Synthesis and Reactivity of Palladium and Nickel β-Diimine Complexes: Application as Catalysts for Heck, Suzuki, and Hiyama Coupling Reactions†

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The synthesis of a range of sterically hindered β-diimine ligands and their complexes with palladium(II) and nickel(II) of the formula Pd(κ^2*N*,*N*-RN=CHC$(CH_2)_n$−CH=NR)(Cl_2) (R = 2,6-*i*-Pr_2Ph, 2,6-Me_2Ph, Cy, *t*-Bu, n = 4, 5) and Ni(κ^2*N*,*N*-RN=CHC$(CH_2)_4$−CH=NR)(Br_2) (R = 2,6-*i*-Pr_2Ph, 2,6-Me_2Ph) has been investigated. Representative X-ray structures of both ligands and complexes have been determined. The use of the palladium complexes as catalysts for Suzuki coupling of aryl halides and arylboronic acids has been examined. In addition, it has been shown that the palladium complexes are also active in the Heck reaction of aryl bromides and methyl acrylate as well as in the Hiyama coupling of aryl halides and phenyltrimethoxysilane.

Introduction

Nickel and palladium complexes containing sterically demanding α-diimine (diazabutadiene) ligands are highly efficient catalysts for olefin polymerizations,[1−3] for alkyne cyclotrimerizations,[4] and as shown recently also for Suzuki cross-coupling reactions.[5] On the other hand, few investigations have focused on the chemistry of analogous nickel and palladium β-diimine complexes. Feldman et al. reported the synthesis of a sterically hindered β-diimine ligand bearing no substitutents at the C_β atom and examined its reactions with Pd(II) and Ni(II) catalyst precursors.[6] However, β-diimines lacking substituents at the central carbon atom typically form hydrogen-bridged β-iminoamine tautomers. Accordingly, in the presence of base, e.g., under catalytic conditions, facile deprotonation occurs giving rise to the formation of β-diketiminate complexes[7] and other products[8] rather than β-diimine complexes. Consequently, the poor catalytic activity of these compounds as polymerization catalysts may be attributed to such reactions. Recently, Woods and co-workers synthesized several β-diimine ligands in which the problematic CH acidity has been removed by diimine dialkylation.[9] In a subsequent paper, these authors described the synthesis of some palladium β-diimine complexes and provided structural comparisons with the corresponding α-diimine analogues.[10] The catalytic activity of these complexes has not been studied so far.

Here we wish to report on the synthesis and characterization of a series of palladium and nickel complexes containing sterically demanding new β-diimine ligands. To ascertain that the ligands maintain their diimine form even under basic conditions, the central carbon atoms of these ligands are part of five- and six-membered-ring systems. In addition, we describe the use of these palladium complexes in the catalytic cross-coupling of various aryl halides with arylboronic acids (Suzuki reaction),[11] methyl acrylate (Heck reaction),[12] and phenyltrimethoxysilane (Hiyama reaction).[13]

† Dedicated to Prof. Fritz Sauter on the occasion of his 75th birthday.

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Scheme 1

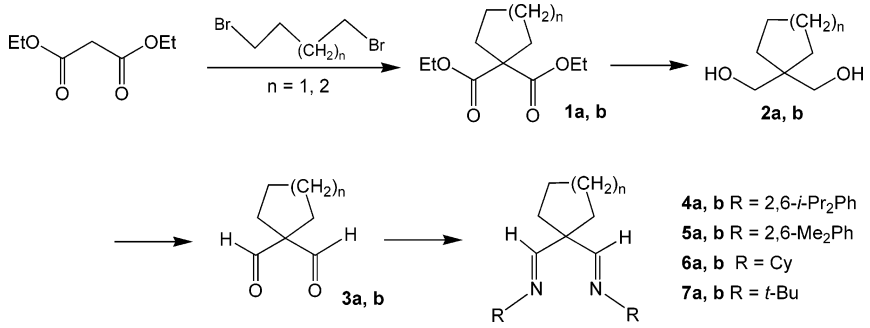

Table 1. Details for the Crystal Structure Determinations of Complexes 4a, 4b, 8a, 8b·3CHCl$_3$, 11a·CHCl$_3$, 12, and 13

	4a	**4b**	**8a**	**8b**·3CHCl$_3$	**11a**·CHCl$_3$	**12**	**13**
formula	$C_{31}H_{44}N_2$	$C_{32}H_{46}N_2$	$C_{31}H_{44}Cl_2N_2Pd$	$C_{35}H_{49}Cl_{11}N_2Pd$	$C_{16}H_{29}Cl_5N_2Pd$	$C_{31}H_{44}Cl_4N_2Pd_2$	$C_{31}H_{44}Br_2N_2Ni$
fw	444.68	458.71	621.98	994.11	533.06	799.28	663.21
cryst size, mm	0.70 × 0.30 × 0.25	0.72 × 0.39 × 0.32	0.25 × 0.08 × 0.05	0.42 × 0.30 × 0.24	0.35 × 0.26 × 0.21	0.18 × 0.06 × 0.06	0.41 × 0.31 × 0.25
space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$Pna2_1$ (no. 33)	$P2_12_12_1$ (no. 19)	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)
a, Å	14.513(1)	11.6301(5)	21.2936(11)	12.1042(5)	10.8303(7)	26.0226(10)	15.1188(7)
b, Å	27.241(2)	11.6674(5)	12.1438(6)	17.2671(7)	18.3935(11)	19.7160(7)	13.3814(6)
c, Å	14.662(1)	11.9371(5)	12.0665(7)	21.1808(8)	11.8584(7)	16.4642(6)	17.6356(8)
α, deg	90	77.150(1)	90	90	90	90	90
β, deg	92.308(1)	71.050(1)	90	90	91.664(1)	126.375(1)	115.189(1)
γ, deg	90	69.572(1)	90	90	90	90	90
V, Å^3	5791.6(6)	1424.7(1)	3120.2(3)	4426.9(3)	2361.3(3)	6769.6(4)	3228.6(3)
Z	8	2	4	4	4	8	4
ρ_{calc}, g cm^{-3}	1.020	1.069	1.324	1.492	1.499	1.568	1.364
T, K	297(2)	173(2)	296(2)	173(2)	297(2)	297(2)	297(2)
μ, mm^{-1} (Mo Kα)	0.058	0.061	0.787	1.111	1.354	1.401	3.096
F(000)	1952	504	1296	2024	1080	3232	1368
θ_{max}, deg	25	27	30	30	30	25	30
no. of rflns measd	59 867	17 396	45 629	59 221	34 950	35 120	25 095
no. of unique rflns	10 152	6196	9046	12 865	6883	5964	9368
no. of rflns $I>2\sigma(I)$	6768	5119	7602	11 413	5556	4320	6882
no. of params	611	307	325	446	217	352	325
R_1 ($I > 2\sigma(I)$)[a]	0.0578	0.0423	0.0274	0.0391	0.0408	0.0395	0.0334
R_1 (all data)	0.0858	0.0516	0.0377	0.0480	0.0549	0.0647	0.0537
wR_2 (all data)	0.1922	0.1193	0.0655	0.1031	0.1032	0.0931	0.0924
diff Fourier peaks min./max., e Å^{-3}	−0.18/0.30	−0.21/0.26	−0.27/0.30	−0.73/1.05	−0.46/1.04	−0.58/1.00	−0.42/0.62

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

Results and Discussion

Ligand Synthesis. The β-diimines **4**−**7** were synthesized according to the four-step procedure summarized in Scheme 1. The diesters **1a**,**b** were obtained in good yields using an improved and simplified method[14] by alkylation of diethyl malonate with terminal dibromoalkanes and sodium ethoxylate as base. Reduction with $LiAlH_4$[15] in THF as the solvent led to the formation of the dialcohols **2a**,**b**. In contrast to the procedure described in the literature,[16] the dialdehydes **3a**,**b** were generated by a Swern oxidation under standard conditions[17] in reasonable isolated yields. Condensation with different amines in the presence of *p*-toluenesulfonic acid afforded finally the desired new β-diimines **4**−**7** in good yields. Characterization of the diimines was accomplished by a combination of elemental analysis and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. In addition, the solid state structures of **4a** and **4b** were determined by single-crystal X-ray diffraction. Crystal data are presented in Table 1. ORTEP diagrams are depicted in Figures 1 and 2. Despite their chemical similarity, the two compounds crystallize in entirely different crystal lattices, namely, **4a** in a monoclinic lattice with two independent molecules and **4b** in a triclinic lattice with only one independent molecule (Table 1). However, all the molecules do exhibit similar key bond lengths and angles (Table 2 and Supporting Information). They are also related in conformations including the property that the electron lone pairs of nitrogens N1 and N2 point in diverging directions and do not participate in any significant interaction with surrounding H atoms. The β-diimine ligand studied by Woods and co-workers[10]

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Table 2. Selected Distances and Angles (Å, deg) of Complexes 4a, 4b, 8a, 8b·3CHCl$_3$, 11a·CHCl$_3$, 12, and 13

	4a	4b	8a	8b·3CHCl$_3$	11a·CHCl$_3$	12	13
Pd−Cl1/Ni−Br1			2.276(1)	2.292(1)	2.305(1)	2.323(1)	2.3295(3)
Pd−Cl2/Ni−Br2			2.279(1)	2.292(1)	2.305(1)	2.324(1)	2.3581(3)
Pd−N1			2.054(2)	2.050(2)	2.016(2)	2.013(3)	2.006(2)
Pd−N2			2.041(2)	2.046(2)	2.023(2)	2.008(4)	1.998(2)
N1−C1	1.244(2)	1.258(1)	1.272(3)	1.271(4)	1.260(3)	1.277(5)	1.270(2)
N2−C3	1.245(2)	1.258(1)	1.270(3)	1.268(4)	1.269(4)	1.278(5)	1.267(2)
C1−C2	1.511(3)	1.511(1)	1.488(3)	1.502(3)	1.508(4)	1.493(6)	1.496(2)
C2−C3	1.500(3)	1.510(1)	1.487(3)	1.507(3)	1.510(4)	1.482(6)	1.498(3)
N1−C11	1.431(2)	1.435(1)	1.468(3)	1.456(4)	1.517(4)	1.459(5)	1.455(2)
N2−C21	1.434(2)	1.427(1)	1.461(3)	1.463(3)	1.514(4)	1.459(6)	1.453(2)
Cl1−Pd−Cl2/Br1−Ni−Br2			89.52(3)	88.89(3)	89.05(3)	84.00(5)	120.34(1)
Cl1−Pd−N1			91.22(5)	91.62(7)	92.80(7)	93.43(11)	
Cl2−Pd−N2			89.44(6)	90.15(7)	93.78(7)	92.92(11)	
N1−Pd−N2			90.38(7)	90.06(9)	83.95(9)	89.85(15)	91.24(6)
rms aplanarity[a]			0.097	0.111	0.075	0.057	
boat angle 1[b]			48.3(2)	41.3(2)	88.0(2)	47.6(3)	41.4(2)
boat angle 2[c]			35.1(1)	31.1(2)	65.5(2)	35.4(2)	30.4(1)

[a] rms aplanarity: root-mean-square deviation (Å) of the atoms Pd, Cl1, Cl2, N1, and N2 from a common least-squares plane. [b] Boat angle 1: angle between the planes N1−Pd−N2 and C1−C2−C3. [c] Boat angle 2: angle between the least-squares planes Pd−N1−C1−C2 and Pd−N2−C3−C2.

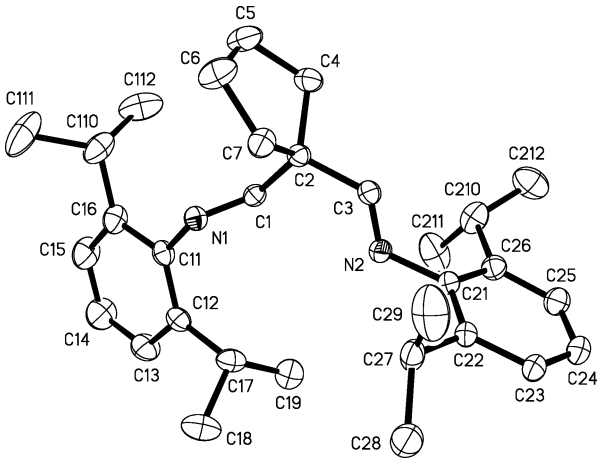


Figure 1. Structural view of **4a** showing 20% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Only one of the two independent molecules in this structure is shown.

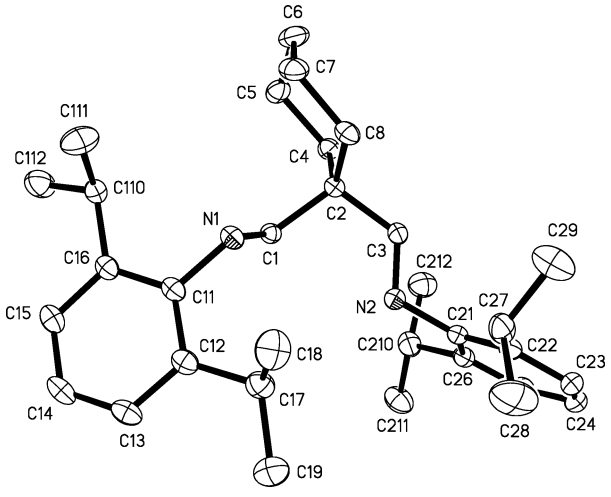
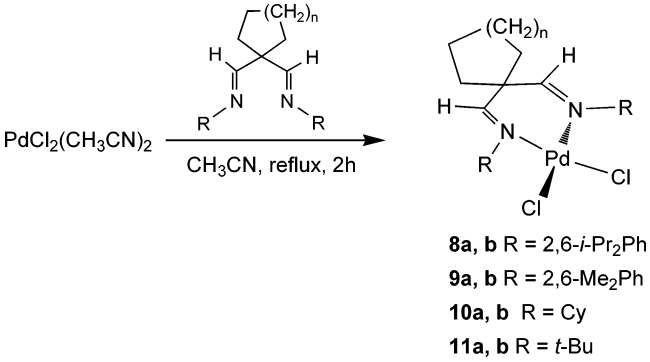


Figure 2. Structural view of **4b** showing 40% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

adopts in free state a conformation of the approximate symmetry C_2 and differs in this respect from **4a** and **4b**.

Synthesis of Pd and Ni β-Diimine Complexes. Treatment of $PdCl_2(CH_3CN)_2$ with the ligands **4**−**7** in

Scheme 2



boiling CH_3CN for 2 h afforded complexes **8**−**11** cleanly in good isolated yields (Scheme 2). All complexes are thermally robust yellow or brown solids that are stable to air both in the solid state and in solution.

The identity of the compounds was established by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and by elemental analysis. The NMR spectra of **8**−**11** bear no unusual features, and it is sufficient to point out that the proton of the imine CH=N moiety of the β-diimine ligands gives a characteristic singlet resonance in the range 7.26−7.77 ppm. Likewise, in the ^{13}C{^{1}H} NMR spectra the imine carbon atom exhibits a singlet resonance at about 174 ppm. Structural views of **4a**, **4b**, and **11a**, as determined by X-ray crystallography (Table 1), are depicted in Figures 3−5. Selected geometric data are reported in Table 2. The expected bidentate coordination of the diimine nitrogen atoms to the Pd(II) center, forming distorted square-planar coordination environments, is found for all three complexes (Figures 3−5, Table 2).[1−3,6,10] As in related Pd(II) β-diimine complexes,[10] the six-membered chelate ring adopts a boat conformation. This boat conformation is the result of the presence of two planar Pd−N(sp^2)=CH(sp^2)−C systems and two comparatively low bond angles N1−Pd−N2 ≈ 90° and C1−C2−C3 ≈ 108° in the chelate ring. It can be noted that the degree of the boat conformation is strongly dependent on the space requirement of the N substituent R (e.g., *t*-Bu vs 2,6-*i*-P_2Ph): In case of the less demanding *t*-Bu substituent (complex **11a**) the boat conformation of the six-membered chelate ring is most

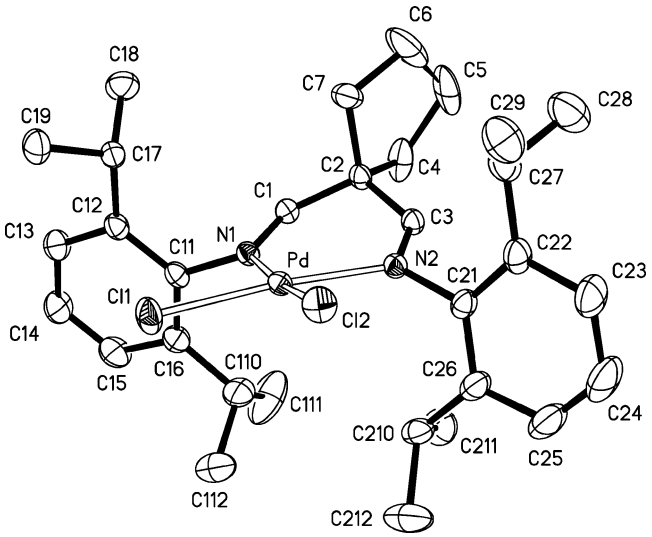


Figure 3. Structural view of **8a** showing 20% thermal ellipsoids.

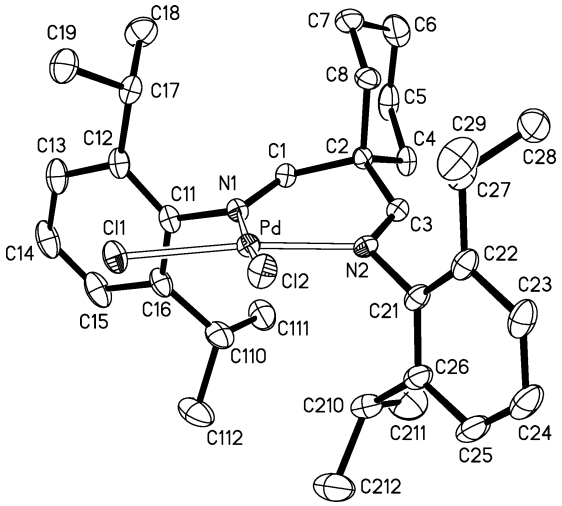


Figure 4. Structural view of **8b**·3$CHCl_3$ showing 40% thermal ellipsoids. Hydrogen atoms and $CHCl_3$ molecules are omitted for clarity.

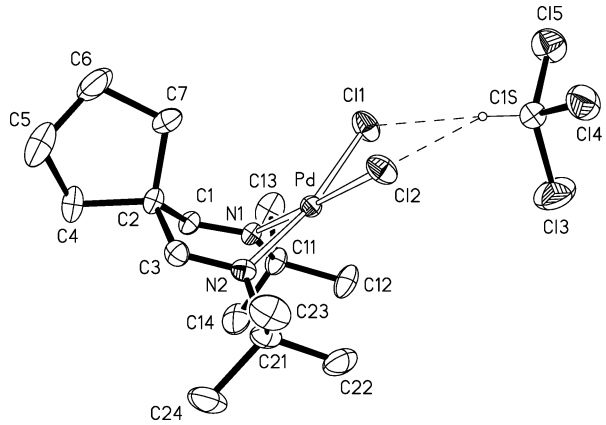
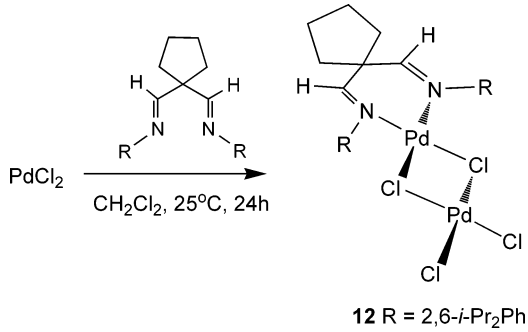


Figure 5. Structural view of **11a**·$CHCl_3$ showing 20% thermal ellipsoids. Most hydrogen atoms are omitted. The broken lines from Cl(1) and Cl(2) to H(1s)−C(1s) represent a symmetrically branched C−H···Cl hydrogen bond.

pronounced (Figure 5). On replacement of the *t*-Bu by the much bulkier 2,6-*i*-Pr_2Ph substituent (complexes **8a**, **8b**, **12**, and **13**), the boat conformation is forced to be distinctly flatter because of mutual *i*-Pr interferences

Scheme 3



12 R = 2,6-*i*-Pr_2Ph

at one side of the complex with consequent short separations between C(110) and C(210) and their hydrogen atoms (cf. Figures 3 and 4). Quantities showing this feature have been included in Table 2. The protruding character of the two chloride ions in these complexes makes them prone to further interactions or reactions (vide infra). In the case of **8b** and **11a** this leads to the formation of the well-crystallized solvates **8b**·3$CHCl_3$ and **11a**·$CHCl_3$, which are both stabilized by C−H···Cl hydrogen bonds from chloroform to chloride. In particular **11a**·$CHCl_3$ stands out in having an almost perfectly symmetrically bifurcated C−H···Cl interaction (H(16)···Cl(1) = 2.64 Å, H(16)···Cl(1) = 2.67 Å) (Figure 5).

It has to be noted that if $PdCl_2$ is reacted overnight with **4a** in CH_2Cl_2 at room temperature, the dinuclear complex **12** is obtained in 36% isolated yield (Scheme 3). For comparison, an analogous complex with the same structural motif has been reported recently by Woods and co-workers.[10] Spectroscopic features are very similar to those of **8a** and are not discussed here. An ORTEP diagram is depicted in Figure 6. Selected bond distances of this complex, not given in Table 2, are reported in the caption.

The corresponding β-diimine complexes of Ni(II) (**13**, **14**) were readily prepared by reaction of $NiBr_2$(DME) with the ligands **4a** and **4b** in 86 and 65% isolated yields (Scheme 4). The purple complexes are paramagnetic and

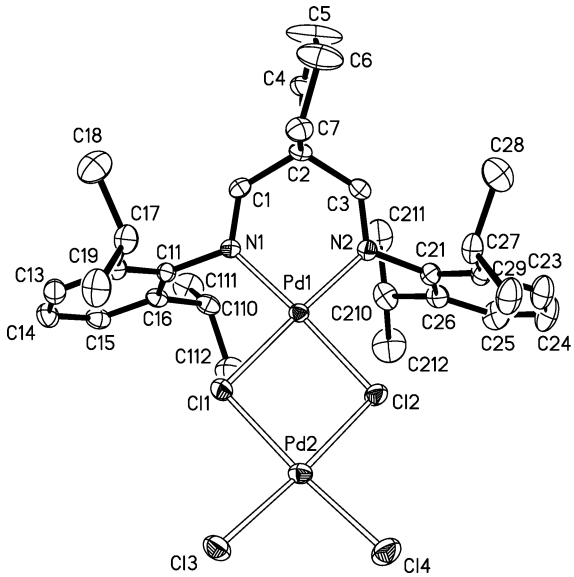
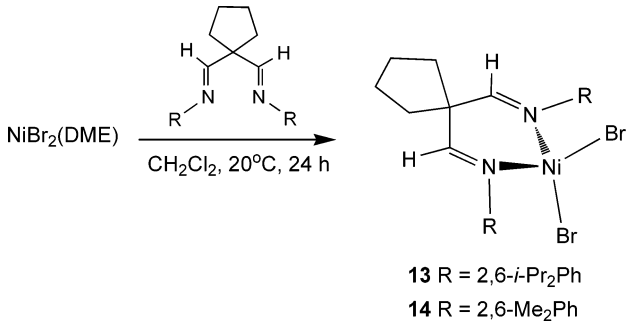


Figure 6. Structural view of **12** showing 20% thermal ellipsoids. Selected distances (Å; for further data see Table 2): Pd2-Cl1 2.334(1), Pd2−Cl3 2.270(1), Pd2−Cl2 2.327(1), Pd2−Cl4 2.266(2).

Scheme 4



display contact-shifted ^{1}H NMR spectra with relatively narrow line widths at room temperature. The X-ray crystal structure of **13** is shown in Figure 7. The Ni(II) atom adopts a pseudo-tetrahedral coordination geometry. In analogy with the above-described Pd complexes, the six-membered chelate ring adopts a boat conformation of flat shape similar to the Pd complexes.

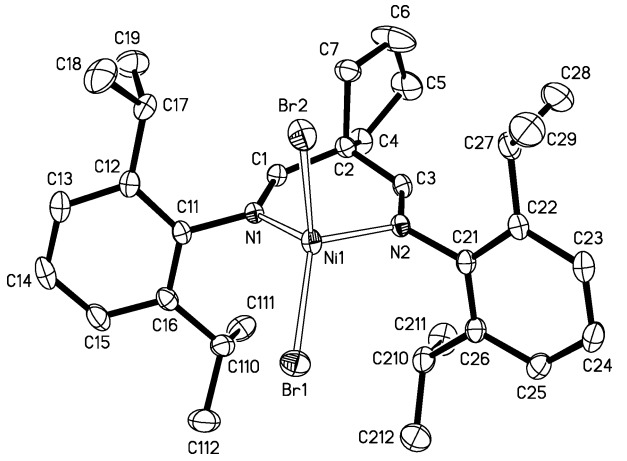


Figure 7. Structural view of **13** showing 20% thermal ellipsoids.

Suzuki Coupling. Palladium complexes containing α-diimine ligands are excellent catalysts for the Suzuki coupling.[5] On the basis of these findings we were interested in whether palladium complexes containing *β*-diimine ligands exhibit similar reactivities in C−C bond coupling reactions. Accordingly, we investigated the activity of $PdCl_2$ in the presence of *β*-diimine ligands **4**−**7** as well as the activity of complexes **8**−**11** as catalysts for the coupling of various aryl halides with aryl boronic acids. The results of this study are summarized in Table 3. In all cases the reactions were performed with 3 mol % of catalysts in dioxane at 80 °C with Cs_2CO_3 acting as base. These conditions have not been optimized.

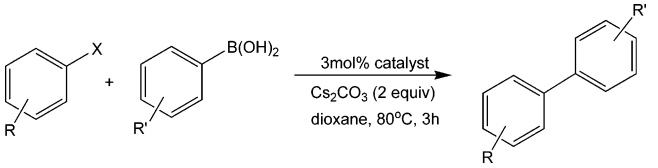
In general, the coupling reaction is more efficient if complexes **8**−**11** are used (entries 10−17) instead of $PdCl_2$ in the presence of 1 equiv of ligands **4**−**7** (entries 2−9). While it is difficult to establish any clear trends in the catalytic activity of complexes **8**−**11** on these preliminary data, on average complexes **8** and **9** show higher activity than complexes **10** and **11** (entries 10−17). This reactivity trend suggests that the stronger donating ability of alkyl substituents, making the ligand more electron-rich, renders the catalyst less active.

We observed that the coupling of 4-bromoacetophenone and 4-bromotoluene with phenylboronic acid proceeded smoothly to give 4-acetylbiphenyl and 4-methylbiphenyl in high yields (entries 10−17, 19). Moreover, with the electronically deactivated and thus more challenging substrate 4-bromoanisole, good conversions could be achieved (entry 20). Even the sterically demanding 2-bromotoluene and 2-bromoanisole gave acceptable yields (entries 18 and 21). On the other hand, little or no activity was observed for 2,6-disubstituted substrates (entries 22−24). Attempts to couple 4-bromotoluene with the *meta*-substituted 3-methoxyphenylboronic acid resulted in reasonable yields (entry 25). In contrast, with *meta*-substituted substrates low yields were observed in the case of palladium α-diimine complexes.[5] Finally, the catalytic effect was confirmed by running the standard reaction on 4-bromotoluene without ligand (entry 1). The reaction proceeds, but led to only low yields.

Finally, it has to be mentioned that attempts to couple arylbromides with phenylboronic acid in the presence of nickel *β*-diimine complexes proved to be little effective, resulting in yields < 10%. Accordingly, the nickel-catalyzed Suzuki coupling has not been further investigated.

Heck and Hiyama Coupling. Catalytic reactions other than the Suzuki cross-coupling were also probed. The Heck reaction between various aryl bromides and

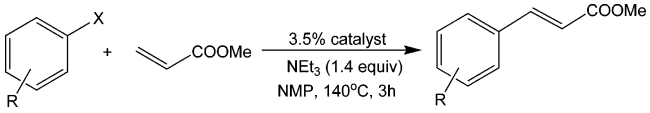
Table 3. Suzuki Cross-Coupling of Aryl Halides with Arylboronic Acids[a]



entry	X	R	R′	catalyst	isolated yield (%)
1	Br	4-Me	H	$PdCl_2$	18[b]
2	Br	4-Me	H	$PdCl_2$, **4a**	65 (82[b])
3	Br	4-Me	H	$PdCl_2$, **4b**	80[b]
4	Br	4-Me	H	$PdCl_2$, **5a**	74[b]
5	Br	4-Me	H	$PdCl_2$, **5b**	73[b]
6	Br	4-Me	H	$PdCl_2$, **6a**	97[b]
7	Br	4-Me	H	$PdCl_2$, **6b**	96[b]
8	Br	4-Me	H	$PdCl_2$, **7a**	93[b]
9	Br	4-Me	H	$PdCl_2$, **7b**	76[b]
10	Br	4-Me	H	**8a**	89
11	Br	4-Me	H	**8b**	98[b]
12	Br	4-Me	H	**9a**	83
13	Br	4-Me	H	**9b**	95[b]
14	Br	4-Me	H	**10a**	74 (97[b])
15	Br	4-Me	H	**10b**	93[b]
16	Br	4-Me	H	**11a**	73 (89[b])
17	Br	4-Me	H	**11b**	90[b]
18	Br	2-Me	H	**8a**	56
19	Br	4-COMe	H	**8a**	96
20	Br	4-OMe	H	**8a**	82[c]
21	Br	2-OMe	H	**8a**	57
22	Br	2,6-Me	H	**8a**	7
23	Br	2,6-Me	H	**8a**	41[c]
24	Br	4-Me	2,6-Me	**8a**	6
25	Br	4-Me	3-OMe	**8a**	53
26	Cl	4-Me	H	**8a**	9[d]
27	Cl	4-Me	H	**8a**	18[c]
28	Cl	4-COMe	H	**8a**	25[e]
29	Cl	4-COMe	H	**8a**	51[c]
30	Cl	4-COMe	H	**9a**	35[e]
31	Cl	4-OMe	H	**8a**	0[c]

[a] Reaction conditions: aryl halide (1.0 mmol), boronic acid (1.5 mmol), Cs_2CO_3 (2.0 mmol) and catalyst (3 mol %). [b] Determined by GC. [c] The reaction was stirred for 18 h. [d] The reaction was stirred for 4.5 h. [e] The reaction was stirred for 4 h.

Table 4. Heck Cross-Coupling of Aryl Halides with Olefins[a]



entry	X	R	catalyst	isolated yield (%)
1	I	H	$PdCl_2$	66[c]
2	I	H	$PdCl_2$, **4a**	99[c]
3	I	H	$PdCl_2$, **5a**	96[c]
4	I	H	**8a**	93[c]
5	I	H	**9a**	98[c]
6	Br	4-COMe	$PdCl_2$	53[b]
7	Br	4-COMe	$PdCl_2$, **4a**	39[b]
8	Br	4-COMe	$PdCl_2$, **4b**	74[b]
9	Br	4-COMe	$PdCl_2$, **5a**	27[b]
10	Br	4-COMe	$PdCl_2$, **5b**	74[b]
11	Br	4-COMe	$PdCl_2$, **6a**	73[b]
12	Br	4-COMe	$PdCl_2$, **6b**	62[b]
13	Br	4-COMe	$PdCl_2$, **7a**	86[b]
14	Br	4-COMe	$PdCl_2$, **7b**	87[b]
15	Br	4-COMe	**8a**	87
16	Br	4-COMe	**8b**	82[b]
17	Br	4-COMe	**9a**	85
18	Br	4-COMe	**9b**	93[b]
19	Br	4-COMe	**10a**	100[b]
20	Br	4-COMe	**10b**	66[b]
21	Br	4-COMe	**11a**	99[b]
22	Br	4-COMe	**11b**	100[b]
23	Br	4-Me	**8a**	15
24	Br	4-Me	**8a**	16[d]
25	Br	2-OMe	**8a**	0
26	Br	2,6-Me	**8a**	5[d]

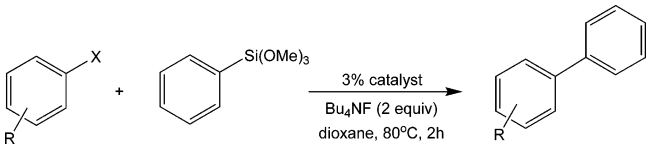
[a] Reaction conditions: aryl halide (1.0 mmol), methyl acrylate (1.2 mmol), NEt_3 (1.4 mmol), and catalyst (3.5 mol %). [b] Determined by GC. [c] The reaction was stirred for 2 h. [d] The reaction was stirred for 18 h.

methyl acrylate has been studied utilizing both $PdCl_2$ in the presence of β-diimine ligands **4**−**7** and complexes **8**−**11** as catalyst precursors. The results are summarized in Table 4. In all cases the reactions were performed with 3.5 mol % of catalysts in NMP as the solvent at 140 °C with NEt_3 (1.4 equiv) acting as base. Again, the conditions have not been optimized.

In the case of aryl iodides, coupling products are formed in essentially quantitative yield independent of whether complexes **8**−**11** are used directly (entries 2−5) or whether $PdCl_2$ is used with 1 equiv of ligands **4**−**7** (entries 7−14). In the case of 4-bromoacetophenone, however, the Heck reaction is clearly more efficient if complexes **8**−**11** are used directly (entries 15−22). There is no clear trend in the catalytic activity of complexes **8**−**11**. With the electronically deactivated and/or sterically demanding aryl bromides little or no activity was observed (entries 23−26). This may be attributed to catalyst deactivation due to the observed formation of palladium black.

The Hiyama coupling was evaluated with $PdCl_2$/**4a** and **8a** as catalyst precursors. The results of this study are summarized in Table 5. Both 4-bromo- and 4-chloroacetophenone can be coupled with phenyltrimethoxysilane in dioxane at 80 °C in reasonable yields (entries 1, 2, and 6). The catalyst/ligand system was not suitable for electronically deactivated and/or sterically demanding substrates. The reaction with 4-bromoanisole and 1-bromo-2,6-dimethylbenzene gave only 33 and 29% yield, respectively, while with 2-bromoanisole no conversion could be achieved (entries 3−5).

Table 5. Hiyama Cross-Coupling of Aryl Halides with Phenyltrimethoxysilane[a]



entry	X	R	catalyst	isolated yield (%)
1	Br	4-COMe	$PdCl_2$, **4a**	64
2	Br	4-COMe	**8a**	87
3	Br	4-OMe	**8a**	33[b]
4	Br	2-OMe	**8a**	0[b]
5	Br	2,6-Me	**8a**	29[b]
6	Cl	4-COMe	**8a**	62[b]

[a] Reaction conditions: aryl halide (1.0 mmol), phenyltrimethoxysilane (2 mmol), Bu_4NF (2.0 mmol), and catalyst (3 mol %). [b] The reaction was stirred for 18 h.

Conclusion

We report the efficient synthesis of new sterically hindered *N*,*N*′-diaryl and dialkyl β-diimines with the central carbon atom being part of both five- and six-membered-ring systems to avoid the formation of β-diketiminates. These compounds are excellent ligands for the preparation of Pd(II) and Ni(II) complexes. The use of the palladium complexes in the catalytic cross-coupling of various aryl halides with arylboronic acids, methyl acrylate, and phenyltrimethoxysilane is described. These complexes proved to be active as catalysts for Suzuki coupling reactions and are comparable to related α-dimine systems, thus representing an interesting alternative to existing catalytic systems. In preliminary results the investigated palladium β-diimine complexes turned out to be less efficient for Heck and Hiyama coupling reactions under the reaction conditions chosen. Attempts to optimize these processes are currently in progress.

Experimental Section

General Information. All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[18] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $PdCl_2(CH_3CN)_2$ and $NiBr_2$(DME) were prepared according to the literature.[19,20] ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AVANCE-200 and -250 spectrometers and were referenced to $SiMe_4$. ^1H and $^{13}C\{^1H\}$ NMR signal assignments were confirmed by ^1H-COSY, DEPT-135, and HMQC($^1H-^{13}C$) experiments.

1,1-Cyclopentanedicarboxylicacid Diethyl Ester (1a). Malonic acid ethyl ester (40.8 g, 255 mmol) was added dropwise to a solution of sodium ethoxide and dry ethanol freshly prepared from sodium (11.7 g, 508 mmol) and dry ethanol (250 mL). The mixture was refluxed for 30 min. After dilution with dry ethanol (165 mL) 1,4-dibromobutane (50.0 g, 232 mmol) was added dropwise, and the mixture was kept boiling for 3 h and was stirred then at room temperature for 18 h. After evaporation of the solvent the residue was dissolved

(18) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: New York, 1988.
(19) Hartley, F. R.; Murray, S. G.; McAuliffe, C. A. *Inorg. Chem.* **1979**, *18*, 1394.
(20) Casalnuovo, A. L.; RajanBabu, T. V.; Ayers, T. A.; Warren, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9869.

in water (270 mL) and extracted with Et_2O (5 × 100 mL). The combined organic layers were washed with saturated NaCl solution (2 × 100 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated and the crude product was purified by vacuum distillation to give a colorless liquid. Yield: 46.8 g (94%). ^{1}H NMR ($CDCl_3$): δ 4.11 (q, 4H, $^3J_{HH}$ = 7.1 Hz, $COOCH_2CH_3$), 2.18−2.03 (m, 4H, $C(CH_2CH_2)_2$), 1.67−1.55 (m, 4H, $C(CH_2CH_2)_2$), 1.17 (t, 6H, $^3J_{HH}$ = 7.1 Hz, $COOCH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 172.44 ($COOCH_2CH_3$), 60.96 ($COOCH_2CH_3$), 60.18 ($C(CH_2CH_2)_2$), 34.26 ($C(CH_2CH_2)_2$), 25.27 ($C(CH_2CH_2)_2$), 13.84 ($COOCH_2CH_3$). Bp: 110−114 °C/15 mbar.

1,1-Cyclohexanedicarboxylic Acid Diethyl Ester (1b). Malonic acid ethyl ester (30.0 g, 187 mmol) and 1,5-dibromopentane (39.1 g, 170 mmol) gave analogously to the procedure described for **1a** a colorless liquid. Yield: 21.3 g (59%). ^{1}H NMR ($CDCl_3$): δ 4.12 (q, 4H, $^3J_{HH}$ = 7.0 Hz, $COOCH_2CH_3$), 1.98−1.83 (m, 4H, $C(CH_2CH_2)_2CH_2$), 1.56−1.27 (m, 6H, $C(CH_2CH_2)_2CH_2$), 1.18 (t, 6H, $^3J_{HH}$ = 7.0 Hz, $COOCH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 171.75 ($COOCH_2CH_3$), 60.85 ($COOCH_2CH_3$), 54.74 ($C(CH_2CH_2)_2CH_2$), 31.17 ($C(CH_2CH_2)_2CH_2$), 25.06 ($C(CH_2CH_2)_2CH_2$), 22.56 ($C(CH_2CH_2)_2CH_2$), 13.88 ($COOCH_2CH_3$). Bp: 116−122 °C/11 mbar.

1,1-Cyclopentanedimethanol (2a). A solution of 1,1-cyclopentanedicarboxylic acid diethyl ester (10.2 g, 47 mmol) in dry THF (50 mL) was added dropwise over a period of 30 min to a suspension of $LiAlH_4$ (4.0 g, 104 mmol) in dry THF (100 mL) at 5 °C. The reaction mixture was stirred at room temperature for 90 min. After cooling to 5 °C EtOAc (50 mL) was added, and the resulting solution was poured into 2 M HCl (125 mL). After separation of the layers, the water layer was extracted with EtOAc (5 × 80 mL). The combined organic layers were washed with saturated NaCl solution (2 × 80 mL), dried over Na_2SO_4, and filtered. The solvent was removed, and the crude solid was recrystallized from a mixture of EtOAc and petroleum ether to give colorless crystals. Yield: 5.1 g (82%). ^{1}H NMR ($CDCl_3$): δ 3.60 (s, 4H, CH_2OH), 2.73 (s, 2H, OH), 1.68−1.56 (m, 4H, $C(CH_2CH_2)_2$), 1.49−1.35 (m, 4H, $C(CH_2CH_2)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 70.11 (CH_2OH), 48.30 ($C(CH_2CH_2)_2$), 31.77 ($C(CH_2CH_2)_2$), 25.12 ($C(CH_2CH_2)_2$). Mp: 94−95 °C.

1,1-Cyclohexanedimethanol (2b). Cyclohexane-1,1-dicarboxylic acid diethyl ester (28.4 g, 124 mmol) gave analogously to the procedure described for **2a** colorless crystals. Yield: 12.7 g (71%). ^{1}H NMR ($CDCl_3$): δ 3.76 (s, 2H, OH), 3.45 (s, 4H, CH_2OH), 1.44−1.13 (m, 10H, $C(CH_2CH_2)_2CH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 68.94 (CH_2OH), 38.01 ($C(CH_2CH_2)_2CH_2$), 29.45 ($C(CH_2CH_2)_2CH_2$), 26.24 ($C(CH_2CH_2)_2CH_2$), 21.16 ($C(CH_2CH_2)_2CH_2$). Mp: 96−97 °C.

1,1-Cyclopentanedicarbaldehyde (3a). A solution of dry dimethyl sulfoxide (9.6 mL, 135.2 mmol) in dry CH_2Cl_2 (20 mL) was added dropwise at −78 °C to oxalyl chloride (5.8 mL, 67.6 mmol) in dry CH_2Cl_2 (40 mL). After stirring for 30 min at this temperature, 1,1-cyclopentanedimethanol (4.0 g, 30.7 mmol) in dry CH_2Cl_2 (40 mL) was added dropwise at a temperature of −78 to −70 °C. After stirring for 90 min at −70 °C the mixture was cooled to −78 °C, NEt_3 (30.6 mL, 215 mmol) was added slowly, and the mixture was stirred for 30 min at this temperature. The reaction mixture was allowed to warm to room temperature over the course of 1 h. The reaction was terminated by addition of saturated NH_4Cl solution (75 mL), and the two layers were separated. The aqueous layer was extracted with CH_2Cl_2 (4 × 50 mL), and the combined organic layers were washed with 2 M HCl (5 × 70 mL) and saturated NaCl solution (2 × 70 mL). The solution was dried over Na_2SO_4, and after filtration the solvent was evaporated. The crude liquid was purified by bulb-to-bulb distillation to give a colorless liquid. Yield: 2.0 g (52%). ^{1}H NMR ($CDCl_3$): δ 9.67 (s, 2H, CHO), 2.14−1.99 (m, 4H, $C(CH_2CH_2)_2$), 1.77−1.60 (m, 4H, $C(CH_2CH_2)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 199.62 (CHO), 69.81 ($C(CH_2CH_2)_2$), 29.15 ($C(CH_2CH_2)_2$), 25.90 ($C(CH_2CH_2)_2$). Bp: 20−22 °C/0.01 mbar.

1,1-Cyclohexanedicarbaldehyde (3b). 1,1-Cyclohexanedimethanol (4.4 g, 30.7 mmol) gave analogously to the procedure described for **3a** a colorless liquid. Yield: 2.1 g (49%). ^{1}H NMR ($CDCl_3$): δ 9.46 (s, 2H, CHO), 1.92−1.77 (m, 4H, $C(CH_2CH_2)_2CH_2$), 1.55−1.29 (m, 4H, $C(CH_2CH_2)_2CH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 200.40 (CHO), 63.51 ($C(CH_2CH_2)_2CH_2$), 26.43 ($C(CH_2CH_2)_2CH_2$), 24.70 ($C(CH_2CH_2)_2CH_2$), 21.61 ($C(CH_2CH_2)_2CH_2$). Bp: 40−45 °C/0.05 mbar.

***N,N′*-(1,1-Cyclopentylidenedimethylidyne)bis(2,6-bis(1-methylethyl)benzenamine) (4a).** 1,1-Cyclopentanedicarbaldehyde (0.30 g, 2.38 mmol), 2,6-diisopropylaniline (0.84 g, 4.76 mmol), *p*-toluenesulfonic acid monohydrate (0.09 g, 0.48 mmol), and toluene (10 mL) was heated under reflux over a Dean−Stark trap for 6 h. After cooling to room temperature the solvent was evaporated and saturated Na_2CO_3 solution (10 mL) and Et_2O (10 mL) were added to the residue. The mixture was stirred for 10 min, the layers were separated, and the water layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with water (1 × 10 mL) and saturated NaCl solution (1 × 10 mL). The solution was dried over Na_2SO_4 and filtered, and the solvent was evaporated. The oily residue was purified by bulb-to-bulb distillation to give colorless crystals. Yield: 8.90 g (84%). ^{1}H NMR ($CDCl_3$): δ 7.84 (s, 2H, CHN), 7.18−7.03 (m, 6H, H_{aromat}), 3.01 (septet, 4H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 2.32−2.18 (m, 4H, $C(CH_2CH_2)_2$), 1.98−1.86 (m, 4H, $C(CH_2CH_2)_2$), 1.17 (d, 24H, $^3J_{HH}$ = 7.0 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 168.76 (CHN), 148.82 (C_{aromat}), 137.40 (C_{ortho}), 123.86 (C_{para}), 122.78 (C_{meta}), 58.39 ($C(CH_2CH_2)_2$), 33.32 ($C(CH_2CH_2)_2$), 27.66 ($CH(CH_3)_2$), 25.54 ($C(CH_2CH_2)_2$), 23.38 ($CH(CH_3)_2$). Bp: 110−120 °C/0.02 mbar. Mp: 56−58 °C. Anal. Calcd for $C_{31}H_{44}N_2$ (444.71): C, 83.73; H, 9.97; N, 6.30. Found: C, 83.78; H, 10.10; N, 6.28.

***N,N′*-(1,1-Cyclohexylidenedimethylidyne)bis(2,6-bis(1-methylethyl)benzenamine) (4b).** 1,1-Cyclohexanedicarbaldehyde (1.00 g, 7.93 mmol) and 2,6-diisopropylaniline (3.10 g, 15.86 mmol) gave analogously to the procedure described for **4a** colorless crystals. Yield: 2.08 g (57%). ^{1}H NMR ($CDCl_3$): δ 7.66 (s, 2H, CHN), 7.09−6.93 (m, 6H, H_{aromat}), 2.94 (septet, 4H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 2.04−1.89 (m, 4H, $CH(CH_2CH_2)_2CH_2$), 1.75−1.61 (m, 4H, $CH(CH_2CH_2)_2CH_2$), 1.60−1.43 (m, 2H, $CH(CH_2CH_2)_2CH_2$), 1.07 (d, 24H, $^3J_{HH}$ = 7.0 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.59 (CHN), 148.85 (C_{aromat}), 137.38 (C_{ortho}), 123.90 (C_{para}), 122.81 (C_{meta}), 50.41 ($C(CH_2CH_2)_2CH_2$), 21.12 ($C(CH_2CH_2)_2CH_2$), 27.61 ($CH(CH_3)_2$), 25.59 ($C(CH_2CH_2)_2CH_2$), 23.48 ($CH(CH_3)_2$), 22.07 ($C(CH_2CH_2)_2CH_2$). Bp: 110−120 °C/0.05 mbar. Mp: 81−82 °C. Anal. Calcd for $C_{32}H_{46}N_2$ (458.74): C, 83.79; H, 10.11; N, 6.11. Found: C, 83.75; H, 10.29; N, 6.04.

***N,N′*-(1,1-Cyclopentylidenedimethylidyne)bis(2,6-dimethylbenzenamine) (5a).** 1,1-Cyclopentanedicarbaldehyde (0.30 g, 2.38 mmol) and 2,6-dimethylaniline (0.58 g, 4.76 mmol) gave analogously to the procedure described for **4a** a colorless oil. Yield: 0.61 g (77%). ^{1}H NMR ($CDCl_3$): δ 7.73 (s, 2H, CHN), 6,97−6.88 (m, 4H, H_{meta}), 6.87−6.77 (m, 2H, H_{para}), 2.18−2.05 (m, 4H, $C(CH_2CH_2)_2$), 2.01 (s, 12H, CH_3), 1.85−1.74 (m, 4H, $C(CH_2CH_2)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.48 (CHN), 150.90 (C_{aromat}), 127.93 (C_{meta}), 126.73 (C_{ortho}), 123.42 (C_{para}), 58.45 ($C(CH_2CH_2)_2$), 33.26 ($C(CH_2CH_2)_2$), 25.26 ($C(CH_2CH_2)_2$), 18.26 (CH_3). Bp: 80−100 °C/0.02 mbar.

***N,N′*-(1,1-Cyclohexylidenedimethylidyne)bis(2,6-dimethylbenzenamine) (5b).** 1,1-Cyclohexanedicarbaldehyde (0.50 g, 3.56 mmol) and 2,6-dimethylaniline (1.06 g, 8.72 mmol) gave analogously to the procedure described for **4a** a colorless oil. Yield: 0.96 g (70%). ^{1}H NMR ($CDCl_3$): δ 7.73 (s, 2H, CHN), 7.11−7.02 (m, 4H, H_{meta}), 7.01−6.89 (m, 2H, H_{para}), 2.16 (s, 12H, CH_3), 1.89−1.72 (m, 4H, $CH(CH_2CH_2)_2CH_2$), 1.71−1.55 (m, 4H, $CH(CH_2CH_2)_2CH_2$), 1.54−1.35 (m, 2H, $CH(CH_2CH_2)_2CH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.13 (CHN), 150.95 (C_{aromat}), 127.93 (C_{meta}), 126.55 (C_{ortho}), 123.43 (C_{para}), 50.59 ($C(CH_2CH_2)_2CH_2$), 31.17 ($C(CH_2CH_2)_2CH_2$), 25.64 ($C(CH_2$-

$CH_2)_2CH_2$), 22.21 ($C(CH_2CH_2)_2CH_2$), 18.45 (CH_3). Bp: 110−115 °C/0.05 mbar.

***N,N′*-(1,1-Cyclopentylidenedimethylidyne)bis(cyclohexaneamine) (6a).** 1,1-Cyclopentanedicarbaldehyde (0.42 g, 3.32 mmol) and cyclohexanamine (0.72 g, 7.32 mmol) gave analogous to the procedure described for **4a** a colorless oil. Yield: 0.67 g (70%). ^{1}H NMR ($CDCl_3$): δ 7.60 (s, 2H, C*H*N), 3.01−2.76 (m, 2H, C*H*$(CH_2CH_2)_2CH_2$), 1.90−1.01 (m, 28H, Cy + Cp). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.10 (*C*HN), 69.36 (*C*H$(CH_2CH_2)_2CH_2$), 56.23 (*C*$(CH_2CH_2)_2$), 34.26 (CH(*C*$H_2CH_2)_2$CH$_2$), 33.86 (C(*C*$H_2CH_2)_2$), 25.59 (C$(CH_2CH_2)_2$), 24.72 (CH$(CH_2CH_2)_2CH_2$), 24.65 (CH$(CH_2CH_2)_2CH_2$). Bp: 60−70 °C/0.05 mbar.

***N,N′*-(1,1-Cyclohexylidenedimethylidyne)bis(cyclohexaneamine) (6b).** 1,1-Cyclohexanedicarbaldehyde (0.60 g, 4.28 mmol) and cyclohexanamine (1.05 g, 10.47 mmol) gave analogously to the procedure described for **4a** a colorless oil. Yield: 0.61 g (47%). ^{1}H NMR ($CDCl_3$): δ 7.40 (s, 2H, C*H*N), 3.00−2.75 (m, 2H, C*H*$(CH_2CH_2)_2CH_2$), 1.83−0.99 (m, 30H, Cy + Cp). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.60 (*C*HN), 69.80 (*C*H$(CH_2CH_2)_2CH_2$), 47.58 (*C*$(CH_2CH_2)_2CH_2$), 34.28 (CH(*C*$H_2CH_2)_2$CH$_2$), 32.02 (C(*C*$H_2CH_2)_2CH_2$), 25.85 (C$(CH_2CH_2)_2$*C*H$_2$), 25.54 (CH$(CH_2CH_2)_2$*C*H$_2$), 24.69 (CH$(CH_2$*C*H$_2)_2CH_2$), 22.06 (C$(CH_2$*C*H$_2)_2CH_2$). Bp: 60−70 °C/0.05 mbar.

***N,N′*-(1,1-Cyclopentylidenedimethylidyne)bis(1,1-dimethylethaneamine) (7a).** 1,1-Cyclopentanedicarbaldehyde (0.50 g, 3.96 mmol) and *tert*-butylamine (0.65 g, 8.71 mmol) gave analogously to the procedure described for **4a** a colorless oil. Yield: 0.52 g (55%). ^{1}H NMR ($CDCl_3$): δ 7.51 (s, 2H, C*H*N), 1.90−1.77 (m, 4H, C(C*H*$_2CH_2)_2$), 1.58−1.47 (m, 4H, C$(CH_2$*CH*$_2)_2$), 1.06 (s, 18H, C(C*H*$_3)_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 161.70 (*C*HN), 56.39 (*C*$(CH_2CH_2)_2$), 33.45 (C(*C*$H_2CH_2)_2$), 29.64 (C(*C*$H_3)_3$), 24.68 (C$(CH_2CH_2)_2$). Bp: 40−50 °C/0.05 mbar.

***N,N′*-(1,1-Cyclohexylidenedimethylidyne)bis(1,1-dimethylethaneamine) (7b).** 1,1-Cyclohexanedicarbaldehyde (0.60 g, 4.27 mmol) and *tert*-butylamine (0.78 g, 10.47 mmol) gave analogously to the procedure described for **4a** a colorless oil. Yield: 0.68 g (57%). ^{1}H NMR ($CDCl_3$): δ 7.31 (s, 2H, C*H*N), 1.79−1.58 (m, 4H, C(C*H*$_2CH_2)_2CH_2$), 1.49−1.24 (m, 6H, C$(CH_2$C*H*$_2)_2$C*H*$_2$), 1.07 (s, 18H, C(C*H*$_3)_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.28 (*C*HN), 56.67 (*C*$(CH_2CH_2)_2CH_2$), 31.92 (CH(*C*$H_2CH_2)_2CH_2$), 29.62 (C(*C*$H_3)_3$), 25.33 (CH$(CH_2CH_2)_2$*C*H$_2$), 22.18 (C$(CH_2$*C*H$_2)_2CH_2$). Bp: 40−50 °C/0.05 mbar.

Pd{*N,N′*-(1,1-Cyclopentylidenedimethylidyne)bis(2,6-bis(1-methylethyl)benzenamine)}Cl_2 (8a). A suspension of $PdCl_2$ (200 mg, 1.13 mmol) in CH_3CN (10 mL) was refluxed until a clear orange solution of $Pd(CH_3CN)_2Cl_2$ was formed. **4a** (500 mg, 1.13 mmol) was then added, whereupon the color of the solution changed from orange to yellow. After the mixture was refluxed for 2 h, the solvent was removed under vacuum, and the resulting yellow solid was collected on a glass frit and washed twice with Et_2O (10 mL). Yield: 698 mg (99%). Anal. Calcd for $C_{31}H_{44}Cl_2N_2Pd$ (622.01): C, 59.86; H, 7.13; N, 4.50. Found: C, 58.59, H, 7.24; N, 4.30. ^{1}H NMR ($CDCl_3$): δ 7.47 (s, 2H, *H*C═N), 7.26−7.14 (m, 6H, H_{aromat}), 3.42−3.37 (m, J_{HH} = 6.62 Hz, 2H, C*H*$(CH_3)_2$), 2.44 (bs, 4H, C(C*H*$_2CH_2)_2$), 1.98 (bs, 4H, C$(CH_2$C*H*$_2)_2$), 1.48−1.46 (d, J_{HH} = 6.55 Hz, 12H, CH(C*H*$_3)_2$), 1.17−1.14 (d, J_{HH} = 6.85 Hz, 12H, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 172.95 (H*C*═N), 145.84 (C_{aromat}), 140.38 (C_{ortho}), 128.15 (C_{para}), 123.55 (C_{meta}), 58.18 (*C*$(CH_2CH_2)_2$), 38.93 (C(*C*$H_2CH_2)_2$), 28.80 (*C*H$(CH_3)_2$), 25.60 (C$(CH_2$*C*H$_2)_2$), 24.79 (CH(*C*$H_3)_2$).

Pd{*N,N′*-(1,1-Cyclohexylidenemethylidyne)bis(2,6-bis(1-methylethyl)benzenamine)}Cl_2 (8b). This complex has been prepared analogously to **8a** with $PdCl_2$ (194 mg, 1.10 mmol) and **4b** (500 mg, 1.10 mmol) as the starting materials. Yield: 500 mg (72%). Anal. Calcd for $C_{32}H_{46}Cl_2N_2Pd$ (636.03): C, 60.43; H, 7.29; N, 4.40. Found: C, 60.29, H, 7.34; N, 4.25. ^{1}H NMR ($CDCl_3$): δ 7.77 (s, 2H, *H*C═N), 7.29−7.20 (m, 6H, H_{aromat}), 3.40−3.29 (m, J_{HH} = 6.85 Hz, 2H, C*H*$(CH_3)_2$), 1.97−1.93 (m, 4H, C(C*H*$_2CH_2)_2CH_2$), 1.77−1.62 (m, 6H, CH$(CH_2$C*H*$_2)_2$-CH_2 and CH$(CH_2CH_2)_2$C*H*$_2$), 1.46−1.44 (d, J_{HH} = 6.70 Hz, 12H, CH(C*H*$_3)_2$), 1.21−1.18 (d, J_{HH} = 7.31 Hz, 12H, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 173.50 (H*C*═N), 145.91 (C_{aromat}), 140.44 (C_{ortho}), 128.17 (C_{para}), 123.64 (C_{meta}), 51.15 (*C*$(CH_2CH_2)_2CH_2$), 34.70 (C(*C*$H_2CH_2)_2CH_2$), 28.65 (*C*H$(CH_3)_2$), 24.06 (C$(CH_2$-$CH_2)_2$CH_2), 23.56 (CH(*C*$H_3)_2$), 21.22 (C$(CH_2CH_2)_2CH_2$).

Pd{*N,N′*-(1,1-Cyclopentylidenemethylidyne)bis(2,6-dimethylbenzenamine)}Cl_2 (9a). This complex has been prepared analogously to **8a** with $PdCl_2$ (267 mg, 1.50 mmol) and **5a** (500 mg, 1.50 mmol) as the starting materials. Yield: 690 mg (90%). Anal. Calcd for $C_{23}H_{28}Cl_2N_2Pd$ (509.80): C, 54.19; H, 5.54; N, 5.50. Found: C, 54.22, H, 5.48; N, 5.60. ^{1}H NMR ($CDCl_3$): δ 7.52 (s, 2H, *H*C═N), 7.18−7.11 (m, 6H, Ph), 2.66 (s, 12H, C*H*$_3$), 2.40−1.79 (m, 8H, CH(C*H*$_2CH_2)_2$ and CH-(CH$_2$C*H*$_2)_2$. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.54 (H*C*═N), 146.32 (C_{aromat}), 139.70 (C_{ortho}), 129.14 (C_{para}), 122.34 (C_{meta}), 51.26 (*C*$(CH_2CH_2)_2$), 34.85 (C(*C*$H_2CH_2)_2$), 25.72 (C$(CH_2$*C*H$_2)_2$), 18.42 (*C*H_3).

Pd{*N,N′*-(1,1-Cyclohexylidenemethylidyne)bis(2,6-dimethylbenzeneamine)}Cl_2 (9b). This complex has been prepared analogously to **8a** with $PdCl_2$ (307 mg, 1.73 mmol) and **5b** (600 mg, 1.73 mmol) as the starting materials. Yield: 750 mg (84%). Anal. Calcd for $C_{24}H_{30}Cl_2N_2Pd$ (523.82): C, 55.03; H, 5.77; N, 5.35. Found: C, 54.87, H, 5.79; N, 5.41. ^{1}H NMR ($CDCl_3$): δ 7.61 (s, 2H, *H*C═N), 7.13−7.04 (m, 6H, Ph), 2.44 (s, 12H, C*H*$_3$), 1.40−1.70 (m, 10H, CH(C*H*$_2CH_2)_2CH_2$, CH-(CH$_2$C*H*$_2)_2$CH$_2$ and CH$(CH_2CH_2)_2$C*H*$_2$). ^{13}C{^{1}H} NMR (CD-Cl_3): δ 174.76 (H*C*═N), 148.53 (C_{aromat}), 129.96 (C_{meta}), 128.48 (C_{ortho}), 127.64 (C_{para}), 51.19 (*C*$(CH_2CH_2)_2CH_2$), 31.54 (C(*C*H_2-$CH_2)_2CH_2$), 27.97 (C$(CH_2CH_2)_2$*C*H$_2$), 21.86 (C$(CH_2$*C*H$_2)_2CH_2$), 19.93 (*C*H_3).

Pd{*N,N′*-(1,1-Cyclopentylidenemethylidyne)bis(cyclohexaneamine)}Cl_2 (10a). This complex has been prepared analogously to **8a** with $PdCl_2$ (247 mg, 1.40 mmol) and **6a** (400 mg, 1.40 mmol) as the starting materials. Yield: 350 mg (55%). Anal. Calcd for $C_{19}H_{32}Cl_2N_2Pd$ (465.78): C, 48.99; H, 6.92; N, 6.01. Found: C, 48.86, H, 6.81; N, 6.10. ^{1}H NMR ($CDCl_3$): δ 7.26 (s, 2H, *H*C═N), 4.28−4.33 (t, J_{HH} = 10.39 Hz, 2H, C*H*$(CH_2CH_2)_2CH_2$), 1.90−1.11 (m, 28H, Cy + Cp). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 168.96 (H*C*═N), 66.15 (*C*H$(CH_2CH_2)_2CH_2$), 60.42 (*C*$(CH_2CH_2)_2$), 35.12 (CH(*C*$H_2CH_2)_2$CH$_2$), 33.25 (C(*C*H_2-$CH_2)_2$), 31.55 (C$(CH_2$*C*H$_2)_2$), 27.84 (CH$(CH_2$*C*H$_2)_2CH_2$), 26.41 (CH$(CH_2CH_2)_2$*C*H$_2$).

Pd{*N,N′*-(1,1-Cyclohexylidenemethylidyne)bis(cyclohexaneamine)}Cl_2 (10b). This complex has been prepared analogously to **8a** with $PdCl_2$ (130 mg, 0.73 mmol) and **6b** (220 mg, 0.73 mmol) as the starting materials. Yield: 290 mg (83%). Anal. Calcd for $C_{20}H_{34}Cl_2N_2Pd$ (479.81): C, 50.07; H, 7.14; N, 5.84. Found: C, 50.12, H, 7.02; N, 5.73. ^{1}H NMR ($CDCl_3$): δ 7.26 (s, 2H, *H*C═N), 4.42−4.34 (t, J_{HH} = 9.82 Hz, 2H, C*H*$(CH_2$-$CH_2)_2CH_2$), 2.00−1.12 (m, 30H, Cy + Cp). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 168.10 (H*C*═N), 66.61 (*C*H$(CH_2CH_2)_2CH_2$), 52.99 (*C*$(CH_2CH_2)_2CH_2$), 35.11 (CH(*C*$H_2CH_2)_2$CH$_2$), 33.26 (C(*C*H_2-$CH_2)_2$CH$_2$), 25.49 (C$(CH_2CH_2)_2$*C*H$_2$), 25.21 (CH$(CH_2CH_2)_2$*C*H$_2$), 24.71 (CH$(CH_2$C*H*$_2)_2CH_2$), 22.59 (C$(CH_2$*C*H$_2)_2CH_2$).

Pd{*N,N′*-(1,1-Cyclopentylidenemethylidyne)bis(1,1-dimethylethaneamine)}Cl_2 (11a). This complex has been prepared analogously to **8a** with $PdCl_2$ (247 mg, 1.40 mmol) and **7a** (330 mg, 1.40 mmol) as the starting materials. Yield: 450 mg (78%). Anal. Calcd for $C_{15}H_{28}Cl_2N_2Pd$ (413.71): C, 43.55; H, 6.82; N, 6.77. Found: C, 43.45, H, 6.76; N, 6.81. ^{1}H NMR ($CDCl_3$): δ 7.47 (s, 2H, *H*C═N), 2.40 (bs, 4H, C(C*H*$_2$-$CH_2)_2$), 1.98 (bs, 4H, C$(CH_2$C*H*$_2)_2$), 1,58 (s, 18H, C(C*H*$_3)_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 174.12 (H*C*═N), 65.37 (*C*$(CH_3)_3$), 62.49 (*C*$(CH_2CH_2)_2$), 37.76 (C(*C*$H_2CH_2)_2$), 32.14 (C(*C*$H_3)_3$), 26.61 (C$(CH_2$*C*H$_2)_2$).

Pd{*N,N′*-(1,1-Cyclohexylidenemethylidyne)bis(1,1-dimethylethaneamine)}Cl_2 (11b). This complex has been prepared analogously to **8a** with $PdCl_2$ (297 mg, 1.70 mmol) and **7b** (420 mg, 1.70 mmol) as the starting materials. Yield: 600 mg (82%). Anal. Calcd for $C_{16}H_{30}Cl_2N_2Pd$ (427.73): C,

44.93; H, 7.07; N, 6.55. Found: C, 44.72, H, 6.98; N, 6.59. ^{1}H NMR ($CDCl_3$): δ 7.31 (s, 2H, *H*C═N), 1.75−1.31 (m, 28H, Cy and ^{t}Bu C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 160.97 (H*C*═N), 47.00 (*C*(CH_2CH_2)$_2$$CH_2$), 31.58 (CH(*C*$H_2CH_2$)$_2$$CH_2$), 29.64 (C(*C*$H_3$)$_3$), 25.66 (CH($CH_2CH_2$)$_2$*C*$H_2$), 21.75 (C($CH_2$*C*$H_2$)$_2$$CH_2$).

Pd{*N,N′*-(1,1-Cyclopentylidenemethylidyne)bis(2,6-bis-(1-methylethyl)benzeneamine)}(μ-Cl$_2$)PdCl$_2$ (12). A solution of **4a** (300 mg, 0.68 mmol) in CH_2Cl_2 (10 mL) was treated with $PdCl_2$ (121 mg, 0.68 mmol) and stirred overnight. After removal of the solvent under reduced pressure, a dark yellow solid was obtained, which was collected on a glass frit, washed twice with *n*-hexane, and dried under vacuum. Yield: 193 mg (36%). Anal. Calcd for $C_{31}H_{44}Cl_4N_2Pd_2$ (799.31): C, 46.58; H, 5.55; N, 3.50. Found: C, 46.66, H, 5.34; N, 3.52. ^{1}H NMR ($CDCl_3$): δ 7.26−7.09 (m, 8H, *H*C═N and H_{aromat}), 3.21−3.10 (m, J_{HH} = 6.74 Hz, 2H, C*H*(CH_3)$_2$), 2.90−2.47 (m, 4H, C(C*H*$_2$-CH_2)$_2$), 2.11−1.84 (m, 4H, C(CH_2C*H*$_2$)$_2$), 1.26−1.15 (m, 24H, CH(C*H*$_3$)$_2$).

Ni{*N,N′*-(1,1-Cyclopentylidenedimethylidyne)bis(2,6-bis(1-methylethyl)benzenamine)}Br$_2$ (13). To a solution of $NiBr_2$(DME) (150 mg, 0.49 mmol) in CH_2Cl_2 (10 mL) was added **4a** (216 mg, 0.49 mmol), and the mixture was stirred overnight at room temperature. Insoluble materials were removed by filtration, and the solution was evaporated to dryness. The remaining purple solid was collected on a glass frit, washed twice with Et_2O, and dried under vacuum. Yield: 300 mg (86%). Anal. Calcd for $C_{31}H_{44}Br_2N_2Ni$ (663.22): C, 56.14; H, 6.69; N, 4.22. Found: C, 56.12, H, 6.58; N, 4.18. ^{1}H NMR (CD_2Cl_2): δ 22.82 (s, 4H, H_{meta}), 7.30 (s, 2H, *H*C═N), 5.33 (s, 4H, C*H*(CH_3)$_2$), 4.21 (s, 12H, CH(C*H*$_3$)$_2$), 3.10 (s, 12H, CH(C*H*$_3$)$_2$), −0.04 (s, 4H, C(C*H*$_2$$CH_2$)$_2$), −2.63 (s, 4H, C($CH_2$C*H*$_2$)$_2$), −10.68 (s, 2H, H_{para}).

Ni{*N,N′*-(1,1-Cyclopentylidenemethylidyne)bis-(2,6-dimethylbenzenamine)}Br$_2$ (14). This complex has been prepared analogously to **13** with $NiBr_2$DME (278 mg, 0.90 mmol) and **5a** (300 mg, 0.9 mmol) as the starting materials. Yield: 320 mg (65%). Anal. Calcd for $C_{23}H_{28}Br_2N_2Ni$ (551.00): C, 50.14; H, 5.12; N, 5.08. Found: C, 50.19, H, 5.14; N, 5.00. ^{1}H NMR (CD_2Cl_2): δ 26.36 (s,12H, C*H*$_3$), 23.56 (s, 4H, H_{meta}), 5.35 (s, 2H, *H*C═N), −0.08 (s, 4H, C(C*H*$_2$$CH_2$)$_2$), −2.52 (s, 4H, C($CH_2$C*H*$_2$)$_2$), −11.61 (s, 2H, H_{para}).

General Suzuki Procedure. Under an atmosphere of argon a solution of catalyst (0.03 mmol) and ligand (0.03 mmol) in dry dioxane (3 mL) was stirred at 80 °C for 30 min. Arylhalide (1 mmol), phenylboronic acid (1.5 mmol), and Cs_2CO_3 (2 mmol) were added, and the mixture was stirred at 80 °C for an additional 3 h. After addition of 1 M NaOH solution (10 mL), the mixture was stirred for 15 min at room temperature. The layers were separated, and the water layer was extracted with Et_2O (5 × 5 mL). The combined organic layers were washed with water (2 × 10 mL) and a saturated NaCl solution (1 × 10 mL), dried over Na_2SO_4, and filtered. After evaporation of the solvent, the crude product was purified by flash chromatography.

General Heck Procedure. Under an atmosphere of argon a solution of catalyst (0.035 mmol) and ligand (0.035 mmol) in dry 1-methyl-2-pyrrolidinone (3 mL) was stirred at 140 °C for 30 min. Arylbromide (1 mmol), methyl acrylate (1.2 mmol), and NEt_3 (1.4 mmol) were added, and the mixture was stirred at 140 °C. A saturated NH_4Cl solution (10 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with 2 M HCl (5 × 10 mL), water (1 × 10 mL), and saturated NaCl solution (2 × 10 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated, and the crude product was purified by flash chromatography.

General Hiyama Procedure. Under an atmosphere of argon a solution of catalyst (0.03 mmol) and ligand (0.03 mmol) in dry dioxane (3 mL) was stirred at 80 °C for 30 min. Arylhalide (1.0 mmol), phenyltrimethoxysilane (2.0 mmol), and Bu_4NF (2.0 mmol, from 1 M solution in THF) were added, and the mixture was stirred at 80 °C. After addition of water (30 mL), the mixture was extracted with Et_2O (4 × 30 mL). The combined organic layers were washed with saturated NaCl solution (2 × 30 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated, and the crude product was purified by flash chromatography.

X-ray Structure Determination for 4a, 4b, 8a, 8b·3CHCl$_3$, 11a·CHCl$_3$, 12, and 13. Crystals were obtained at room temperature by solvent evaporation (**4a** and **4b** from ethanol; **8b** and **11a** from $CHCl_3$) or by diffusion of diethyl ether into CH_2Cl_2 solutions (**8a**, **12**, and **13**). X-ray data were collected on a Bruker Smart APEX CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å, 0.3° ω-scan frames covering usually complete spheres of the reciprocal space up to $2\theta_{max}$). The frame data were integrated with the program SAINT.[21] Corrections for detector effects, crystal decay, and absorption were applied using the multiscan method and the program SADABS.[19] The structures were solved by direct methods using the program SHELXS97.[22] Structure refinement on F^2 was carried out with the program SHELXL97.[22] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded.

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Supporting Information Available: Complete crystallographic and structural data of **4a**, **4b**, **8a**, **8b**·3$CHCl_3$, **11a**·$CHCl_3$, **12**, and **13** in CIF form. This material is available free of charge via the Internet at http://pubs.acs.org.

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