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Room-Temperature Synthesis of Tetra-*ortho*-Substituted Biaryls by NHC-Catalyzed Suzuki–Miyaura Couplings**

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Transition-metal-catalyzed cross couplings have become some of the most powerful and widely used methods to construct C–C bonds.[1] Among them, the Suzuki–Miyaura coupling,[2] has emerged as a particularly attractive and practical tool for synthetic organic chemistry.[3] Indeed, over the last decade, several limitations of this methodology have been successfully addressed by using bulky, electron-rich monodentate phosphines or sterically demanding NHC ligands (NHC = N-heterocyclic carbene).[4] One of the few challenges remaining in the Suzuki–Miyaura coupling reaction involves transformations with sterically demanding substrates that lead to tetra-*ortho*-substituted products. Especially in cases where aryl chlorides are used, the relatively poor nucleophilicity of the arylboron reagents results in diminished catalytic activities.[5] In 2004, Glorius and co-workers showed for the first time that aryl chlorides can indeed be coupled to aryl boronic acids to generate such tetra-*ortho*-substituted biaryls at elevated temperature (110 °C) by employing a very bulky, yet flexible derivative of their bioxazoline-derived NHC ligands in combination with a Pd^{II} metal salt.[6] More recently in 2009 and following the same concept of 'flexible steric bulk' of the NHC ligand, Organ and co-workers used the complex Pd-PEPPSI-IPent as the catalyst for the Suzuki–Miyaura couplings to form bulky tetra-*ortho*-substituted biaryls at milder conditions (65 °C).[7] Since then, various other ligand systems have been shown to effect similar couplings involving aryl chlorides when appropriate heating is employed.[8] To date, systems that work at room temperature have not been reported for the construction of these important tetra-*ortho*-substituted biaryl structures by way of the Suzuki–Miyaura coupling.[9]

Recently, we have presented a new class of saturated NHC ligands with naphthyl-derived side chains that showed excellent reactivities in a variety of catalytic applications.[10] In related studies,[11] we noticed that a ligand with a cyclooctyl group in position 2 of the naphthalene moieties led to significantly increased reactivity. On the basis of these observations, we now report the application of such NHC ligand systems in the palladium-catalyzed Suzuki–Miyaura couplings to give tetra-*ortho* substituted biaryls and present conclusive evidence concerning the reasons leading to their superior behavior in these reactions.

Reaction of NHC ligands with saturated[10c] and unsaturated N-heterocycles incorporating 2- or 2,7-cyclooctyl groups on the naphthalene side chains with a Pd(cin)Cl dimer (cin = cinnamyl) and appropriate workup gave the four complexes depicted in Table 1 in good yield as single isomers (*anti*-configured).[12]

To explore the effect of these new NHC ligands on biaryl formation in difficult Suzuki–Miyaura couplings, we chose the reaction between 2,4,6-trimethylphenyl chloride and 2,6-dimethylphenyl boronic acid (Table 1). Under optimized reaction conditions,[12] the four new catalyst systems were benchmarked against the commercially available, SIPr/IPr-modified congeners (Nolan's catalysts) as well as Organ's Pd-PEPPSI-IPent system, currently the most powerful pre-catalyst for such transformations. At room temperature, these reference systems resulted in low product yields (Table 1, entries 1–5, GC yields).[13] In entries 4 and 5 in Table 1, we used Organ's previously reported reaction conditions,[7] which deteriorated the reaction outcome. Gratifyingly, all catalysts incorporating the new NHC structures showed higher conversions and yields than the benchmark systems. Among the four substructures tested, *anti*-**C** clearly stands out as being particularly effective as it shows both high conversions and yields at room temperature.

We then proceeded in evaluating the coupling of a variety of hindered aryl bromides (Table 2) and aryl chlorides (Table 3) employing precatalyst *anti*-**C**. As can be seen from the data reported in Table 2, high isolated product yields were normally obtained at room temperature within short reaction times when employing aryl bromides. In entry 2 in Table 2, where the coupling proceeded very slowly at room temperature, slight heating (65 °C) was applied, leading to a

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[**] NHC = N-heterocyclic carbene.

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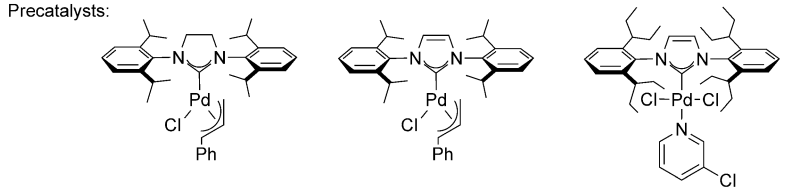
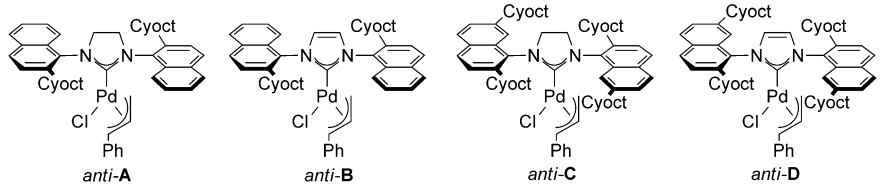
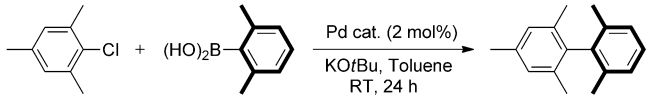
Table 1. Screening of precatalysts in a representative example of room-temperature Suzuki–Miyaura coupling.[a] Cyoct = cyclooctyl.

Precatalysts:





Reaction:



Entry	Pd complex	Conversion [%]	Yield [%]
1	(SIPr)Pd(cin)Cl	39	35
2	(IPr)Pd(cin)Cl	40	33
3	Pd-PEPPSI-IPent	33	29
4	Pd-PEPPSI-IPent	20	14[b]
5	Pd-PEPPSI-IPent	7	< 5[c]
6	*anti*-**A**	45	39
7	*anti*-**B**	60	51
8	*anti*-**C**	95	90
9	*anti*-**D**	65	61

[a] Conditions: 25 °C, toluene (1 mL), 24 h, Ar–Cl (0.125 mmol), Ar–$(BOH)_2$ (0.250 mmol), KO*t*Bu (0.312 mmol), 2 mol% Pd cat.; conversions and yields determined by GC with internal standard. [b] KO*t*Bu (0.375 mmol), *t*BuOH (0.5 mL), 4 Å molecular sieves. [c] KOH (0.375 mmol), dioxane (0.5 mL).

dramatic increase in reactions rates. Indeed, entry 5 in Table 2 shows that as little as 0.2 mol% of catalyst suffices for the reaction to go to completion. More sterically demanding 2,6-diethylphenyl bromide could also be coupled with 2,6-dimethylphenyl boronic acid at room temperature in acceptable yield (Table 2, entry 10). Two representative tetrasubstituted heterobiaryls were also successfully synthesized in good yields (in Table 2, entries 11 and 12).

Table 3 shows examples for the synthesis of tetra-*ortho*-substituted biaryls starting from the corresponding aryl chlorides. Again, a variety of hindered biaryls were prepared smoothly at room temperature. In two cases when sterically demanding and electron-rich aryl chlorides were used, slight heating was necessary for complete conversion (Table 3, entries 2 and 3). In other cases, slight heating permitted the use of much lower catalyst loadings (Table 3, entries 8, 12, and 13). Using the corresponding NHC/$[Pd(dba)_2]$ precatalyst system (dba = dibenzylideneacetone) instead of *anti*-**C** completely suppresses the coupling reaction at room temperature (Table 3, entries 4 vs. 5), meaning that the catalytically active 12-electron NHC–Pd^0 complex is not generated in the former case. Interestingly, the present system also displayed excellent chemoselectivity, favoring Suzuki–Miyaura couplings over the Heck reaction scenario (Table 3, entries 15 and 16). Precatalyst *anti*-**C** also promotes less difficult Suzuki–Miyaura coupling reactions, as evidenced from data gathered in Table 3, entry 18. The last two entries in Table 3 also highlight just how different the reactivities are when moving from a tri- to a tetra-*ortho*-substituted coupling product.

This last observation, together with the uniquely high reactivity of *anti*-**C**, prompted us to investigate the present catalytic system further. As a first approach, we grew single crystals of *anti*-**C** and of the unsaturated NHC–Pd derivative that lacks the 7-cyclooctyl groups on the naphthalene units (*anti*-**B**) to compare their structures in the solid state (Figure 1).[14]

One notes that these *anti*-configured NHCs lead to idealized C_2-symmetry of the ligand framework, in contrast to the commonly used IPr/SIPr or Organ's IPent ligands, which result in structures with C_{2v} symmetry. Between the NHC ligands in *anti*-**B** and *anti*-**C**, the main difference resides in the way the naphthyl side chains are twisted with respect to the central metal atom. The introduction of additional steric crowding (7-cyclooctyl) leads to a structure in *anti*-**C**, in which the 2-cyclooctyl groups point into the space occupied by the metal.[15]

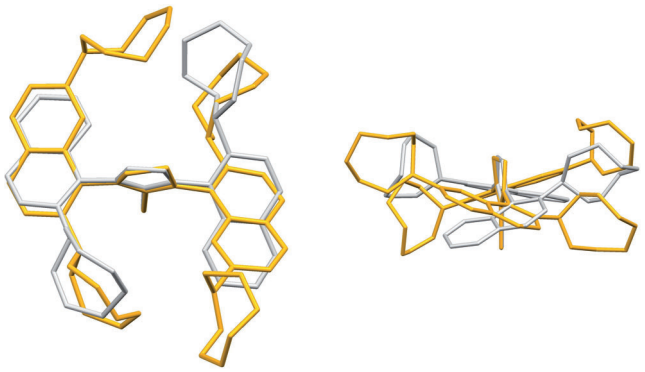
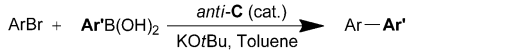
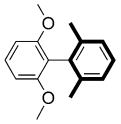
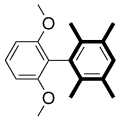
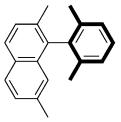
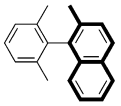
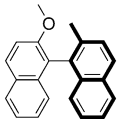
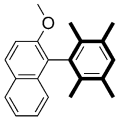
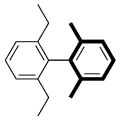
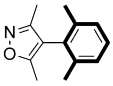
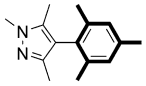


Figure 1. Overlay of the molecular structures of *anti*-**B** (gray) and *anti*-**C** (yellow). Cinnamyl, chloride and hydrogens omitted for clarity.

To further understand the difference between the catalytically preferred NHC ligand of *anti*-(2,7)-SICyoctNap and the more established SIPr ligand, we calculated the buried % V_{Bur} of the two NHC ligands.[16,17] The simple % V_{Bur} of

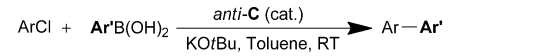
Table 2. Suzuki–Miyaura couplings generating tetra-*ortho*-substituted products starting with aryl bromides catalyzed by *anti*-**C**.[a]

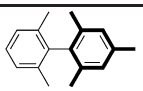
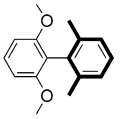
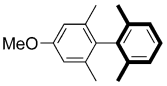
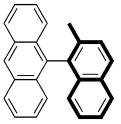
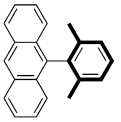
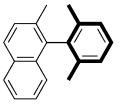
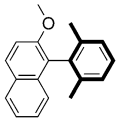
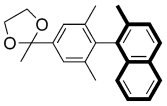
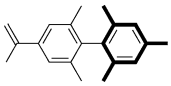
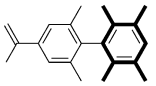
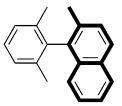
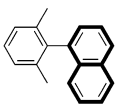


Entry	Ar–**Ar′**	Pd [mol%]	Time [h]	Yield [%]
1		2	12	96
2		2	72	80
3		1	2	96[b]
4		0.5	3	92[b,c]
5		0.2	12	97[b,c]
6		2	15	92
7		2	12	85
8		1	16	95
9		2	10	91
10		2	18	67
11		2	20	70
12		2	20	88

[a] Conditions: 25 °C, toluene (3.2 mL), Ar–Br (0.4 mmol), Ar–B(OH)$_2$ (0.6 mmol), KO*t*Bu (1.0 mmol); isolated products yields. [b] 65 °C. [c] Toluene (2 mL).

Table 3. Suzuki–Miyaura couplings generating tetra-*ortho*-substituted products starting with aryl chlorides catalyzed by *anti*-**C**.[a]



Entry	Ar-**Ar′**	Pd [mol%]	Time [h]	Yield [%]
1		2	8	78
2		1	8	80[b]
3		2	2	72[b]
4		2	20	92
5		2	20	<10[c]
6		2	20	86
7		2	8	89
8		0.5	1.5	85[b,d]
9		2	16	82
10		1	10	90
11		1	1	91[b]
12		0.5	1.5	88[b,d]
13		0.2	7	80[b,d]
14		2	20	78
15		2	18	71
16		2	24	72
17		2	12	91
18		0.05	15	80[e]

[a] Conditions: 25 °C, Toluene (3.2 mL), Ar–Cl (0.4 mmol), Ar–B(OH)$_2$ (0.8 mmol), KO*t*Bu (1.0 mmol), *anti*-**C**; isolated products yields. [b] 65 °C. [c] 2 mol% [Pd(dba)$_2$]/(2,7)-SICyoctNap. [d] 2 mL toluene. [e] 25 °C, *i*PrOH (0.5 mL), Ar–Cl (0.5 mmol), Ar–B(OH)$_2$ (1.1 equiv), 0.05 mol% *anti*-**C**, KO*t*Bu (1.3 equiv).

the NHC ligands in *anti*-**C** (41.5%) and (SIPr)Pd(cin)Cl (34.9%) show that our ligand is bulkier than SIPr. That an overall more bulky NHC ligand behaves better in catalysis involving sterically more demanding substrates is not unusual and the term 'flexible steric bulk' has been introduced to account for this phenomenon.[4b,6a,7] At least in a catalytic coupling scheme that follows the classical path (i.e. no secondary reactivity/decomposition), this concept is nevertheless at odds with what one would expect. For this reason we decided to perform a more detailed analysis by evaluating the % V_{Bur} in the single quadrants around the Pd center and plotted them as steric contour maps (Figure 2) for both (SIPr)Pd(cin)Cl (left) and *anti*-**C** (right).[16a,d,e] Splitting the total % V_{Bur} into quadrant contributions quantifies any asymmetry in the way the ligand wraps around the metal.[18] Within this approach, the quadrant % V_{Bur} of SIPr is rather

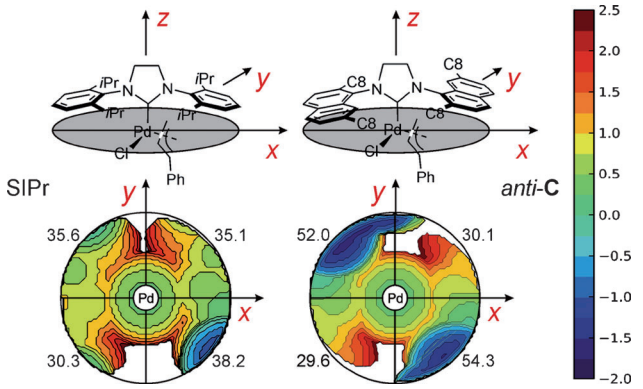


Figure 2. Steric maps of the NHC ligands in (SIPr)Pd(cin)Cl and *anti*-**C** complexes.

constant (% V_{Bur} ca. 35%), while the quadrant % V_{Bur} values of *anti*-(2,7)-SICyoctNap are largely different. Two quadrants heavily hindered (top left and bottom right, % V_{Bur} ca. 53%), two quadrants clearly more open (top right and bottom left, % V_{Bur} ca. 30%) creating a groove that possibly can host bulky substrates.

We therefore turned our attention to the catalytic step where sterics play the crucial role, namely the transmetallated (NHC)Pd(Ar)(Ar′) [where Ar = 2,4,6-trimethylphenyl and Ar′ = 2,6-dimethylphenyl] intermediate and the following reductive elimination. We first calculated the total energy of the system when going from the starting naked (NHC)Pd^0 species (set at 0 kcal mol^{-1}), to the transmetallated (NHC)Pd(Ar)(Ar′) intermediate according to Equation (1).[19]

$$(NHC)Pd + ArCl + Ar'B(OH)_2 + KO\mathit{t}Bu \rightarrow \rightarrow (NHC)Pd(Ar)(Ar') + KCl + \mathit{t}BuOB(OH)_2 \quad (1)$$

This approach eliminates the specific way the two aryl moieties are loaded onto the metal. Loading of these two aryls onto the (NHC)Pd^0 species [Eq. (1)] is favored for both (SIPr)Pd (by 23.8 kcal mol^{-1}) and [*anti*-(2,7)-SICyoctNap]Pd (by 30.7 kcal mol^{-1}). This in turn means that the groove created by the *anti*-(2,7)-SICyoctNap ligand is able to more readily accommodate (by 6.9 kcal mol^{-1}) the bulky aryl fragments than SIPr. An identical preference (6.9 kcal mol^{-1}) is also calculated at the level of the following transition state (overall 15 kcal mol^{-1} higher in energy) leading to the coupled Ar–Ar' product (see Figure S2 in the Supporting Information). Representations of these transition states for both complexes show a distorted T-shaped geometry (Figure 3). As already evidenced by the steric contour map of Figure 2, the structures shown in Figure 3 perfectly illustrate how the open quadrants in *anti*-(2,7)-SICyoctNap are able to host the *ortho* methyl groups of the aryl substituent *cis* to the NHC ligand. Differently, in presence of the SIPr ligand the same *ortho* methyl groups interact repulsively with the NHC ligand. In other words, the special steric characteristics of *anti*-(2,7)-SICyoctNap facilitate loading and releasing of the bulky aryl groups from the metal by creating a groove that is able to accommodate the *ortho* methyl groups of the aryl moieties. Together with the overall very bulky nature of this ligand, this translates into the clearly superior catalytic performance that we see in these Suzuki–Miyaura couplings.

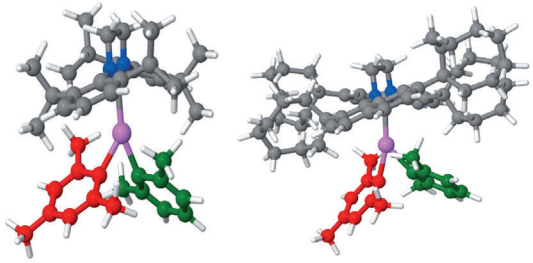


Figure 3. Transition state of the reductive elimination for (SIPr)Pd(Ar)(Ar′) (left) and [*anti*-(2,7)-SICyoctNap]Pd(Ar)(Ar′) (right).

In summary, we disclose the first catalyst system that is able to efficiently perform the Suzuki–Miyaura coupling to form bulky tetra-*ortho*-substituted biaryls from aryl bromides and chlorides at room temperature. The central feature of the catalyst sees the introduction of a C_2-symmetric NHC ligand with appropriately substituted naphthyl side chains. This simple modification to the well-known ligand systems allows a dramatic increase in catalytic performance in these difficult Suzuki–Miyaura coupling reactions, apparently leaving the already high activity in less demanding coupling reactions unaffected. Advanced DFT calculations show how the ligand's special steric properties, which are inherently associated with its symmetry, leave two of the four quadrants relatively open. This enhances the reactivity of the system with respect to the crucial, sterically demanding NHC–Pd(Ar)(Ar′) intermediate and the following reductive elimination step.

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[14] CCDC-832037 (*anti*-**B**), and CCDC-832038 (*anti*-**C**) 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.

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[19] See the Supporting Information for details on the DFT calculations.

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