RSC Advances

PAPER

View Article Online
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Cite this: *RSC Adv.*, 2015, **5**, 25723

NCN pincer palladium complexes based on 1,3-dipicolyl-3,4,5,6-tetrahydropyrimidin-2-ylidenes: synthesis, characterization and catalytic activities†

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Received 28th January 2015
Accepted 5th March 2015

DOI: 10.1039/c5ra01706h

www.rsc.org/advances

The synthesis of novel pincer palladium complexes containing ring expanded six-membered N-heterocyclic carbenes (NHCs) *via* direct metallation of the precursors tetrahydropyrimidin-1-ium hexafluorophosphates in the presence of $NaN(SiMe_3)_2$ is presented. The structure has been characterized unambiguously by X-ray single crystal analysis. Catalytic activity investigation showed that the complexes catalyzed the Heck reaction of aryl bromides with acrylate/styrene efficiently when using Et_3N as base and DMA as solvent.

Introduction

Since the successful isolation and characterization of the first stable N-heterocyclic carbene (NHC) by Arduengo *et al.* in 1991,[1] these molecules have been widely used as ancillary ligands for the preparation of transition-metal-based catalysts.[2] Today, NHC metal complexes rank among the most powerful tools in organic chemistry, with numerous publications related to their coordination chemistry and catalytic properties being reported.[3] NHC palladium complexes are attracting a considerable amount of interest because of their easy accessibility, high thermal stability, and remarkable catalytic activities in various C–C coupling reactions. Numerous functionalized NHC palladium complexes have been synthesized and applied to catalytic hydrogenation, hydrophosphination, C–H functionalization, Suzuki–Miyaura reactions, Mizoroki–Heck reactions, Buchwald–Hartwig reactions, *etc.* successfully.[4] However, most of the reported NHC ligands are based on five-membered heterocyclic rings (imidazol-2-ylidenes, imidazolin-2-ylidenes, or benzimidazolin-2-ylidene, *etc.*).

In recently years, the ring expanded NHCs based on six-, seven-, or eight-membered heterocyclic rings began to attract extensive attention due to the enhanced σ-donor ability and easy tunability of the electronic property and steric effect of the ligands.[5] Various kinds of ring expanded NHC metal complexes, including Ag,[6] Au(I),[7] Pd,[8] Ni,[9] Cu,[10] Ru,[11] Rh,[12] and Ir,[13] *etc.* have been synthesized, characterized, and applied to organic transformations successfully. For example, the ring expanded six-, or seven-membered NHC copper(I) complexes have been proved to be effective catalysts for the 1,3-dipolar cycloaddition of alkynes and azide.[10a] A ring-expanded six-membered NHC Nickel(I) complex has been reported to be a useful precursor for catalytic hydrodehalogenation.[9] Palladium(II) complexes bearing ring expanded NHCs have been demonstrated to be effective catalysts for the intramolecular aerobic oxidative amination of alkenes,[8a] the Heck reaction of aliphatic and aromatic vinyl compounds with aryl bromides and chlorides,[8c] Suzuki–Miyaura cross-coupling of aryl bromide and chloride, and the catalytic dehalogenation of aryl chloride.[5a]

The pincer architecture, which provides a preorganised backbone featuring unique properties of high stability and modular variability has also been extensively studied in a wide range of fields.[14] Therefore, the inclusion of NHC donors within pincer systems has attracted an increasing level of interest, with a particular emphasis on their catalytic potential.[15] Multiple pincer-type NHC palladium complexes carrying different donor moieties have been prepared and employed as catalysts for a number of catalytic organic transformations (Fig. 1).[16] For example, the palladium complexes of phosphine/NHC-based pincer ligand $PC^{NHC}P$ (**B**) have been reported to be active catalysts for Suzuki coupling and Heck coupling reactions.[16b,16c] All these systems, however, contain NHC scaffolds based on five-membered heterocyclic rings.

Based on the reports mentioned above, it would be of interest to explore whether the introduction of ring expanded NHCs to a pincer framework will result in new pincer complexes displaying novel reactivity and enhanced catalytic activities. While to the best of our knowledge, the only report on the pincer ring expanded NHC complexes was about the phosphine functionalized dihydroperimidine-based NHC Rh, Ir complexes

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† Electronic supplementary information (ESI) available: ^1H NMR and ^{13}C NMR spectra of compounds **1–4**, DEPT 135 of **4b**, COSY of **4b**, HSQC of **4b**, and characterization data of the products of the catalytic Heck reaction. CCDC 1038971 and 1038972. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ra01706h

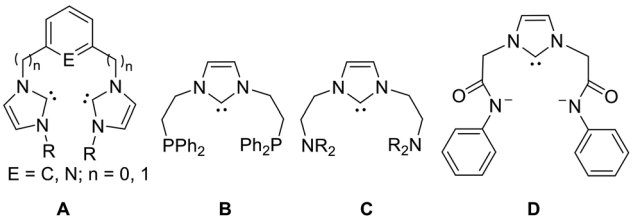


Fig. 1 NHC-based pincer ligands.

generated *via* chelate-assisted double C–H activation of substituted 2,3-dihydroperimidine proligands.[17] In view of the strong donating properties of the ring expanded NHCs and obvious rare of precedent studies on their pincer metal complexes, here we report the synthesis, characterization and catalytic activity of picolyl functionalized pincer six-membered NHC palladium complexes based on tetrahydropyrimidin-2-ylidenes. As expected, the pincer six-membered NHC palladium complexes proved remarkably stable toward air and moisture, and showed high catalytic activity toward Heck reaction. These results underline the high potential of this class of carbene ligands in catalysis.

Results and discussion

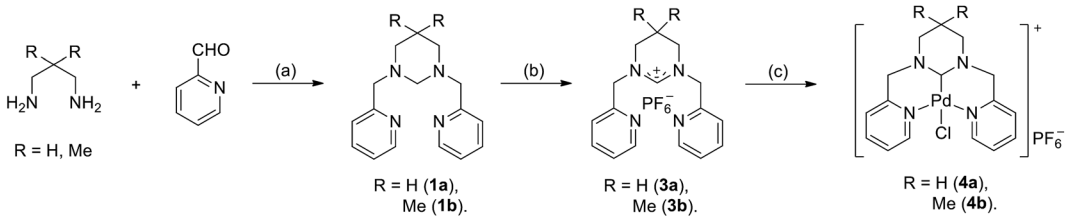
Synthesis of tetrahydropyrimidin-1-ium derivatives

In literature report, dehydrogenation of hexahydropyrimidine by NBS have been used quite often to synthesis tetrahydropyrimidin-1-iums salts, along with other procedures, including quarterisation of tetrahydropyrimidine, and direct cyclization of *N*,*N*′-dialkylpropan-1,3-diamines with methyl orthoformate catalyzed by acid.[18] It features the obvious advantages of high yield and repeatability, and easy purification of the product. Here we synthesized the pincer six-membered NHC precursors 1,3-dipicolyl-3,4,5,6-tetrahydropyrimidin-1-ium salts through the dehydrogenation of 1,3-disubstituted hexahydropyrimidine by NBS. The synthetic procedure is shown in Scheme 1. Condensation of 1,3-propandiamines with pyridine-2-formaldehyde in methanol produced Schiff bases in high yields. Reduction of the resulting Schiff bases with $NaBH_4$ lead to the formation of *N*,*N*′-dialkylpropan-1,3-diamines. The following reaction with aqueous formaldehyde in methanol afforded the 1,3-dipicolyl-hexahydropyrimidines (**1a–b**), which were then treated by NBS to obtain the tetrahydropyridin-1-ium bromides (**2a–b**). Anion exchange with NH_4PF_6 in ethanol/H_2O produced the corresponding tetrahydropyridin-1-ium hexafluorophosphates (**3a–b**). The ligands **3a–b** were obtained analytically pure in high yields after recrystallization. Their structures were fully characterized by various NMR techniques and mass spectra measurement, and in the case of complex **3b**, by X-ray crystallographic determination. In hexahydropyrimidines **1a–b**, the proton resonances of the methylene groups on picolyl occurred as singlet signals at 3.61 and 3.51, respectively. The resonances of N*CH*$_2$N protons appeared at 3.19 and 3.06 ppm, respectively. While in the corresponding tetrahydropyridin-1-ium salts (**2a–b**, **3a–b**), the proton resonances of the methylene groups on picolyl downfielded within the range of 4.86–4.84 ppm, and the resonances of N*CH*N protons downfielded within the range of 9.07–8.91 ppm, respectively. Single crystals of **3b** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether to a dichloromethane solution of **3b**.

Fig. 2 shows the molecular structure of **3b** with selected bond lengths and bond angles listed in the caption. The bonding within the pyrimidinyl ring indicates a pattern of delocalization that extends from N(1) to N(2) through C(1), with N(1)–C(1) [1.305(3) Å] and N(2)–C(1) [1.305(4) Å] being significantly shorter than those between N(1)–C(2) [1.463(4) Å] and N(2)–C(4) [1.465(4) Å]. The nitrogen donors of the picolyl groups are rotated away from C(1), showing that the donor arms rotating freely to take up positions suitable for chelation to a metal ligated at C(1).

Synthesis of pincer NHC palladium complexes

Following a similar literature report,[19] the pincer NHC–Pd complexes (**4a–b**) were prepared by heating the corresponding tetrahydropyridin-1-ium hexafluorophosphates (**3a** or **3b**) and $PdCl_2$ in the presence of $NaN(SiMe_3)_2$ as a base in pyridine at 140 °C (Scheme 1). The formation of the pincer NHC palladium complexes was observed from the studies of NMR spectra, showing the conspicuous absence of the N*CH*N resonances of the reacting cationic tetrahydropyrimidin-1-ium hexafluorophosphates and the appearance of the highly downfield shifted at 174.9 (**4a**) and 174.0 (**4b**) ppm in the ^{13}C NMR spectra, which should be attributed to the new Pd–$C_{carbene}$ resonance. In addition, the proton resonances of the methylene groups on picolyl occurred as a doublet of doublets at 5.30 and 4.80 (**4a**), and 5.38 and 4.78 (**4b**) ppm, respectively. This confirms the formation of the chelate ring, which makes the two protons of the methylene group on the picolyl magnetic unequal. At the same time, the pyridine proton resonances appeared within the ranges of 9.00–7.63 (**4a**) and 9.01–7.65 (**4b**) ppm, obviously downfielded compared to those of the tetrahydropyrimidin-1-ium hexafluorophosphates **3a** (8.63–7.41 ppm) and **3b**



Scheme 1 Synthesis of the ligands and pincer ring expanded NHC–Pd complexes. (a) (i) MeOH; (ii) $NaBH_4$, MeOH, 0–70 °C; (iii) HCHO, MeOH; (b) (i) NBS, DME; (ii) NH_4PF_6, EtOH/H_2O; (c) $PdCl_2$, $NaN(SiMe_3)_2$, pyridine, 140 °C.

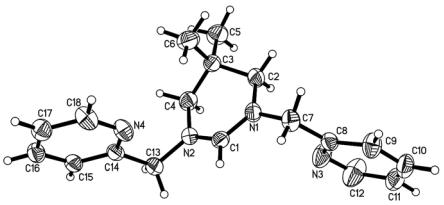


Fig. 2 Molecular structure of **3b** (counter ion omitted, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): N(1)–C(1) 1.305(3), N(1)–C(2) 1.463(4), N(1)–C(7) 1.458(4), N(2)–C(1) 1.305(4), N(2)–C(4) 1.465(4), N(2)–C(13) 1.458(3), N(1)–C(1)–N(2) 124.1(2), C(1)–N(1)–C(2) 120.3(2), C(1)–N(2)–C(4) 121.3(2), C(1)–N(1)–C(7) 120.1(2), C(2)–N(1)–C(7) 119.2(2), C(1)–N(2)–C(13) 119.9 (2), C(4)–N(2)–C(13) 118.6 (2).

(8.94–7.41 ppm), supporting the coordination of pyridine to the palladium center. The complex **4b** has been further characterized unambiguously by the single-crystal X-ray diffraction studies.

Slow diffusion of diethyl ether to a concentrated acetonitrile solution of **4b** produced single crystals suitable for X-ray diffraction analysis. The molecular structure is shown in Fig. 3, selected bond lengths and bond angles listed in the caption.

As shown in Fig. 3, the palladium atom in **4b** adopts a slightly distorted square-planar coordination bonded to carbene and two pyridinyl nitrogen donors, with the two fused six-membered chelate rings of the 'pincer' both exist in boat conformation. As complex **4b** represents the only example of a structurally characterized pincer six-membered NHC palladium complex that we are aware of, we compare the structure with pincer five-member NHC palladium complexes, and non-chelating six-membered NHC palladium complex, respectively. The Pd–$C_{carbene}$ bond distance of 1.975(5) Å is slightly longer than those found in the dipicolyl functionalized pincer NHC palladium bearing imidazol-2-ylidene (1.929(4) Å) or imidazolin-2-ylidene (1.936(2) Å),[20] while very similar to those found in the pincer NHC palladium complexes bearing diphosphine-substituted benzimidazolin-2-ylidene (1.974(5) Å and 1.980(6) Å) or imidazol-2-ylidene (1.983(7) Å) ligands reported by Hahn and Lee,[16b,c] and non-chelating six-membered NHC palladium complex reported by Cavell (1.983(3) Å) and Ghosh (1.9812(19) Å).[5a,19]

The Pd–N distances (2.037(4) Å and 2.035(4) Å) and Pd–Cl distance (2.3619(14) Å), are very similar to those of the picolyl functionalized NHC palladium carrying imidazol-2-ylidene (2.073(3) Å and 2.062(3) Å, 2.3737(3) Å) or imidazolin-2-ylidene (2.066(2) Å and 2.054(4) Å, 2.3688(5) Å).[20]

Catalytic studies

Initially, running the Heck reaction of bromobenzene and *n*-butyl acrylate catalyzed by 1.0% complex **4a** in DMA as a model reaction, a brief screening of the base and solvent was conducted (Table 1). Among the bases tested, organic base NEt_3 afforded the moderate yield. Inorganic bases *t*-BuOK, K_2CO_3, Na_2CO_3, and Cs_2CO_3 all produced very low yields (Table 1, entries 1–5). Tests of different solvents proved DMA to be the proper solvent. Reaction in DMF and toluene produced the target product in low yields, and the reaction in DME or dioxane did not occur at all (Table 1, entries 6–9). Increasing the catalyst loading to 2.5% raised yield to 98%.

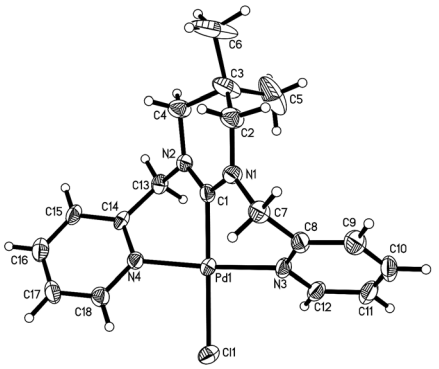
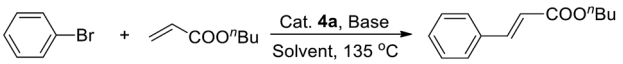


Fig. 3 Molecular structure of **4b** (counter ion omitted, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Pd(1)–C(1) 1.975(5), Pd(1)–N(3) 2.037(4), Pd(1)–N(4) 2.035(4), Pd(1)–Cl(1) 2.3619(14), N(1)–C(1) 1.334(7), N(1)–C(2) 1.452(7), N(1)–C(7) 1.468(7), N(2)–C(1) 1.316(7), N(2)–C(4) 1.467(8), N(2)–C(13) 1.453(7), C(1)–Pd(1)–Cl(1) 176.89(16), N(3)–Pd(1)–N(4) 175.83(18), C(1)–Pd(1)–N(3) 87.8(2), C(1)–Pd(1)–N(4) 88.08(19), N(3)–Pd(1)–Cl(1) 91.65(14), N(4)–Pd(1)–Cl(1) 92.51(13), N(1)–C(1)–N(2) 120.6(5), C(1)6N(1)–C(2) 122.0(5), C(1)–N(2)–C(4) 122.8(5), C(1)–N(1)–C(7) 120.1(2), C(2)–N(1)–C(7) 119.5(5), C(1)–N(2)–C(13) 119.0(5), C(4)–N(2)–C(13) 117.9(5).

Under the standard conditions, using Et_3N as base and DMA as solvent, the catalytic activity of complexes **4a** and **4b** towards Heck reaction of a series of aryl bromides with olefins (acrylate and styrene) were investigated and the results are summarized in Table 2. The results showed that complexes **4a** and **4b** presented almost equally catalytic efficiency, producing the target products in moderate to high yields. The substituents on the phenyl ring of the aryl bromides did not show any obvious

Table 1 Screening of the base and solvent effect



Entry[a]	Solvent	Base	Cat. (mol%)	Yield[b] (%)
1	DMA	Et_3N	1.0	54
2	DMA	*t*-BuOK	1.0	<5
3	DMA	K_2CO_3	1.0	<5
4	DMA	Na_2CO_3	1.0	<5
5	DMA	Cs_2CO_3	1.0	<5
6	DMF	Et_3N	1.0	40
7	DME	Et_3N	1.0	0
8	Toluene	Et_3N	1.0	36
9	Dioxane	Et_3N	1.0	0
10	DMA	Et_3N	1.5	70
11	DMA	Et_3N	2.5	98

[a] Reaction condition: 0.5 mmol bromobenzene, 0.75 mmol *n*-butylacrylate, 0.75 mmol base, 2 mL solvent, 135 °C, 12 h. [b] Yields determined by HPLC.

electronic effect, while the steric effect was obvious. In some cases of *ortho*-substituted phenyl bromide and 1-naphthyl bromide, comparatively low yields were obtained (Table 2, entries 10–15, 23 and 24).

The Heck reaction of phenyl bromide or *para*-substituted phenyl bromide with olefines was achieved in less time or lower catalyst loading, using pincer diphosphine-substituted imidazol-2-ylidene palladium complex,[16c] than the results reported here for complexes **4a** and **4b**. While for the Heck reaction of *ortho*-substituted phenyl bromide or 1-naphthyl bromide, moderate to good yields were obtained using complexes **4a** and **4b**. This suggests that there is considerable potential to improve the activity of these complexes, with the possibility of developing these complexes as catalysts for the Heck reaction of more substituted, sterically demanding substrates.

Experimental section

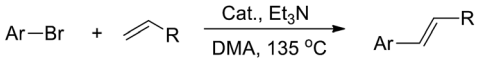
General consideration

All solvents and chemicals were used as received or dried with standard methods and freshly distilled prior to use if needed. NMR spectra were recorded at 25 °C on a 400 MHz Bruker spectrometer. Chemical shifts (δ in ppm, coupling constants J in Hz) were referenced to the residual solvent resonances. Elemental analyses were obtained from a thermo Flash 2000. ESI-MS spectra were recorded on a Bruker Esquire 3000.

Synthesis of 1,3-dipicolyl hexahydropyrimidines (1a–b)

A methanol solution (50 mL) containing pyridine-2-formaldehyde (30 mmol, 3.21 g) and 1,3-propanediamine (15 mmol, 1.11 g) were stirred at room temperature for 5 h. Infrared detection showed the disappearance of the carbonyl group. Additional 20 mL methanol was added and the mixture was put into an ice-bath, then $NaBH_4$ (120 mmol, 4.54 g) was added portion-wise for 1 h. The mixture was then warmed up to room temperature and then heated to 70 °C overnight. The solvent was then evaporated and the residue was poured into a mixture of water (40 mL) and CH_2Cl_2 (40 mL). The resulting suspension liquid was filtered and the filtrate was extracted by CH_2Cl_2 (20 mL) for 3 times. The combined organic phase was evaporated and the residue obtained was dissolved in methanol (10 mL) for the following reaction directly. The solution was then treated with aqueous HCHO solution (36.5%, 15 mmol). The mixture was stirred at room temperature for 6 h before being evaporated. Purification of the residue by flash chromatography (silica, acetone/CH_2Cl_2/Et_3N = 2/8/1, v/v/v) afforded the pure products.

Table 2 Heck reaction of aryl bromides with olefines



Entry[a]	Ar–Br	Olefines	Products	Yields[b] (%) Cat. **4a**	Cat. **4b**
1	C_6H_5Br	Methyl acrylate	5a	95	93
2	C_6H_5Br	*n*-Butyl acrylate	5b	94	90
3	C_6H_5Br	Styrene	5c	88	86
4	2-Me–C_6H_4–Br	Methyl acrylate	5d	89	88
5	2-Me–C_6H_4–Br	*n*-Butyl acrylate	5e	89	87
6	2-Me–C_6H_4–Br	Styrene	5f	76	80
7	4-Me–C_6H_4–Br	Methyl acrylate	5g	93	90
8	4-Me–C_6H_4–Br	*n*-Butyl acrylate	5h	91	89
9	4-Me–C_6H_4–Br	Styrene	5i	78	75
10	2,4-Me_2–C_6H_3–Br	Methyl acrylate	5j	82	80
11	2,4-Me_2–C_6H_3–Br	*n*-Butyl acrylate	5k	78	79
12	2,4-Me_2–C_6H_3–Br	Styrene	5l	70	68
13	2-OCH_3–C_6H_4–Br	Methyl acrylate	5m	81	83
14	2-OCH_3–C_6H_4–Br	*n*-Butyl acrylate	5n	78	80
15	2-OCH_3–C_6H_4–Br	Styrene	5o	68	72
16	4-OCH_3–C_6H_4–Br	Methyl acrylate	5p	91	88
17	4-OCH_3–C_6H_4–Br	*n*-Butyl acrylate	5q	88	85
18	4-OCH_3–C_6H_4–Br	Styrene	5r	76	80
19	4-$COCH_3$–C_6H_4–Br	Methyl acrylate	5s	95	94
20	4-$COCH_3$–C_6H_4–Br	*n*-Butyl acrylate	5t	89	87
21	4-$COCH_3$–C_6H_4–Br	Styrene	5u	79	76
22	1-$C_{10}H_7$–Br	Methyl acrylate	5v	87	84
23	1-$C_{10}H_7$–Br	*n*-Butyl acrylate	5w	65	60
24	1-$C_{10}H_7$–Br	Styrene	5x	70	68

[a] Reaction condition: 0.5 mmol aryl bromide 0.75 mmol olefine, 0.75 mmol Et_3N, 0.0125 mmol **4a** or **4b**, 2 mL solvent, 135 °C, 12 h. [b] Isolated yields.

1,3-Dipicolyl hexahydropyrimidine (1a). Yellow oil (3.50 g, 87%, based on the starting pyridine-2-formaldehyde). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37–8.35 (m, 2H, Py–H), 7.48–7.44 (m, 2H, Py–H), 7.32 (d, J = 7.6 Hz, 2H, Py–H), 6.99–6.96 (m, 2H, Py–H), 3.60 (s, 4H, picolyl–CH_2), 3.19 (s, 2H, pyrimidine–CH_2), 2.51 (s, 4H, pyrimidine–CH_2), 1.61 (s, 2H, pyrimidine–CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 148.8, 136.2, 122.8, 121.8, 75.2, 60.7, 52.2, 22.6 ppm. ESI-MS (m/z): 269.0 $[M + H]^+$.

5,5-Dimethyl-1,3-dipicolyl hexahydropyrimidine (1b). Yellow oil (3.96 g, 89%, based on the starting pyridine-2-formaldehyde). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35–8.34 (m, 2H, Py–H), 7.50–7.40 (m, 4H, Py–H), 6.99–6.95 (m, 2H, Py–H), 3.51 (s, 4H, picolyl–CH_2), 3.06 (bs, 2H, pyrimidine–CH_2), 2.03 (bs, 4H, pyrimidine–CH_2), 0.87 (s, 6H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 148.7, 136.3, 122.5, 121.8, 76.7, 64.6, 61.5, 31.2, 25.9 ppm. ESI-MS (m/z): 297.1 $[M + H]^+$, 319.2 $[M + Na]^+$.

Synthesis of 1,3-dipicolyl tetrahydropyrimidin-1-ium bromides (2a–b)

Hexahydropyrimidine (**1a** or **1b**, 5 mmol) was dissolved in DME (20 mL). NBS (5 mmol, 0.89 g) was added portion-wise and the resulting mixture was stirred at room temperature for 3 h, during which time a white precipitate formed. The precipitate was filtered and washed with DME. Crystallization of the precipitate from CH_2Cl_2/diethyl ether produced the pure products.

1,3-Dipicolyl tetrahydropyrimidin-1-ium bromides (2a). Colorless crystal (1.40 g, 81%). Mp: 158–159 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.91 (s, 1H, pyrimidine–CH), 8.63 (d, J = 4.8 Hz, 2H, Py–H), 7.93–7.89 (m, 2H, Py–H), 7.52 (d, J = 7.7 Hz, 2H, Py–H), 7.44–7.41 (m, 2H, Py–H), 4.85 (s, 4H, picolyl–CH_2), 3.33 (t, J = 5.8 Hz, 4H, pyrimidine–CH_2), 1.96 (t, J = 5.6 Hz, 2H, pyrimidine–CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 153.0, 149.4, 137.2, 123.4, 123.2, 58.8, 53.7, 43.1, 18.7 ppm. ESI-MS (m/z): 267.1 $[M - Br]^+$.

5,5-Dimethyl-1,3-dipicolyl tetrahydropyrimidin-1-ium bromides (2b). Colorless crystal (1.45 g, 77%). Mp: 239 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.07 (s, 1H, pyrimidine–CH), 8.63 (t, J = 2.4 Hz, 2H, Py–H), 7.93–7.89 (m, 2H, Py–H), 7.57 (d, J = 7.8 Hz, 2H, Py–H), 7.44–7.41 (m, 2H, Py–H), 4.86 (s, 4H, picolyl–CH_2), 3.07 (s, 4H, pyrimidine–CH_2), 0.82 (s, 6H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.5, 154.1, 150.1, 137.9, 124.1, 123.6, 58.9, 54.0, 27.2, 23.7 ppm. ESI-MS (m/z): 295.1 $[M - Br]^+$.

Synthesis of 1,3-dipicolyl tetrahydropyrimidin-1-ium hexafluorophosphates (3a–b)

NH_4PF_6 (3 mmol, 0.49 g) was dissolved in water (5 mL). The water solution was then combined with an ethanol (25 mL) solution of tetrahydropyrimidin-1-ium bromides (**2a** or **2b**, 2 mmol) and the mixture was then stirred at room temperature for 5 h. The solvent was then evaporated and the residue was poured into a mixture of water (10 mL) and CH_2Cl_2 (10 mL). The resulting solution was then extracted by CH_2Cl_2 (10 mL) for 3 times. The combined organic phase was then washed by water, dried and evaporated. Crystallization of the resulting white powder from CH_2Cl_2/diethyl ether produced the pure products.

1,3-Dipicolyl tetrahydropyrimidin-1-ium hexafluorophosphate (3a). Colorless crystal (0.78 g, 95%). Mp: 107–108 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.84 (s, 1H, pyrimidine–CH), 8.63 (d, J = 4.2 Hz, 2H, Py–H), 7.93–7.89 (m, 2H, Py–H), 7.52 (d, J = 7.8 Hz, 2H, Py–H), 7.44–7.41 (m, 2H, Py–H), 4.85 (s, 4H, picolyl–CH_2), 3.37–3.32 (m, 4H, pyrimidine–CH_2), 2.02–1.95 (m, 2H, pyrimidine–CH_2) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.6, 154.3, 150.1, 137.9, 124.0, 123.1, 59.0, 43.5, 18.8 ppm. ESI-MS (m/z): 267.2 $[M - PF_6]^+$.

5,5-Dimethyl-1,3-dipicolyl tetrahydropyrimidin-1-ium hexafluorophosphate (3b). Colorless crystal (0.83 g, 94%). Mp: 109 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.94 (s, 1H, pyrimidine–CH), 8.64 (d, J = 4.2 Hz, 2H, Py–H), 7.93–7.89 (m, 2H, Py–H), 7.54 (d, J = 7.7 Hz, 2H, Py–H), 7.44–7.41 (m, 2H, Py–H), 4.84 (s, 4H, picolyl–CH_2), 3.07 (s, 4H, pyrimidine–CH_2), 0.82 (s, 6H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.5, 154.0, 150.1, 137.9, 124.1, 123.6, 58.9, 54.0, 27.2, 23.7 ppm. ESI-MS (m/z): 295.1 $[M - PF_6]^+$.

Synthesis of 1,3-dipicolyl-3,4,5,6-tetrahydropyrimidin-2-ylidenes palladium complexes (4a–b)

A mixture of tetrahydropyrimidin-1-ium hexafluorophosphate (**3a** or **3b**, 2.0 mmol), $PdCl_2$ (2.0 mmol, 0.35 g) and $NaN(SiMe_3)_2$ (1.2 mL, 2.0 M in THF) in pyridine (6 mL) was heated at 140 °C for 12 h. The reaction mixture was then evaporated and purification of the residue by column chromatography (silica, $CHCl_3$/diethyl ether, gradient elution) produced the pure palladium complexes.

(1,3-Dipicolyl-3,4,5,6-tetrahydropyrimidin-2-ylidenes) PdCl·PF$_6$ (4a). Colorless crystal (0.64 g, 58%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.00–8.98 (m, 2H, Py–H), 8.22–8.18 (m, 2H, Py–H), 7.88 (d, J = 7.1 Hz, 2H, Py–H), 7.67–7.63 (m, 2H, Py–H), 5.30 (d, J = 15.1 Hz, 2H, picolyl–CH_2), 4.80 (d, J = 15.3 Hz, 2H, picolyl–CH_2), 3.58–3.48 (m, 4H, pyrimidine–CH_2), 1.92 (t, J = 5.8 Hz, 2H, pyrimidine–CH_2) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 174.9, 154.8, 154.0, 141.4, 125.6, 125.2, 61.6, 47.5, 20.8 ppm. Anal. cacld for $C_{16}H_{18}ClF_6N_4PPd$ (551.99): C, 34.74; H, 3.28; N, 10.13. Found: C, 34.56; H, 3.02; N, 9.89%.

(5,5-Dimethyl-1,3-dipicolyl-3,4,5,6-tetrahydropyrimidin-2-ylidenes)PdCl·PF$_6$ (4b). Light yellow solid (0.70 g, 60%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.01 (d, J = 4.9 Hz, 2H, Py–H), 8.23–8.19 (m, 2H, Py–H), 7.86 (d, J = 7.4 Hz, 2H, Py–H), 7.68–7.65 (m, 2H, Py–H), 5.38 (d, J = 15.1 Hz, 2H, picolyl–CH_2), 4.77 (d, J = 15.2 Hz, 2H, picolyl–CH_2), 3.28 (d, J = 3.2 Hz, 4H, pyrimidine–CH_2), 0.79 (s, 6H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 174.0, 154.9, 154.0, 141.5, 125.5, 125.2, 61.6, 58.7, 28.1, 23.5 ppm. Anal. cacld for $C_{18}H_{22}ClF_6N_4PPd$ (580.02): C, 37.20; H, 3.82; N, 9.64. Found: C, 36.93; H, 3.87; N, 9.49%.

General procedure for the Heck reaction

The Heck reaction was conducted in a parallel reactor. In a typical reaction, A Schlenk tube was charged with aryl bromides (0.5 mmol), acrylate or styrene (0.75 mmol), base (0.75 mmol), pincer NHC–Pd complex **4a** or **4b**, and solvent (2 mL). The

mixture was stirred at 135 °C for 12 h under Ar. After cooling, the reaction mixture was evaporated. Purification of the residue by flash chromatography on silica gel (hexanes/CH_2Cl_2 = 20 : 1) afforded the pure products, which were characterized by ^{1}H NMR and ^{13}C NMR. The analytical data of the products were shown in the ESI.†

X-ray diffraction studies

The crystal data of **3b** and **4b** (ESI†) were collected on a Xcalibur, Eos, Gemini diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals were kept at 291.15 K during data collection. Using Olex2,[21] the structure was solved with the ShelXS[22] structure solution program using Direct Methods and refined with the ShelXL[22] refinement package using Least Squares minimization.

Conclusions

Two novel NCN pincer ring expanded six-membered NHC palladium complexes based on 1,3-dipicolyl-3,4,5,6-tetrahydropyrimidin-2-ylidenes have been synthesized *via* the direct metallation of the corresponding tetrahydropyridin-1-ium salts. The structure were characterized unambiguously X-ray structure analysis, showing that the complex adopts a slightly distorted square-planar coordination with the two fused six-membered chelate rings of the 'pincer' both exist in boat conformation. Catalytic activity investigation showed that the complexes catalyzed the Heck reaction of aryl bromides with acrylate/styrene efficiently in DMA when using Et_3N as base. The catalytic activity of this novel type of NHC complexes towards other organic transformation are currently in progress in our group.

Acknowledgements

The authors are grateful to the National Natural Science Foundation of China (nos: 21172055 and 21302042), the Program for Innovative Research Team from Zhengzhou (131PCXTD605), and the Plan for Scientific Innovation Talent of Henan University of Technology (11CXRC10) for financial support to this work.

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