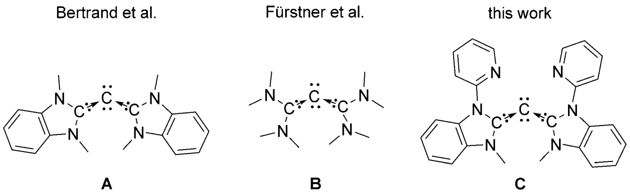
DOI: 10.1002/ange.201406481

Carbodicarbenes

Synthesis and Isolation of an Acyclic Tridentate Bis(pyridine)carbodicarbene and Studies on Its Structural Implications and Reactivities**

Yu-Chen Hsu, Jiun-Shian Shen, Bo-Chao Lin, Wen-Ching Chen, Yi-Tsu Chan, Wei-Min Ching, Glenn P. A. Yap, Chao-Ping Hsu, and Tiow-Gan Ong**

***Abstract:** The simple synthetic development of acyclic pincer bis(pyridine)carbodicarbene is depicted herein. Presented is the first isolated structural pincer carbodicarbene with a C-C-C angle of 143°, larger than the monodentate framework. More importantly, theoretical analysis showed that this carbodicarbene embodies a more allene-like character. Palladium complexes supported by this pincer ligand are active catalysts for Heck–Mizoroki and Suzuki–Miyaura coupling reactions.*



Scheme 1. Known and new carbodicarbenes.

Steady research efforts toward the development of unique bonding environments for carbon species, with the aim of defying the "octet rule", have been a fundamental challenge in organic chemistry for centuries. This curiosity-driven work eventually led to the isolation of stable free six-electron carbon species, namely phosphino–silyl carbenes[1a,b] and N-heterocyclic carbenes (NHC).[1c,d] More importantly, the discovery of NHCs also generated numerous breakthroughs in organometallic chemistry and catalysis.[2]

A few years ago, the groups of Bertrand[3] and Fürstner[4] pioneered a rather peculiar carbon(0)-based class of compounds, coined as "carbodicarbenes" or "bent allenes", by synthesizing the corresponding compounds **A** and **B**, respectively (Scheme 1). Subsequently, our laboratory has undertaken the synthetic endeavor of increasing the structural diversity of carbodicarbene **A**, with the hopes of extending its utility in organometallic chemistry.[5] To date, the reported carbodicarbenes and their metal complexes are limited essentially to a monodentate framework.[6] Therefore, the need exists to develop a pincer or multidentate-type carbodicarbene to explore new chemical reactivity. Moreover, metal complexes supported by pincer ligands are gaining increasing momentum in contemporary science, owing to their ability to activate strong bonds[7] and their utility in catalysis.[8] We envisioned that a rationally designed pincer bis(pyridine)carbodicarbene with rigid tridentate chelation, such as that shown in **C**, would be desirable, as such a ligand design will lead to the accumulation of new chemical knowledge as well as new potential catalytic applications.[9] Herein, we report the synthesis and characterization of bis(pyridine)carbodicarbene and its pincer palladium complexes. At this stage, these captodative, carbogenic compounds are still largely regarded as a laboratory curiosity, rarely used for supporting metal-mediated catalytic reactions. In order to evaluate the catalytic activity of the palladium complexes supported by pincer carbodicarbene, we have also reported their utility in catalyzing C−C cross-couplings such as Heck–Mizoroki and Suzuki–Miyaura reactions.

The preliminary synthesis of the dicationic salt **4**, the precursor of an acyclic pincer-type carbodicarbene, was initiated with a commercially available 1-iodo-2-nitrobenzene (Scheme 2), which undergoes palladium-mediated amination with 2-aminopyridine to give **1**, from which diamine **2** is furnished in excellent yield (92%) through hydrogenation. Compound **2** was then heated at reflux with diethyl malonate to afford **3** in high yield. Bismethylation of **3** with iodomethane in acetonitrile results in the dicationic salt **4**, confirmed by single-crystal X-ray diffraction (Figure 1, left).[10] Double deprotonation of **4** with $NaN(SiMe_3)_2$ afforded the air-sensitive carbodicarbene **5** in 50% yield. In the ^1H NMR spectrum of **5**, the methylene resonance of **4** at $\delta = 5.91$ ppm has disappeared and the singlet methyl resonance with an integration of six protons has shifted from 4.14 ppm to 2.68 ppm, thus suggesting that **5** is a free carbodicarbene. The molecular structure of **5** was further elucidated by single-crystal X-ray diffraction (Figure 1, right). To the best of our knowledge, compound **5** represents the first isolated free form of a pincer-type, acyclic carbodicarbene. The connectivity of the bent allenic moiety, C6-C14-C16, was confirmed, with bond distances of 1.333(2) and 1.324(2) Å,

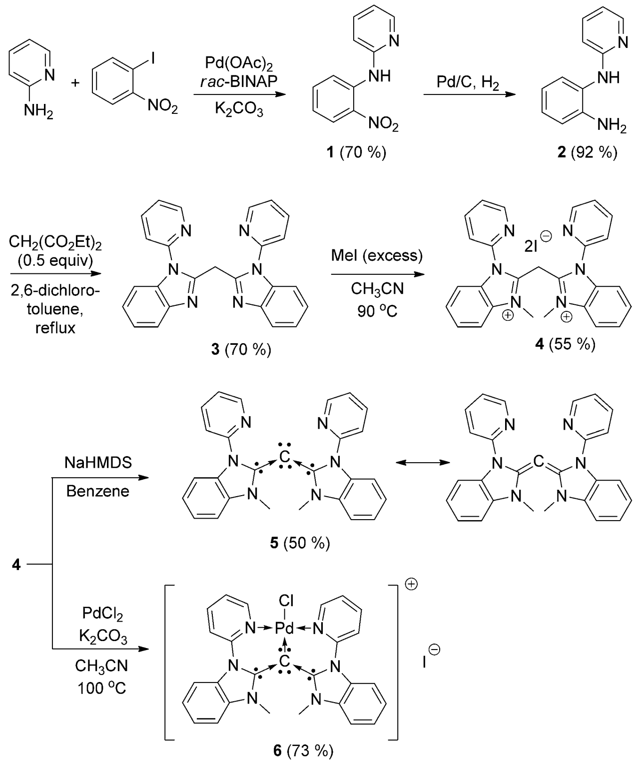
---

[*] J. Shen,[+] Dr. B. Lin, Dr. W. Chen, Dr. W. Ching, Dr. C. Hsu, Dr. T. Ong
Institute of Chemistry, Academia Sinica
Taipei, Taiwan (Republic of China)
E-mail: tgong@gate.sinica.edu.tw
Dr. T. Ong
Department of Applied Chemistry, National Chiao Tung University
Taiwan (Republic of China)
Y. Hsu,[+] Prof. Y. Chan
Department of Chemistry, National Taiwan University
Taipei, Taiwan (Republic of China)
Prof. G. Yap
Department of Chemistry & Biochemistry
University of Delaware (USA)

[+] These authors contributed equally to this work.

[**] This work was financially supported by the Ministry of Science & Technology of Taiwan. (NSC-101-2628M-001-002-MY grant) and Academia Sinica Funding.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201406481.



Scheme 2. Synthetic routes toward carbodicarbene **5** and its palladium complex **6**.

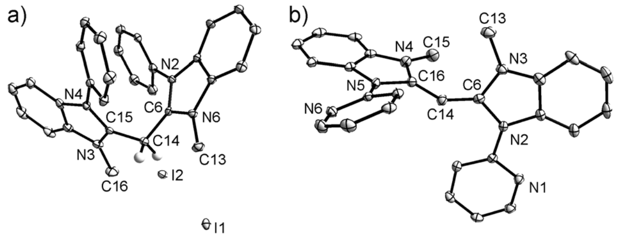


Figure 1. Crystal structures of compounds a) **4** and b) **5** with thermal ellipsoids depicted at 30% probability. Solvent molecules and hydrogen atoms (except for those on the methylene group of **4**) have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: **4:** C6–C14 1.496(6), C14–C15 1.493(6), N2–C6 1.352(5), N6–C6 1.330(5), N3–C15 1.333(6), N4–C15 1.346(5); C15-C14-C6 115.8(3). **5:** C6–14 1.333(2), C14–C16 1.324(2), N2–C6 1.418(2), N3–C6 1.389(2), N4–C16 1.3993(18), N5–C16 1.4242(18); C6-C14-C16 143.61(15).

which are comparable to the previous reports by our group[5a] and Bertrand and co-workers.[3] However, the bond angle of 143.6° in the allenic moiety of **5** is larger than that reported for other acyclic carbodicarbenes (134.8°), despite the relative lack of steric hindrance. More interestingly, the two N4-C16-N5 and N2-C6-N3 planes are twisted by 84°, a feature that bears resemblance to an allene (90°). Finally, the lone pairs residing at pyridine and those of the carbodicarbene are oriented in an *anti* manner, presumably to avoid unfavorable stereoelectronic interactions.

To investigate the coordination chemistry of the carbodicarbene, dicationic salt **4** in CH_3CN was introduced to $PdCl_2$ in the presence of K_2CO_3 as a base at 100 °C, affording complex **6** in good yield. In **6** (Figure 2), the cationic palladium center has a square planar environment with a tridentate NCN coordination. The palladium−carbodicarbene bond in **6** (1.973(3) Å) is shorter than that in our previously reported non-pincer NHC−Pd complexes (2.101(4) Å).[5a] The rather short Pd−C bond is attributed to a tight pincer effect. Not surprisingly, the C center of the carbodicarbene ligand contributes a strong *trans* influence on the chloride ligand opposite to it, thus lengthening the Pd−Cl distance to 2.4090(8) Å.[11] This result is consistent with previous reports of related tridentate pincer-type structures of LCL complexes.[12] Interestingly, the geometry around Pd is close to idealized square-planar, but both benzimidazolium (or pyridine) rings are puckered with respect to each other to avoid unfavorable steric interactions invoked by the methyl side arms in the framework.

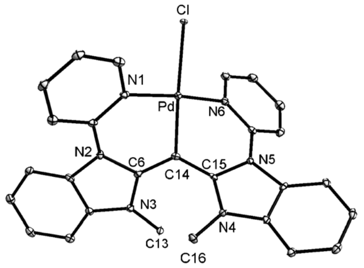


Figure 2. Crystal structure of complex **6** with thermal ellipsoids depicted at 30% probability. Hydrogen atoms and the iodine counterion have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1–Cl1 2.4090(8), Pd1–N1 2.035(3), Pd1–N6 2.033(3), Pd1–C14 1.973(3), C14–C6 1.369(5), C14–C15 1.398(5); C6-C14-C15 126.5(3), Cl1-Pd1-C14 177.24(10).

To further understand the molecular structures and their implication in molecular properties, we further employed DFT calculation. At the level of B3LYP/Lan2Ldz/6-31G*, the optimized structures of **5** and **6** were obtained, which are in good agreement with the X-ray crystal structures (see Figure 3 and the Supporting Information for details). Additionally, we have modeled the molecular structure of **5′**, based on structure **6** excluding the palladium atom, to examine the stereoelectronic interaction of the lone pairs. Both lone pairs at the pyridyl fragments of **5′** are directed toward the central carbodicarbene region (Figure 3 b). The model structure of **5′** is 23.0 kcal mol^{-1} higher in energy than **5**, thus indicating unfavorable stereoelectronic interactions among those lone pairs. Figure 3 a and b shows the two highest occupied molecular orbitals HOMO and HOMO-1 of **5** and **5′**. The HOMO-1 of **5** is clearly a σ-type orbital and localized at the central carbon atom C14. The HOMO of **5** is a π-type lone-pair orbital that has also the largest coefficient at C14 with respect to the C-C-C plane. We note that these results for **5** are similar to previous computational results for a number of carbodicarbenes.[13] Interestingly, the frontier orbital arrangement for **5′** is reverse with respect to **5**.

One of intriguing questions worth considering at this juncture is the nature of the C-C-C moiety of **5**. A larger C6-

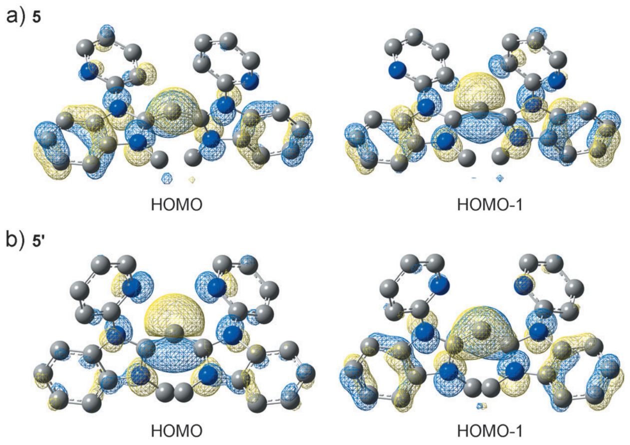


Figure 3. Plots of the HOMO and HOMO-1 of a) **5** and b) **5′** based on calculations at B3LYP/Lan2Ldz/6-31G* level.

C14-C16 angle with almost orthogonal torsional angles compared to **A** and **C** would conceivably mean some allenic character in **5**. To examine the extend of the allene-like character of bis(pyridine)carbodicarbene, we used the program "TopMod" to perform the electron localization function (ELF) analysis[14] on **5** and **5′**. The electron localization function (ELF) is a useful method to study the disposition of electron density of bonding and lone pairs. The ELF[14] analyses of **5** and **5'** with their contour plots are displayed in Figure 4. A lone pair close to the central C14 is observed for both **5** and **5′**. The valence basin near this central atom (denoted as $V(C_{14})$) has electronic populations of $1.54\,e^-$ and $2.10\,e^-$ for **5** and **5′**, respectively. This result supports a pronounced carbene character at the central C14 atom in both conformers. Yet, the lower electron population in compound **5** suggests that it possesses significant allene-like character. Similar ELF results were reported previously for a bent allene of 1,2-cyclopentadiene.[14d] We also performed a natural population analysis (NPA) to map out the charge distribution of **5** and **6**.[15] NPA showed that the NHC fragments in **6** carry a significant amount of positive charge, but not as much in **5**,[16] suggesting a lack of a strong electron-donating contribution from C6 and C15 in **5**. Again, the NPA is consistently in line with the ELF interpretation that carbodicarbene **5** has embodied a more allene-like character compared to previously known carbodicarbenes **A** and **B**. We speculate that the pyridine moieties, which are an electron-withdrawing entity in **5**, may play a role in that respect.

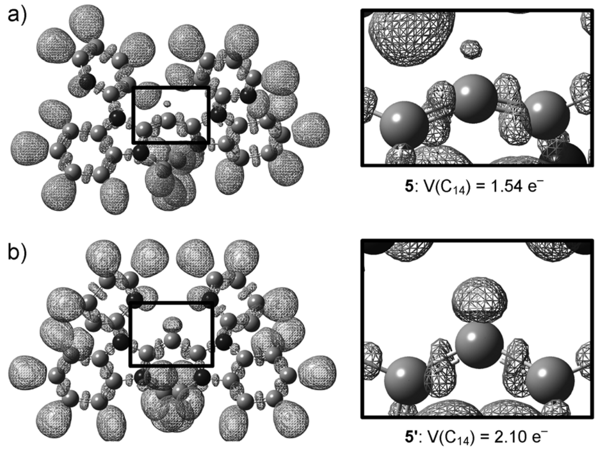
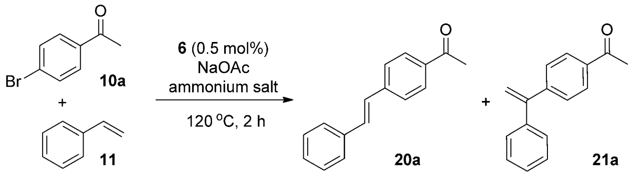


Figure 4. Electron localization function (ELF) analysis of a) **5** and b) **5′**, with the magnification of the central carbodicarbene (or bent allenic) moieties on the right. Basin populations for the valence lone pair at the central C14 atom are also given.

Recent years have seen increasing interest in the development of NHC-promoted metal-mediated homogeneous catalysis. Interestingly, endeavors using carbodicarbene-based catalysts are still lacking. Thus, the development of carbodicarbenes as an NHC alternative for catalysis is definitely worthwhile to pursue. To evaluate the catalytic activity of the palladium complexes supported by pincer carbodicarbene, we studied these compounds as potential catalysts for the Mizoroki–Heck cross-coupling reaction. To our delight, even during the preliminary studies for optimization of reaction conditions (Table 1), the coupling product **20a** was obtained in good yield (entry 1).[17]

Table 1: Optimization of the Mizoroki–Heck reaction catalyzed by complex **6**.[a]

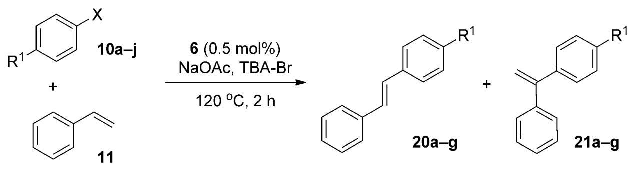


Entry	Ammonium salt	Yield[b] [%] (**20a**:**21a**)
1	TBA-Br	97 (92:5)
2	TBA-BF_4	20 (20:1)
3	TBA-HSO_3	54 (49:5)
4	TBA-Cl	88 (85:3)
5	TBA-PF_6	no reaction

[a] Reactions were carried out with aryl bromide (1.0 mmol), styrene (1.45 mmol), NaOAc (1.18 mmol), Pd catalyst **6** (0.5 mol%), ammonium salt (2 g) at 120°C for 2 h. [b] Yield and regioselectivity determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. TBA = tetrabutylammonium.

With the optimized reaction conditions in hand, the scope of the Mizoroki-Heck reaction mediated by catalyst **6** was studied further (Table 2). Excellent yields (entries 1–3) were observed for aryl bromide bearing ketone (**10a**), cyanide (**10b**), and aldehyde (**10c**). Similarly, derivatives (**10d–f**) with more electron-donating groups did not seem to affect the yield of the reaction. The amino substituent (**10g**) is also compatible with the reaction conditions, giving a high yield of product (82%). Encouragingly, the less expensive aryl chloride can be used for the coupling process, giving good yields (entries 8–10). It is noteworthy, that all reactions mediated by complex **6** were performed under organic-solvent-free conditions using aqueous media with ammonium salts. The scope of this protocol was further expanded to butyl acrylate with various aryl bromides (Table 3). Remarkably, levels of the coupling products **22a–d** were consistently high

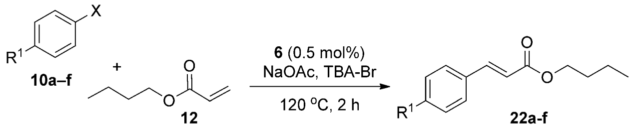
Table 2: Scope of Mizoroki–Heck reactions with styrene.[a]



Entry	10	X	R1	20	Yield [%] (**20**:**21**)
1	**10a**	Br	$COCH_3$	**20a**	97 (92:5)
2[d]	**10b**	Br	CN	**20b**	99 (95:4)
3[d]	**10c**	Br	COH	**20c**	94 (89:5)
4[d]	**10d**	Br	H	**20d**	90 (90:0)
5[c]	**10e**	Br	CH_3	**20e**	91 (85:6)
6[b]	**10f**	Br	OMe	**20f**	93 (84:9)
7	**10g**	Br	NH_2	**20g**	82 (75:7)
8[e]	**10h**	Cl	$COCH_3$	**20a**	94 (90:4)
9[e]	**10i**	Cl	CN	**20b**	90 (85:5)
10[d]	**10j**	Cl	COH	**20c**	97 (91:6)

[a] Reactions were carried out with aryl halide (1.0 mmol), styrene (1.45 mmol), NaOAc (1.18 mmol), **6** (0.5 mol%), TBA-Br (2 g) at 120°C for 2 h. [b] 3-Chloropyridine (2.65 mol%) was added. [c] 2,6-Dimethylpyridine (2.65 mol%) was added. [d] 3-Chloropyridine (2.65 mol%) was added, 4 h, 140°C. [e] Performed at 140°C. Yields and regioselectivity determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

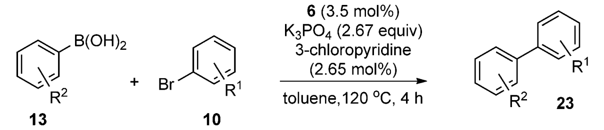
Table 3: Scope of Mizoroki–Heck reactions with butyl acrylate.[a]

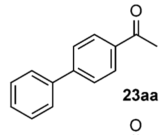
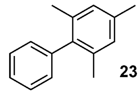
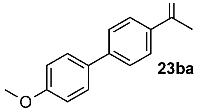
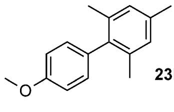
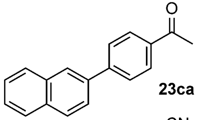
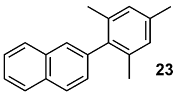
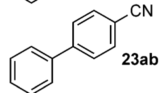
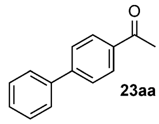
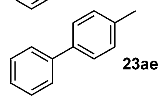
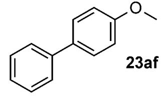
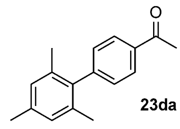


Entry	10	R1	22	Yield [%]
1	**10a**	$COCH_3$	**22a**	92
2	**10b**	CN	**22b**	94
3	**10c**	COH	**22c**	92
4	**10d**	H	**22d**	90
5	**10e**	CH_3	**22e**	78
6	**10f**	OMe	**22f**	79

[a] Reactions were carried out with aryl halide (1.0 mmol), butyl acrylate (1.45 mmol), NaOAc (1.18 mmol), **6** (0.5 mol%), TBA-Br (2 g) at 120°C for 2 h. Yields determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

Table 4: Suzuki–Miyaura cross-coupling reaction.[a]



Entry	Product	Yield [%][b]	Entry	Product	Yield [%][b]
1	 **23aa**	93[c]	7	 **23ag**	84
2	 **23ba**	93	8	 **23bg**	85
3	 **23ca**	91	9	 **23cg**	82
4	 **23ab**	99	10[d,e]	 **23aa**	85
5	 **23ae**	77			
6	 **23af**	71	11[e]	 **23da**	17

[a] Reactions were carried out with aryl bromide (1 mmol), aryl boronic acid (1.3 mmol), **6** (3.5 mol%), K_3PO_4 (2.67 mmol), 3-chloropyridine (2.65 mol%) in toluene (2 mL) at 120°C for 4 h. [b] Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as internal standard. [c] Yields of isolated products. [d] Aryl chloride was used instead of aryl bromide. [e] H_2O (0.3 mL) was added.

(>90%), while the methyl and methoxy analogues (**10e**–**10f**) gave satisfactory conversion.

To further demonstrate the versatility of the catalyst, **6** was tested for the Suzuki–Miyaura coupling reaction (Table 4) between aryl boronic acids and aryl halides. To our delight, a highly efficient cross coupling of boronic reagent **13a** and acetophenyl bromide **10a** to product **23aa** can be achieved with 3.5 mol% of Pd catalyst **6** in the presence of around three equivalents of K_3PO_4 as base and 3-chloropyridine as additive (Table 4, entry 1). High yields were observed with several boronic reagents, such as **13b** and **13c** (products **23ba** and **23ca**, respectively; Table 4, entries 2 and 3). Likewise, aryl bromides that contain electron-withdrawing (**10b**) and electron-donating groups (**10e** and **10f**) are suitable substrates, but gave the products (**23ab**, **23ae**, and **23af**; Table 4, entries 4–6) in moderate yields typical for electron-donating derivatives. Relatively hindered 2-bromo-1,3,5-trimethyl benzene (**10g**) was also a capable coupling partner for different boronic reagents (Table 4, entries 7–9), but the sterically bulky mesitylboronic acid (**13d**) gave the product **23da** only in a low yield (entry 11). Finally, less active 4′-chloroacetophenone is also a suitable reagent for this reaction (Table 4, entry 10).

In summary, a new type of pincer bis(pyridine)-carbodicarbene framework has been prepared, isolated, and fully characterized. The pincer carbodicarbene **5** embodies a more allene-like character compared to previously known monodentate carbodicarbenes **A** and **B**. The corresponding tridentate palladium complexes have also been successfully prepared and shown to be active catalysts in Heck and Suzuki C−C cross-coupling reactions. This work represents a proof-of-concept of carbodicarbene-promoted metal catalysis. Further studies of the mechanistic pathways of cross-coupling reactions catalyzed by carbodicarbene–Pd complexes are under way.

Experimental Section

Preparation of compound **5**: In a 100 mL, one-necked, round-bottomed flask, **4** (3.44 g, 5 mmol) was placed in anhydrous benzene (10 mL). A solution of $NaN(SiMe_3)_2$ (NaHDMS) (1.85 g, 10 mmol) in benzene (30 mL) was added dropwise to the flask. The reaction mixture was stirred at ambient temperature for 3 h, followed by filtration of the reaction mixture through a celite plug. The filtrate was concentrated in vacuo, and the residue washed with diethyl ether and dried in vacuo to afford 1.08 g of **5** (50 %) as a yellow solid. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 8.36$ (br, 2H), 8.31 (br, 1H), 8.29 (br, 3H), 7.03 (t, $J = 7.6$ Hz, 2H), 6.97 (br, 4H), 6.43 (s, 4H), 2.69 ppm (s, 6H); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 153.8$, 148.5, 139.1, 137.5, 136.3, 133.3, 122.7, 120.5, 119.9, 119.1, 117.3, 113.4, 105.9, 29.6 ppm; HR-MS(FAB): calculated for $[C_{27}H_{22}N_6]^+$: 431.1984; Found: 431.1982.

CCDC 1005971 (**4**), 1005972 (**5**), and 1005973 (**6**) 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.

Received: June 23, 2014
Revised: July 29, 2014
Published online: August 28, 2014

Keywords: carbenes · carbodicarbenes · C–C coupling · ligand design · palladium

---

[1] a) A. Igau, H. Grutzmacher, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **1988**, *110*, 6463 – 6466; b) A. Igau, A. Baceiredo, G. Trinquier, G. Bertrand, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 621 – 622; *Angew. Chem.* **1989**, *101*, 617 – 618; c) A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361 – 363; d) A. J. Arduengo, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530 – 5534.

[2] a) W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290 – 1309; *Angew. Chem.* **2002**, *114*, 1342 – 1363; b) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122 – 3172; *Angew. Chem.* **2008**, *120*, 3166 – 3216; c) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612 – 3676; d) G. C. Fortman, S. P. Nolan, *Chem. Soc. Rev.* **2011**, *40*, 5151 – 5169; e) D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* **2007**, *107*, 5606 – 5655; f) L. Schaper, S. J. Hock, W. A. Herrmann, F. E. Kühn, *Angew. Chem. Int. Ed.* **2013**, *52*, 270 – 289; *Angew. Chem.* **2013**, *125*, 284 – 304; g) L. M. Slaughter, *ACS Catal.* **2012**, *2*, 1802 – 1816.

[3] a) C. A. Dyker, V. Lavallo, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2008**, *47*, 3206 – 3209; *Angew. Chem.* **2008**, *120*, 3250 – 3253; b) I. Fernăndez, C. A. Dyker, A. DeHope, B. Donnadieu, G. Frenking, G. Bertrand, *J. Am. Chem. Soc.* **2009**, *131*, 11875 – 11881; c) M. Melaimi, M. Soleihavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 8810 – 8849; *Angew. Chem.* **2010**, *122*, 8992 – 9032.

[4] A. Fürstner, M. Alcarazo, R. Goddard, C. W. Lehmann, *Angew. Chem. Int. Ed.* **2008**, *47*, 3210 – 3214; *Angew. Chem.* **2008**, *120*, 3254 – 3258.

[5] a) W.-C. Chen, Y.-C. Hsu, C.-Y. Lee, G. P. A. Yap, T.-G. Ong, *Organometallics* **2013**, *32*, 2435 – 2442; b) W.-C. Chen, C.-Y. Lee, B.-C. Lin, Y.-C. Hsu, J.-S. Shen, C.-P. Hsu, G. P. A. Yap, T.-G. Ong, *J. Am. Chem. Soc.* **2014**, *136*, 914 – 917.

[6] a) A. DeHope, B. Donnadieu, G. Bertrand, *J. Organomet. Chem.* **2011**, *696*, 2899 – 2903; b) C. Pranckevicius, D. W. Stephan, *Organometallics* **2013**, *32*, 2693 – 2697; c) M. Alcarazo, C. W. Lehmann, A. Anoop, W. Thiel, A. Fürstner, *Nat. Chem.* **2009**, *1*, 295 – 301; d) M. Alcarazo, T. Stork, A. Anoop, W. Thiel, A. Fürstner, *Angew. Chem. Int. Ed.* **2010**, *49*, 2542 – 2546; *Angew. Chem.* **2010**, *122*, 2596 – 2600; e) M. Alcarazo, *Dalton Trans.* **2011**, *40*, 1839 – 1845.

[7] W. Leis, H. A. Mayer, W. C. Kaska, *Coord. Chem. Rev.* **2008**, *252*, 1787 – 1797.

[8] a) C. I. Lee, J. Zhou, O. V. Ozerov, *J. Am. Chem. Soc.* **2013**, *135*, 3560 – 3566; b) N. Selander, K. J. Szabo, *Chem. Rev.* **2011**, *111*, 2048 – 2076; c) J. C. DeMott, N. Bhuvanesh, O. V. Ozerov, *Chem. Sci.* **2013**, *4*, 642 – 649; d) J. Choi, A. H. Roy MacArthur, M. Brookhart, A. S. Goldman, *Chem. Rev.* **2011**, *111*, 1761 – 1779; e) D. Benito-Garagorri, K. Kirchner, *Acc. Chem. Res.* **2008**, *41*, 201 – 213.

[9] During the preparation of this manuscript, Meek and co-workers reported a pincer-based cyclic bis(phosphine)carbodicarbene and its rhodium complexes. M. J. Goldfogel, C. C. Roberts, S. J. Meek, *J. Am. Chem. Soc.* **2014**, *136*, 6227 – 6230.

[10] Of more interest are the intramolecular π-stacked interactions adopted by both the benzimidazolium and pyridine moieties, causing the two benzimidazolium planes in **4** to twist by 62°, an angle that is smaller than that in the previously reported analogue bearing an isopropyl side arm (87.2°).[5a]

[11] The average Pd–Cl distance reported for (NHC)Pd(allyl)Cl complexes is approximately 2.35 Å; a) H. Clavier, A. Correa, L. Cavallo, E. C. Escudero-Adán, J. Benet-Buchholz, A. M. Z. Slawin, S. P. Nolan, *Eur. J. Inorg. Chem.* **2009**, 1767 – 1773; b) M. S. Viciu, O. Navarro, R. F. Germaneau, R. A. Kelly III, W. Sommer, N. Marion, E. D. Stevens, L. Cavallo, S. P. Nolan, *Organometallics* **2004**, *23*, 1629 – 1635.

[12] a) K. Takenaka, M. Minakawa, Y. Uozumi, *J. Am. Chem. Soc.* **2005**, *127*, 12273 – 12281; b) S. Stallinger, C. Reitsamer, W. Schuh, H. Kopacka, K. Wurst, P. Peringer, *Chem. Commun.* **2007**, 510 – 512; c) L.-Y. Wu, X.-Q. Hao, Y.-X. Xu, M.-Q. Jia, Y.-N. Wang, J.-F. Gong, M.-P. Song, *Organometallics* **2009**, *28*, 3369 – 3380; d) B. Ding, Z. Zhang, Y. Xu, T. Liu, M. Sugiya, T. Imamoto, W. Zhang, *Org. Lett.* **2013**, *15*, 5476 – 5479.

[13] a) R. Tonner, G. Frenking, *Angew. Chem. Int. Ed.* **2007**, *46*, 8695 – 8698; *Angew. Chem.* **2007**, *119*, 8850 – 8853; b) R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3260 – 3272; c) R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3273 – 3289; d) R. Tonner, G. Heydenrych, G. Frenking, *ChemPhysChem* **2008**, *9*, 1474 – 1480.

[14] a) B. Silvi, A. Savin, *Nature* **1994**, *371*, 683 – 686; b) A. Savin, R. Nesper, S. Wengert, T. F. Fässler, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1808 – 1832; *Angew. Chem.* **1997**, *109*, 1892 – 1918; c) S. Noury, X. Krokidis, F. Fuster, B. Silvi, *Comput. Chem.* **1999**, *23*, 597 – 604; d) M. M. Hänninen, A. Peuronen, H. M. Tuononen, *Chem. Eur. J.* **2009**, *15*, 7287 – 7291.

[15] a) A. E. Reed, F. J. Weinhold, *Chem. Phys.* **1983**, *78*, 4066 – 4073; b) A. E. Reed, R. B. Weinstock, F. J. Weinhold, *Chem. Phys.* **1985**, *83*, 735 – 746.

[16] See the Supporting Information for further details.

[17] We also performed the solvent-free Heck cross-coupling reaction with various Pd catalysts supported by NHCs and PPh_3. The survey of the experiments under similar conditions suggested that catalyst **5** was much more effective than IMes, IPr, and PPh_3 (see Table S1b in the Supporting Information).