

A palladium Chugaev carbene complex as a modular, air-stable catalyst for Suzuki–Miyaura cross-coupling reactions

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Abstract—A new Chugaev-type palladium carbene complex was prepared via a convenient metal-templated route and fully characterized by X-ray crystallography, NMR, and IR. This complex proved effective as a precatalyst for Suzuki–Miyaura cross-coupling reactions of a range of aryl bromides, even under aerobic conditions, and its modular synthesis should allow for further catalyst fine-tuning.

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Recent advances in ligand design have dramatically improved the scope and utility of metal-catalyzed cross-coupling reactions.¹ This is exemplified by the palladium-catalyzed Suzuki–Miyaura coupling of aryl halides with arylboron reagents,² a reaction that has attracted growing interest due to its high functional group tolerance as well as the prevalence of biaryl moieties in natural products, organic materials, and new ligands.³ A guiding theme has been the combination of strong σ -donor ligands, which are thought to facilitate aryl halide oxidative addition, with steric bulk, which promotes biaryl reductive elimination.⁴ Little and Fu⁵ and Buchwald and co-workers⁶ first demonstrated that electron-rich, sterically hindered phosphine ligands facilitate Suzuki–Miyaura couplings of electron-rich aryl chlorides, a substrate class that had previously been inaccessible. Rational modification of bulky phosphines by Buchwald and co-workers has led to a general catalyst system that shows high coupling activity for a wide range of aryl bromides and chlorides, in many cases at room temperature.⁷

Parallel to the development of phosphines, N-heterocyclic carbene (NHC) ligands (e.g., **a**, Fig. 1)⁸ have been pursued in cross-coupling catalysis primarily due to their potentially stronger σ -donating ability⁹ and enhanced stability to air and high temperature.¹⁰ Follow-

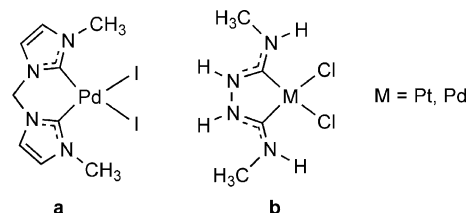


Figure 1. Chelating NHC (**a**, Ref. 11) and Chugaev carbene (**b**) ligands.

ing Herrmann's initial report of Suzuki coupling with a palladium–NHC catalyst,¹¹ Nolan and co-workers developed catalyst systems based on palladium precursors combined with imidazolium salts that allowed practical Suzuki–Miyaura coupling of deactivated aryl chlorides.^{4,12} Palladium complexes of bulky NHC's were reported by Herrmann and co-workers to catalyze Suzuki–Miyaura coupling of unhindered aryl chlorides at room temperature.¹³ Subsequently, Glorius and co-workers achieved the formation of di- and tri-*ortho*-substituted biaryls at room temperature from aryl chlorides using an NHC ligand containing 'flexible steric bulk',¹⁴ and systematic variation of ligand sterics by these authors recently resulted in the unprecedented Suzuki–Miyaura synthesis of a range of tetra-*ortho*-substituted biaryls from aryl chlorides.¹⁵

Given the recent successes in tuning cross-coupling catalyst activity through ligand modification, a ligand design that combines strong σ -donor groups with a

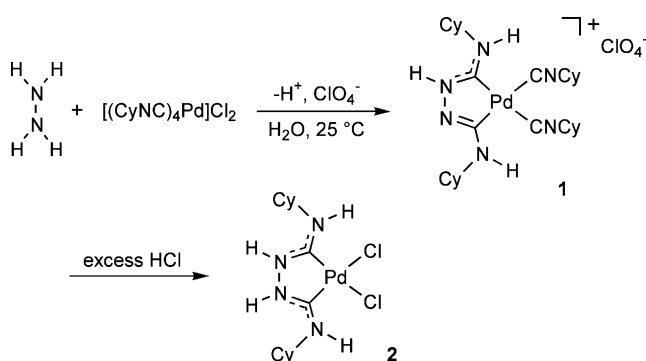
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readily altered structural framework would clearly be advantageous. While investigating synthetically flexible routes to chelating carbenes that possess these attributes, we became intrigued by ‘Chugaev-type’ carbenes (**b**, Fig. 1),¹⁶ a relatively unexplored class of chelate ligands that are formed via the metal-templated addition of hydrazines or other bifunctional nucleophiles to *cis*-coordinated isocyanides. Platinum complexes of these ligands were prepared as early as 1915,¹⁶ but their structures were unknown until spectroscopic studies by Rouschias and Shaw¹⁷ and crystallographic studies by Balch and co-workers¹⁸ in 1970 revealed their chelating nature. These ligands contain nitrogen-stabilized carbene donors analogous to NHC’s, but they have never been investigated in catalysis. Additionally, reports of similar chelate ligands synthesized from diamines such as 2,6-diaminopyridine¹⁹ and 1,2-ethylenediamine²⁰ suggest that the metal-templated synthetic strategy could be extended to a wide range of structures, potentially including sterically hindered or chiral examples.

As a starting point to explore the scope of Chugaev carbene synthesis, we targeted palladium dicarbene complexes derived from hydrazine and bulky isocyanides. Palladium complexes of methylisocyanide-derived Chugaev carbenes are known,¹⁸ but the only reported example synthesized from a sterically encumbered isocyanide is a platinum dicarbene complex prepared from *tert*-butylisocyanide.²¹ Herein we report a new Chugaev carbene complex of palladium and its use as an air-stable catalyst for Suzuki–Miyaura cross-coupling reactions. The convenient synthesis of this complex opens new opportunities for the modular design of novel chelating carbene ligands.

Addition of excess hydrazine hydrate to a stirred solution of $[\text{Pd}(\text{CNCy})_4]\text{Cl}_2$,²² generated in situ from PdCl_2 and cyclohexylisocyanide, provided a yellow precipitate, which was washed with aqueous LiClO_4 and water and then dried in vacuo.²³ Consistent with the original reports of methylisocyanide-derived Chugaev carbene complexes,^{17,18} this product is assigned as $[\text{Pd}(\text{C}_{14}\text{H}_{25}\text{N}_4)(\text{CNCy})_2][\text{ClO}_4]$ (**1**, Scheme 1), containing a deprotonated form of the chelating dicarbene ligand. Treatment of an acetonitrile solution of **1** with 3 M HCl followed by addition of Et_2O afforded neutral $\text{Pd}(\text{C}_{14}\text{H}_{26}\text{N}_4)\text{Cl}_2$ **2** in 65% yield.²⁴ Characteristic spec-



Scheme 1. Synthesis of palladium Chugaev carbene complexes.

troscopic changes accompanied the conversion of **1** into **2**, including replacement of three NH peaks in the ^1H NMR ($\text{DMSO}-d_6$) of **1** (δ 4.49, 6.79, 10.09) with two NH peaks for **2** (δ 7.71, 11.15), as well as disappearance of the isocyanide stretches of **1** ($\nu(\text{C}\equiv\text{N})$ 2220, 2210 cm^{-1}) in the IR spectrum.

X-ray crystallographic analysis of **2**²⁵ revealed the expected chelating carbene ligand with a planar NCNCCN backbone (Fig. 2). The coordination about palladium is almost perfectly planar (sum of angles $359.96(9)^\circ$), but the five-membered chelate ring of the dicarbene constrains the C–Pd–C angle to a small value of $79.91(6)^\circ$. The N–C_{carbene} distances of the ligand (average 1.326 Å) are slightly smaller than the normal range of 1.34–1.37 Å for imidazolium-based NHC ligands, indicating substantial π -interaction within the dicarbene unit. In addition, the Pd–C_{carbene} distances (1.9583(15), 1.9638(15) Å) are slightly shorter than those in comparable Pd–NHC complexes (typically 1.99–2.00 Å),^{8,11} suggesting possibly stronger binding to the metal. The steric bulk of the cyclohexyl groups is directed away from the palladium coordination sphere and does not substantially perturb the ligand backbone. Thus, the use of even larger isocyanides appears feasible. An intriguing feature is hydrogen bonding of the backbone NH units with DMSO solvent molecules. Interestingly, X-ray quality crystals could only be grown from DMSO.

In view of the similarity of Chugaev carbene ligands to NHC’s, we have tested the catalytic activity of **2** in Suzuki–Miyaura cross-coupling reactions. Complex **2** is stable to air and moisture, and therefore we regarded it as potentially useful under aerobic conditions. The ability to operate under air would greatly increase the practicality of the reaction. However, only a few palladium Suzuki catalysts have been reported to function under air,²⁶ primarily involving nitrogen ligands,²⁷ with only one example of an aerobic Suzuki reaction reported using a Pd–NHC catalyst.²⁸

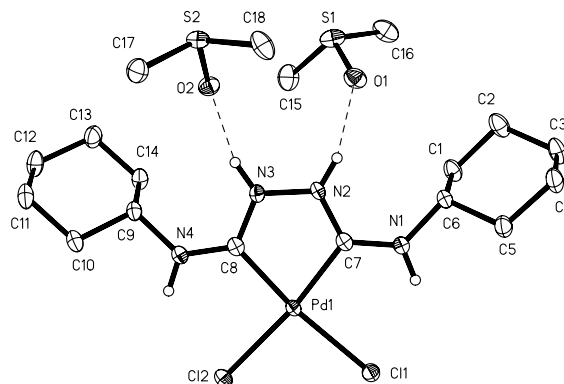


Figure 2. ORTEP diagram of **2** (50% probability ellipsoids). Selected distances (Å) and angles ($^\circ$): Pd(1)–C(7) = 1.9583(15), Pd(1)–C(8) = 1.9638(15), C(7)–N(1) = 1.3205(19), C(7)–N(2) = 1.332(2), C(8)–N(3) = 1.3311(19), C(8)–N(4) = 1.3191(19), C(7)–Pd(1)–C(8) = $79.91(6)$, C(7)–Pd(1)–Cl(1) = $93.26(5)$, C(8)–Pd(1)–Cl(2) = $92.97(4)$, Cl(1)–Pd(1)–Cl(2) = $93.818(14)$.

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