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Square-Planar Diacetatopalladium Complexes with *trans*-Configured Secondary Amine Ligands that Avoid Orthometalation: Ligand Synthesis, Coordination, Molecular Structure and Catalytic Potential for Suzuki Cross-Coupling Reactions

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Keywords: Cross-coupling / Palladium / N ligands / Amines / Homogeneous catalysis

The *trans*-configured square-planar palladium complexes $[Pd(OAc)_2(LN{t}Bu)_2]$ (**1**), $[Pd(OAc)_2(\eta^2\text{-}LN{\cap}N{t}Bu)]$ (**2**), $[Pd(OAc)_2(LNPh)_2]$ (**3**), and $[Pd(OAc)_2(\eta^2\text{-}LN{\cap}NPh)]$ (**4**), have been synthesized by treating palladium acetate with the amines $NH{t}BuCH_2\text{-}2,4,6\text{-}Me_3C_6H_2$ ($LN{t}Bu$) or $NHPhCH_2\text{-}2,4,6\text{-}Me_3C_6H_2$ (LNPh) or with the diamines $NH{t}BuCH_2\text{-}2,4,6\text{-}Me_3C_6H\text{-}CH_2\text{-}2,4,6\text{-}Me_3C_6H\text{-}CH_2\text{-}NH{t}Bu$ ($LN{\cap}N{t}Bu$) or $NHPh\text{-}CH_2\text{-}2,4,6\text{-}Me_3C_6H\text{-}CH_2\text{-}2,4,6\text{-}Me_3C_6H\text{-}CH_2\text{-}NHPh$ ($LN{\cap}NPh$). The single-crystal X-ray structure analysis of complexes **1**–**3** confirms a *trans* arrangement of the two acetato groups and of the two nitrogen atoms. Orthometalation leading to palladacycles is impossible in all cases as the *ortho* positions in the benzylic rings are blocked by methyl substituents. All complexes are found to catalyze Suzuki cross-coupling reactions of deactivated and even sterically hindered arene substrates.

Introduction

The Suzuki cross-coupling reaction is one of the most important methods for the selective assembly of biaryls in the synthesis of natural products, pharmaceuticals, and advanced materials.[1] Although many palladium(II) or palladium(0) complexes catalyze this coupling reaction, significant efforts have been made to design ligands that can increase the catalytic activity of the palladium center. Some of the most widely studied Suzuki catalysts are palladium phosphane complexes that are susceptible to orthometalation or palladacycle formation.[2] However, the most efficient catalysts so far reported are palladium phosphane complexes that cannot undergo orthometalation.[3] These very active phosphane complexes require rigorous exclusion of air and water, however, due to the air sensitivity of the phosphane ligands, which is the main reason for the growing interest in Ncoordinating ligands for Suzuki catalysts. Indeed, many N-based ligands have been reported to be efficient for the Suzuki cross-coupling reactions, especially tertiary amines and imines.[4] These ligands are air-stable and are therefore easier to synthesize and handle. Boykin et al. have screened several simple and commercially available amines as ligands with palladium acetate in the Suzuki cross-coupling reaction and found that bulky primary and secondary amines appear to be better ligands than comparable tertiary amines that do not form stable complexes with palladium acetate.[5] Although these catalytic systems are efficient at low temperature and under aerobic conditions, a significantly higher amount of palladium acetate (2 mol-%) is needed compared to the molar ratio generally required with phosphane ligands (0.01 mol-%) in order to afford similar turnover numbers.

Our laboratory has recently designed new ligands that impose a *trans* geometry at the metal center, thereby preventing orthometalation.[6] As the palladium complex *trans*-$[PdCl_2(P{\cap}P)]$, which contains the diphosphane ligand $PPh_2CH_2\text{-}2,4,6\text{-}Me_3C_6H\text{-}CH_2\text{-}2,4,6\text{-}Me_3C_6H\text{-}CH_2\text{-}PPh_2$ ($P{\cap}P$) is an active Suzuki catalyst for the cross-coupling of deactivated or hindered aryl bromides, we decided to synthesize the analogous amine ligands $NH{t}Bu\text{-}CH_2\text{-}2,4,6\text{-}Me_3C_6H_2$ ($LN{t}Bu$), $NHPh\text{-}CH_2\text{-}2,4,6\text{-}Me_3C_6H_2$ (LNPh), $NH{t}Bu\text{-}CH_2\text{-}2,4,6\text{-}Me_3C_6H\text{-}CH_2\text{-}2,4,6\text{-}Me_3C_6H\text{-}CH_2\text{-}NH{t}Bu$ ($LN{\cap}N{t}Bu$), and $NHPh\text{-}CH_2\text{-}2,4,6\text{-}Me_3C_6H\text{-}CH_2\text{-}2,4,6\text{-}Me_3\text{-}C_6H\text{-}CH_2\text{-}NHPh$ ($LN{\cap}NPh$) in order to study their coordination to palladium acetate as well as the catalytic potential of these complexes for Suzuki reactions.

Results and Discussion

Synthesis and Characterization of New Secondary Amine Ligands

The secondary amines $NH{t}Bu\text{-}CH_2\text{-}2,4,6\text{-}Me_3C_6H_2$ ($LN{t}Bu$), $NH{t}Bu\text{-}CH_2\text{-}2,4,6\text{-}Me_3C_6H\text{-}CH_2\text{-}2,4,6\text{-}Me_3C_6H\text{-}CH_2\text{-}NH{t}Bu$ ($LN{\cap}N{t}Bu$), and $NHPh\text{-}CH_2\text{-}2,4,6\text{-}Me_3C_6H\text{-}CH_2\text{-}2,4,6\text{-}Me_3C_6H\text{-}CH_2\text{-}NHPh$ ($LN{\cap}NPh$) are accessible in one step from the corresponding bromide and the corre-

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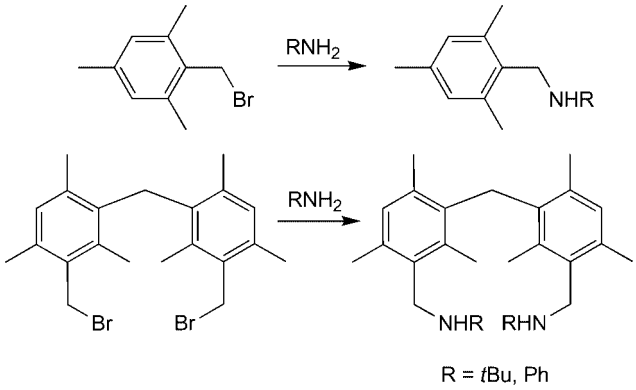
sponding amine (Scheme 1). The synthesis of (2,4,6-trimethylbenzyl)aniline (LNPh) has been described previously.[7]

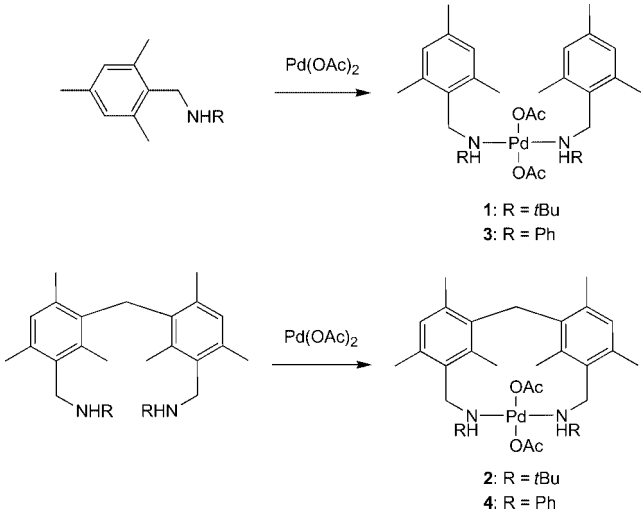


Scheme 1. Synthesis of the secondary amines LN*t*Bu, LNPh, LN∩N*t*Bu, and LN∩NPh.

All new compounds were characterized by NMR (^{1}H, ^{13}C) spectroscopy, mass spectrometry, and elemental analysis.

Synthesis and Molecular Structure of *trans*-Palladium Complexes

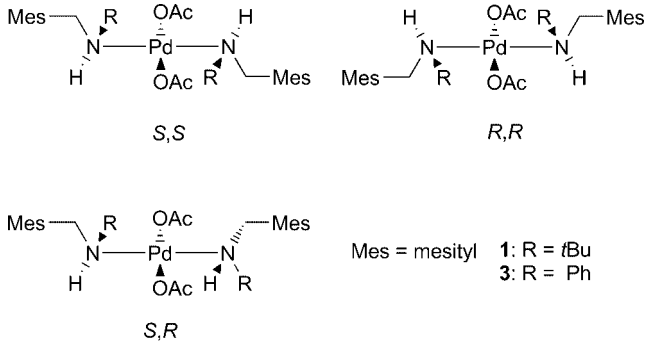
The *trans*-palladium complexes [Pd(OAc)$_2$(LN*t*Bu)$_2$] (**1**), [Pd(OAc)$_2$(η^2-LN∩N*t*Bu)] (**2**), [Pd(OAc)$_2$(LNPh)$_2$] (**3**), and [Pd(OAc)$_2$(η^2-LN∩NPh)] (**4**) were synthesized by treating [Pd(OAc)$_2$] with the corresponding amines or diamines in toluene at 50 °C and simple workup of the reaction mixture (Scheme 2).



Scheme 2. Synthesis of the palladium complexes *trans*-[Pd(OAc)$_2$(LN*t*Bu)$_2$](**1**), *trans*-[Pd(OAc)$_2$(η^2-LN∩N*t*Bu)](**2**), *trans*-[Pd(OAc)$_2$(LNPh)$_2$] (**3**), and *trans*-[Pd(OAc)$_2$(η^2-LN∩NPh)] (**4**).

The question of stereochemistry needs to be addressed for complexes containing secondary amine ligands with three different substituents as the nitrogen atom is stereogenic (asymmetric tetrahedral geometry) due to coordination to the metal center. This problem has been solved by NMR spectroscopy and X-ray crystallography for complexes **1**–**4**.

The two asymmetric nitrogen centers in the bis-amine complexes **1** and **3** give rise, in principle, to three isomers − a pair of enantiomers (*R*,*R* and *S*,*S*) and a *meso* isomer (*R*,*S*), as shown in Scheme 3. In both cases, all three isomers are indeed formed upon coordination of LN*t*Bu or LNPh to [Pd(OAc)$_2$] as the NMR spectra show the expected signals of both diastereoisomers.



Scheme 3. Representation of the stereoisomeric configurations of complexes **1** and **3**.

While it did not prove possible to separate the three isomers of complex **3**, we succeeded in separating the diastereoisomers of **1** by extraction with diethyl ether. However, the separated diastereoisomers (*R*,*R*)/(*S*,*S*)-**1** and (*R*,*S*)-**1** were found to isomerize in solution over a period of several minutes so it was only possible to record ^{1}H NMR spectra of diastereomerically pure **1a** and **1b**, but not the ^{13}C{^{1}H} NMR spectra. Crystallization from chloroform gave only the *meso* isomer (*R*,*S*) for both complexes **1** and **3**.

The single-crystal X-ray structure analysis of **1** and **3** revealed that, in contrast to solutions of these complexes, which contain all isomers, the crystals isolated in both cases represent only the *meso* isomer. The molecular structures of **1** and **3** show the palladium atom to be in a square-planar geometry surrounded by two acetato ligands and two nitrogen atoms in a *trans* coordination geometry (Figures 1 and 2, respectively).

There are intramolecular hydrogen bonds in the crystal structures of **1** and **3** between the NH of the amino function and the C=O group of the acetato ligands [N–O 2.846(5) Å, N–H···O 141.7° in **1** and N–O 2.714(3) Å, N–H···O 150.4° in **3**; Figure 3]. The N···O distances and N–H···O angles are similar to those observed in analogous *trans* acetato(amino)-palladium complexes.[5a,8]

The rigid diamine backbone in the diamine complexes **2** and **4** generates an additional chirality upon coordination, with two enantiomers (*P* and *M*) being generated depending on the sense of helicity. Complexes **2** and **4** therefore possess three chiral elements (two chiral nitrogen atoms and a helical chirality element) and thus eight stereoisomeric species can theoretically be obtained (Scheme 4).

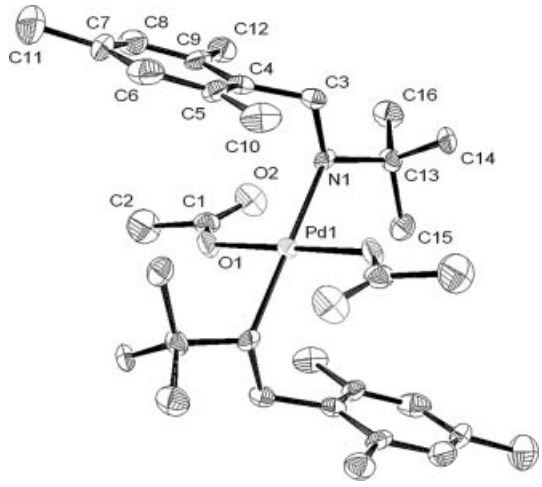


Figure 1. ORTEP drawing of **1** showing ellipsoids at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–O(1) 2.038(4), Pd(1)–N(1) 2.097(5), O(1)–C(1) 1.239(7), O(2)–C(1) 1.236(9), C(2)–C(1) 1.506(11), N(1)–C(3) 1.501(5), N(1)–C(13) 1.509(9), C(3)–C(4) 1.497(10); O(1)–Pd(1)–O(1)^{i} 180.0(4), N(1)–Pd(1)–O(1) 87.3(2), N(1)–Pd(1)–N(1)^{i} 180.0(1). (i = –*x*, –*y*, –*z*).

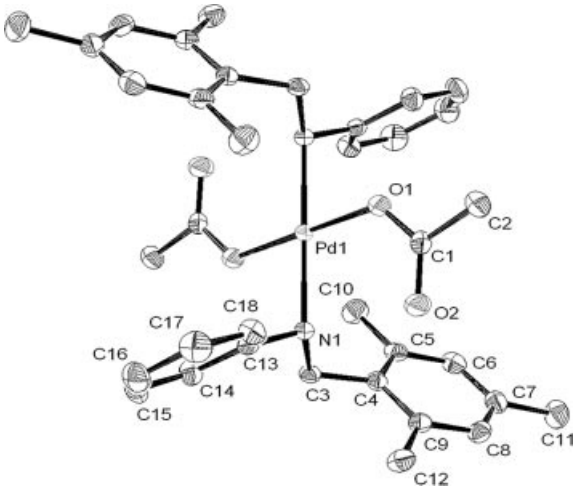


Figure 2. ORTEP drawing of **3** showing ellipsoids at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–O(1) 2.013(2), Pd(1)–N(1) 2.079(2), O(1)–C(1) 1.280(3), O(2)–C(1) 1.230(3), C(2)–C(1) 1.504(4), N(1)–C(3) 1.500(3), N(1)–C(13) 1.446(3), C(3)–C(4) 1.506(3); O(1)–Pd(1)–O(1)^{i} 180.0(1), N(1)–Pd(1)–O(1) 96.14(8), N(1)–Pd(1)–N(1)^{i} 180.0. (i = –*x*, –*y*, 1 – *z*).

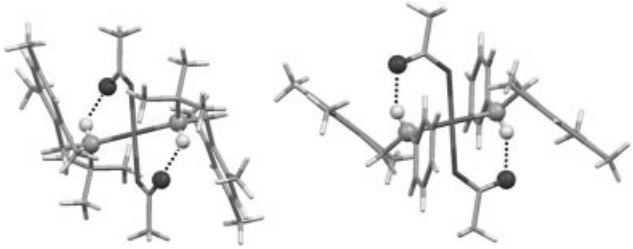
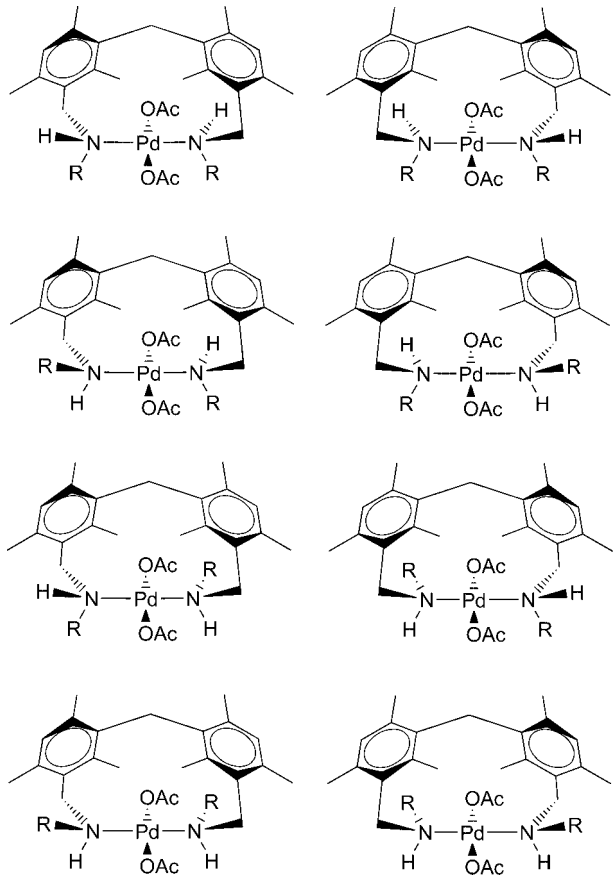


Figure 3. Intramolecular hydrogen-bonded systems in **1** (left) and **3** (right).

However, as suggested by ^{1}H NMR spectroscopy and confirmed by the X-ray structure analysis of **2**, only one pair of enantiomers is observed for **2** and **4**.



Scheme 4. Representation of the possible stereoconfigurations of complexes **2** and **4**.

Despite the high number of theoretically possible isomers, the ^{1}H NMR spectra of complexes **2** and **4** are not complex and show only the expected signals for the ligands, thereby suggesting that only one isomer or pair of enantiomers is present in solution. As neither **2** nor **4** shows a signal in its CD spectrum, it can be assumed that both complexes exist as a pair of enantiomers. The single-crystal X-ray structure analysis of **2** confirmed this hypothesis since it reveals a racemic crystal containing two enantiomers, with the square-planar palladium center being *trans* coordinated to two acetato ligands and to the two nitrogen atoms of the diamine ligand (Figure 4).

The coordination of the chelating diamino ligand in **2** imposes a slight distortion of the planar geometry. Thus, unlike in **1** and **3**, where the O–Pd–O and N–Pd–N axes are perfectly linear by symmetry, the corresponding angles in **2** are 179.1(4)° and 178.8(4)°, respectively. A strong distortion is imposed on the diphenylmethane spacer such that the angle between the two planes of the phenyl rings is much more acute (56.4°; Figure 5) than the corresponding angle in diphenylmethane[9] (80.5°), the analogous *trans*-diphosphane complex [$PdCl_2$(P∩P)][6] (65.9°), and in the structurally constrained dinuclear chromium complex [(μ_2-η^6,η^6-di-

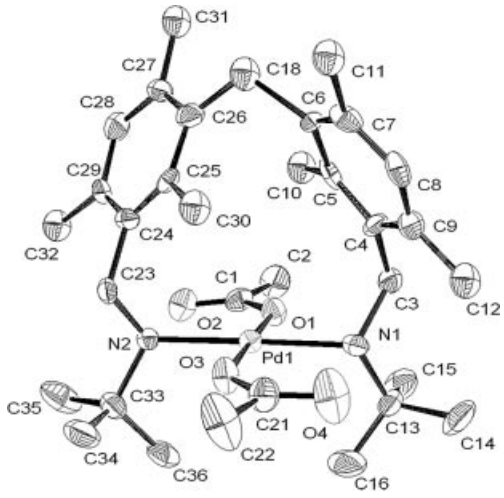


Figure 4. ORTEP drawing of **2** showing ellipsoids at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–O(1) 1.999(9), Pd(1)–O(3) 2.012(9), Pd(1)–N(1) 2.112(11), Pd(1)–N(2) 2.102(10), O(1)–C(1) 1.260(16), O(3)–C(21) 1.268(18), N(1)–C(3) 1.504(16), N(1)–C(13) 1.552(17), N(2)–C(23) 1.528(16), N(2)–C(33) 1.531(16), C(3)–C(4) 1.537(19), C(23)–C(24) 1.517(16); O(1)–Pd(1)–O(3) 179.1(4), N(1)–Pd(1)–O(1) 83.9(4), N(1)–Pd(1)–O(3) 95.5(4), N(1)–Pd(1)–N(2) 178.8(4), C(6)–C(18)–C(26) 111.4(12).

phenylmethane)-(μ_2-1,1,2,2-tetramethyldiphosphane-*P*,*P*′)-bis(dicarbonylchromium)] (71.9°).[10] Intramolecular hydrogen bonds are observed between the N–H amino function and the C=O oxygen of an acetato group in the crystal structure of **2**, as in **1** and **3** (Figure 5). The N···O distances are 2.801(16) and 2.765(15) Å with N–H···O angles of 149.0° and 150.3°, respectively.

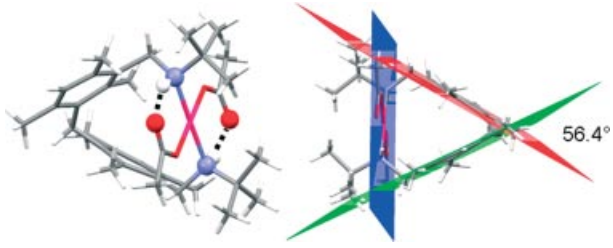
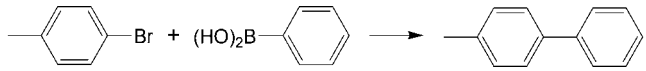


Figure 5. Intramolecular hydrogen-bonded system in **2** (left) and axial view in **2** (right).

Catalytic Activity of Complexes 1–4 for Suzuki Cross-Coupling Reactions

The *trans*-palladium complexes **1**–**4** were studied as catalyst precursors for Suzuki cross-coupling reactions. As we wanted to study the real influence of the ligands and the geometry they impose, we decided to compare the results of these four complexes with the ligand-free compound [$Pd(OAc)_2$], which is suspected to catalyze the Suzuki cross-coupling due to nanoparticle formation, depending on the catalyst concentration.[11]

We studied two Suzuki-type reactions, namely the cross-coupling of phenylboronic acid with 4-bromotoluene, which is a deactivated bromo derivative, and the cross-coupling of phenylboronic acid with 1-bromo-2,4,6-trimethylbenzene, which is both deactivated and sterically hindered. The cross-coupling of phenylboronic acid with aliphatic bromides, which was recently reported to occur with [$Pd(OAc)_2$] in the presence of sterically hindered phosphanes,[12,13] does not work with our complexes [<5% of product formation with $CH_3(CH_2)_{11}Br$; catalyst/substrate ratio: 1:20; dioxane, *t*BuOK, 30–90 °C].



The results summarized in Table 1 show that the efficiency of the catalysts depends mainly on the temperature. Thus, at 90 °C the highest catalytic turnover number (86000) is achieved with [$Pd(OAc)_2$], which is not surprising given that recent work has shown [$Pd(OAc)_2$] to be an excellent source of highly active palladium nanoparticles during cross-coupling reactions.[14] However, at 60 °C complexes **1** and **2** are more efficient than [$Pd(OAc)_2$] and the other complexes, thereby indicating that the ligands have a strong influence on the catalytic performance − the electronic and steric effect of the *tert*-butyl groups on secondary amines is stronger than that of phenyl groups. Finally, this sequence changes again at 30 °C, since complex **2** becomes the least efficient one. This is due to the rigidity of the ligand, which means that the complex requires more energy to perform the catalytic reaction.

Table 1. Catalytic turnover numbers (TON), indicating the mol of product formed per mol of catalyst used after 18 h, for the Suzuki cross-coupling of 4-bromotoluene and phenylboronic acid catalyzed by **1**–**4** and [$Pd(OAc)_2$]. Solvent: toluene; base: K_2CO_3; reaction time: 18 h. Average of two runs.

T [°C]	Catalyst/ substrate	**1**	**2**	**3**	**4**	[$Pd(OAc)_2$]
30	1:1000	410	250	130	230	240
30	1:10000	2700	0	600	900	460
60	1:1000	620	960	360	390	1000
60	1:10000	4800	6200	2300	2200	3800
60	1:100000	36000	38000	7000	12000	21000
90	1:1000	800	1000	710	710	1000
90	1:10000	6200	9100	4000	4900	9600
90	1:100000	45000	58000	28000	29000	86000

Nevertheless, as the TONs of the four complexes have the same order of magnitude as that of [$Pd(OAc)_2$], we compared complex **2** and [$Pd(OAc)_2$] kinetically at 60 °C with a catalyst/substrate ratio of 1:10000.

Figure 6 shows that the two precursors behave differently during the catalytic reaction. Thus, whereas [$Pd(OAc)_2$] shows a relatively constant activity, complex **2** undergoes an induction period of almost one hour, thereby indicating that it is also only a precatalyst. As we cannot exclude nanoparticle formation in the case of **2**, we performed poisoning tests with metallic mercury using a catalyst/substrate ratio of 1:1000. At 60 °C, **2** attains a TON of 300 after 1 h, while it is 960 after 18 h. When 400 equiv. of mercury is added at the beginning of the reaction, the TON falls to

480 after 18 h, and if mercury is added after one hour of reaction the TON is 660 after 18 h. Under the same conditions, the catalytic turnover of $[Pd(OAc)_2]$ drops to 84 or 267 if 400 equiv. of mercury is added at the beginning or after 1 h, respectively. Since the catalytic activity of metallic palladium nanoparticles should be suppressed completely by metallic mercury, we can conclude that the molecular catalysis pathway dominates for complex **2** while in the case of palladium acetate the nanoparticle pathway is dominant.

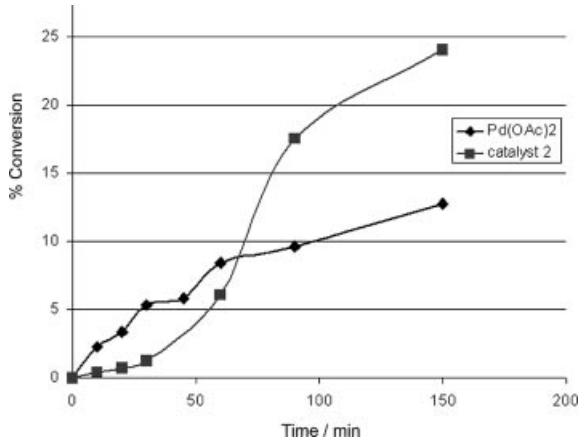
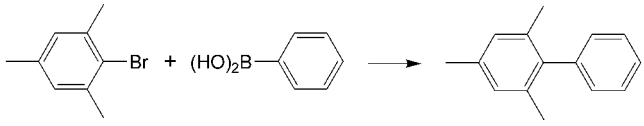


Figure 6. Kinetic comparison of complex **2** and $[Pd(OAc)_2]$ at 60 °C with a ratio of 1:10000.



The results of the Suzuki cross-coupling of 1-bromo-2,4,6-trimethylbenzene with phenylboronic acid are summarized in Table 2. As expected with a sterically hindered and deactivated bromide, the TONs are lower than those observed for the previous reaction. Complex **2** is less active than **1** at 30 °C because of the rigidity of the ligand backbone. However, at temperatures above 60 °C complex **2** shows the best catalytic performance for sterically hindered substrates.

Table 2. Catalytic turnover numbers (TON) indicating the mol of product formed per mol of catalyst used after 18 h for the Suzuki cross-coupling of 2,4,6-trimethylphenyl bromide and phenylboronic acid catalyzed by **1**–**4** and $[Pd(OAc)_2]$. Solvent: toluene; base: K_2CO_3; reaction time: 18 h. Average of two runs.

T [°C]	Catalyst/ substrate	**1**	**2**	**3**	**4**	$[Pd(OAc)_2]$
30	1:1000	297	66	18	60	86
60	1:1000	430	620	80	160	200
60	1:10000	2790	2900	300	900	420
90	1:1000	550	730	140	140	270
90	1:10000	3200	4900	800	1000	1300

Conclusions

The *trans*-secondary amino complexes **1**–**4**, in which orthometalation is impossible because of the methyl substituents in the *ortho*-positions, catalyze the Suzuki cross-coupling of 4-bromotoluene and even of 2,4,6-trimethylphenyl bromide with phenylboronic acid. Whereas the TONs of the four complexes show the same order of magnitude as $[Pd(OAc)_2]$ in both reactions, it seems that the new ligands give rise to the formation of catalytically active molecular species rather than to metallic nanoparticles. Furthermore, we have shown that, at temperatures above 60 °C, the rigidity of the ligand backbone and the *tert*-butyl substituents increase the catalytic performance in the Suzuki cross-coupling of sterically hindered and deactivated bromides.

Experimental Section

General: All reactions were carried out under argon using standard Schlenk techniques. Thf was distilled from sodium benzophenone under N_2 to avoid water and oxygen contamination. Toluene, *n*-hexane, and diethyl ether were purchased from Merck (puriss., pro analysi) and, along with distilled water, were saturated with argon prior to use. Dichloromethane was distilled from CaH_2 and saturated with N_2. $[Pd(OAc)_2]$ was purchased from Aldrich and used as received. Deuterated chloroform was used as received, and all NMR spectra were performed with a Bruker spectrometer [400 MHz for ^1H and 100 MHz for $^{13}C\{^1H\}$]. All GC analyses were performed using a GC DANI 86.10 equipped with a fused-silica capillary column OPTIMA δ-3 (0.5 μm, 30 m × 0.25 mm) and an SP-4400 integrator.

Synthesis of NH*t*Bu-CH_2-2,4,6-$Me_3C_6H_2$ (LN*t*Bu): *tert*-Butylamine (2.11 mL, 20 mmol) was added to a suspension of 1-(bromomethyl)-2,4,6-trimethylbenzene (1.278 g, 6 mmol) and K_2CO_3 (2.76 g, 20 mmol) in toluene (20 mL). The mixture was refluxed for 15 h, then cooled to room temperature, and filtered through filter pulp. The filtrate was evaporated to dryness to give 793 mg of an oil (yield 64%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.91 (s, 2 H), 3.75 (s, 2 H), 2.44 (s, 6 H), 2.32 (s, 3 H), 1.27 (s, 9 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 136.74, 136.09, 134.25, 128.95, 50.43, 40.37, 28.89, 20.84, 19.21 ppm. EI-MS: *m*/*z* 206 $[M + H]^+$. $C_{14}H_{23}N$ (205.34): calcd. C 81.89, H 11.29, N 6.82; found C 81.95, H 11.34, N 6.75.

Synthesis of NH*t*Bu-CH_2-2,4,6-Me_3C_6H-CH_2-2,4,6-Me_3C_6H-CH_2-NH*t*Bu (LN∩N*t*Bu): *tert*-Butylamine (2.11 mL, 20 mmol) was added to a suspension of bis[3-(bromomethyl)-2,4,6-trimethylphenyl]methane (1.313 g, 3 mmol) and K_2CO_3 (2.76 g, 20 mmol) in toluene (20 mL) and the mixture refluxed for 15 h. The solution was then filtered through filter pulp at room temperature and the filtrate dried in vacuo (yield 80%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.78 (s, 2 H), 4.02 (s, 2 H), 3.63 (s, 4 H), 2.32 (s, 6 H), 2.08 (s, 12 H), 1.15 (s, 18 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 136.41, 135.87, 135.15, 135.13, 133.99, 130.54, 50.46, 41.07, 32.39, 28.90, 21.07, 19.37, 15.74 ppm. $C_{29}H_{46}N_2$ (422.69): calcd. C 82.40, H 10.97, N 6.63; found C 82.56, H 11.04, N 6.57.

Synthesis of NHPh-CH_2-2,4,6-Me_3C_6H-CH_2-2,4,6-Me_3C_6H-CH_2-NHPh (LN∩NPh): Phenylamine (2 mL, 20 mmol) was added to a suspension of bis[3-(bromomethyl)-2,4,6-trimethylphenyl]methane (1.313 g, 3 mmol) and K_2CO_3 (2.76 g, 20 mmol) in toluene (20 mL) and the mixture refluxed for 24 h. The solution was then filtered through filter pulp at room temperature and the filtrate dried in vacuo. The white residue was washed with *n*-hexane (20 mL) to remove an excess of phenylamine (yield 968 mg, 70%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.35–7.24 (m, 4 H), 6.91 (s, 2 H),

6.88–6.69 (m, 6 H), 4.22 (s, 4 H), 4.15 (s, 2 H), 2.38 (s, 6 H), 2.19 (s, 6 H), 2.16 (s, 6 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 148.20, 136.48, 136.22, 134.77, 133.09, 130.68, 129.25, 129.01, 128.20, 125.28, 117.42, 115.16, 112.62, 43.15, 32.36, 21.09, 19.53, 16.12 ppm. EI-MS: *m*/*z* 463 $[M + H]^+$. $C_{33}H_{38}N_2$ (462.67): calcd. C 85.67, H 8.28, N 6.05; found C 85.89, H 8.46, N 5.90.

Synthesis of $[Pd(OAc)_2(LNtBu)_2]$ (1): A solution of LN*t*Bu (102.5 mg, 0.5 mmol) in toluene (40 mL) was added to a suspension of $[Pd(OAc)_2]$ (56 mg, 0.25 mmol) in toluene (40 mL) and the mixture stirred at 50 °C for 3 h. The red solution became clear after 20 min, although towards the end of the reaction it became slightly cloudy again. After 3 h the cloudy solution was concentrated in vacuo to 40 mL and then filtered through filter pulp to remove the solid precipitate. The filtrate was evaporated to dryness and the residue washed with *n*-hexane (40 mL) to give analytically pure **1** as a mixture of isomers (total yield 65%). Complex **1** was separated into two diastereoisomers by extraction with diethyl ether (40 mL). After stirring at room temperature for 10 min, the diethyl ether extract was filtered through a cannula equipped with filter paper and the solvents evaporated to dryness to give isomer **1a**; diastereoisomer **1b** remained as a solid.

1a: ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.60 (br. d, $^3J_{H,H}$ = 9.6 Hz, 2 H, NH), 6.87 (s, 4 H), 3.69 (dd, $^3J_{H,H}$ = 12.8, 9.6 Hz, 2 H), 3.05 (dd, $^3J_{H,H}$ = 12.8, 2.2 Hz, 2 H), 2.40 (s, 6 H), 2.19 (s, 12 H), 1.80 (s, 6 H), 1.63 (s, 18 H) ppm. $C_{32}H_{52}N_2O_4Pd$ (635.19): calcd. C 63.72, H 8.69, N 4.64; found C 63.96, H 8.85, N 4.44.

1b: ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.11 (br. d, $^3J_{H,H}$ = 10.6 Hz, 2 H, NH), 6.90 (s, 4 H), 3.64 (t, $^3J_{H,H}$ = 10.6 Hz, 2 H), 3.00 (dd, $^3J_{H,H}$ = 12.8, 2.0 Hz, 2 H), 2.45 (s, 12 H), 2.32 (s, 6 H), 1.70 (s, 6 H), 1.41 (s, 18 H) ppm. $C_{32}H_{52}N_2O_4Pd$ (635.19): calcd. C 63.72, H 8.69, N 4.64; found C 63.88, H 8.78, N 4.50.

Synthesis of $[Pd(OAc)_2(\eta^2\text{-}LN\cap NtBu)]$ (2): A solution of LN∩N*t*Bu (105 mg, 0.25 mmol) in toluene (50 mL) was added to a suspension of $[Pd(OAc)_2]$ (56 mg, 0.25 mmol) in toluene (50 mL) and the mixture stirred at 50 °C for 15 h. The red solution became clear after 20 min. After 15 h the solvent was evaporated to dryness to give a yellow powder, which was washed with diethyl ether (10 mL). Yield 80%. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.71 (d, $^3J_{H,H}$ = 10.6 Hz, 2 H), 6.86 (s, 2 H), 4.16 (s, 2 H), 3.61 (dd, $^3J_{H,H}$ = 12.3, 10.6 Hz, 2 H), 2.93 (d, $^3J_{H,H}$ = 12.6 Hz, 2 H), 2.51 (s, 6 H), 3.32 (s, 6 H), 1.72 (s, 6 H), 1.67 (s, 18 H), 1.66 (s, 6 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 180.16, 140.47, 138.95, 136.26, 135.70, 132.40, 129.94, 59.47, 42.90, 32.39, 28.85, 24.80, 21.48, 20.59, 18.46 ppm. $C_{33}H_{52}N_2O_4Pd$ (647.20): calcd. C 61.24, H 8.10, N 4.33; found C 61.48, H 8.28, N 4.28.

Synthesis of $[Pd(OAc)_2(LNPh)_2]$ (3): A solution of LNPh (225 mg, 1 mmol) in toluene (50 mL) was added to a suspension of $[Pd(OAc)_2]$ (112 mg, 0.5 mmol) in toluene (50 mL) and the mixture stirred at 50 °C for 3 h. The red solution became clear after 20 min, although towards the end of the reaction the solution became slightly cloudy again. After 3 h the cloudy solution was concentrated in vacuo to 50 mL and then filtered through filter pulp to remove the solid precipitate. The filtrate was evaporated to dryness and the residue washed with diethyl ether (20 mL) to give analytically pure **3** as a mixture of isomers (total yield 60%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.35 (m), 9.06 (m), 7.22–7.07 (m), 6.82 (s), 6.78 (s), 4.41–4.20 (m), 3.79 (dd, $^3J_{H,H}$ = 13.4, 4.6 Hz), 3.63 (dd, $^3J_{H,H}$ = 13.4, 4.7 Hz), 2.37 (s), 2.33 (s), 2.28 (s), 1.81 (s), 1.76 (s) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 180.78, 147.21, 138.35, 137.87, 129.52, 129.42, 129.20, 129.08, 128.90, 125.61, 122.96, 122.26, 50.78, 49.84, 29.32, 24.22, 23.15, 21.27, 20.39, 20.26 ppm. $C_{36}H_{44}N_2O_4Pd$ (675.17): calcd. C 61.20, H 6.10, N 4.46; found C 61.48, H 6.12, N 4.42.

Synthesis of $[Pd(OAc)_2(\eta^2\text{-}LN\cap NPh)]$ (4): A solution of LN∩NPh (230 mg, 0.5 mmol) in toluene (50 mL) was added to a suspension of $[Pd(OAc)_2]$ (112 mg, 0.5 mmol) in toluene (50 mL) and the mixture stirred at 50 °C for 15 h. The red solution became clear after 20 min, although towards the end of the reaction the solution became slightly cloudy again. After 15 h the cloudy solution was con-

Table 3. Crystallographic and selected experimental data for **1**–**3**.

	1	**2**	**3**
Chemical formula	$C_{32}H_{52}N_2O_4Pd$	$C_{33}H_{52}N_2O_4Pd$	$C_{36}H_{44}N_2O_4Pd$
Formula weight	635.16	647.17	675.13
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Crystal color and shape	yellow block	yellow block	yellow block
Crystal size [mm]	0.35 × 0.22 × 0.20	0.18 × 0.15 × 0.13	0.23 × 0.22 × 0.18
a [Å]	9.095(3)	12.5014(12)	8.8590(9)
b [Å]	9.113(2)	14.5192(10)	9.1797(10)
c [Å]	10.093(2)	19.354(3)	11.2241(12)
α [°]	107.71(3)		66.176(12)
β [°]	99.14(3)	110.856(10)	71.855(12)
γ [°]	91.95(3)		75.525(12)
V [Å^3]	783.8(3)	3282.8(6)	785.34(14)
Z	1	4	1
T [K]	173(2)	173(2)	173(2)
D_c [g cm^{-3}]	1.346	1.309	1.428
μ [mm^{-1}]	0.629	0.602	0.633
Scan range [°]	$4.30 < 2\theta < 51.80$	$4.42 < 2\theta < 51.90$	$4.90 < 2\theta < 51.92$
Unique reflections	1552	6379	2852
Reflections used $[I > 2\sigma(I)]$	1494	3759	2745
R_{int}	0.0166	0.1243	0.0287
R indices $[I > 2\sigma(I)]$[a]	0.0364, wR_2 0.0739	0.1587, wR_2 0.4129	0.0253, wR_2 0.0630
R indices (all data)	0.0302, wR_2 0.0898	0.1927, wR_2 0.4256	0.0287, wR_2 0.0739
Goodness-of-fit	1.224	1.518	1.151
Max, min $\Delta\rho$ [e Å^{-3}]	0.535, –0.686	13.775, –2.481	0.575, –0.998

[a] Structures were refined on F_o^2: $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$, where $w^{-1} = [\Sigma(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

centrated in vacuo to 50 mL and then filtered through filter pulp to remove the solid precipitate. The filtrate was evaporated to dryness and the residue washed with diethyl ether (20 mL) to give **4** (yield 60%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.34 (d, $^3J_{H,H}$ = 10.0 Hz, 2 H, NH), 7.35–7.31 (m, 4 H), 7.27–7.15 (m, 6 H), 6.98 (s, 2 H), 4.39 (dd, $^3J_{H,H}$ = 12.1, 10.0 Hz, 2 H), 4.23 (s, 2 H), 3.08 (d, $^3J_{H,H}$ = 12.1 Hz, 2 H), 2.56 (s, 6 H), 2.28 (s, 6 H), 1.90 (s, 6 H), 1.79 (s, 6 H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ = 181.20, 148.43, 140.28, 138.23, 136.90, 136.23, 131.37, 130.18, 129.44, 125.37, 121.29, 49.00, 32.38, 25.34, 21.62, 19.67, 18.59 ppm. $C_{37}H_{44}N_2O_4Pd$ (687.18): calcd. C 64.67, H 6.45, N 4.08; found C 64.90, H 6.59, N 3.99.

X-ray Crystallographic Study: Crystals of **1**–**3** were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer and a Mo-K_α graphite-monochromated radiation source (λ = 0.71073 Å). Data were collected in the ϕ range 0–200°, in increments of 1.0°, 1.2°, and 1.0°, respectively, with the 2θ range 2.0–26° and D_{max}–D_{min} = 12.45–0.81 Å. The structures were solved by direct methods using the program SHELXS-97.[15] Refinement and all further calculations were carried out using SHELXL-97.[16] The H-atoms were included in calculated positions in all complexes and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically using weighted full-matrix least-squares on F^2. Crystallographic details are summarized in Table 3. Figures 1, 2, and 4 were drawn with ORTEP[17] and Figures 3 and 5 with MERCURY.[18]

CCDC-647487 (for **1**), -647488 (for **2**), and -647489 (for **3**) contain 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.

Catalytic Reactions: The catalyst was added (in the molar ratio given in Tables 1 and 2) to a solution of $K_2CO_3 \cdot 1.5H_2O$ (138 mg, 0.8 mmol), phenylboronic acid (91 mg, 0.75 mmol), and the aryl bromide (0.5 mmol) in toluene (5 mL) in a Schlenk tube and the mixture heated to the desired temperature (Tables 1 and 2) and stirred for 18 h. After cooling, the solution was filtered through a small silica gel column then the silica gel was eluted with diethyl ether (20 mL). The filtrate was combined with the ether washings and the solution obtained analyzed by GC.

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