

Synthesis of chiral mono(N-heterocyclic carbene) palladium and gold complexes with a 1,1'-biphenyl scaffold and their applications in catalysis

Lian-jun Liu¹, Feijun Wang¹, Wenfeng Wang¹, Mei-xin Zhao¹ and Min Shi^{*1,2}

Full Research Paper

Open Access

Address:

¹Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 MeiLong Road, Shanghai 200237, People's Republic of China and ²State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, People's Republic of China, Fax: 86-21-64166128

Email:

Min Shi* - Mshi@mail.sioc.ac.cn

* Corresponding author

Keywords:

chiral mono(N-heterocyclic carbene) complex; Heck–Mizoroki reaction; hydroamination; Suzuki–Miyaura reaction

Beilstein J. Org. Chem. **2011**, *7*, 555–564.

doi:10.3762/bjoc.7.64

Received: 21 January 2011

Accepted: 04 March 2011

Published: 04 May 2011

This article is part of the Thematic Series "Gold catalysis for organic synthesis".

Guest Editor: F. D. Toste

© 2011 Liu et al; licensee Beilstein-Institut.

License and terms: see end of document.

Abstract

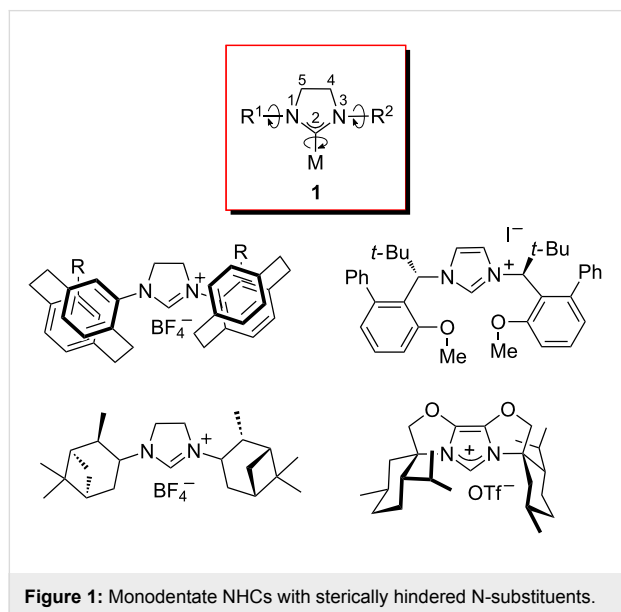
Axially chiral mono(NHC)–Pd(II) and mono(NHC)–Au(I) complexes with one side shaped 1,1'-biphenyl backbone have been prepared from chiral 6,6'-dimethoxybiphenyl-2,2'-diamine. The complexes were characterized by X-ray crystal structure diffraction. The Pd(II) complex showed good catalytic activities in the Suzuki–Miyaura and Heck–Mizoroki coupling reactions, and the (S)-Au(I) complexes also showed good catalytic activities in the asymmetric intramolecular hydroamination reaction to give the corresponding product in moderate ee.

Introduction

N-heterocyclic carbene (NHC) ligands, which have intrinsic characteristics such as strong σ -donor but poor π -acceptor abilities, easy preparation, air and thermal stability of their metal complexes, and convenient introduction of chiral elements, have been widely used as promising ligands in metal-catalyzed transformations [1–13]. Numbers of novel chiral NHCs and NHC–metal-catalyzed asymmetric transformations have been

developed in a dramatic expansion of this area of chemistry during the past decade; however, up to 2010 only a very few efficient chiral NHCs or NHCs metal catalysts have been described [14–18]. From the typical configuration of NHC metal complex **1** (Figure 1), NHCs are generally more or less cone-shaped with flat heterocyclic structures, and that R¹, R² and M can rotate flexibly around the R¹–N, R²–N and C–M bonds, res-

pectively. Such internal rotations cause the active chiral space at the metal center to be relatively ill-defined, which is a key factor for their low enantioselectivity in asymmetric catalysis. As a result, many monodentate NHCs (Figure 1) with sterically hindered R^1 , R^2 groups have been designed, and these have been shown to be good to excellent catalysts in chiral induction reactions [19–25].



The axially chiral biaryl framework, widely used in the design of chiral ligands such as BINAP [26,27], BINOL [28,29], and boxax [30], has proved to be very rigid, and was introduced in the development of NHC ligands by the Hoveyda group [31–36] and ours [37–44] (Figure 2). Several highly efficient asymmetric catalytic processes with these novel chiral NHCs-bonded metal catalysts have so far been reported. Encouraged by these results, we attempted to develop a new type of mono(NHC) metal complex **2** with a biaryl framework, in which one of biaryl groups bearing a substituent might provide steric hindrance to limit the rotation of the N–Ar bond. Herein we

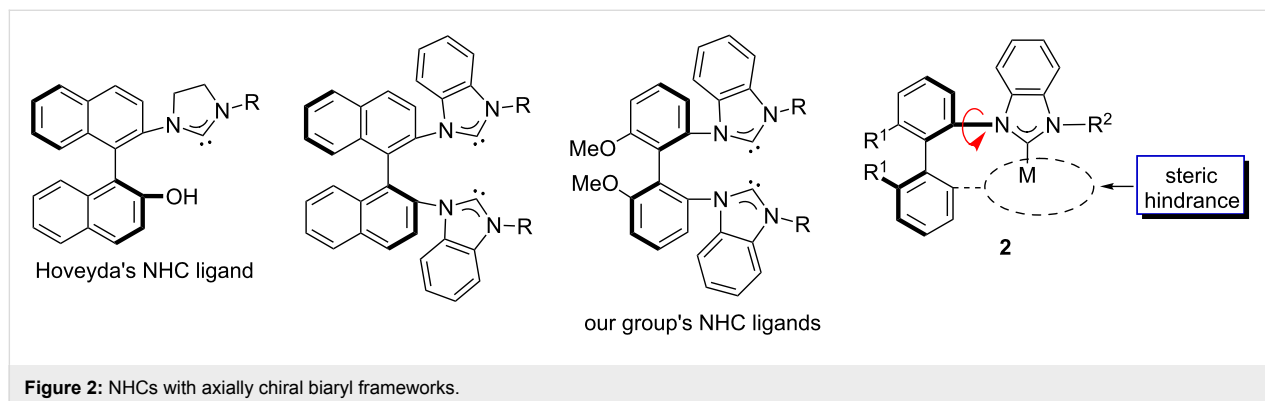
wish to report the synthesis of novel chiral [(NHC)Pd(allyl)]I and mono(NHC)–Au complexes bearing an axially chiral biphenyl framework, and their application in catalysis.

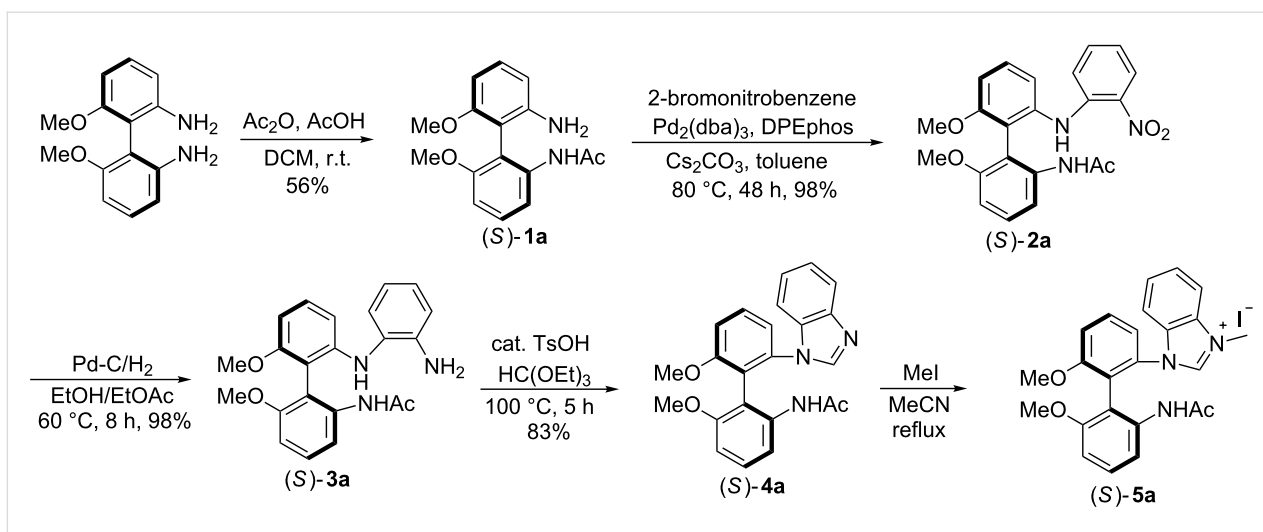
Results and Discussion

Synthesis of the NHC–Pd(II) and NHC–Au(I) complexes

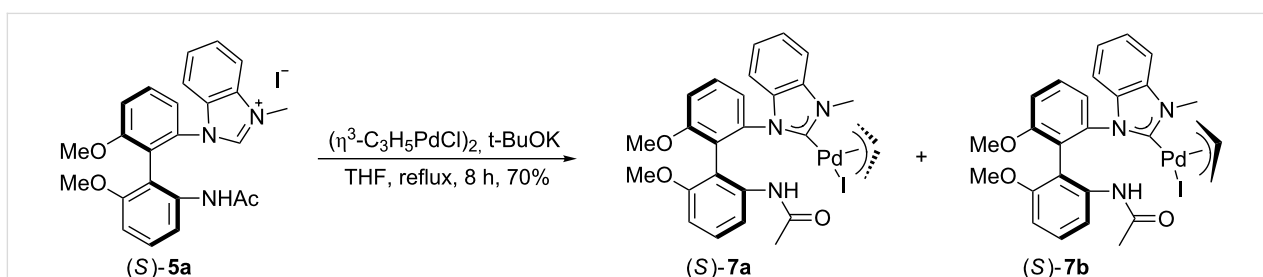
The synthesis of the chiral benzimidazolium salt (*S*)-**5a** is shown in Scheme 1. Thus (*S*)-6,6'-dimethoxybiphenyl-2,2'-diamine was reacted with acetic anhydride in the presence of acetic acid at room temperature (25 °C) in DCM to afford the corresponding amide (*S*)-**1a** in 56% yield. The coupling reaction of (*S*)-**1a** with 2-bromonitrobenzene was achieved by the use of bis(2-diphenylphosphinophenyl)ether (DPEphos) as a ligand and Pd₂(dba)₃ as the catalyst in the presence of Cs₂CO₃ to give the desired compound (*S*)-**2a** in 98% yield. Reduction of (*S*)-**2a** by means of Pd–C/H₂ for 8 h gave (*S*)-**3a** in 98% yield. Subsequent cyclization with triethyl orthoformate catalyzed by *p*-toluenesulfonic acid at 100 °C for 5 h afforded (*S*)-**4a** in 83% yield. Quaternization of the benzimidazole ring of (*S*)-**4a** by heating with methyl iodide in acetonitrile provided the corresponding benzimidazolium salt (*S*)-**5a** in quantitative yield.

With the NHC precursor (*S*)-**5a** in hand, its coordination with Pd or Au metal salts was examined. Benzimidazolium salt (*S*)-**5a** was treated with (η³-C₃H₅PdCl)₂ in tetrahydrofuran (THF) in the presence of *t*-BuOK at 50 °C to give [(NHC)Pd(allyl)]I complex (*S*)-**7** in 70% yield as a yellow solid after purification by silica gel column chromatography (Scheme 2) [45,46]. Due to the stereochemical orientation of π-allyl group relative to the unsymmetrical carbene ligand, this NHC–Pd complex exists as two stereoisomers in solution, (*S*)-**7a** and (*S*)-**7b**, which could be easily distinguished in its ¹H NMR spectrum recorded at 23 °C [47–50]. The ratio of (*S*)-**7a** and (*S*)-**7b** was found to be 1.2:1 on the basis of ¹H NMR spectroscopic data. It appears that (*S*)-**7a** is slightly more stable than (*S*)-**7b** presumably due to the steric repulsion between the π-allyl group and the acetylated amino group in another phenyl group. However, we were





Scheme 1: Synthesis of N-heterocyclic carbene precursor.



Scheme 2: Synthesis of mono(NHC)–Pd(II) complex.

unable to isolate either stereoisomer in a pure form by silica gel column chromatography. After recrystallization from DCM and pentane (1:3), one of the two stereoisomers, [(NHC)Pd(allyl)I] (*S*)-**7a**, was obtained as a crystalline compound and its structure was confirmed by the X-ray single crystal diffraction (Figure 3) [51].

Benzimidazolium salt (*S*)-**5a** also complexed Au(I). According to the previously reported procedure [52–55], (*S*)-**5a** reacted with AuCl·S(Me)₂ on heating in THF for 8 h in the presence of KI and *t*-BuOK to give the expected chiral NHC–Au(I) complex (*S*)-**6a** in 65% yield (Scheme 3). Its structure was also confirmed by X-ray diffraction (Figure 4) [56]. It was found that the Au–carbene distance is 2.036 Å which is consistent with other reported NHC–Au complexes [57–59].

The NHC–metal complex [(NHC)Pd(allyl)I] complex **7** and NHC–Au(I) complex (*S*)-**6a**, are air and moisture stable both in the solid state and in solution, and can be used as catalysts. Therefore, the catalytic activities of these complexes were investigated in Pd-catalyzed coupling reactions and a Au-catalyzed asymmetric reaction, respectively.

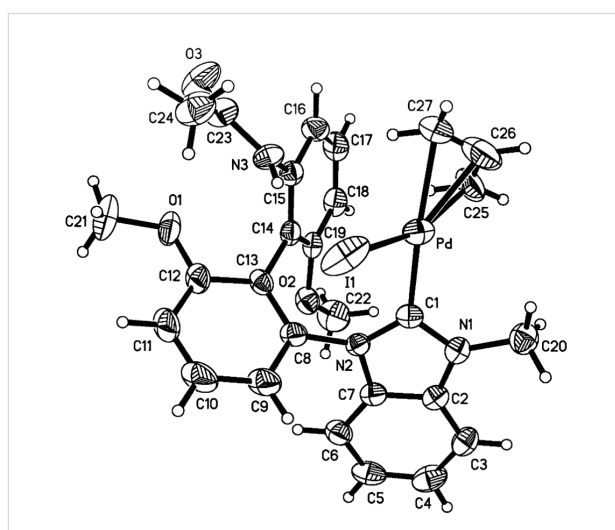


Figure 3: ORTEP drawing of NHC–Pd(II) complex (*S*)-**7a** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Pd–C1 = 2.050(5), Pd–C25 = 2.154(7), Pd–C26 = 2.128(9), Pd–C27 = 2.168(8), Pd–I1 = 2.6404(7), N1–C1–Pd = 125.6(4), N2–C1–Pd = 128.8(4), C1–Pd–I1 = 99.52(13), C1–Pd–C25 = 98.3(3), C1–Pd–C26 = 132.3(5), C1–Pd–C27 = 163.7(4), I1–Pd–C25 = 161.9(3), I1–Pd–C26 = 126.5(5), I1–Pd–C27 = 95.9(3), C25–Pd–C27 = 66.0(4), C25–Pd–C26 = 37.5(4), C26–Pd–C27 = 34.8(4).

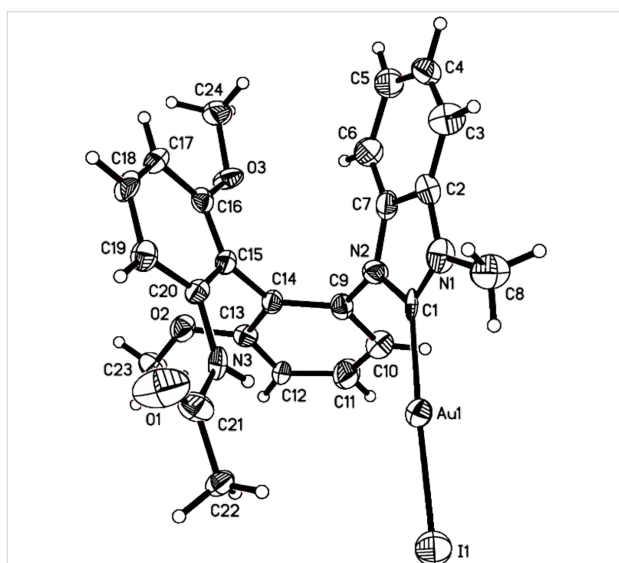
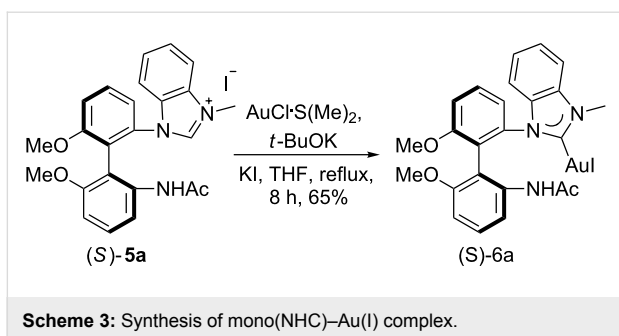
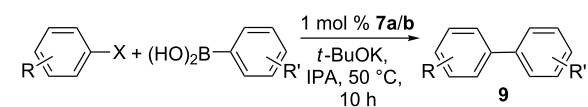


Figure 4: ORTEP drawing of NHC–Au(I) complex (S)-6a with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Au1–C1 = 2.036(14), Au1–I1 = 2.5093(13), C1–Au1–I1 = 176.5(3), N1–C1–Au1 = 125.7(9), N2–C1–Au1 = 126.1(9).

Suzuki–Miyaura and Heck–Mizoroki coupling reactions catalyzed by NHC–Pd(II) complex

The Pd-catalyzed coupling reaction is one of the most powerful methods for the formation of carbon–carbon bonds in organic synthesis [60–66]. NHC–Allylpalladium complexes have been employed and showed good catalytic activities in carbon–carbon bond coupling reactions [67–70]. Stereoisomeric complex **7** was firstly applied as the catalyst in the catalyze Suzuki–Miyaura coupling reaction. On the basis of screening of the solvent and base in the reaction of phenylboronic acid with bromobenzene, it was found that using *t*-BuOK as the base in *i*PrOH at 50 °C for 10 h, the coupling product **9a** was obtained in the highest yield (81% yield) (Supporting Information File 1). Under the optimized conditions, the reactions of various aryl halides with arylboronic acids were carried out, and it was found that the electronic properties of the R groups and halide atoms significantly affected the reaction yield of the Suzuki–Miyaura reactions. The results have been summarized in Table 1.

Table 1: Suzuki–Miyaura reaction catalyzed by NHC–Pd(II) complex **7**^a.



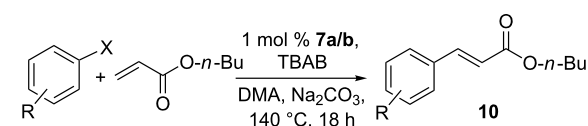
Entry	R	R'	X	Product	Yield (%) ^b
1	4-Me	H	Br	9a	81
2	4-COMe	H	Br	9b	98
3	2-NO ₂	H	Br	9c	96
4	2-MeO	H	Br	9d	89
5	2-Me	H	Br	9e	80
6	4-COMe	4-Me	Br	9f	97
7	4-MeO	4-Me	Br	9g	81
8	4-Me	2-Cl	Br	9h	74
9	H	4-Me	I	9a	>99
10	H	4-Me	Cl	9a	<5

^aReaction conditions: 1 mmol aryl halide, 1.3 mmol arylboronic acid, 1.3 mmol *t*-BuOK, 0.01 mmol NHC–Pd(II) complex, 2.0 mL IPA.

^bIsolated yields.

The [(NHC)Pd(allyl)I] complex **7** was also examined in the Heck–Mizoroki coupling reaction. Under optimized conditions (Supporting Information File 1), the reactions of various aryl halides with *n*-butyl acrylate were carried out in the presence of Na₂CO₃ in *N,N*-dimethylacetamide (DMA) at 140 °C. [(NHC)Pd(allyl)I] complex **7** showed good catalytic activities in the reaction of arylbromides or iodobenzene with *n*-butyl acrylate to afford the coupling products **10** in up to 97% yield. The results have been summarized in Table 2.

Table 2: Heck–Mizoroki reaction catalyzed by NHC–Pd(II) complex **7**^a.



Entry	R	X	Time (h)	Product	Yield (%) ^b
1	H	Br	18	10a	82
2	4-Me	Br	18	10b	79
3	4-MeO	Br	18	10c	80
4	4-CHO	Br	18	10d	85
5	2-Me	Br	18	10e	76
6	H	I	18	10a	97
7	H	Cl	18	10a	<5

^aReaction conditions: **7** (1 mol % Pd), Na₂CO₃ (2.0 mmol), TBAB (0.1 mmol), aryl halide (1.0 mmol) and *n*-butyl acrylate (1.5 mmol) in DMA (3.0 mL) at 140 °C for 18 h.

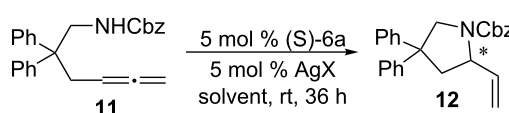
^bIsolated yield after silica gel column chromatography.

Intramolecular hydroamination reaction catalyzed by NHC–Au(I) complex (S)-6a

Since the first example of NHC–Au complex was reported in 1989 [71], a variety of neutral or cationic NHC–Au complexes has been synthesized and applied in many catalytic reactions [72,73]. For example, recently, NHC–Au showed good catalytic activity in the intramolecular [4 + 2] cycloadditions of 1,3-enynes or arylalkynes [74], rearrangement of allylic acetates [75,76], carbene-transfer reactions from ethyl diazoacetate [77], formation of conjugated enones and enals [78], regio- and stereoselective synthesis of fluoroalkenes [79], and so on [80–85]. However, reports on NHC–Au catalyzed asymmetric reactions are rare [86]. The NHC–Au(I) complex (S)-6a was consequently investigated as the catalyst in the asymmetric intramolecular hydroamination of allenes. This reaction has been achieved with high enantioselectivity by a chiral phosphine–Au(I) complex [87–93]. Treatment of allene **11** with (S)-6a and AgSbF₆ (5 mol %) in DCM at room temperature for 36 h afforded pyrrolidine derivative **12** in 53% yield with an ee of only 10%. When THF or toluene was used as solvent, only traces of compound **12** were formed. Further screening of AgX revealed that the combination of (S)-6a and AgClO₄ gave the best catalytic activity in this reaction (Table 3).

We assumed that the ill-defined chiral space at the Au center may be the cause of the low ee, and that a more sterically bulky group than an acetyl group in another phenyl framework may be required to improve the enantioselectivity. Accordingly, the original acetyl group was replaced by a more sterically bulky group such as *tert*-butoxycarbonyl group and adamantanecarbonyl group.

Table 3: NHC–Au complex (S)-6a catalyzed asymmetric intramolecular hydroamination.

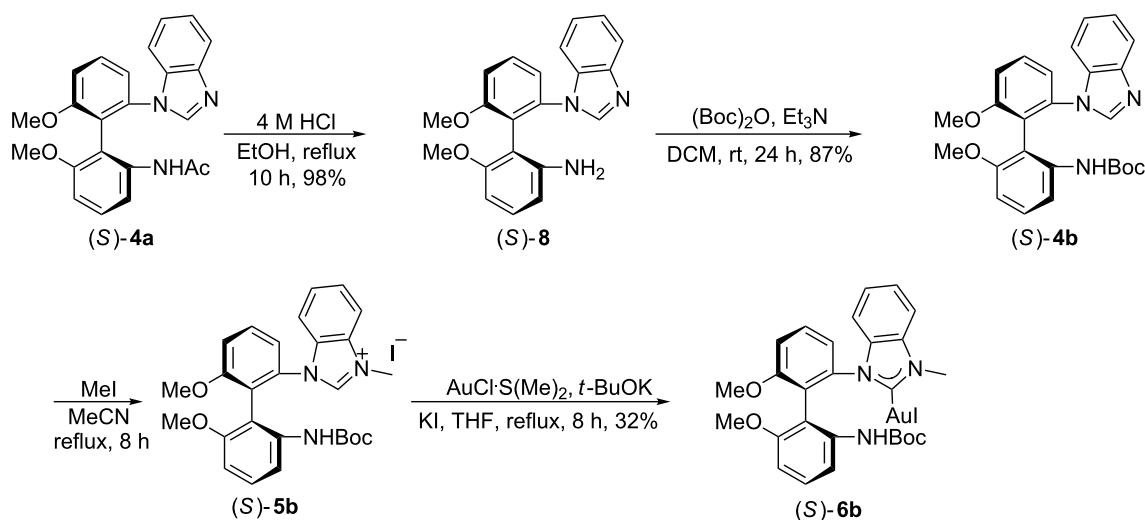


Entry	Solvent	AgX	Time (h)	Yield (%) ^a	ee (%) ^b
1	THF	AgSbF ₆	36	trace	— ^c
2	Toluene	AgSbF ₆	36	trace	—
3	DCM	AgSbF ₆	36	53	10
4	DCE	AgSbF ₆	36	43	7
5	DCM	AgClO ₄	36	63	10
6	DCM	AgOTf	36	42	10
7	DCM	AgOTs	36	— ^d	—
8	DCM	AgBF ₄	36	46	0

^aIsolated yield.
^bDetermined by chiral HPLC.
^cnot determined.
^dno reaction.

Synthesis of the NHC–Au(I) complexes (S)-6b and 6c

The synthesis of (S)-6b is shown in Scheme 4: Thus (S)-4a was heated under reflux with 4 M HCl in EtOH to afford the corresponding amide (S)-8 in 98% yield. Amine (S)-8 was then treated with (Boc)₂O in the presence of Et₃N at room temperature for 24 h to give the corresponding BOC derivative (S)-4b in 87% yield. Quaternization of the benzimidazole ring of (S)-4b with methyl iodide in acetonitrile gave the corresponding benzimidazolium salt (S)-5b in quantitative yield. Benzimidazolium salt (S)-5b was then treated with AuCl·S(Me)₂ and *t*-BuOK in THF to give the corresponding mono(NHC)–Au(I) complex (S)-6b in 32% yield.



Scheme 4: Synthesis of mono(NHC)–Au(I) complex (S)-6b.

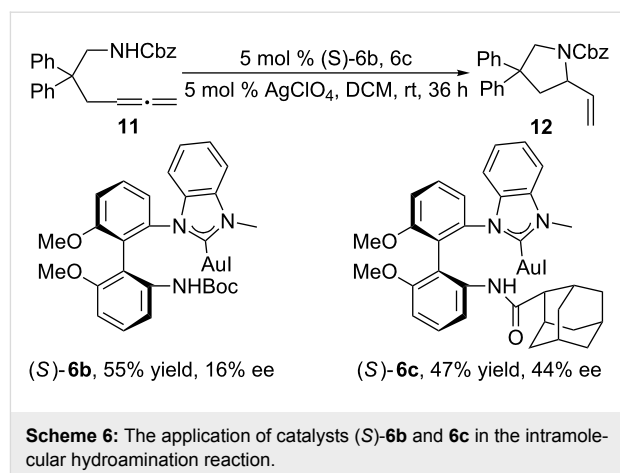
zolium salt (*S*)-**5b** was then complexed with Au (I) as described above for (*S*)-**6a** (AuCl·S(Me)₂) in the presence of KI and *t*-BuOK in THF for 8 h) to produce the expected chiral NHC–Au(I) complex (*S*)-**6b** in 32% yield.

For the preparation of (*S*)-**6c**, (*S*)-6,6'-dimethoxybiphenyl-2,2'-diamine was treated with adamantane-2-carbonyl chloride in the presence of Et₃N at room temperature (25 °C) in DCM to afford the corresponding amide (*S*)-**1c** in 71% yield. According to the synthetic method for the synthesis of compound (*S*)-**6a**, NHC–Au complex (*S*)-**6c** was successfully prepared in 45% yield (Scheme 5).

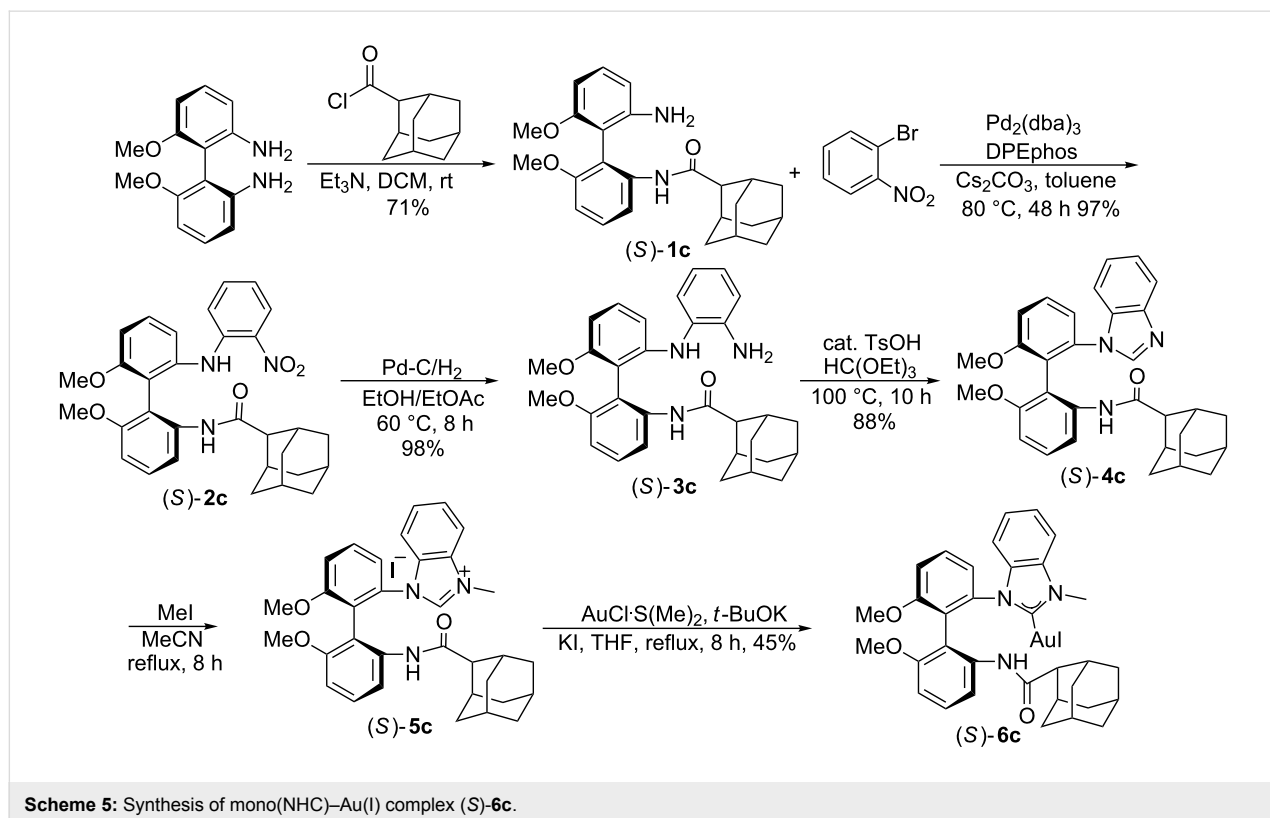
Under the optimized conditions, (*S*)-**6b** and (*S*)-**6c** were used as catalysts to examine their chiral induction abilities in the intramolecular hydroamination reaction (Scheme 6). As expected, the corresponding pyrrolidine derivative **12** was obtained in higher ee value but in lower isolated yield: With (*S*)-**6c** as catalyst, **12** was obtained in 47% yield with an ee of 44% whereas with (*S*)-**6b** as catalyst, **12** was obtained in 55% yield but the ee was only 16%.

Conclusion

Axially chiral mono(NHC)–Pd(II) and mono(NHC)–Au(I) complexes with one side shaped 1,1'-biphenyl backbone have been prepared from chiral 6,6'-dimethoxybiphenyl-2,2'-diamine.



The Pd(II) complex showed good catalytic activity in the Suzuki–Miyaura and Heck–Mizoroki coupling reactions. The (*S*)-Au(I) complex also showed moderate catalytic activities along with moderate chiral inductions in the asymmetric intramolecular hydroamination reaction. Using chiral Au complex (*S*)-**6c**, having a sterically hindered 2-adamantanecarbonyl group, as the catalyst gave the corresponding intramolecular hydroamination product in higher enantioselectivity (44% ee). Efforts are underway to extend the scope and limitations of these chiral (NHC) Pd(II) and Au(I) complexes in other asymmetric catalytic reactions.



Experimental

Synthesis of NHC–Pd(II) complex **7**

Compound **5a** (105.8 mg, 0.2 mmol) and [PdCl(η^3 -allyl)]₂ (109.1 mg, 0.3 mmol), *t*-BuOK (56 mg, 0.5 mmol) were heated under reflux in THF (10 mL) for 8 h. The volatiles were then removed under reduced pressure and the residue purified by a silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate, 2:1–0:1) to give **7** as a mixture of two isomers (117.0 mg, 70%). A single crystal grown from racemic complex **7** in a saturated solution of DCM:pentane (1/3) was suitable for X-ray crystal structure analysis. (*S*)-**7**, light yellow solid; mp: 124.6–125.3 °C; [α]_D²⁰ +13.0 (*c* 0.25, CHCl₃); IR (DCM) ν 3303, 3037, 2933, 2838, 1688, 1688, 1594, 1520, 1464, 1378, 1256, 1125, 1090, 1062, 1004, 976, 939, 733, 560, 530 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ [2.07 (s, CH₃), 2.14 (s, CH₃), 1:1.2, 3H], [2.53 (d, *J* = 12.0 Hz, CH₂), 2.71 (d, *J* = 13.2 Hz, CH₂), 1:1.2, 1H], [2.84 (s, OCH₃), 2.88 (s, OCH₃), 1:1.2, 3H], [3.07 (d, *J* = 13.2 Hz, CH₂), 3.65 (d, *J* = 6.8 Hz, CH₂), 1.2:1, 1H], [3.76 (s, OCH₃), 3.79 (s, OCH₃), 1:1.2, 3H], [3.81 (s, CH₃), 3.92 (s, CH₃), 1:1.2, 3H], 4.23 (brs, 1H, CH₂), [4.86–4.95 (m, CH), 5.19–5.29 (m, CH), 1:1.2, 1H], [6.35 (d, *J* = 8.4 Hz, CH₂), 6.39 (d, *J* = 8.0 Hz, CH₂), 1:1.2, 1H], 7.09–7.23 (m, 3H, ArH), 7.29–7.36 (m, 4H, ArH), 7.43–7.69 (m, 3H, ArH), [8.10 (s, NH), 8.18 (s, NH), 1:1.2, 1H]; MS (ESI) *m/z* (%): 675 (M⁺, 60.07), 402 (M⁺–273, 100), 274 (M⁺–401, 28.80); Anal. Calcd. for C₂₇H₂₈IN₃O₃Pd requires: C, 47.98; H, 4.18; N, 6.22%. Found: C₂₇H₂₈IN₃O₃Pd, C 47.78, H 4.68, N 5.78%.

Synthesis of NHC–Au(I) complex (*S*)-**6a**

Compound (*S*)-**5a** (105.8 mg, 0.2 mmol) and AuCl·S(Me)₂ (58.8 mg, 0.2 mmol), KI (49.8 mg, 0.3 mmol) *t*-BuOK (56 mg, 0.5 mmol) were heated under reflux in THF (10 mL) for 8 h. The volatiles were then removed under reduced pressure and the residue purified by a silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate, 2:1–0:1) to give **8** as a white solid (94 mg, 65%). A single crystal grown from racemic complex **6a** in a saturated solution of DCM/pentane (1:3) was suitable for X-ray crystal structure analysis. (*S*)-**6a**: white solid; mp: 184.3–129.6 °C; [α]_D²⁰ +5.0 (*c* 0.25, CHCl₃); IR (DCM) ν 3407, 2929, 2835, 1697, 1591, 1468, 1438, 1286, 1083, 1002, 852, 779, 747, 657 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.19 (s, CH₃, 3H), 3.21 (s, OCH₃, 3H), 3.81 (s, OCH₃, 3H), 3.97 (s, CH₃, 3H), 6.36 (d, *J* = 8.4 Hz, Ar, 1H), 7.11–7.25 (m, Ar and NH, 5H), 7.32–7.37 (m, Ar, 4H), 7.47 (d, *J* = 8.0 Hz, Ar, 1H), 7.62 (t, *J* = 8.0 Hz, Ar, 1H); MS (ESI) *m/z* (%): 551 (M⁺, 10.05), 598 (M⁺–127, 100), 612 (M⁺–113, 22.10); Anal. Calcd. for C₂₄H₂₃IN₃O₃Au requires: C, 39.74; H, 3.20; N, 5.79%. Found: C₂₄H₂₃IN₃O₃Au C 40.64, H 3.08, N 5.72%.

General procedure for the intramolecular hydroamination reaction catalyzed by NHC–Au(I) complex (*S*)-**6a**

A mixture of NHC–Au(I) (*S*)-**6a** (7.2 mg, 5 mol %) and AgX (5 mol %) in DCM (0.4 mL) was stirred at rt for 5 min. A solution of compound **11** (76.6 mg, 0.20 mmol) in DCM (0.6 mL) was added to the resulting solution and the mixture stirred at rt for 36 h. Column chromatography of the reaction mixture gave the desired product. The enantiomeric purity of the product was determined by chiral HPLC analysis.

Supporting Information

Supporting Information File 1

Experimental procedures and characterization data of compounds given in this article.

[<http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-7-64-S1.pdf>]

Supporting Information File 2

Crystal structure data for NHC–Pd(II) complex **7a**.

[<http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-7-64-S2.pdf>]

Supporting Information File 3

Crystal structure data for NHC–Au(I) complex **6a**.

[<http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-7-64-S3.pdf>]

Supporting Information File 4

Crystal structure information file of compound **6a**.

[<http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-7-64-S4.cif>]

Supporting Information File 5

Crystal structure information file of compound **7a**.

[<http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-7-64-S5.cif>]

Acknowledgements

Financial support from the Shanghai Municipal Committee of Science and Technology (08dj1400100-2), the Fundamental Research Funds for the Central Universities, National Basic Research Program of China (973)-2010CB833302, the Fundamental Research Funds for the Central Universities and the National Natural Science Foundation of China (21072206, 20902019, 20472096, 20872162, 20672127, 20732008, 20821002, and 20702013) are gratefully acknowledged.

References

- Rogers, M. M.; Stahl, S. S. N-Heterocyclic Carbenes as Ligands for High-Oxidation-State Metal Complexes and Oxidation Catalysis. In *N-Heterocyclic Carbenes in Transition Metal Catalysis*; Glorius, F., Ed.; Topics in Organometallic Chemistry, Vol. 21; Springer: Berlin Heidelberg, 2007. doi:10.1007/3418_025
- Glorius, F., Ed. *N-Heterocyclic Carbenes as Ligands for High-Oxidation-State Metal Complexes and Oxidation Catalysis*; Topics in Organometallic Chemistry, Vol. 21; Springer: Berlin Heidelberg, 2007. doi:10.1007/11603795
- Arduengo, A. J.; Bertrand, G. *Chem. Rev.* **2009**, *109*, 3209–3210. doi:10.1021/cr900241h
- Schuster, O.; Yang, L.; Raubenheimer, H. G.; Albrecht, M. *Chem. Rev.* **2009**, *109*, 3445–3478. doi:10.1021/cr8005087
- Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B. *Chem. Rev.* **2009**, *109*, 3561–3598. doi:10.1021/cr8005153
- Arnold, P. L.; Casely, I. J. *Chem. Rev.* **2009**, *109*, 3599–3611. doi:10.1021/cr8005203
- Poyatos, M.; Mata, J. A.; Peris, E. *Chem. Rev.* **2009**, *109*, 3677–3707. doi:10.1021/cr800501s
- Corberán, R.; Mas-Marzá, E.; Peris, E. *Eur. J. Inorg. Chem.* **2009**, 1700–1716. doi:10.1002/ejic.200801095
- Hahn, F. E.; Jahnke, M. C. *Angew. Chem.* **2008**, *120*, 3166–3216. doi:10.1002/ange.200703883
Angew. Chem., Int. Ed. **2008**, *47*, 3122–3172. doi:10.1002/anie.200703883
- Bourissou, D.; Guerret, O.; Gabba, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–92. doi:10.1021/cr940472u
- Pugh, D.; Danopoulos, A. A. *Coord. Chem. Rev.* **2007**, *251*, 610–641. doi:10.1016/j.ccr.2006.08.001
- Braband, H.; Kückmann, T. I.; Abram, U. J. *Organomet. Chem.* **2005**, *690*, 5421–5429. doi:10.1016/j.jorganchem.2005.07.014
- Herrmann, W. A. *Angew. Chem.* **2002**, *114*, 1342–1363. doi:10.1002/1521-3757(20020415)114:8<1342::AID-ANGE1342>3.0.CO;2-A
Angew. Chem., Int. Ed. **2002**, *41*, 1290–1309. doi:10.1002/1521-3773(20020415)41:8<1290::AID-ANIE1290>3.0.CO;2-Y
- Powell, M. T.; Hou, D.-R.; Perry, M. C.; Cui, X.; Burgess, K. *J. Am. Chem. Soc.* **2001**, *123*, 8878–8879. doi:10.1021/ja016011p
- Seiders, T. J.; Ward, D. W.; Grubbs, R. H. *Org. Lett.* **2001**, *3*, 3225–3228. doi:10.1021/ol0165692
- He, M.; Bode, J. W. *J. Am. Chem. Soc.* **2008**, *130*, 418–419. doi:10.1021/ja0778592
- Lee, Y.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 3160–3161. doi:10.1021/ja809382c
- Hauwert, P.; Boerleider, R.; Warsink, S.; Weigand, J. J.; Elsevier, C. J. *J. Am. Chem. Soc.* **2010**, *132*, 16900–16910. doi:10.1021/ja1062407
- Song, C.; Ma, C.; Ma, Y.; Feng, W.; Ma, S.; Chai, Q.; Andrus, M. B. *Tetrahedron Lett.* **2005**, *46*, 3241–3244. doi:10.1016/j.tetlet.2005.03.026
- Kündig, E. P.; Seidel, T. M.; Jia, Y.-X.; Bernardinelli, G. *Angew. Chem.* **2007**, *119*, 8636–8639. doi:10.1002/ange.200703408
Angew. Chem., Int. Ed. **2007**, *46*, 8484–8487. doi:10.1002/anie.200703408
- Jia, Y.-X.; Hillgren, J. M.; Watson, E. L.; Marsden, S. P.; Kündig, E. P. *Chem. Commun.* **2008**, 4040–4042. doi:10.1039/b810858g
- Marsden, S. P.; Watson, E. L.; Raw, S. A. *Org. Lett.* **2008**, *10*, 2905–2908. doi:10.1021/ol801028e
- Hillgren, J. M.; Marsden, S. P. *J. Org. Chem.* **2008**, *73*, 6459–6461. doi:10.1021/jo8010842
- Lee, S.; Hartwig, J. F. *J. Org. Chem.* **2001**, *66*, 3402–3415. doi:10.1021/jo005761z
- Würtz, S.; Lohre, C.; Fröhlich, R.; Bergander, K.; Glorius, F. *J. Am. Chem. Soc.* **2009**, *131*, 8344–8345. doi:10.1021/ja901018g
- Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932–7934. doi:10.1021/ja00547a020
- Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008–2022. doi:10.1002/1521-3773(20020617)41:12<2008::AID-ANIE2008>3.0.CO;2-4
- Chen, Y.; Yekta, S.; Yudin, A. K. *Chem. Rev.* **2003**, *103*, 3155–3212. doi:10.1021/cr020025b
- Brunel, J. M. *Chem. Rev.* **2005**, *105*, 857–898. doi:10.1021/cr040079g
- Uozumi, Y.; Kyota, H.; Kishi, E.; Kitayama, K.; Hayashi, T. *Tetrahedron: Asymmetry* **1996**, *7*, 1603–1606. doi:10.1016/0957-4166(96)00193-0
- Hoveyda, A. H. Catalytic Asymmetric Olefin Metathesis. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003.
- Schrock, R. R.; Hoveyda, A. H. *Angew. Chem.* **2003**, *115*, 4740–4782. doi:10.1002/ange.200300576
Angew. Chem., Int. Ed. **2003**, *42*, 4592–4633. doi:10.1002/anie.200300576
- Hoveyda, A. H.; Schrock, R. R. *Chem.–Eur. J.* **2001**, *7*, 945–950. doi:10.1002/1521-3765(20010302)7:5<945::AID-CHEM945>3.0.CO;2-3
- Luchaco-Cullis, C. A.; Mizutani, H.; Murphy, K. E.; Hoveyda, A. H. *Angew. Chem.* **2001**, *113*, 1504–1508. doi:10.1002/1521-3757(20010417)113:8<1504::AID-ANGE1504>3.0.CO;2-V
Angew. Chem., Int. Ed. **2001**, *40*, 1456–1460. doi:10.1002/1521-3773(20010417)40:8<1456::AID-ANIE1456>3.0.CO;2-T
- Murphy, K. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 4690–4691. doi:10.1021/ja0300618
- Kacprzynski, M. A.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2004**, *126*, 10676–10681. doi:10.1021/ja0478779
- Duan, W.-L.; Shi, M.; Rong, G.-B. *Chem. Commun.* **2003**, 2916–2917. doi:10.1039/b309185f
- Chen, T.; Jiang, J.-J.; Xu, Q.; Shi, M. *Org. Lett.* **2007**, *9*, 865–868. doi:10.1021/ol063061w
- Xu, Q.; Gu, X.; Liu, S.; Dou, Q.; Shi, M. *J. Org. Chem.* **2007**, *72*, 2240–2242. doi:10.1021/jo062453d
- Zhang, T.; Shi, M. *Chem.–Eur. J.* **2008**, *14*, 3759–3764. doi:10.1002/chem.200701982
- Ma, G.-N.; Zhang, T.; Shi, M. *Org. Lett.* **2009**, *11*, 875–878. doi:10.1021/ol802861s
- Liu, L.-J.; Wang, F.; Shi, M. *Eur. J. Inorg. Chem.* **2009**, 1723–1728. doi:10.1002/ejic.200801207
- Liu, L.-J.; Wang, F.; Shi, M. *Organometallics* **2009**, *28*, 4416–4420. doi:10.1021/om900320c
- Liu, Z.; Shi, M. *Organometallics* **2010**, *29*, 2831–2834. doi:10.1021/om100331z
- Viciu, M. S.; Navarro, O.; Germaneau, R. F.; Kelly, R. A., III; Sommer, W.; Marion, N.; Stevens, E. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2004**, *23*, 1629–1635. doi:10.1021/om034319e

46. Viciu, M. S.; Germaneau, R. F.; Navarro-Fernandez, O.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2002**, *21*, 5470–5472. doi:10.1021/om020804i
47. Roland, S.; Cotet, W.; Mangeney, P. *Eur. J. Inorg. Chem.* **2009**, 1796–1805. doi:10.1002/ejic.200801157
48. Wang, C.-Y.; Liu, Y.-H.; Peng, S.-M.; Chen, J.-T.; Liu, S.-T. *J. Organomet. Chem.* **2007**, *692*, 3976–3983. doi:10.1016/j.jorganchem.2007.06.007
49. Peng, H. M.; Song, G. Y.; Li, Y. X.; Li, X. W. *Inorg. Chem.* **2008**, *47*, 8031–8043. doi:10.1021/ic800361v
50. Ketz, B. E.; Cole, A. P.; Waymouth, R. M. *Organometallics* **2004**, *23*, 2835–2837. doi:10.1021/om049838b
51. The crystal data of **7** have been deposited at the CCDC with number 754776. Empirical Formula: $C_{27}H_{28}IN_3O_3Pd$; Formula Weight: 675.82; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.309 x 0.250 x 0.191 mm; Crystal System: Monoclinic; Lattice Type: Primitive; Lattice Parameters: $a = 9.8872(8)\text{Å}$, $b = 16.8643(14)\text{Å}$, $c = 16.8744(15)\text{Å}$, $\alpha = 90^\circ$, $\beta = 100.713(2)^\circ$, $\gamma = 90^\circ$, $V = 2764.6(4)\text{Å}^3$; Space group: $P2(1)/c$; $Z = 4$; $D_{calc} = 1.624\text{ g/cm}^3$; $F_{000} = 1336$; Diffractometer: Bruker Smart CCD.
52. Baker, M. V.; Barnard, P. J.; Berners-Price, S. J.; Brayshaw, S. K.; Hickey, J. L.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2005**, *690*, 5625–5635. doi:10.1016/j.jorganchem.2005.07.013
53. Lemke, J.; Pinto, A.; Niehoff, P.; Vasylyeva, V.; Metzler-Nolte, N. *Dalton Trans.* **2009**, 7063–7070. doi:10.1039/b906140a
54. de Frémont, P.; Scott, N. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 2411–2418. doi:10.1021/om050111c
55. Ray, L.; Shaikh, M. M.; Ghosh, P. *Organometallics* **2007**, *26*, 958–964. doi:10.1021/om060834b
56. The crystal data of **8** have been deposited at the CCDC with number 782844. Empirical formula: $C_{24}H_{23}AuIN_3O_3$; formula weight: 725.32; crystal size: 0.277 x 0.268 x 0.224 mm; crystal color, habit: colorless, prismatic; crystal system: monoclinic; lattice type: primitive; lattice parameters: $a = 9.2786(7)\text{Å}$, $b = 25.5371(19)\text{Å}$, $c = 10.1633(14)\text{Å}$, $\alpha = 90^\circ$, $\beta = 104.9480(10)^\circ$, $\gamma = 90^\circ$, $V = 2326.7(3)\text{Å}^3$; Space group: $P-1$; $Z = 4$; $D_{calc} = 2.071\text{ g/cm}^3$; $F_{000} = 1376$; $R1 = 0.0478$, $wR2 = 0.1273$. Diffractometer: Bruker Smart CCD.
57. Ray, L.; Katiyar, V.; Barman, S.; Raihan, M. J.; Nanavati, H.; Shaikh, M. M.; Ghosh, P. *J. Organomet. Chem.* **2007**, *692*, 4259–4269. doi:10.1016/j.jorganchem.2007.06.033
58. Jothibasu, R.; Huynh, H. V.; Koh, L. L. *J. Organomet. Chem.* **2008**, *693*, 374–380. doi:10.1016/j.jorganchem.2007.11.003
59. Zhang, X.; Gu, S.; Xia, Q.; Chen, W. *J. Organomet. Chem.* **2009**, *694*, 2359–2367. doi:10.1016/j.jorganchem.2009.03.031
60. Eisnor, C. R.; Gossage, R. A.; Yadav, P. N. *Tetrahedron* **2006**, *62*, 3395–3401. doi:10.1016/j.tet.2006.01.046
61. Taylor, S. R.; Ung, A. T.; Pyne, S. G. *Tetrahedron* **2007**, *63*, 10889–10895. doi:10.1016/j.tet.2007.08.080
62. Yip, K.-T.; Yang, V.; Law, K.-L.; Zhu, N.-Y.; Yang, D. *J. Am. Chem. Soc.* **2006**, *128*, 3130–3131. doi:10.1021/ja060291x
63. Cropper, E. L.; Yuen, A.-P.; Ford, A.; White, A. J. P.; Hii, K. K. *Tetrahedron* **2009**, *65*, 525–530. doi:10.1016/j.tet.2008.10.098
64. Pratap, R.; Parrish, D.; Gunda, P.; Venkataraman, D.; Lakshman, M. K. *J. Am. Chem. Soc.* **2009**, *131*, 12240–12249. doi:10.1021/ja902679b
65. Marion, N.; Ecarnot, E. C.; Navarro, O.; Amoroso, D.; Bell, A.; Nolan, S. P. *J. Org. Chem.* **2006**, *71*, 3816–3821. doi:10.1021/jo060190h
66. Chai, D. I.; Lautens, M. J. *J. Org. Chem.* **2009**, *74*, 3054–3061. doi:10.1021/jo900053b
67. Marion, N.; Navarro, O.; Mei, J.; Stevens, E. D.; Scott, N. M.; Nolan, S. P. *J. Am. Chem. Soc.* **2006**, *128*, 4101–4111. doi:10.1021/ja057704z
68. Viciu, M. S.; Germaneau, R. F.; Nolan, S. P. *Org. Lett.* **2002**, *4*, 4053–4056. doi:10.1021/ol026745m
69. Winkelmann, O. H.; Riekstins, A.; Nolan, S. P.; Navarro, O. *Organometallics* **2009**, *28*, 5809–5813. doi:10.1021/om900677v
70. Navarro, O.; Kaur, H.; Mahjoor, P.; Nolan, S. P. *J. Org. Chem.* **2004**, *69*, 3173–3180. doi:10.1021/jo035834p
71. Bonati, F.; Burini, A.; Pietroni, B. R.; Bovio, B. J. *J. Organomet. Chem.* **1989**, *375*, 147–160. doi:10.1016/0022-328X(89)85094-6
72. Marion, N.; Nolan, S. P. *Chem. Soc. Rev.* **2008**, *37*, 1776–1782. doi:10.1039/b711132k
73. Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351–3378. doi:10.1021/cr068430g
74. Nieto-Oberhuber, C.; López, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 6178–6179. doi:10.1021/ja042257t
75. Gourlaouen, C.; Marion, N.; Nolan, S. P.; Maseras, F. *Org. Lett.* **2009**, *11*, 81–84. doi:10.1021/ol802430m
76. Marion, N.; Gealageas, R.; Nolan, S. P. *Org. Lett.* **2007**, *9*, 2653–2656. doi:10.1021/ol070843w
77. Fructos, M. R.; Belderrain, T. R.; de Frémont, P.; Scott, N. M.; Nolan, S. P.; Díaz-Requejo, M. M.; Pérez, P. J. *Angew. Chem.* **2005**, *117*, 5418–5422. doi:10.1002/ange.200501056
Angew. Chem., Int. Ed. **2005**, *44*, 5284–5288. doi:10.1002/anie.200501056
78. Marion, N.; Carlqvist, P.; Gealageas, R.; de Frémont, P.; Maseras, F.; Nolan, S. P. *Chem.–Eur. J.* **2007**, *13*, 6437–6451. doi:10.1002/chem.200700134
79. Gorske, B. C.; Mbofana, C. T.; Miller, S. J. *Org. Lett.* **2009**, *11*, 4318–4321. doi:10.1021/ol9016782
80. Lavallo, V.; Frey, G. D.; Donnadiou, B.; Soleilhavoup, M.; Bertrand, G. *Angew. Chem.* **2008**, *120*, 5302–5306. doi:10.1002/ange.200801136
Angew. Chem., Int. Ed. **2008**, *47*, 5224–5228. doi:10.1002/anie.200801136
81. Zeng, X.; Frey, G. D.; Kinjo, R.; Donnadiou, B.; Bertrand, G. *J. Am. Chem. Soc.* **2009**, *131*, 8690–8696. doi:10.1021/ja902051m
82. van der Vlugt, J. I. *Chem. Soc. Rev.* **2010**, *39*, 2302–2322. doi:10.1039/b925794m
83. Zeng, X.; Kinjo, R.; Kinjo, R.; Donnadiou, B.; Bertrand, G. *Angew. Chem.* **2010**, *122*, 954–957. doi:10.1002/ange.200905341
Angew. Chem., Int. Ed. **2010**, *49*, 942–945. doi:10.1002/anie.200905341
84. Klinckenberg, J. L.; Hartwig, J. F. *Angew. Chem.* **2011**, *123*, 88–98. doi:10.1002/ange.201002354
Angew. Chem., Int. Ed. **2011**, *50*, 86–95. doi:10.1002/anie.201002354
85. Lavallo, V.; Frey, G. D.; Kousar, S.; Donnadiou, B.; Bertrand, G. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 13569–13573. doi:10.1073/pnas.0705809104
86. Matsumoto, Y.; Selim, K. B.; Nakanishi, H.; Yamada, K.; Yamamoto, Y.; Tomioka, K. *Tetrahedron Lett.* **2010**, *51*, 404–406. doi:10.1016/j.tetlet.2009.11.039
87. LaLonde, R. L.; Sherry, B. D.; Kang, E. J.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 2452–2453. doi:10.1021/ja068819l
88. Johansson, M. J.; Gorin, D. J.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 18002–18003. doi:10.1021/ja0552500
89. Zhang, Z.; Liu, C.; Kinder, R. E.; Han, X.; Qian, H.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2006**, *128*, 9066–9073. doi:10.1021/ja062045r
90. Zhang, Z.; Bender, C. F.; Widenhoefer, R. A. *Org. Lett.* **2007**, *9*, 2887–2889. doi:10.1021/ol071108n

91. Zhang, Z.; Bender, C. F.; Widenhoefer, R. A. *Org. Lett.* **2007**, *9*, 2887–2889. doi:10.1021/ol071108n
92. Li, H.; Widenhoefer, R. A. *Org. Lett.* **2009**, *11*, 2671–2674. doi:10.1021/ol900730w
93. Zhang, Z.; Bender, C. F.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2007**, *129*, 14148–14149. doi:10.1021/ja0760731

License and Terms

This is an Open Access article under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/2.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The license is subject to the *Beilstein Journal of Organic Chemistry* terms and conditions: (<http://www.beilstein-journals.org/bjoc>)

The definitive version of this article is the electronic one which can be found at:
[doi:10.3762/bjoc.7.64](https://doi.org/10.3762/bjoc.7.64)