyst activation proceeds most likely via aryl boronic acid homocoupling.

Experimental Section

General Procedures. All reactions and manipulations with air-sensitive compounds were performed under dry argon, using standard Schlenk and drybox techniques. Solvents were distilled from sodium benzophenone ketyl. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried, and distilled prior to use. NMR spectra were obtained using either a Bruker ARX 250, Bruker MSL 300, Bruker DRX 500, or Varian Unity Inova 400 or 300 spectrometer. Chemical shifts are reported in ppm relative to the deuterated solvent. GC analyses were conducted with an Agilent 6890N Network GC System. Elemental analyses were carried out using an Elementar Vario EL III analyzer. Some of the carbon values are a little lower than 0.5% due to the formation of silicium carbide. GC/MS was performed on a HP 5890/II gas chromatograph with a HP 5971/A MSD, a HP1 (cross-linked methyl silicone) column, and helium as carrier gas. Molecular masses were determined by GPC using a Merck-Hitachi L 6200 chromatograph equipped with a differential refractive index detector and viscosity index detector (Viscotek 200), SDV-gel columns from Polymer Standards Service in THF calibrated against polystyrene standards (Polymer Laboratories). Interpretation of the results was done using software of Polymer Standards Service. X-ray crystal structure analyses were performed using a STOE-IPDS I or II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement was accomplished using SIR97,[35] SHELXL97,[36] and WinGX.[37] Crystallographic details are summarized in Table 1. CCDC-263853

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(compound **4**), -263855 (compound **5**), -263854 (compound **6**), -263856 (compound **7**), and -263857 (compound **8**) contain the supplementary crystallographic data for this publication. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44-1223-336-033; E-mail deposit@ccdc.cam.ac.uk).

Ligand Synthesis. Synthesis of 2. $[Pd_2(dba)_3]$ (0.137 g, 0.15 mmol) (dba = dibenzylideneacetone), BINAP (*rac*-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) (0.186 g, 0.3 mmol), and sodium *tert*-butoxide (1.4 g, 14.5 mmol) were placed in an ACE tube, and 10 mL of xylene was added. 2-Bromo-4-methylpyridine (1.72 g, 1.12 mL, 10 mmol) and an excess of *tert*-butylamine (3.45 g, 5 mL, 21 mmol) were added, and the solution was stirred at 120 °C for 2 days. The reaction mixture was allowed to cool to room temperature, and water (50 mL) and diethyl ether (50 mL) were added. The two phases were separated, the organic phase was dried over $MgSO_4$, and the solvent was removed in a vacuum. After distillation **2** was isolated as a colorless liquid in 80% yield (1.3 g). Anal. Found for $C_{10}H_{16}N_2$ ($M_r = 164.04$): C, 72.66; H, 9.88; N, 17.09. Calcd: C, 73.15; H, 9.75; N, 17.07.

^1H (C_6D_6): $\delta = 1.42$ (s, 9 H, ^tBu), 1.92 (s, 3 H, CH_3), 3.99 (s, 1 H, NH), 5.80 (s, 1H), 6.21 (d, 1 H), 8.17 (d, 1 H). ^{13}C (C_6D_6): $\delta = 21.61$, 30.29, 51.57, 110.52, 114.57, 147.57, 148.8, 160.1.

Complex Synthesis. Synthesis of 4. Compound **1** (0.425 mL, 0.36 g, 2 mmol) was dissolved at −40 °C in diethyl ether (12 mL), and *n*-BuLi (1.25 mL of a 1.6 M hexane solution, 2 mmol) was added. After 20 min the reaction mixture was allowed to warm to room temperature and stirred for 1 h. $[(dme)NiCl_2]$ (1 mmol, 0.219 g) was suspended in THF (12 mL) and added to the above-mentioned reaction mixture at −30 °C. After being stirred for 4 h at −30 °C, the solution was stored overnight at this temperature. Solvent was removed under reduced pressure at −30 °C. The residue was extracted with hexane to give a green solution, which was concentrated and stored at −30 °C to give green crystals. Yield: 0.220 g (0.264 mmol, 53%). Anal. Found for $C_{36}H_{60}N_8Ni_2Si_4$ ($M_r = 833.74$): C, 51.04; H, 7.27; N, 13.54. Calcd: C, 51.81; H, 7.19; N, 13.43). ^1H (C_6D_6): $\delta = 0.11$ (s, 9 H, TMS), 1.30 (s, 9 H, TMS), 1.71 (s, 3 H, CH_3), 1.81 (s, 3 H, CH_3), 5.33 (s, 1 H), 5.67 (d, 1 H), 5.87 (d, 1 H), 6.11 (s, 1 H), 7.18 (d, 1 H), 9.17 (d, 1 H). ^{13}C NMR (C_6D_6): $\delta = 2.67$, 4.04, 21.08, 22.42, 108.9, 109.69, 111.07, 116.65, 142.55, 144.86, 149.36, 149.74, 170.27, 173.81.

Synthesis of 5. A solution of compound **2** (0.47 mL, 0.4 g, 2.44 mmol) in diethyl ether (12 mL) was treated with *n*-BuLi (1.53 mL) in hexane (1.6 M, 2.44 mmol) at −40 °C. After the solution was stirred for 20 min at this temperature, the cooling bath was removed, and after another 1 h, a suspension of $[(cod)PdCl_2]$ (0.348 g, 1.22 mmol) in THF (12 mL) was added at −30 °C. The reaction mixture was stirred for 3 h and then stored at −30 °C overnight. Now the solvent was removed in a vacuum, and the residue was extracted with hexane. The red-brown solution was concentrated and gave red crystals at room temperature. Yield: 0.338 g (0.67 mmol, 55%). Anal. Found for $C_{24}H_{38}N_4OPd$ ($M_r = 504.21$): C, 56.44; H, 7.51; N, 10.90. Calcd: C, 57.08; H, 7.58; N, 11.09. ^1H (C_6D_6): $\delta =$ 1.22 (s, 9H, *tert*Bu), 1.75 (s, 3 H, CH_3), 5.45 (d, 1 H), 5.73 (s, 1H), 7.40 (d, 1H). ^{13}C NMR (C_6D_6): $\delta = 29.8$, 31.7, 104.72, 108.72, 145.88, 148.95, 158.73.

Attempts To Synthesize the Analogous Nickel Complex of 5. A solution of **2** (0.51 mL, 0.44 g, 2.7 mmol) in diethyl ether (12 mL) was treated with *n*-BuLi (1.7 mL of a 1.6 M hexane solution, 2.7 mmol) at −40 °C. After the solution was stirred for 20 min at this temperature, the cooling bath was removed, and after another 1 h, a suspension of $[(dme)NiCl_2]$ (0.295 g, 1.35 mmol) in THF (12 mL) was added at −30 °C. The reaction mixture was stirred for 3 h at −30 °C and then stored overnight at this temperature. The solvent was removed under reduced pressure, and the residue was extracted with hexane. The red-brown solution was filtered and concentrated. After the mixture was standing at room temperature, yellow (**6**) and red (**7**) crystals were obtained, which could be separated manually. Yield of **7**: 0.246 g (0.44 mmol, 33%). Anal. Found for $C_{30}H_{46}N_6Ni$ ($M_r = 548.69$): C, 65.28; H, 8.51; N, 14.88. Calcd: C, 65.58; H, 8.44; N, 15.30. Yellow crystals of **6** were obtained as a byproduct. Yield: 0.090 g (0.11 mmol, 24%).

Synthesis of 8. To a stirred solution of **2** (0.522 g, 3.18 mmol) in 7 mL of diethyl ether was added *n*-BuLi (2 mL of a 1.6 M hexane solution, 3.2 mmol) at −40 °C. This “ligand solution” was allowed to warm slowly to room temperature and was stirred for 90 min. $[(dme)NiCl_2]$ (0.349 g, 1.59 mmol) was suspended in 8 mL of THF, and 4-*tert*-butylpyridine (3.2 mmol, 0.29 mL) was added. The “ligand solution” was added to this suspension at −30 °C, and the color changed slowly to red brown. The solution was stirred at this temperature until all starting material dissolved. The solvent was removed in a vacuum, and the residue was extracted with hexane. After the concentration of this hexane solution, green crystals were formed at room temperature. Yield: 0.426 g (0.65 mmol, 41%). Anal. Found for $C_{38}H_{56}N_6Ni$ ($M_r = 654.72$): C, 69.05; H, 8.77; N, 12.32. Calcd: C, 69.65; H, 8.55; N, 12.83. ^1H (C_6D_6) (paramagnetic compound): $\delta = 3.77$ (s, b), 5.21 (s, b), 19.65 (s, b), 43.48 (s, vb), 58.48 (s, vb), 68.4 (s, vb), 93.14 (s, vb).

Cross-Coupling Experiments. The cross-coupling experiments were performed using a parallel apparatus (12 tubes) on the basis of Schlenk techniques. K_3PO_4 was dried for 24 h at 130 °C prior to use, and 1.2 mmol was added into each tube. After the base, the substrates (1 mmol of aryl halide, 1.2 mmol of phenyl boronic acid) and catalyst were added from stock solutions and the reaction mixture was stirred and heated to the corresponding temperature. The reactions were quenched with water after the given reaction time and allowed to cool to room temperature before they were extracted with diethyl ether. Samples were analyzed by GC using *n*-dodecane as an internal standard. For the kinetic studies a 100 mL Schlenk-flask was filled with 4 mmol of 3-chloropyridine, 4.8 mmol of phenyl boronic acid, 1.02 g of K_3PO_4, dodecane (internal standard), and 23 mL of dioxane. Small amounts of the reaction mixture (about 0.25 mL) were taken after the given reaction times and quenched directly into water, extracted with diethyl ether, and measured via GC analysis. The investigation of the homocoupling was made under the same conditions without the addition of 3-chloropyridine.

Polymerization Procedure. Starting material (1 g/11 mmol of MeH_2SiSiH_2Me) and 1 mol % catalyst were mixed in a flask and stirred at room temperature. The course of the reaction was followed by GC/MS in the beginning and later by ^{29}Si NMR of aliquot samples. Workup consisted of passing a toluene solution of the reaction mixture through a short column of Florisil, which was followed by evaporation of the solvent.

Magnetic Susceptibility Measurements. Magnetic properties of **7** and **8** samples were studied by using a commercial quantum design SQUID (superconducting quantum interference device) magnetometer (Cryogenic Consultant Ltd S-600). Magnetic moment measurements were performed on the air- and moisture-sensitive polycrystalline samples stored inside sealed capillary glass tubes

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that were placed into plastic straws. Data were recorded in zero-field-cooled conditions (ZFC) at the applied field of 0.0105 T and in the temperature range 5−300 K. The data were corrected for the diamagnetism (Pascal corrections). The very small diamagnetic contribution of the glass capillary container has a negligible contribution to the overall magnetization, which is dominated by the sample signal.

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