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A Cyclobutene-1,2-bis(imidazolium) Salt as Preligand for Palladium-Catalyzed Cross-Coupling Reactions: Properties and Applications

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Spectroscopic investigations and the results of calculations on the title bis-imidazolium salt, its mono- and bis-carbenes, and its interactions with palladium are presented. In addition, we report on the scope and limitations of metal-catalyzed cross-coupling reactions performed with the title bis-imidazolium salt. The salt proved to be an efficient ligand precursor in room-temperature Suzuki–Miyaura reactions, C–C couplings with sterically extremely hindered biaryls, selective thiophene arylations, and couplings with vinylic chlorides.

Palladium-catalyzed cross-coupling reactions are of ever-growing importance in organic synthesis.[1] They are key steps in numerous total syntheses of natural products, pharmaceuticals, starting materials, liquid crystals, polymers, and new functional materials. Undoubtedly, the Suzuki–Miyaura reaction is one of the most widely applied cross-coupling reactions and remarkable progress has been achieved in the syntheses of sterically extremely hindered biaryls, syntheses with low catalyst loadings, and cross-coupling reactions under very mild conditions.[2] In this respect, N-heterocyclic carbenes[3] play important roles as ligands due to their valuable properties, for example, their tunable electronic characteristics, ability to form complexes[4] with a broad range of electron-rich (Pd^0,[5] Rh^+[6]) as well as electron-poor metals (Mg,[7] Be,[8] Nb[9]), and the stability of the $C_{carbene}$–metal bond. The last-mentioned property enables reactions with low catalyst loadings. Meanwhile, numerous structural modifications of N-heterocyclic carbenes and related species have been performed with a view to enhancing the electron density at the carbene center and thus influencing the σ-donating capacity of catalytically active metal complexes. Figure 1 shows some examples, the "classical" NHC imidazol-2-ylidene, the abnormal N-heterocyclic carbene (*a*NHC) imidazol-4-ylidene,[10] the remote N-heterocyclic carbene (*r*NHC)[11] pyrazol-4-ylidene, and the cyclic alkyl(amino)carbene (CAAC).[12] In the latter species, a nitrogen is replaced by a strongly σ-donating carbon. The limitations of N-heterocyclic carbenes in transition-metal-catalyzed cross-coupling reactions are undesired insertion reactions,[13] reductive eliminations,[14] or C–H bond activation at sites other than those expected.[15]

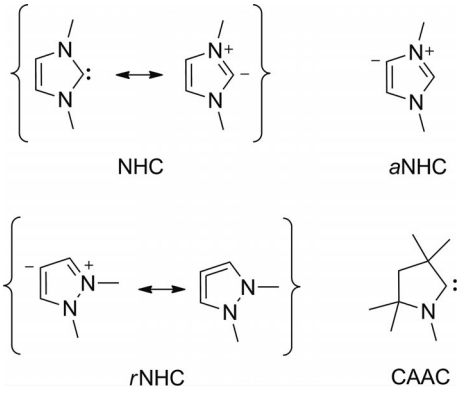

Figure 1. Selected types of carbenes.

Therefore robust bis-N-heterocyclic carbene precursors and complexes have been developed. Their catalytic activity is governed by several geometric parameters. The dihedral angle N–$C_{carbene}$–M–$C_{carbene}$ (*α*), the bite angle $C_{carbene}$–M–$C_{carbene}$,[16] the bond length M–$C_{carbene}$, and the in-plane distortion angle [$\theta = (\beta - \gamma)/2$] play important roles (Figure 2).

As a continuation of our interest in N-heterocyclic carbenes,[17] heterocyclic mesomeric betaines,[18] and organic polycation chemistry,[19] we became interested in developing a new bis-imidazolium salt with a relatively large bite angle as a catalyst precursor for Suzuki–Miyaura cross-coupling reactions. Cyclobutene seemed to be a suitable linker between the two imidazolium rings as the two C=C–N bond angles are compelled to adopt values of about 90° (Fig-

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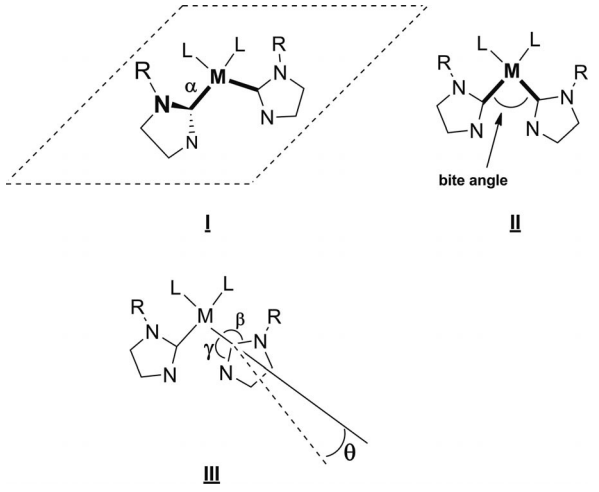


Figure 2. Geometric parameters governing the catalytic properties of bidentate ligands.

ure 3). A literature search revealed that only one 1,2-bis-imidazolium salt attached to a cyclobutene has been described, but its catalytic activity has not been examined.[20]

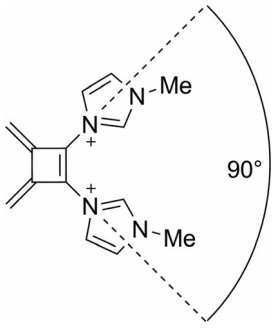


Figure 3. Enlarged bite angle in a bis-imidazolium salt with cyclobutene as the core element.

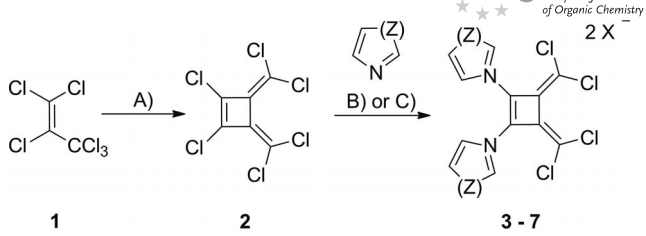
We report herein results on the scope and limitations of Suzuki–Miyaura reactions employing a cyclobutene-1,2-diyl bis-imidazolium salt as well as experimental and theoretical investigations of the ligand structure.

Results and Discussion

Synthesis

On treatment with Al/Hg, perchloropropene (**1**) formed 1,2-dichloro-3,4-bis(dichloromethylene)cyclobut-1-ene (**2**), which is susceptible to nucleophilic substitution reactions at the ring chlorine atoms (Scheme 1).

We first examined a selection of heteroaromatics and found that the reaction of **2** with 1-methylimidazole, 4-(dimethylamino)pyridine, 4-(morpholin-1-yl)pyridine, 4-(pyrrolidin-1-yl)pyridine, and 4-aminopyridine as nucleophiles led to the bis-hetarenium salts **3**–**7** in good yields, respectively. As the chlorides crystallized with water of crystallization and proved to be hygroscopic, we exchanged the anion of the imidazolium derivative to tetrafluoroborate because of its potential use as a preligand in catalytic reactions. Thus, tetrafluoroborate **3** was formed in 73% yield from **2**.[21] The salt **3** possesses no water of crystallization and its purification is simple.



A) Al/Hg, Et_2O, reflux
B) 1,2-dichlorobenzene, 60 °C, 4h; then $NaBF_4$, H_2O
C) 1,2-dichlorobenzene, 70 °C - 100 °C, 3 h

	(Z)-N	method	X	yield
3	N-Me	A	BF_4^-	73 %
4	NMe_2	B	Cl^-	76 %
5	O	B	Cl^-	66 %
6		B	Cl^-	59 %
7	NH_2	B	Cl^-	68 %

Scheme 1. Synthesis of cyclobutene-1,2-bis(hetarenium) salts.

Structure and Carbene Formation

Single crystals of the bis-imidazolium salt were obtained by slow diffusion of diethyl ether into a solution of **3** in CH_3CN for 1 week. The molecular structure of a single-crystal X-ray analysis is shown in Figure 4. The substance crystallizes in the monoclinic space group *C*2/*c* (no. 15) with four molecular units in the unit cell. The structure consists of layers of cations and anions along [010]. The chlorine atoms are coplanar to the four carbon atoms forming the cyclobutene. This core shows different bond lengths, which indicates that no electron delocalization has occurred.

The bond lengths of the cyclobutene are as follows: The double bond (C1–C2) has a length of 135.2(2) pm. The C2–C3 and C1–C4 bonds of the four-membered ring are identical and were determined to be 148.8(2) pm. The C3–C4 bond has a length of 152.9(2) pm, which is close to that of a C–C single bond. The imidazole rings are twisted out of planarity. The dihedral angles $C1–C2–N1_{imidazole}–C5_{imidazole}$ and $C2–C1–N1'_{imidazole}–C5'_{imidazole}$ were determined to be –43.2(2) and 16.8(2)°, respectively. The dihedral angles $C1–C2–N1_{imidazole}–C2_{imidazole}$ and $C2–C1–N1'_{imidazole}–C2'_{imidazole}$ are identical and were determined to be 132.1(2)°. The bond angles $C1–N1'_{imidazole}–C2'_{imidazole}$ and $C2–N1_{imidazole}–C2_{imidazole}$ are also identical

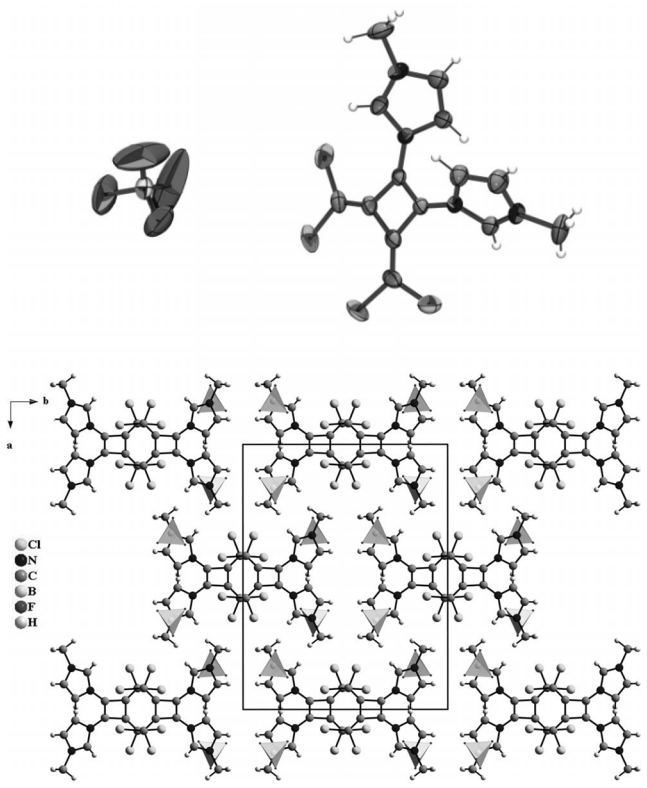
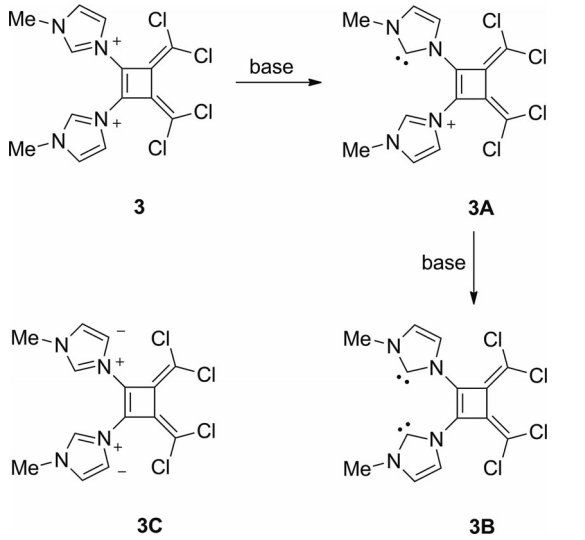


Figure 4. Molecular structure of **3** as a result of an X-ray single-crystal analysis and the elemental cell.

and are 128.3(2)°. The C1–$N1_{imidazole}$ and C2–$N1_{imidazole}$ bonds each have a length of 138.8(2)°pm, which is shorter than a normal C–N bond.

We performed NMR titrations with bases to gain an insight into the formation of N-heterocyclic carbenes. Consecutive deprotonations of **3** to mono-NHC **3A** and bis-carbene **3B** are shown in Scheme 2. A – hypothetical, see below – bis-*a*NHC **3C**, which possesses two imidazol-4-ylidene rings, is also shown.



Scheme 2. Consecutive deprotonations of **3** to a bis-carbene **3B**.

The mono-carbene **3A** can be seen in the ^{1}H NMR analysis; when **3** in [D_3]MeCN was treated with substoichiometric amounts of *n*BuLi in [D_3]MeCN, the signals of the 2-H of the imidazolium rings of **3** decreased with the concomitant appearance of signals of an imidazol-2-ylidene at δ = 6.94 (4-H) and δ = 7.02 ppm (5-H). The signal of the methyl groups of **3** shift from δ = 3.92 to δ = 3.66 ppm on mono-carbene formation. ESI-MS measurements are in agreement with the NMR results. Due to the chlorine isotopes, the salt **3** can be detected at *m*/*z* = 189.1 (100%), 188.1 (78%), and 190.1 (48%) [*M* = 378.1; *z* = 2]. On addition of potassium carbonate to an acetonitrile solution of **3**, the peaks of the mono-carbene **3A** at *m*/*z* = 377.0 (100%), 375.0 (78%), and 379 (48%) become the most prominent peaks of the spectrum.

To examine the bis-carbene **3B** spectroscopically, we took advantage of the different solubilities of salt **3**, mono-carbene **3A**, and bis-carbene **3B** in nonpolar solvents, and repeated the NMR measurements in [D_8]toluene. We exposed the salt **3** to 2.1 equiv. of *n*BuLi in [D_8]toluene at 0 °C over a period of 3 h under an inert atmosphere and filtered off unreacted salt. The ^{1}H NMR spectra show the bis-carbene **3B** with resonance frequencies for 4-H and 5-H at δ = 7.01 and 7.12 ppm, respectively. In addition, the ^{13}C chemical shift of C-$2_{imidazolium}$ disappeared in favor of a new signal at δ = 203.6 ppm, which can be assigned to the lithium adduct of bis-carbene **3B**. On addition of 15-crown-5 to complex the lithium cation, spontaneous decomposition occurred. Clearly the uncomplexed bis-carbene **3B** is not stable under these conditions. Again, ESI-MS measurements supplemented our knowledge on carbene formation: Analysis of a sample of **3** in MeCN after the addition of *n*BuLi gives prominent peaks between *m*/*z* = 383.3 and 386.6, which can be attributed to the bis-carbene **3B** plus one Li cation. In addition, a group of peaks is detectable between 194.2 and 196.2, attributable to the bis-carbene **3B** plus two Li cations.

The structures of **3A** and **3B** were investigated by DFT calculations. Several conformers differing in the orientation of the heterocyclic rings can be identified as energy minima on the two potential energy surfaces. The most stable rotamers display weak intramolecular C–H···C interactions, which appear to be more enhanced in the cationic ligand **3A** (see Figure 5). The calculations indicate that proton

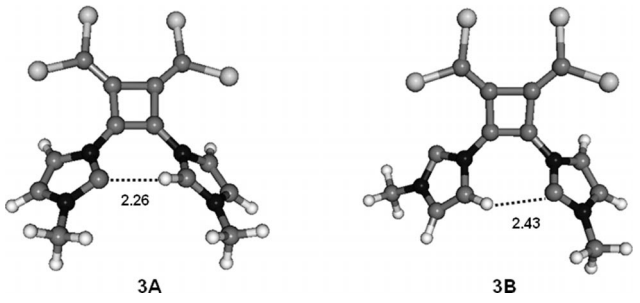


Figure 5. Most stable conformations of mono-carbene **3A** and bis-carbene **3B** as obtained by DFT calculations. Interatomic distances are given in Å.

transfer between the two heterocycles can easily occur in **3A**. The energy barrier of this process is predicted to be only 8 kcal/mol. The **3C** form of the bis-carbene, that is, the *a*NHC, is found to be strongly disfavored energetically as it is 33 kcal/mol less stable than the bis-NHC **3B**.

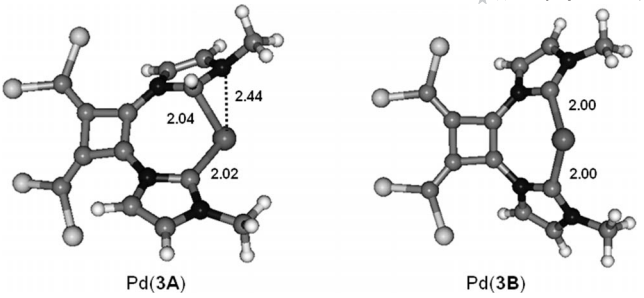


Figure 6. Equilibrium structures of the [Pd(**3A**)] and [Pd(**3B**)] complexes. Selected interatomic distances are given in Å.

Characterization of Pd Complexes

In view of the capability of the bis-imidazolium salt **3** to serve as an efficient catalyst precursor in Suzuki–Miyaura reactions (see below), we studied the interactions of **3** with palladium under various conditions. Thus, NMR experiments were repeated with equimolar amounts of $Pd(OAc)_2$ to gain an insight into the carbene–Pd interaction. The salt **3** gives ^{1}H NMR signals of the imidazolium ring at δ = 8.02, 7.72, and 7.66 ppm in [D_8]toluene. No changes in chemical shifts were observed on treatment of the aforementioned bis-carbene **3B**–lithium adduct with $Pd(OAc)_2$ after a period of 10 h at 50 °C. After charging the tube with 15-crown-5 and traces of water, however, signals of a Pd complex of **3A** appeared spontaneously at δ = 7.66, 7.57, 7.08, and 6.99 ppm in [D_8]toluene. A new ^{13}C chemical shift at δ = 162.0 ppm was also detected, attributed to a $C_{carbene}$–Pd group, in addition to the signal of C-2–H at δ = 141.8 ppm. The chemical shifts are in agreement with other Pd–NHC complexes (δ = 145–175 ppm),[22] including [Pd(imidazole-2-ylidene)Br_2] (157.7–169.57 ppm).[23,24]

The results of analogous measurements in [D_3]MeCN were similar. The Pd complex with **3A** gives a ^{13}C NMR signal at δ = 164.9 ppm. After 3 days at room temperature, the integral of the 2-H proton of the imidazolium ring also started to decrease with a concomitant appearance of an additional ^{13}C chemical shift at δ = 166.7 ppm, which can be assigned to the bis-carbene complex [Pd(**3B**)$_2$]. In summary, 24 signals can be detected, 6 from each of the symmetric structures **3** and [Pd(**3B**)$_2$] plus 12 from the nonsymmetric structure of the Pd complex with **3A**. These complexes can also be detected by ESI-MS: Analysis of a mixture of **3** and $Pd(OAc)_2$ in a 1:1 ratio from MeCN gives a complicated ESI mass spectrum with a prominent group of peaks between *m*/*z* = 858.4 and 863.5 (with the strongest peak detectable at *m*/*z* = 860.7) due to the isotopes of chlorine and palladium. These peaks correspond to the proton adduct of [Pd(**3B**)$_2$]. In addition, a group of peaks are detectable between *m*/*z* = 424.5 and 430.9 (with the strongest peak at *m*/*z* = 426.0) under the same conditions. These masses correspond to a dicationic complex formed from two molecules of the mono-carbene, [Pd(**3A**)$_2$]. Masses of higher aggregates can also be detected under these conditions.

The coordination of ligands **3A** and **3B** to a single Pd atom has also been examined computationally. The structures of the [PdL] and [PdL_2] complexes (L = **3A** or **3B**) identified by geometry optimizations are depicted in Figures 6 and 7.

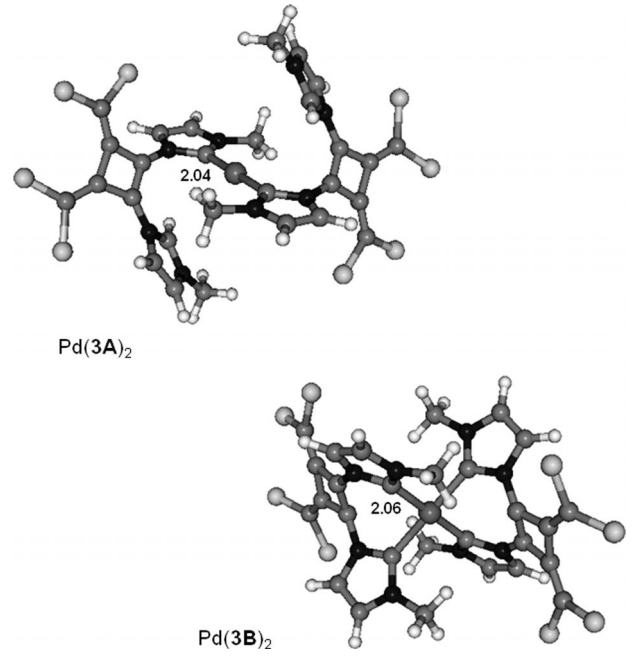


Figure 7. Equilibrium structures of the [Pd(**3A**)$_2$] and [Pd(**3B**)$_2$] complexes. Selected interatomic distances are given in Å.

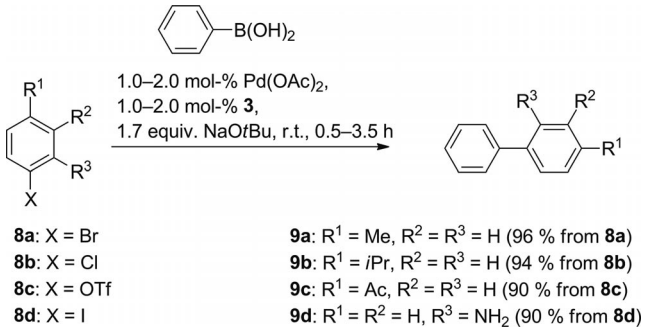
Both **3A** and **3B** act as chelating ligands upon coordination to Pd. As expected, the carbene group forms a strong covalent bond with the metal atom by σ donation, whereas the imidazolium ring in [Pd(**3A**)] interacts with the metal center through its π system. The latter interaction, however, appears to be much weaker, as indicated by the computed ligand binding energies {45 and 62 kcal/mol for [Pd(**3A**)] and [Pd(**3B**)], respectively}. The chelating nature of the ligands is also maintained in the [Pd(**3B**)$_2$] complex, which has a square-planar coordination environment, as is also found in the NHC–Pd^{II} complexes of [Pd(imidazol-2-ylidene)$_2$$Br_2$],[23] [Pd(imidazol-2-ylidene)$_2$$Cl_2$],[24] [Pd(imidazol-2-ylidene)$_2$$I_2$],[25] [Pd(imidazol-2-ylidene)Pd(OAc)(κ^2-OAc)],[26] [(imidazol-2-ylidene)Pd($OOCCF_3$)$_2$(H_2O)],[26] and Pd–benzimidazol-2-ylidene complexes.[27]

In the [Pd(**3A**)$_2$] complex, both ligands are monodentate as only the carbene units are bound to Pd in a linear arrangement, which has also been observed in [Pd^0(imidazole-2-ylidene)$_2$] complexes.[28] The [Pd(**3B**)$_2$] complex is predicted to be stable thermodynamically (the binding energy

of the second ligand is 27 kcal/mol) unlike the [Pd(**3A**)$_2$] species, which is predicted to be 15 kcal/mol less stable than the Pd(**3A**) + **3A** dissociation limit.[29]

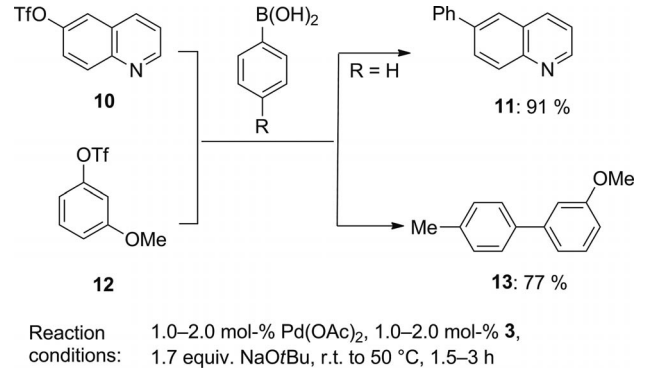
Applications

The bis-imidazolium salt **3** proved to be a highly effective precatalyst for Suzuki–Miyaura reactions, which proceeded at room temperature starting from electron-rich as well as electron-poor aromatic and heteroaromatic bromides, chlorides, triflates, and iodides to give excellent-to-very-good yields (Scheme 3).[30]



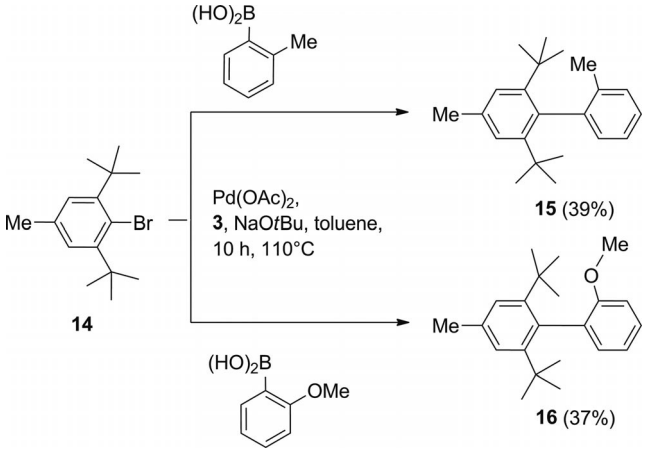
Scheme 3. Room-temperature Suzuki–Miyaura reactions.

Reactions with heteroaromatic triflates such as **10** proceeded to give **11** (Scheme 4). The triflate **12** required slightly higher temperatures for the coupling to give **13**. Raising the temperature from 25 to 50 °C increased the yield from 43 to 77%.



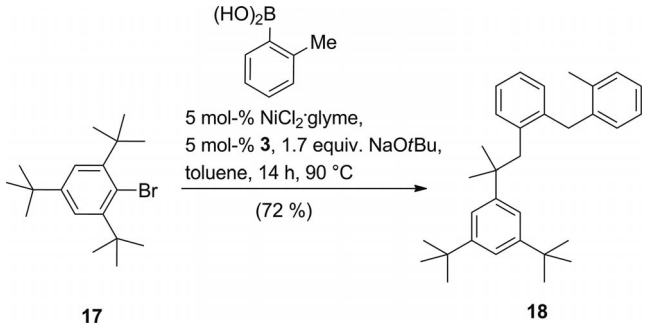
Scheme 4. Triflates as substrates in Suzuki–Miyaura reactions.

Bis(imidazolium) salt **3** is also able to catalyze syntheses of sterically extremely hindered biaryls such as 2,6-di-*tert*-butyl-2′,4-dimethylbiphenyl (**15**) and its methoxy derivative **16** (Scheme 5).[21] These reactions, however, which are the first examples to the best of our knowledge, occur at reflux temperature. With 2-(2′,6′-dimethoxybiphenyl)dicyclohexylphosphane as ligand in the coupling of 2,4,6-tri-*tert*-butylbromobenzene and 2-methylphenylboronic acid, C–H activation occurred but no aryl–aryl coupling was observed.[31]



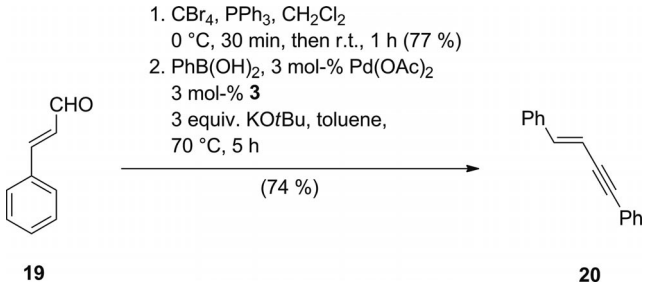
Scheme 5. First syntheses of sterically extremely hindered biaryls.

In our case, when a nickel(II) chloride–glyme complex was used, C–H activation was the main route of the reaction pathway. Thus, we isolated a good yield of **18** (Scheme 6).



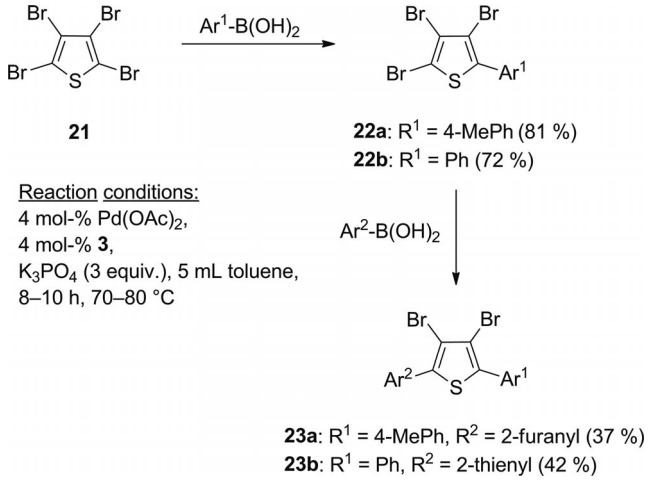
Scheme 6. C–H activation with nickel chloride and **3**.

The sequence of Corey–Fuchs-type reaction and tandem Suzuki–Miyaura cross-coupling/dehydrobromination enabled the synthesis of alkynes from aldehydes in good yields when **3** was used as the precatalyst (Scheme 7).[32]



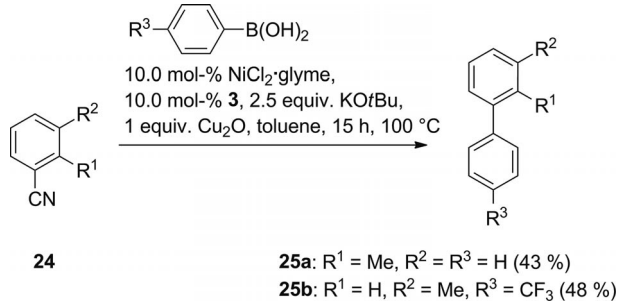
Scheme 7. Synthesis of alkynes.

Sequential arylations of tetrabromothiophene at the 2- and 5-positions were governed by the addition of stoichiometric amounts of boronic acid when **3** was used as ligand precursor (Scheme 8).[33]



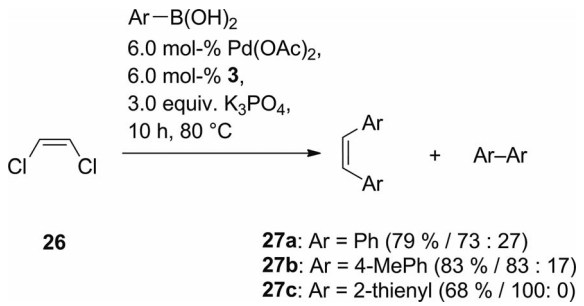
Scheme 8. Sequential arylations of tetrabromothiophene.

Nitriles were also used as substrates although modification of the reaction conditions was necessary. Thus, 2- and 3-methylbenzonitrile reacted with arylboronic acids in the presence of the nickel(II) chloride–glyme complex, the bisimidazolium salt **3**, copper(I) oxide, and potassium *tert*-butoxide to yield the 2- and 3-methylbiphenyls **25a** and **25b** in moderate yields, respectively (Scheme 9).



Scheme 9. Nitriles as substrates in the coupling reactions.

Vinylic chlorides can also be submitted to C–C cross-coupling reactions. Thus, *cis*-1,2-dichloroethene reacted with phenylboronic acid to give *cis*-1,2-diphenylethene. Likewise, 4-methylphenylboronic acid also underwent this cross-coupling reaction. In the case of phenyl- and 4-methylphenylboronic acids, some homocoupling products, that is, biphenyls, were formed. Application of the reaction conditions to 2-thienylboronic acid resulted in the formation of *cis*-1,2-bis(thiophen-2-yl)ethene in 68% yield without any traces of homocoupling products (Scheme 10). We were unable to isolate monosubstituted ethenes under these conditions.



Scheme 10. Formation of (het)arylated ethenes.

Conclusions

The cyclobutene-1,2-bis(imidazolium) salt **3** is an effective ligand precursor in metal-catalyzed reactions. Thus, palladium-catalyzed Suzuki–Miyaura reactions proceed under very mild conditions. At elevated temperatures, sterically hindered biaryls can be synthesized. The catalyst system is less effective in nickel-catalyzed couplings and when using nitriles as substrates. The salt forms mono- and biscarbenes on treatment with bases, and both species are able to form complexes with palladium, as evidenced by NMR and ESI-MS analyses and DFT calculations.

Experimental Section

General: Toluene was dried with sodium according to standard procedures. The ligand was synthesized as reported earlier.[21] Flash column chromatography was performed with silica gel 60 (0.040–0.063 mm). NMR spectra were obtained with Bruker Avance 400 and Avance III 600 MHz spectrometers. ^{1}H NMR spectra were recorded at 400 or 600 MHz and ^{13}C NMR spectra were recorded at 100 or 150 MHz with the solvent peak or tetramethylsilane used as the internal reference. Multiplicities are described by the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. FTIR spectra were obtained with a Bruker Vektor 22 spectrometer in the range of 400 to 4000 cm^{-1}. Solids were measured as pellets (2.5%) in KBr and oils were measured as films in NaCl plates. The mass spectra were measured with a Varian 320 MS Triple Quad GC/MS/MS with a Varian 450-GC. Melting points were determined with a Dr. Tottoli (Büchi) apparatus. To weigh small amounts of the catalyst (palladium source + ligand) easily and precisely, $Pd(OAc)_2$ (1 mmol, 224.5 mg) and the ligand (1.1 mmol, 604.9 mg) were weighed and mixed in a mortar. The resulting fine powder was stored in a capped vial in a desiccator.

X-ray Structure Analysis for $C_{14}H_{12}B_2Cl_4F_8N_4$: A suitable single crystal of the title compound was selected under a polarization microscope and mounted in a glass capillary (d = 0.3 mm). The crystal structure was determined by X-ray diffraction analysis using graphite-monochromated Mo-K_α radiation (0.71073 Å) [T = 223(2) K] and the scattering intensities were collected with a single-crystal diffractometer (STOE IPDS II). The crystal structure was solved by direct methods using SHELXS-97 and refined by using alternating cycles of least-squares refinements against F^2 (SHELXL-97).[34] All non-hydrogen atoms were located in difference Fourier maps and were refined with anisotropic displacement parameters. The H positions were determined by a final difference Fourier synthesis.

$C_{14}H_{12}B_2Cl_4F_8N_4$, M_r 551.70, monoclinic space group $C2/c$ (no. 15), a = 19.425(2), b = 14.664(2), c = 8.0255(11) Å, β = 102.39(1)°, V = 2232.9(6) Å^3, Z = 4, $d_{calcd.}$ = 1.641 g cm^{-3}, $F(000)$ = 1096 using

2032 independent reflections and 169 parameters. $R1$ = 0.0990, $wR2$ = 0.1373 [$I > 2\sigma(I)$], goodness of fit on $F2$ = 1.039, residual electron density = 1.283 and –0.912 e Å^{-3}.

CCDC-812624 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for the Preparation of Bis(heteroarenium) Cyclobutenes 3–7: A stirred solution of the nucleophile [0.246 g (3.0 mmol) of 1-methylimidazole, 0.366 g (3.0 mmol) of 4-dimethylaminopyridine, 0.492 g (3.0 mmol) of 4-morpholinopyridine, 0.444 g (3.0 mmol) of 4-pyrrolidinopyridine, or 0.282 g (3.0 mmol) of 4-aminopyridine] in anhydrous 1,2-dichlorobenzene (DCB, 25 mL) was treated with perchloro-3,4-dimethylenecyclobutene (0.284 g, 1 mmol) in DCB (5 mL) and heated. The precipitate was rapidly filtered off under nitrogen, washed with anhydrous ethyl acetate, and dried in vacuo. These crude compounds were crystallized in CH_3CN/CH_3OH (98:2) to give the corresponding salts. Anion exchange of the bis-imidazolium salt was accomplished as described previously.[21]

1,1′-[3,4-Bis(dichloromethylene)cyclobut-1-ene-1,2-diyl]bis(4-dimethylaminopyridinium) Chloride (4): After stirring for 3 h at 80 °C the precipitate was filtered off and washed to give 0.401 g (76%) of light-green crystals after recrystallization; m.p. 169–170 °C. ^{1}H NMR (400 MHz, D_2O): δ = 8.07 (d, J = 7.7 Hz, 4 H, α-H), 7.03 (d, J = 7.7 Hz, 4 H, β-H), 3.32 (s, 12 H, Me) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 155.9 (2 C), 138.8 (4 C), 135.6 (2 C), 128.2 (2 C), 114.4 (2 C), 107.5 (4 C), 39.4 (4 C) ppm. IR (KBr): $\tilde{\nu}$ = 3060, 2039, 1720, 1589, 1407, 1220, 821 cm^{-1}. MS (ESI): m/z = 229 $[M/2]^{2+}$. $C_{20}H_2Cl_6N_4{\cdot}4H_2O$ (583.0): calcd. C 39.96, H 4.69, N 9.32; found C 40.12, H 4.71, N 9.28.

1,1′-[3,4-Bis(dichloromethylene)cyclobut-1-ene-1,2-diyl]bis(4-morpholinopyridinium) Chloride (5): After stirring for 3 h at 100 °C, the precipitate was filtered off and washed to give 0.4 g (66%) of a yellow solid after recrystallization; m.p. 181 °C (dec.). ^{1}H NMR (400 MHz, D_2O): δ = 8.22 (d, J = 7.7 Hz, 4 H, α-H), 7.31 (d, J = 7.7 Hz, 4 H, β-H), 3.62 (m, 8 H), 2.43 (m, 8 H) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 156.4 (2 C), 140.1 (4 C), 134.2 (2 C), 125.1 (2 C), 117.3 (2 C), 108.6 (4 C), 47.3 (4 C), 26.7 (4 C) ppm. IR (KBr): $\tilde{\nu}$ = 3047, 2873, 1731, 1573, 1421, 1231, 811 cm^{-1}. MS (ESI): m/z = 271 $[M/2]^{2+}$. $C_{24}H_{24}Cl_6N_4O_2{\cdot}3H_2O$ (667.2): calcd. C 43.20, H 4.53, N 8.40; found C 43.03, H 4.58, N 8.34.

1,1′-[3,4-Bis(dichloromethylene)cyclobut-1-ene-1,2-diyl]bis(4-pyrrolidinopyridinium) Chloride (6): After stirring for 3 h at 80 °C, the precipitate was filtered off and washed to give 0.34 g (59%) of a light-brown solid after recrystallization; m.p. 188 °C (dec.). ^{1}H NMR (400 MHz, [D$_4$]MeOH): δ = 8.09 (d, J = 7.7 Hz, 4 H, α-H), 6.86 (d, J = 7.7 Hz, 4 H, β-H), 3.56 (m, 8 H), 2.13 (m, 8 H) ppm. ^{13}C NMR (100 MHz, [D$_4$]MeOH): δ = 157.3 (2 C), 141.4 (4 C), 131.7 (2 C), 127.1 (2 C), 121.3 (2 C), 108.8 (4 C), 49.5 (4 C), 26.1 (4 C) ppm. IR (KBr): $\tilde{\nu}$ = 3022, 2892, 1724, 1578, 1432, 1211, 807 cm^{-1}. MS (ESI): m/z = 255 $[M/2]^{2+}$. $C_{24}H_{24}Cl_6N_4{\cdot}5\ H_2O$: calcd. C 42.94, H 5.11, N 8.35; found C 42.75, H 5.13, N 8.32.

1,1′-[3,4-Bis(dichloromethylene)cyclobut-1-ene-1,2-diyl]bis(4-aminopyridinium) Chloride (7): After stirring for 3 h at 70 °C, the precipitate was filtered off and washed to give 0.32 g (68%) of a reddish brown solid after recrystallization; m.p. 193 °C (dec.). ^{1}H NMR (400 MHz, D_2O): δ = 8.53 (d, J = 7.7 Hz, 4 H, α-H), 7.14 (d, J = 7.7 Hz, 4 H, β-H) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 159.2 (2 C), 143.2 (4 C), 133.1 (2 C), 128.2 (2 C), 119.7 (2 C), 108.7 (4 C) ppm. IR (KBr): $\tilde{\nu}$ = 3317, 3043, 1729, 1566, 1442, 1216, 812 cm^{-1}. MS (ESI): m/z = 201 $[M/2]^{2+}$. $C_{16}H_{12}Cl_6N_4{\cdot}3H_2O$ (527.1): calcd. C 36.46, H 3.44, N 10.63; found C 36.30, H 3.50, N 10.71.

1-(Biphenyl-4-yl)ethanone (9c): A mixture of phenylboronic acid (146.5 mg, 1.20 mmol), 4-acetylphenyl trifluoromethanesulfonate (268 mg, 1.0 mmol), NaOtBu (163.5 mg, 1.7 mmol), $Pd(OAc)_2$ (5 mg, 0.02 mmol, 2 mol-%), and **3** (11.2 mg, 0.02 mmol) in toluene (5 mL) was stirred at room temperature. A colorless solid was obtained after 80 min in 90% yield (177 mg); m.p. 117–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.6 Hz, 2 H), 7.68 (d, J = 8.6 Hz, 2 H), 7.63–7.61 (m, 2 H), 7.48–7.44 (m, 2 H), 7.41–7.37 (m, 1 H), 2.63 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 145.7, 139.8, 135.8, 129.0, 128.9, 128.2, 127.3, 127.2, 26.6 ppm. IR (KBr): $\tilde{\nu}$ = 3073, 2998, 2916, 1680, 1602, 1403, 1358, 1264, 960, 765 cm^{-1}. MS (70 eV): m/z = 196 $[M]^+$. $C_{14}H_{12}O$ (196.25): calcd. C 85.68, H 6.16; found C 85.57, H 6.03.

6-Phenylquinoline (11): A mixture of phenylboronic acid (146.5 mg, 1.20 mmol), 6-quinolinyl trifluoromethanesulfonate (277.2 mg, 1.0 mmol), NaOtBu (163.5 mg, 1.7 mmol), $Pd(OAc)_2$ (5 mg, 0.02 mmol, 2 mol-%), and **3** (11.2 mg, 0.02 mmol) in toluene (5 mL) was stirred for 90 min at room temperature. Purification by column chromatography gave 186 mg (91%) of the title compound as a light-yellow solid; m.p. 105–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.92 (dd, J = 4.7, 1.4 Hz, 1 H), 8.22–8.14 (m, 2 H), 7.98–7.94 (m, 2 H), 7.70 (d, J = 8.1 Hz, 2 H), 7.50–7.36 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.4, 147.7, 140.3, 139.4, 136.3, 129.9, 129.3, 129.0, 128.5, 127.8, 127.5, 125.5, 121.5 ppm. IR (KBr): $\tilde{\nu}$ = 2852, 1598, 1491, 1372, 1314, 887, 803 cm^{-1}. MS (70 eV): m/z = 205 $[M]^+$. $C_{15}H_{11}N$ (205.26): calcd. C 87.77, H 5.40, N 6.82; found C 88.01, H 5.37, N 6.91.

3-Methoxy-4′-methylbiphenyl (13): A mixture of 4-methylphenylboronic acid (163.2 mg, 1.20 mmol), 3-methoxyphenyl trifluoromethanesulfonate (256 mg, 1.0 mmol), NaOtBu (163.5 mg, 1.7 mmol), $Pd(OAc)_2$ (5 mg, 0.02 mmol, 2 mol-%), and **3** (11.2 mg, 0.02 mmol) in toluene (5 mL) was stirred for 3 h at 50 °C to give 153 mg (77%) of the title compound as a yellow solid after column chromatography; m.p. 77–78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, J = 8.0 Hz, 2 H), 7.34 (dd, J = 7.8, 2.0 Hz, 1 H), 7.25 (d, J = 8.0 Hz, 2 H), 7.19 (dd, J = 8.0, 7.5 Hz, 1 H), 7.13 (d, J = 2.0 Hz, 1 H), 6.89 (dd, J = 7.8, 2.0 Hz, 1 H), 3.79 (s, 3 H), 2.35 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 141.6, 137.2, 136.7, 129.8, 129.3, 126.5, 118.8, 112.6, 111.9, 55.0, 20.7 ppm. IR (KBr): $\tilde{\nu}$ = 3021, 2917, 2828, 1481, 1296, 1221, 817 cm^{-1}. MS (70 eV): m/z = 198 $[M]^+$. $C_{14}H_{14}O$ (198.26): calcd. C 84.81, H 7.12; found C 84.56, H 7.16.

1,3-Di-*tert*-butyl-5-{2-methyl-1-[2-(2-methylbenzyl)phenyl]propan-2-yl}benzene (18): A two-necked dry flask equipped with a stirring bar was charged with 2-methylphenylboronic acid (299.2 mg, 2.2 mmol), NaOtBu (190.75 mg, 1.7 mmol), salt **3** (11.2 mg, 0.02 mmol), and $NiCl_2$·glyme (4.5 mg, 0.02 mmol) and purged with nitrogen three times. 1-Bromo-2,4,6-tri-*tert*-butylbenzene (325.34 mg, 1 mmol) in toluene (5.0 mL) was then added through a syringe and the reaction was stirred at 90 °C for 14 h. After this time, petroleum ether was added (5 mL) and the mixture was filtered through a plug of Celite. The solvent was then evaporated and the residue was purified by flash column chromatography. A colorless oil was obtained in 72% yield (307 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.26 (m, 3 H), 7.17–7.15 (m, 1 H), 7.10–7.02 (m, 5 H), 6.89–6.87 (m, 1 H), 2.87 (s, 2 H), 2.11 (s, 2 H), 1.78 (s, 3 H), 1.47 (s, 6 H), 1.31 (s, 18 H) ppm. ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 149.7, 147.2, 141.6, 137.7, 137.4, 135.8, 131.4, 130.1, 129.8, 129.3, 127.1, 125.8, 125.5, 124.8, 120.5, 119.5, 47.5, 39.7, 34.9, 31.5, 28.5, 19.8, 19.4 ppm. IR (NaCl): $\tilde{\nu}$ = 3067, 3011, 2974, 2853, 1571, 1524, 1452, 1129, 773 cm^{-1}. HRMS (70 eV): calcd. for $C_{32}H_{42}$ 426.3287; found 426.3292.

General Procedure for the C–C Couplings of Nitriles: A mixture of arylboronic acid (1.20 mmol), arylnitrile (1.0 mmol), KO*t*Bu (190.75 mg, 1.7 mmol), Cu_2O (1 equiv.), $NiCl_2$·glyme (21.97 mg, 0.1 mmol, 10 mol-%), and **3** (56 mg, 0.1 mmol) in toluene (5 mL) was stirred at 100 °C for 15 h. The reaction mixture was then diluted with petroleum ether (10 mL), filtered through a thin pad of silica gel, and concentrated under reduced pressure. The crude material obtained was purified by flash chromatography on silica gel (petroleum ether).

2-Methylbiphenyl (25a): The reaction of phenylboronic acid (146.5 mg, 1.20 mmol) and 2-methylbenzonitrile (117.14 mg, 1.0 mmol) gave a colorless oil in 43% yield (72.33 mg) after 15 h at 100 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.50 (m, 3 H), 7.42–7.34 (m, 3 H), 7.29–7.16 (m, 3 H), 2.47 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.1, 141.1, 132.8, 132.7, 130.4, 128.9, 127.4, 127.3, 126.4, 112.9, 20.7 ppm. IR (NaCl): $\tilde{\nu}$ = 3045, 2991, 1563, 1457 cm^{-1}. MS (70 eV): *m*/*z* = 168 $[M]^+$. $C_{13}H_{12}$ (168.24): calcd. C 92.81, H 7.19; found C 92.76, H 7.22.

3-Methyl-4′-(trifluoromethyl)biphenyl (25b): The reaction of 4-trifluoromethylphenylboronic acid (228 mg, 1.20 mmol) and 3-methylbenzonitrile (117.14 mg, 1.0 mmol) gave a colorless oil in 48% yield (113.5 mg) after 15 h at 100 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.67 (s, 4 H), 7.40–7.34 (m, 3 H), 7.21–7.19 (m, 1 H), 2.42 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 139.7, 138.6, 128.9, 128.8, 128.0, 127.4, 125.6 (q, *J* = 3.78 Hz), 124.4, 121.6, 21.5 ppm. IR (NaCl): $\tilde{\nu}$ = 3023, 2897, 1551, 772 cm^{-1}. MS (70 eV): *m*/*z* = 236 $[M]^+$. $C_{14}H_{11}F_3$ (236.23): calcd. C 71.18, H 4.69; found C 71.20, H 4.65.

General Procedure for the Coupling of *cis*-1,2-Dichloroethene: An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with [$Pd(OAc)_2$ + ligand **3**] (46.6 mg, 0.06 mmol, 6 mol-%), K_3PO_4 (636.8 mg, 3 equiv.), and arylboronic acid (2.4 equiv.). The resulting mixture was degassed for 10 min with nitrogen. *cis*-1,2-Dichloroethene (1 mmol, 97 mg) and toluene (3 mL) were added and the mixture was stirred at 80 °C for 10 h.

***cis*-1,2-Diphenylethene (27a):** Colorless oil in 79% total yield. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.57 (m)*, 7.44–7.40 (m)*, 7.25–7.15 (m, 10 H), 6.58 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.3*, 137.3, 130.3*, 128.9, 128.8*, 128.3, 127.3*, 127.2, 127.1 ppm. GC–MS (ratio 2.7:1): *m*/*z* = 154 $[M]^+$, 180 $[M]^+$. * Spectroscopic data for biphenyl, which could not be separated.

***cis*-1,2-Di-*p*-toluylethene (27b):** Colorless oil in 83% total yield. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 7.8 Hz, 1 H)*, 7.2 (d, *J* = 7.8 Hz, 1 H)*, 7.14 (d, *J* = 7.8 Hz, 4 H), 7.00 (d, *J* = 7.8 Hz, 4 H), 6.49 (s, 2 H), 2.36 (s, 1.5 H)*, 2.28 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2*, 136.6, 136.5*, 134.4, 129.4*, 129.3*, 128.8, 128.7, 126.7, 21.2, 21.0 ppm. GC–MS (ratio 4.9:1): *m*/*z* = 182 $[M]^+$, 208 $[M]^+$. * Spectroscopic data for ditoluyl, which could not be separated.

***cis*-1,2-Bis(thiophen-2-yl)ethene (27c):** Colorless oil in 68% (130.5 mg) yield. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.23 (dd, *J* = 5.1, 1.0 Hz, 2 H), 7.1 (dd, *J* = 5.1, 1.0 Hz, 2 H), 6.97 (dd, *J* = 5.1, 3.6 Hz, 2 H), 6.59 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.1, 128.3, 126.9, 126.3, 122.9 ppm. IR (NaCl): $\tilde{\nu}$ = 3103, 3014, 1618, 1507, 1214, 697 cm^{-1}. HRMS (70 eV): calcd. for $C_{10}H_8S_2$ 192.0067; found 192.0069.

Computational Details: The DFT calculations presented in this work were carried out at the B3LYP/SDDP level of theory, with B3LYP referring to the applied exchange-correlation functional[35–37] and SDDP denoting a basis set including the Stuttgart–Dresden relativistic small-core ECP basis set for Pd and the Dunning/Huzinaga DZ+ polarization all-electron basis set for the lighter atoms.[38–41] The structures of all the investigated species were fully optimized. The reported ligand binding energies were obtained from the total electronic energies. The computations were performed by using the Gaussian 03 package.[42]

Supporting Information (see footnote on the first page of this article): Cartesian coordinates and total electronic energies of all calculated structures.

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