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Synthesis and characterization of Palladium(II) complexes of chiral chelating NHC–*N* donor hybrid ligands

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ABSTRACT

A new class of palladium(II) complexes of chelating NHC–*N* donor hybrid ligands, such as NHC–sulfonamide (**6**), NHC–phenoxyimine (**11**), NHC–phenylimine (**14**), and NHC–amine (**15**) have been successfully synthesized in modest yields from 1,1′-binaphthyl-2,2′-diamine (BINAM). These complexes have been characterized by all the spectroscopic data, and the structures of **6**, **11**, and **14** were also confirmed by single-crystal X-ray diffraction studies, exhibiting a tridentate chelating motif around the palladium center.

1. Introduction

Since Arduengo et al. isolated a stable crystalline *N*-heterocyclic carbene (NHC) and first explored its complexation chemistry in the early 1990s,[1] NHCs and their relatives as ancillary ligands for metal-mediated catalysis have attracted increasing attention recently.[2] Thus far, significant advances have been achieved for their applications in achiral catalytic chemistry particularly in Ru-catalyzed metathesis[3] and Pd-mediated cross-coupling reactions,[2j,4] although the successful examples for their asymmetric catalyzes are still limited.[2e,g,k,5] Previously, we have synthesized a series of axially chiral chelating bis(NHC)–Pd(II) complexes **1** and their derivatives from 1,1′-binaphthyl-2,2′-diamine (BINAM) and successfully applied them in several asymmetric catalytic reactions (Fig. 1).[5] However, in agreement with earlier work,[2h,6] these bis(NHC)–Pd(II) complexes displayed poor activities in some reactions, such as asymmetric allylic alkylation,[7] which has been developed commonly using chiral phosphine ligands. Aiming at improving these catalysts' activities and selectivities, these BINAM based NHC ligands should be subjected to the corresponding modifications, and the initial work is commenced on the basis of following considerations.

With respect to electronic features, NHCs have typical strong σ-donor but poor π-acceptor properties[8] in comparison to those of widely used phosphine ligands. Firstly, the strong σ-donation will promote oxidative addition to the metal center and stabilize high oxidation state of metal-containing transition states or the intermediates, but as poor π-acceptors NHCs will reduce the rate of reductive elimination or reactions involving an electrophilic intermediate (e.g., transmetallation, nucleophilic attack).[2h] This may be one potential reason that bis(NHC)–Pd(II) complexes **1** could facilitate the Et_2Zn-mediated enantioselective umpolung allylation of aldehydes but they were ineffective catalysts in the allylic alkylation of nucleophiles.[5e,6d,7] Secondly, strong σ-donation of NHCs often allows the formation of strong NHC–metal bonds[2k,9] and prevents decomposition of these catalysts during the reaction as well as the dissociation of NHC–metal bond (usually upon heating). The resulting stable NHC–metal active species could restrict the number of accessible transition states in a reaction, which may be beneficial to understand the mechanistic details and improve the catalytic activities and selectivities. However, the paucity of a typical ligand coordination–dissociation process was detrimental to giving flexible coordination sites for substrates or products on the metal center, possibly resulting in an inferior catalytic activity.[10]

In addition, chiral NHCs have been most commonly prepared by incorporating chirality at the *N*-substituents or at the C4 and C5 positions of the *N*-heterocyclic framework.[2] While the latter

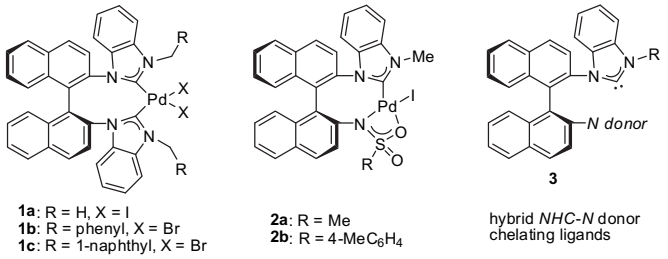

Fig. 1. Bis(NHC)–Pd(II) complexes and hybrid NHC–*N* donor ligands.

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expresses chirality via the bulky *N*-substituents exerting steric influence at the metal center, the chiral information at the *N*-substituents may be imparted to the metal complex by itself (e.g., monodentate NHC) or via chelating motif (e.g., chelating di-NHCs or NHC–hybrid ligands). Since bis(NHC)–metal complexes tended to exhibit poor catalytic activities in some reactions, NHC–hybrid ligands with adjustable electronic diversity may be a better choice as privileged ancillary ligands to improve the catalytic efficiency of their chelating derivatives.[2h,11] Previously, we have synthesized chelating hybrid NHC–sulfonamide–Pd(II) complexes **2** and found that they displayed more promising catalytic activities than bis (NHC)–Pd(II) counterpart **1a** in Suzuki coupling reaction.[12a] Herein we wish to report the synthesis and characterization of palladium (II) complexes of chiral chelating NHC–*N* donor hybrid ligands **3** (Fig. 1), with *N*-donors, such as sulfonamide, imine, and amine.

2. Results and discussion

2.1. Synthesis of palladium(II) complex of NHC–sulfonamide hybrid ligand

Mono-benzimidazole compound (*S*)-**4** was prepared from (*S*)-binaphthyl-2,2′-diamine (BINAM) according to our previously reported procedures with a sequence of palladium catalyzed coupling, methanesulfonylation of primary amine, palladium catalyzed hydrogenation of nitro group, and ring closing with triethyl orthoformate (see the Supplementary data).[12a] By refluxing of **4** (139 mg, 0.3 mmol) and benzylbromide (0.36 mL, 10 equiv) in 1,4-dioxane (3 mL) for several hours, lots of white solids were precipitated in the reaction system. After completely consuming **4**, the resulting suspension was cooled to room temperature and filtered through Celite. The obtained solids were washed with *n*-hexane for three times to give mono-benzimidazolium salt **5** without any further purification. When NHC precursor **5** (160 mg, 0.25 mmol) and $Pd(OAc)_2$ (57 mg, 0.25 mmol) were stirred at room temperature in THF (12 mL) in the presence of Cs_2CO_3 (82 mg, 0.25 mmol), palladium(II) complex **6** of chelating NHC–sulfonamide hybrid ligands was successfully obtained in 38% yield. The low isolated yield was possibly attributed to the side reaction of Pd $(OAc)_2$ with excessive benzylbromide inevitably incorporated in the solids of **5** (Scheme 1).

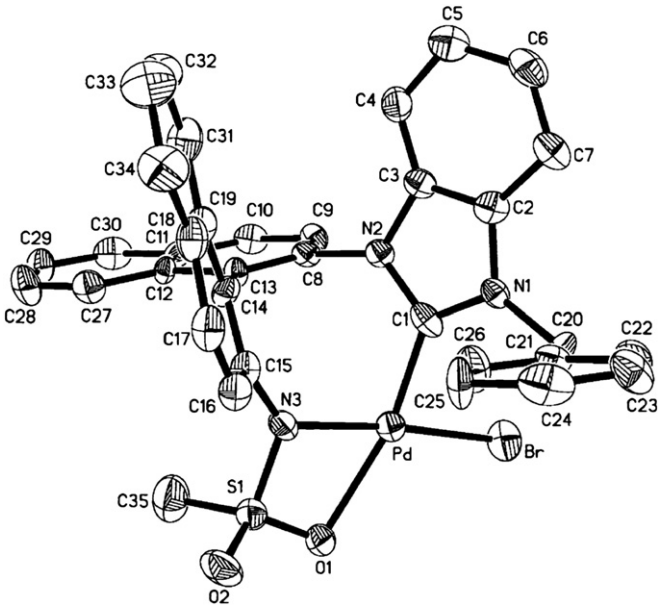
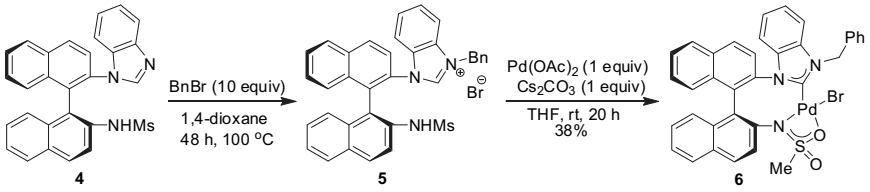


Fig. 2. ORTEP drawing of NHC–Pd(II) complex **6** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Pd–C1=1.931(8), Pd–N3=2.013(7), Pd–O1=2.231(5), Pd–Br=2.3978(10), S1–O2=1.418(6), S1–O1=1.444 (6), S1–N3=1.593(6), N3–C15=1.413(9); C1–Pd–N3=96.1(3), C1–Pd–O1=162.0(3), N3–Pd–O1=66.2(2), C1–Pd–Br=90.5(3), N3–Pd–Br=173.21(18), O1–Pd–Br=107.28 (16), N1–C1–N2=108.0(7).

(1), S(1), and N(3) atoms (S(1)–N(3) bond length: 1.593(6) Å). This NHC–sulfonamide ligand is definitely chelating and coordinates to palladium center through NHC carbon, sulfonamide nitrogen, and one of two oxygen atoms. Although all structural parameters of complex **6** are similar to the analogue **2a**, the bond lengths of Pd–C (1) (1.931(8) Å) and Pd–Br (2.3978(10) Å) are clearly shorter than that of bis(NHC)–Pd(II) complex **1c**, with a length of 1.997(7) Å and 2.4876(11) Å for the cis bonds Pd(1)–C(1) and Pd(1)–Br(1), respectively.[5e] This may reflect the stronger *trans*-influence exerted by the NHC moiety relative to the sulfonamide due to their electronic differentiation.

In comparison to sulfonamide anion, *N*=C double bond is a prominent *N*-donor with unchanging the valance of metal center,



Scheme 1. General procedure for the synthesis of palladium(II) complex **6**.

This NHC–Pd(II) complex **6** was air and moisture stable in solid or solution state and even under the heating conditions. Characteristic ^{1}H NMR spectroscopic data for complex **6** included one singlet signal at δ 2.17 ppm attributable to CH_3 group and two doublet signals at δ 5.35 and 6.54 ppm for the two $PhCH_2$ protons, which were separated and coupled mutually due to the restricted rotation about the $N–CH_2Ph$ bond. Single crystals of complex **6** suitable for an X-ray diffraction study were grown from solutions of (*R*)-**6** in mixed petroleum ether/CH_2Cl_2 (1/1). The molecular structure and selected data are shown in Fig. 2,[13] which reveals a similar distorted-square-planar geometry around the metal center in comparison to complex **2a**. The S(1)–O(1) bond length (1.444 (6) Å) is longer than that of S(1)–O(2) (1.418(6) Å, a typical S=O double bond length), suggesting partial π-conjugation between O which is generally introduced in ancillary ligands, such as Schiff base analogues,[14] oxazoline,[15] and pyridyl pincer-type ligands[16]. Herein the subsequent aim was to prepare NHC–phenolimine and NHC–phenylimine hybrid ligands and their palladium complexes based on the BINAM scaffold (vide infra).

2.2. Synthesis of palladium(II) complex of NHC–phenoxyimine hybrid ligand

Under the acidic conditions, benzimidazole–primary amine **8** was prepared by the hydrolysis of acetyl compound **7**, which was synthesized according to the reported literature (see the Supplementary data).[12b] Refluxing of compound **8** (578 mg,

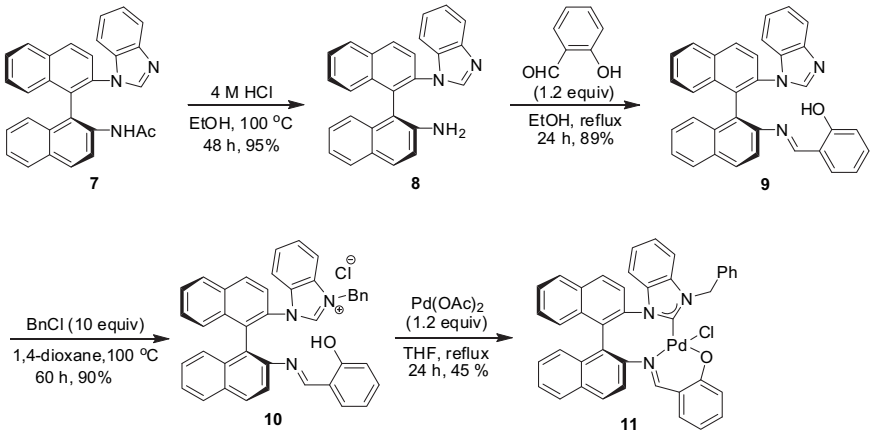
1.5 mmol) and salicylaldehyde (0.19 mL, 1.8 mmol) conveniently afforded phenolimine **9**, which can be purified by a silica gel flash column chromatography without decomposition. The ^{1}H NMR spectra of compound **9** exhibited a signal at ca. δ 12 ppm indicating an intramolecular hydrogen bonding between the phenol *OH* and imine nitrogen atom.[11f,17] Benzimidazolium salt **10** was obtained via a similar work-up for **5** (see the Supplementary data), and without using benzylbromide to avoid a possible substitution at the phenol hydroxy group. Then the reaction of **10** (185 mg, 0.3 mmol) and $Pd(OAc)_2$ (81 mg, 0.36 mmol) occurred smoothly to give palladium(II) complex **11** as a yellow solid in 45% yield, where $Pd(OAc)_2$ provided acetate anion as a weak base for the deprotonation of benzimidazolium and phenol moieties.

The structure of complex **11** was characterized by all the spectroscopic data, and ^{1}H NMR spectra showed several typical features. Two CH_2Ph protons were also separated at different chemical shift (δ 5.36 and 6.66 ppm) and coupled mutually with a coupling constant of 16.0 Hz. The absence of a signal at ca. δ 12 ppm of compound **9** suggested a cleavage of the hydrogen bonding interaction between the *OH* and imine nitrogen atoms. The ESI-MS signal at 684.1 for $[M^+-Cl]$ of complex **11** was consistent with the structure depicted in Scheme 2, with the phenoxy group participating in the coordination about the metal center.

attempted to prepare NHC–phenylimine hybrid ligands and their palladium complexes.

2.3. Synthesis of palladium(II) complex of NHC–phenylimine hybrid ligand

In the presence of 4 Å MS (1.0 g), refluxing of the primary amine **8** (385 mg, 1.0 mmol) and benzaldehyde (0.13 mL, 1.3 mmol) in 5 mL of dry toluene offered phenylimine **12** without further purification until the completion of **8** by ^{1}H NMR spectroscopic monitoring. Then the benzimidazolium salt **13** was obtained from **12** via a similar work-up for **10** and using benzylbromide instead (see the Supplementary data). It should be noted that to some extent the imine moiety of **12** or **13** was inevitably hydrolyzed under the reaction conditions. We next subjected benzimidazolium salt **13** (193 mg, 0.3 mmol) to react with $Pd(OAc)_2$ (101 mg, 0.45 mmol) under the modified standard conditions and fortunately a palladium complex **14** was successfully isolated in up to 45% yield during our initial experiments. The addition of KBr (143 mg, 4 equiv) was intended to circumvent the potential ligand exchange between acetate and bromide anions and subsequent separation problems in the reaction. However, it was found that in the subsequent investigations, complex **14** was obtained in only 18% yield and the



Scheme 2. General procedure for the synthesis of palladium(II) complex **11**.

Furthermore, a single-crystal X-ray diffraction study confirmed this coordination motif of complex **11**, and the molecular structure was shown in Fig. 3.[18] Two molecules of **11** and one molecule of H_2O are present in the asymmetrical unit of single crystals. The geometry around the palladium center is also distorted-square-planar comprising *trans* C^{NHC}–O^{Ph} and N^{imine}–*Cl* moieties with angles of C(1)–Pd(1)–O(1)=169.8(6)° and N(3)–Pd(1)–Cl(1)=174.1(5)°, respectively. While both bond length and angle data of the NHC moiety are similar to that of previously reported NHC–Pd(II) complexes, those for the palladacycle of the phenoxyimine moiety are also unexceptional as compared with that of known palladium(II) Schiff base complexes,[11f,19] for example, Pd(1)–N(3)=2.027(14) Å, Pd(1)–O(1)=2.040(10) Å, N(3)–C(28)=1.32(2) Å, O(1)–C(30)=1.315(15) Å, and N(3)–C(28)–C(29)=125.9(17)°.

Since the tridentate chelating NHC–imine–$O^{phenoxy}$ palladium (II) complex **11** commonly could provide only one coordination site for the reaction, bidentate chelating NHC–imine hybrid ligand may be a promising alternative in the reactions where flexible coordination sites at metal center for substrates or products are required to achieve good activity and selectivity.[2h,11b] Thus we next

major product of the reaction was an another palladium complex **15** isolated in 31% yield with a higher polarity than **14**. After carefully examining the experimental results, such as the thin layer chromatography, it was suggested that complexes **14** and **15** were actually always present in all reaction systems along with varying ratios of **14**/**15**. Aiming at clearly understanding the process, the next important work was to determine the structures of complexes **14** and **15**.

While the ^{1}H NMR spectra of complex **14** only provided two characteristic doublet signals at δ 5.23 and 6.57 ppm attributable to the two separated CH_2Ph protons, its MS spectroscopic data suggested that **14** was not the simple NHC–imine chelating moiety with two bromide anion coordinating at the palladium center.[11b] The ESI-MS signal at 668.1 for $[M^+-Br]$ of complex **14** was consistent with the structure depicted in Scheme 3, where an NHC–imine–C^{phenyl} chelating moiety about the metal center was assumed with one coordinated bromine atom. This structure was further confirmed by an X-ray diffraction study of the single crystals grown from evaporation of a mixed petroleum ether/EtOAc (4/1) solution of **14**. The molecular structure and selected bond distances and angles are shown in Fig. 4.[20] In comparison to the

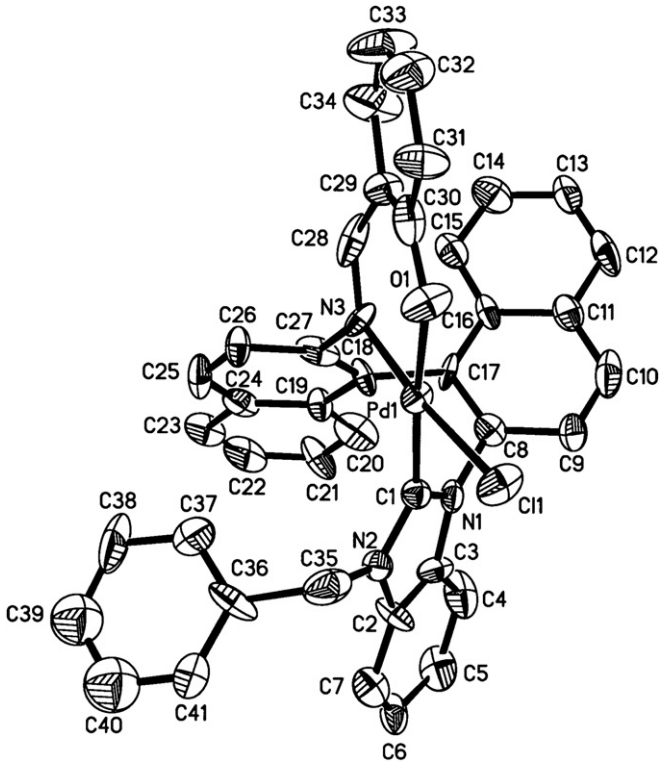


Fig. 3. ORTEP drawing of NHC–Pd(II) complex **11** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Pd1–C1=1.941(16), Pd1–N3=2.027(14), Pd1–O1=2.040(10), Pd1–Cl1=2.312(5), C1–N1=1.40(2), C1–N2=1.328(18), N3–C28=1.32(2), N3–C27=1.502(19), O1–C30=1.315(15); C1–Pd1–N3=99.1(6), C1–Pd1–O1=169.8(6), N3–Pd1–O1=91.0(5), C1–Pd1–Cl1=82.5 (5), N3–Pd1–Cl1=174.1(5), O1–Pd1–Cl1=87.5(4), N1–C1–N2=102.9(14), N3–C28–C29=125.9(17).

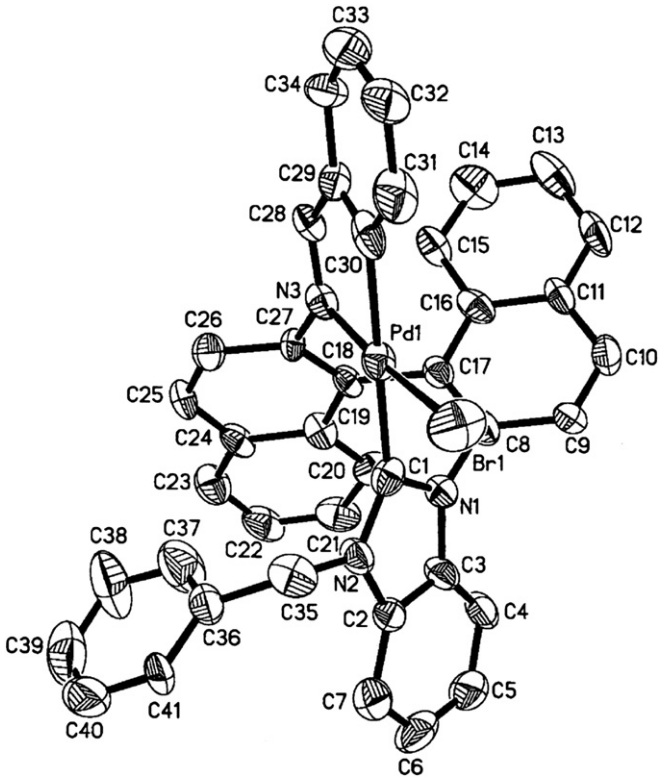
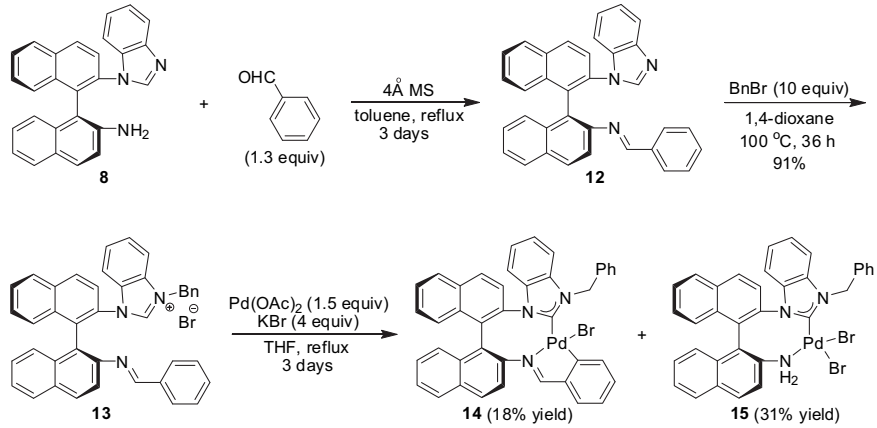


Fig. 4. ORTEP drawing of NHC–Pd(II) complex **14** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Pd1–C1=2.040(12), Pd1–N3=2.044(10), Pd1–C30=2.054(12), Pd1–Br1=2.4104(17), C1–N1=1.400(15), C1–N2=1.366(16), N3–C28=1.277(14), N3–C27=1.429(19); C1–Pd1–N3=97.4(4), C1–Pd1–C30=175.4(5), N3–Pd1–C30=78.4(5), C1–Pd1–Br1=87.5(3), N3–Pd1–Br1 =174.9(3), C30–Pd1–Br1=96.6(4), N2–C1–N1=102.2(9), N3–C28–C29=115.9(11).



Scheme 3. General procedure for the synthesis of palladium(II) complexes **14** and **15**.

chelating NHC–imine–$O^{phenoxy}$ palladium(II) complex **11**, complex **14** has a more crowded palladacycle including the angles for N(3)–Pd(1)–C(30) of 78.4(5)° and N(3)–C(28)–C(29) of 115.9(11)°, with that of **11** showing N(3)–Pd(1)–O(1)=91.0(5)° and N(3)–C(28)–C (29)=125.9(17)°, respectively. Other bond lengths and angles are not considered exceptionally, for example, with Pd(1)–N(3)=2.044 (10) Å and N(3)–C(28)=1.277(14) Å similar to related PdCl (NHC–imine–$O^{phenoxy}$) complex **11**, and with the Pd(1)–C(1)= 2.040(12) Å and Pd(1)–C(30)=2.054(12) Å distances being similar to the previously reported cyclometalated *cis*-chelated bis(NHC)–C^{phenyl} palladium(II) complexes.[21] The formation of this palladium (II) complex **14** of tridentate chelating NHC–imine–C^{phenyl} ligand was possibly attributed to a metalation process involving an *ortho*-mediated C–H activation of the phenylimine moiety in the presence of $Pd(OAc)_2$.[22] Complex **14** was an air and moisture stable solid and soluble in common organic solvents except saturated hydrocarbons without obvious decomposition observed even in 6 months.

Since the coordination moiety of **14** was unambiguously determined, it was much easier to determine the structure of complex **15** from the spectroscopic data. Being similar to complex **14**, the ^{1}H NMR spectra of **15** also provided two characteristic doublet signals

at δ 5.30 and 6.46 ppm for the two separated CH_2Ph protons with a coupling constant of 16.0 Hz. Integrations of ^{1}H NMR spectra for **15** significantly displayed that the imine moiety has been decomposed in comparison to **14**, along with two broad signals at δ 4.66 and 5.42 ppm present for the generated NH_2 group. Being different from the precursor **8** with NH_2 signal at δ 3.55 ppm as a singlet, the obvious downfield shift and separation of the two NH_2 protons indicated a coordination of NH_2 moiety to the metal center for complex **15**. Therefore, a structure of **15** was initially proposed as shown in Scheme 3, which was further corroborated by an ESI-MS signal at 660.0 for [M^+−Br]. Complex **15** was soluble in common organic solvents, such as ethyl acetate except saturated hydrocarbons, indicating that an intermolecular hydrogen bonding was not present here for the NH_2 group, which may result in a one-dimensional chain motif with poor solubility as reported in the literature.[11d] Unfortunately, the growth of single crystals of **15** suitable for an X-ray diffraction study has not been successful to date. The still unclear details for the formation of **15** and the synthesis of other NHC–amine derivatives as hybrid ligands for palladium(II) complexes are currently under investigation in our laboratory. We believe that imine was not stable before it coordinated with Pd salt. Therefore, the amine derived from the decomposition of imine coordinated to the Pd center to give the corresponding complex **15**.

3. Conclusion

In conclusion, we have successfully synthesized a new class of palladium(II) complexes of NHC–*N* donor hybrid ligands, such as NHC–sulfonamide (**6**), NHC–phenoxyimine (**11**), and NHC–phenylimine (**14**), which were characterized by all the spectroscopic data and confirmed by single-crystal X-ray diffraction studies, where all of them displayed a tridentate chelating motif around the palladium center exhibiting NHC–*N*–*O* (Pd), NHC–imine–$O^{phenoxy}$ (Pd) and NHC–imine–C^{phenyl} (Pd), respectively. During the preparation for **14**, a palladium(II) complex **15** of NHC–amine hybrid ligand was also obtained with a proposed bidentate chelating motif about the metal center. Efforts are underway for the synthesis of other NHC–amine derivatives as hybrid ligands and the application of all these palladium(II) complexes of chelating NHC–*N* donor ligands in metal-mediated transformations as well as asymmetric catalysis.

4. Experimental section

4.1. General remarks

Unless otherwise stated, all reactions and manipulations were performed using standard Schlenk techniques. Using standard methods, THF and toluene were dried by distillation over sodium, and dry CH_3CN and CH_2Cl_2 were distilled over CaH_2. Other commercially obtained solvents and reagents were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded by using a Varian Mercury vx 300 MHz or Bruker 400 MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. ^{1}H NMR and ^{13}C NMR chemical shifts were referenced to 0.00 ppm (TMS) and 77.0 ppm ($CDCl_3$), respectively. Coupling constants (J) are given in hertz. Mass spectra were recorded on the HP-5989 instrument by ESI/MALDI methods. Infrared spectra were recorded on a Perkin–Elmer PE-983 spectrometer with absorption in cm^{-1}. Melting points were measured on a Yanagimoto micro melting apparatus and uncorrected. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin–Elmer 341 MC digital polarimeter with a 10 cm cell (c given in g per 100 mL) and $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. Single-crystal X-ray diffraction analysis was performed by using a Bruker Smart-1000 X-ray diffractometer. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out by using 300–400 mesh silica gel at increased pressure.

4.2. General procedure for the synthesis of palladium(II) complex 6

The precursor of mono-benzimidazole compound **4** was prepared from chiral binaphthyl-2,2′-diamine (BINAM) according to our previously reported procedures.[12a] It is a known compound.[12a] White solid; mp 136–138 °C; $[\alpha]_D^{20}$ −244 (c 0.25, $CHCl_3$); IR (direct irradiation) ν 2919, 2850, 1488, 1454, 1320, 1235, 1155, 984, 819, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.91 (s, 3H), 5.99 (br, 1H), 7.15 (d, J=8.4 Hz, 1H), 7.19 (d, J=8.4 Hz, 1H), 7.25–7.31 (m, 2H), 7.34–7.47 (m, 4H), 7.52 (d, J=8.0 Hz, 1H), 7.63–7.67 (m, 1H), 7.69 (d, J=7.6 Hz, 1H), 7.76 (d, J=9.2 Hz, 1H), 7.82 (d, J=8.8 Hz, 1H), 7.89 (d, J=7.6 Hz, 1H), 7.93 (d, J=8.8 Hz, 1H), 8.10 (d, J=8.0 Hz, 1H), 8.27 (d, J=9.2 Hz, 1H).

Compound **4** (139 mg, 0.3 mmol) and benzylbromide (0.36 mL, 10 equiv) were refluxed in 1,4-dioxane (3 mL) until that **4** was completely consumed by TLC monitoring. If lots of white solids were precipitated in the reaction system, the resulting suspension was cooled to room temperature and filtered through Celite to obtain solids. Alternatively, the resulting reaction mixture could be concentrated and dissolved in ca. 0.5 mL of CH_2Cl_2, then the solution was dropped into 30 mL of petroleum ether with vigorously stirring to precipitate lots of white solids followed by the filtration through Celite. The obtained solids via above-mentioned two approaches were washed with n-hexane for three times to give benzimidazolium salt **5** in almost quantitative yield without any further purification.

To a flame-dried Schlenk tube equipped with a septum and stirring bar were added NHC precursor **5** (160 mg, 0.25 mmol), Pd$(OAc)_2$ (57 mg, 0.25 mmol), and Cs_2CO_3 (82 mg, 0.25 mmol). The tube was placed under argon atmosphere and then dry THF (12 mL) was added. After stirring at room temperature for 20 h followed by filtering through Celite, volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 3/1) to give **6** as a yellow solid in 38% yield. Single crystals of complex **6** suitable for an X-ray diffraction study were grown from the solution of (*R*)-**6** in mixed petroleum ether/CH_2Cl_2 (1/1). Mp >300 °C (dec); $[\alpha]_D^{20}$ −275 (c 0.25, $CHCl_3$); IR (direct irradiation) ν 3065, 2923, 2853, 1415, 1402, 1268, 1052, 1041, 883, 752, 739, 701, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.17 (s, 3H), 5.35 (d, J=16.0 Hz, 1H), 6.54 (d, J=15.6 Hz, 1H), 6.96–7.04 (m, 7H), 7.11 (t, J=8.4 Hz, 2H), 7.21–7.31 (m, 4H), 7.36 (t, J=8.0 Hz, 1H), 7.55 (d, J=8.8 Hz, 1H), 7.62–7.68 (m, 2H), 7.72 (d, J=8.8 Hz, 1H), 7.86 (d, J=8.8 Hz, 1H), 8.15 (d, J=8.4 Hz, 1H), 8.35 (d, J=8.8 Hz, 1H); LRMS (ESI) m/e 658.0 [M^+−Br]; HRMS (MALDI) calcd for [$C_{35}H_{26}BrN_3O_2S^{102}Pd$−Br] requires 654.0802, found 654.0796 [M^+−Br].

4.3. General procedure for the synthesis of palladium(II) complex 11

The precursor of mono-benzimidazole compound (*S*)-**7** was prepared from (*S*)-BINAM according to our previously reported procedures.[12b] It is a known compound.[12b] White solid; mp 228–230 °C; $[\alpha]_D^{20}$ −218 (c 0.25, $CHCl_3$); IR (direct irradiation) ν 3223, 3052, 2929, 1656, 1597, 1500, 1488, 1453, 1364, 1275, 1232, 865, 812, 742, 715 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.64 (s, 3H), 6.66 (s, 1H), 7.09–7.11 (m, 1H), 7.24–7.30 (m, 5H), 7.37–7.43 (m, 3H), 7.62–7.68 (m, 2H), 7.79 (d, J=8.8 Hz, 1H), 7.83–7.88 (m, 2H), 8.08 (d, J=8.0 Hz, 1H), 8.22–8.28 (m, 2H).

Acetyl compound **7** (2.14 g, 5.0 mmol) was refluxed in 4 M HCl (50 mL) and ethanol (80 mL) for 1–2 days. The reaction system was cooled to room temperature and neutralized to pH>7 with saturated

NaOH, which was followed by the extraction with CH_2Cl_2 and dried over anhydrous sodium sulfate. The crude product was purified by the flash column chromatography (eluent: petroleum ether/EtOAc, 1/1) to give benzimidazole–primary amine **8** as a white solid in 95% yield. Mp 134–136 °C; $[\alpha]_D^{20}$ −27 (*c* 0.25, $CHCl_3$); IR (direct irradiation) *ν* 3461, 3370, 3318, 3196, 2956, 2925, 2853, 1619, 1488, 1453, 1382, 1285, 1235, 1146, 816, 740, 623 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) *δ* 3.55 (s, 2H), 6.89–6.93 (m, 2H), 7.04–7.12 (m, 2H), 7.17–7.23 (m, 2H), 7.38–7.45 (m, 3H), 7.58–7.68 (m, 5H), 7.77 (d, *J*=8.8 Hz, 1H), 8.05 (d, *J*=8.4 Hz, 1H), 8.17 (d, *J*=8.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) *δ* 109.7, 111.4, 117.7, 120.0, 122.09, 122.14, 123.0, 124.4, 126.4, 126.6, 127.1, 127.6, 128.1, 128.3, 129.8, 129.9, 130.3, 133.1, 133.3, 133.5, 133.7, 134.2, 142.5, 142.9, 143.0; LRMS (ESI) *m*/*e* 386.2 [M^++H]; HRMS (ESI) calcd for [$C_{27}H_{19}N_3$+H] requires 386.1657, found 386.1660 [M^++H].

Compound **8** (578 mg, 1.5 mmol) and salicylaldehyde (0.19 mL, 1.8 mmol) were refluxed in ethanol (40 mL) for 24 h and then cooled to room temperature. After removing the solvent under reduced pressure, the crude product was conveniently purified by a silica gel column chromatography (eluent: petroleum ether/EtOAc, 2/1) to afford phenolimine **9** as a yellow solid in 89% yield. Mp 133–135 °C; $[\alpha]_D^{20}$ −197 (*c* 0.25, $CHCl_3$); IR (direct irradiation) *ν* 3054, 2924, 2852, 1607, 1568, 1487, 1452, 1281, 1235, 1203, 1189, 1150, 818, 799, 742, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) *δ* 6.67–6.74 (m, 3H), 6.86 (d, *J*=6.8 Hz, 1H), 7.00 (t, *J*=7.6 Hz, 1H), 7.17–7.19 (m, 3H), 7.26–7.29 (m, 3H), 7.35–7.38 (m, 3H), 7.47–7.48 (m, 1H), 7.56 (d, *J*=7.6 Hz, 1H), 7.64 (d, *J*=8.8 Hz, 1H), 7.74–7.78 (m, 2H), 7.97–7.99 (m, 2H), 8.12 (d, *J*=8.8 Hz, 1H), 11.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) *δ* 110.4, 116.6, 116.7, 118.6, 119.0, 119.5, 122.0, 122.8, 124.2, 125.8, 125.9, 126.6, 126.9, 127.2, 127.3, 127.4, 128.3, 128.4, 130.0, 130.5, 131.5, 132.1, 132.2, 132.8, 132.9, 133.0, 133.3, 133.7, 134.1, 142.4, 142.6, 143.5, 160.4, 162.5; LRMS (ESI) *m*/*e* 490.2 [M^++H]; HRMS (ESI) calcd for [$C_{34}H_{23}N_3O$+H] requires 490.1919, found 490.1902 [M^++H].

Compound **9** (196 mg, 0.4 mmol) and benzylchloride (0.46 mL, 10 equiv) were refluxed in 1,4-dioxane (2 mL) until that **9** was completely consumed by TLC monitoring. Benzimidazolium salt **10** as a yellow solid was obtained in 90% yield via a similar work-up for **5** from the resulting reaction mixture without any further purification.

Under argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirring bar were added NHC precursor **10** (185 mg, 0.3 mmol) and $Pd(OAc)_2$ (81 mg, 0.36 mmol) followed by the addition of dry THF (10 mL) as the solvent. After refluxing at 70 °C for 24–36 h, the reaction mixture was cooled to room temperature followed by filtering through Celite. Then the volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 2/1) to give **11** as a yellow solid in 45% yield. Single crystals of complex **11** suitable for an X-ray diffraction study were grown from the solution of **11** in mixed petroleum ether/EtOAc/CH_2Cl_2 (1/1/2). Mp >300 °C; $[\alpha]_D^{20}$ −218 (*c* 0.25, $CHCl_3$); IR (direct irradiation) *ν* 3057, 2958, 2923, 2852, 1607, 1583, 1527, 1507, 1485, 1457, 1439, 1410, 1396, 1332, 1254, 1184, 1152, 965, 838, 808, 737, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) *δ* 5.36 (d, *J*=16.0 Hz, 1H), 6.39 (t, *J*=7.2 Hz, 1H), 6.66 (d, *J*=16.0 Hz, 1H), 6.86–6.98 (m, 9H), 7.04–7.13 (m, 3H), 7.19–7.36 (m, 6H), 7.55–7.59 (m, 2H), 7.70 (t, *J*=9.6 Hz, 2H), 7.98 (d, *J*=8.8 Hz, 1H), 8.07 (d, *J*=8.0 Hz, 1H), 8.29 (d, *J*=8.0 Hz, 1H); LRMS (ESI) *m*/*e* 684.1 [M^+−Cl]; HRMS (ESI) calcd for [$C_{41}H_{28}ClN_3OPd$−Cl] requires 684.1267, found 684.1286 [M^+−Cl].

4.4. General procedure for the synthesis of palladium(II) complexes 14 and 15

In the presence of 4 Å MS (1.0 g), refluxing of primary amine **8** (385 mg, 1.0 mmol) and benzaldehyde (0.13 mL, 1.3 mmol) in dry toluene (5 mL) for about 3 days successfully offered phenylimine **12** until completely consuming of **8** by ^1H NMR monitoring. After the volatiles were removed under reduced pressure, **12** as a yellow solid was directly used for the next step without further purification. Mp 129–131 °C; $[\alpha]_D^{20}$ −209 (*c* 0.25, $CHCl_3$); IR (direct irradiation) *ν* 3053, 2961, 2923, 2853, 1612, 1487, 1451, 1283, 1234, 1202, 1100, 1024, 815, 740, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) *δ* 6.82 (t, *J*=7.6 Hz, 1H), 7.06–7.16 (m, 3H), 7.21–7.37 (m, 10H), 7.52–7.56 (m, 2H), 7.60 (d, *J*=8.4 Hz, 1H), 7.64 (d, *J*=8.4 Hz, 1H), 7.82–7.88 (m, 3H), 8.01 (d, *J*=8.4 Hz, 1H), 8.09 (d, *J*=8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) *δ* 110.7, 118.7, 119.7, 122.1, 122.8, 124.0, 124.9, 125.2, 125.5, 126.6, 127.1, 127.2, 128.1, 128.3, 128.4, 128.7, 129.4, 130.3, 131.1, 131.7, 132.0, 132.8, 133.1, 133.7, 134.1, 135.8, 142.9, 148.0, 160.7; LRMS (ESI) *m*/*e* 474.2 [M^++H]; HRMS (ESI) calcd for [$C_{34}H_{23}N_3$+H] requires 474.1970, found 474.1975 [M^++H].

Compound **12** (189 mg, 0.4 mmol) and benzylbromide (0.47 mL, 10 equiv) were refluxed in 1,4-dioxane (4 mL) until that **12** was completely consumed by TLC monitoring. Benzimidazolium salt **13** as a yellow solid was obtained in 91% yield via a similar work-up for **5** from the resulting reaction mixture without any further purification.

Under argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirring bar were added NHC precursor **13** (193 mg, 0.3 mmol), $Pd(OAc)_2$ (101 mg, 0.45 mmol), and KBr (143 mg, 1.2 mmol) followed by the addition of dry THF (15 mL) as the solvent. After refluxing at 70 °C for 2–3 days, the reaction mixture was cooled to room temperature followed by filtering through Celite. Then the volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography to give **14** (eluent: petroleum ether/EtOAc, 4/1) and **15** (eluent: petroleum ether/EtOAc, 2/1) both as yellow solids, and in a representative yield of 18% and 31%, respectively. Single crystals of complex **14** suitable for an X-ray diffraction study were grown from the solution of **14** in mixed petroleum ether/EtOAc (4/1). For complex **14**: mp >300 °C (dec); $[\alpha]_D^{20}$ −60 (*c* 0.25, $CHCl_3$); IR (direct irradiation) *ν* 3054, 2957, 2923, 2852, 1713, 1587, 1467, 1402, 1260, 1206, 1189, 1081, 1017, 967, 816, 803, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) *δ* 5.23 (d, *J*=16.0 Hz, 1H), 6.57 (d, *J*=15.6 Hz, 1H), 6.66–6.70 (m, 2H), 6.95–7.01 (m, 6H), 7.11–7.21 (m, 6H), 7.23–7.33 (m, 4H), 7.54 (t, *J*=7.6 Hz, 1H), 7.75 (d, *J*=8.0 Hz, 1H), 7.87 (d, *J*=8.8 Hz, 1H), 7.91 (d, *J*=8.4 Hz, 1H), 8.04 (d, *J*=8.4 Hz, 1H), 8.09–8.16 (m, 2H), 8.23 (d, *J*=8.8 Hz, 1H); LRMS (ESI) *m*/*e* 668.1 [M^+−Br]; HRMS (ESI) calcd for [$C_{41}H_{28}BrN_3Pd$−Br] requires 668.1318, found 668.1333 [M^+−Br]. For complex **15**: mp >300 °C (dec); $[\alpha]_D^{20}$ −122 (*c* 0.25, $CHCl_3$); IR (direct irradiation) *ν* 3191, 3059, 2956, 2921, 2851, 1712, 1463, 1411, 1277, 1250, 1187, 1080, 965, 818, 742, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) *δ* 4.66 (br, 1H), 5.30 (d, *J*=16.0 Hz, 1H), 5.42 (br, 1H), 6.46 (d, *J*=16.0 Hz, 1H), 6.89–6.93 (m, 5H), 6.98 (d, *J*=6.8 Hz, 2H), 7.08–7.12 (m, 2H), 7.17–7.23 (m, 2H), 7.31–7.37 (m, 3H), 7.43 (t, *J*=8.0 Hz, 1H), 7.61 (d, *J*=8.4 Hz, 2H), 7.71 (t, *J*=8.0 Hz, 1H), 7.99 (d, *J*=8.8 Hz, 1H), 8.19 (d, *J*=8.4 Hz, 1H), 8.40 (d, *J*=8.4 Hz, 1H); LRMS (ESI) *m*/*e* 660.0 [M^+−Br]; HRMS (ESI) calcd for [$C_{34}H_{25}Br_2N_3Pd$−Br] requires 660.0267, found 660.0273 [M^+−Br].

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Supplementary data

Detailed description of experimental procedures, spectral, and analytical data for new compounds shown in Schemes and Figures,

CIF files and X-ray crystal data of complexes **6**, **11**, and **14**. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.01.001.

References and notes

1. (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361–363; (b) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405–3409.
2. For selected books and reviews on NHC ligands, see: (a) *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, Germany, 2006; (b) Glorius, F. *N-Heterocyclic Carbenes in Transition Metal Catalysis*; Springer: Berlin, 2007; (c) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–91; (d) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309; (e) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951–961; (f) Kirmse, W. *Angew. Chem., Int. Ed.* **2004**, *43*, 1767–1769; (g) Cesar, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, *33*, 619–636; (h) Douthwaite, R. E. *Coord. Chem. Rev.* **2007**, *251*, 702–717; (i) Kühl, O. *Chem. Soc. Rev.* **2007**, *36*, 592–607; (j) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768–2813; (k) Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612–3676.
3. For recent selected reviews on metathesis, see: (a) Hoveyda, A. H.; Zhugralin, A. R. Nature 450, 243–251. (b) Shrodi, Y.; Pederson, R. L. *Aldrichimica Acta* **2007**, *40*, 45–52; (c) Samojłowicz, C.; Bieniek, M.; Grela, K. *Chem. Rev.* **2009**, *109*, 3708–3742; (d) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746–1787.
4. For recent selected reviews on cross-coupling reactions, see: (a) Marion, N.; Nolan, S. P. *Acc. Chem. Res.* **2008**, *41*, 1440–1449; (b) Boeda, F.; Nolan, S. P. *Annu. Rep. Prog. Chem., Sect. B* **2008**, *104*, 184–210.
5. (a) Xu, Q.; Duan, W. L.; Lei, Z. Y.; Zhu, Z. B.; Shi, M. *Tetrahedron* **2005**, *61*, 11225–11229; (b) Chen, T.; Jiang, J. J.; Xu, Q.; Shi, M. *Org. Lett.* **2007**, *9*, 865–868; (c) Zhang, T.; Shi, M. *Chem.—Eur. J.* **2008**, *14*, 3759–3764; (d) Ma, G. N.; Zhang, T.; Shi, M. *Org. Lett.* **2009**, *11*, 875–878; (e) Wang, W. F.; Zhang, T.; Shi, M. *Organometallics* **2009**, *28*, 2640–2642; (f) Liu, Z.; Shi, M. *Tetrahedron* **2010**, *66*, 2619–2623; (g) Liu, Z.; Shi, M. *Organometallics* **2010**, *29*, 2831–2834; (h) Xu, Q.; Zhang, R.; Zhang, T.; Shi, M. *J. Org. Chem.* **2010**, *75*, 3935–3937; (i) Zhang, R.; Xu, Q.; Zhang, X.; Zhang, T.; Shi, M. *Tetrahedron: Asymmetry* **2010**, *21*, 1928–1935.
6. (a) Grasa, G. A.; Viciu, M. S.; Huang, J. K.; Nolan, S. P. *J. Org. Chem.* **2001**, *66*, 7729–7737; (b) Lewis, A. K. D.; Caddick, S.; Cloke, F. G. N.; Billingham, N. C.; Hitchcock, P. B.; Leonard, J. *J. Am. Chem. Soc.* **2003**, *125*, 10066–10073; (c) Bonnet, L. G.; Douthwaite, R. E.; Hodgson, R. *Organometallics* **2003**, *22*, 4384–4386; (d) Zhang, T.; Shi, M.; Zhao, M. X. *Tetrahedron* **2008**, *64*, 2412–2418.
7. (a) Tsuji, J. *Innovations in Organic Synthesis*; Wiley: New York, NY, 1995; (b) Trost, B. M.; Jorgensen, K. A. *Chem. Rev.* **1996**, *96*, 395–422; (c) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921–2943.
8. (a) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2000**, *46*, 181–222; (b) Weskamp, T.; Bohm, V. P. W.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, *600*, 12–22; (c) Hillier, A. C.; Nolan, S. P. *Platinum Met. Rev.* **2002**, *46*, 50–64; (d) Strassner, T. *Top. Organomet. Chem.* **2004**, *13*, 1–20; (e) Cavallo, L.; Correa, A.; Costabile, C.; Jacobsen, H. *J. Organomet. Chem.* **2005**, *690*, 5407–5413; (f) Crabtree, R. H. *J. Organomet. Chem.* **2005**, *690*, 5451–5457; (g) Diez-Gonzalez, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874–883.
9. (a) Frenking, G.; Sola, M.; Vyboishchikov, S. F. *J. Organomet. Chem.* **2005**, *690*, 6178–6204; (b) Radius, U.; Bickelhaupt, F. M. *Coord. Chem. Rev.* **2009**, *253*, 678–686; (c) Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. *Coord. Chem. Rev.* **2009**, *253*, 687–703.
10. However, there are also several examples involving a cleavage of NHC–metal bond: (a) Douthwaite, R. E.; Haussinger, D.; Green, M. L. H.; Silcock, P. J.; Gomes, P. T.; Martins, A. M.; Danopoulos, A. A. *Organometallics* **1999**, *18*, 4584–4590; (b) McGuinness, D. S.; Saendig, N.; Yates, B. F.; Cavell, K. J. *J. Am. Chem. Soc.* **2001**, *123*, 4029–4040; (c) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247–2273 And Refs. 6b and 8f.
11. For selected reports on palladium complexes of NHC–N donor hybrid ligands, see: (a) Frøseth, M.; Dhindsa, A.; Røise, H.; Tilset, M. *Dalton Trans.* **2003**, 4516–4524; (b) Bonnet, L. G.; Douthwaite, R. E. *Organometallics* **2003**, *22*, 4187–4189; (c) Douthwaite, R. E.; Houghton, J.; Kariuki, B. M. *Chem. Commun.* **2004**, 698–699; (d) Bonnet, L. G.; Douthwaite, R. E.; Hodgson, R.; Houghton, J.; Kariuki, B. M.; Simonovic, S. *Dalton Trans.* **2004**, 3528–3535; (e) Houghton, J.; Dyson, G.; Douthwaite, R. E.; Whitwood, A. C.; Kariuki, B. M. *Dalton Trans.* **2007**, 3065–3073; (f) Dyson, G.; Frison, J. C.; Simonovic, S.; Whitwood, A. C.; Douthwaite, R. E. *Organometallics* **2008**, *27*, 281–288.
12. (a) Zhang, T.; Wang, W. F.; Gu, X. X.; Shi, M. *Organometallics* **2008**, *27*, 753–757; (b) Zhang, T.; Liu, S. J.; Shi, M.; Zhao, M. X. *Synthesis* **2008**, 2819–2824.
13. The crystal data of **6** have been deposited in CCDC with number 668094. Empirical Formula: $C_{36}H_{28}BrCl_2N_3O_2PdS$; Formula Weight: 823.88; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.223×0.130×0.128 mm; Crystal System: Orthorhombic; Lattice Type: Primitive; Lattice Parameters: a=14.8195(16) Å, b=24.358(3) Å, c=9.3643(10) Å, α=90°, β=90°, γ=90°, V=3380.3(6) Å^3; Space group: $P2(1)2(1)2$; Z=4; D_{calcd}=1.619 g/cm^3; F_{000}=1648; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0548, 0.0979.
14. For selected reviews on Schiff base ligands, see: (a) Che, C. M.; Huang, J. S. *Coord. Chem. Rev.* **2003**, *242*, 97–113; (b) Cozzi, P. G. *Chem. Soc. Rev.* **2004**, *33*, 410–421; (c) Katsuki, T. *Chem. Soc. Rev.* **2004**, *33*, 437–444; (d) Baleizao, C.; Garcia, H. *Chem. Rev.* **2006**, *106*, 3987–4043; (e) Gupta, K. C.; Sutar, A. K. *Coord. Chem. Rev.* **2008**, *252*, 1420–1450.
15. For selected reviews on oxazoline ligands, see: (a) Ghosh, A. K.; Mathivanan, P.; Cappiello, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1–45; (b) Gómez, M.; Muller, G.; Rocamora, M. *Coord. Chem. Rev.* **1999**, *193–195*, 769–835; (c) Rechavi, D.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 3467–3494; (d) Desimoni, G.; Faita, G.; Jørgensen, K. A. *Chem. Rev.* **2006**, *106*, 3561–3651; (e) Gade, L. H.; Bellemin-Laponnaz, S. *Coord. Chem. Rev.* **2007**, *251*, 718–725; (f) Hargaden, G. C.; Guiry, P. J. *Chem. Rev.* **2009**, *109*, 2505–2550.
16. For selected reviews on pyridyl pincer-type ligands incorporating NHCs, see: (a) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239–2246; (b) Pugh, D.; Danopoulos, A. A. *Coord. Chem. Rev.* **2007**, *251*, 610–641.
17. (a) Dudek, G. O. *J. Am. Chem. Soc.* **1963**, *85*, 694–697; (b) Dudek, G. O. *J. Org. Chem.* **1965**, *30*, 548–552.
18. The crystal data of **11** have been deposited in CCDC with number 779495. Empirical Formula: $C_{41}H_{29}ClN_3O_1\cdot 5Pd$; Formula Weight: 729.52; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.269×0.215×0.117 mm; Crystal System: Monoclinic; Lattice Parameters: a=23.087(6) Å, b=9.434(3) Å, c=31.476(9) Å, α=90°, β=92.428(4)°, γ=90°, V=6850(3) Å^3; Space group: $C2$; Z=8; D_{calcd}=1.415 g/cm^3; F_{000}=2968; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0865, 0.1732.
19. (a) Voutsas, G. P.; Keramidas, K. G.; Lalia-Kantouri, M. *Polyhedron* **1996**, *15*, 147–151; (b) Lai, Y. C.; Chen, H. Y.; Hung, W. C.; Lin, C. C.; Hong, F. E. *Tetrahedron* **2005**, *61*, 9484–9489; (c) Naota, T.; Koori, H. *J. Am. Chem. Soc.* **2005**, *127*, 9324–9325.
20. The crystal data of **14** have been deposited in CCDC with number 790888. Empirical Formula: $C_{41}H_{28}BrN_3Pd$; Formula Weight: 748.97; Crystal Color, Habit: colorless; Crystal Dimensions: 0.407×0.211×0.139 mm; Crystal System: Monoclinic; Lattice Parameters: a=24.115(5) Å, b=9.055(2) Å, c=17.154(4) Å, α=90°, β=107.971(4)°, γ=90°, V=3563.0(14) Å^3; Space group: $C2$; Z=4; D_{calcd}=1.396 g/cm^3; F_{000}=1504; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0604, 0.1676.
21. Liu, Z.; Zhang, T.; Shi, M. *Organometallics* **2008**, *27*, 2668–2671.
22. (a) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403–424; (b) Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527–2571; (c) Dupont, J.; Pfeffer, M. In *Palladacycles*; Wiley-VCH: Weinheim, Germany, 2008.