APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 40–44
Materials, Nanoscience and Catalysis **AOC**
DOI:10.1002/aoc.705

Synthesis of an axially chiral Ir–NHC complex derived from BINAM

Min Shi[1]* and Wei-Liang Duan[2]

[1]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, People's Republic of China
[2]School of Chemistry & Pharmaceutics, East China University of Science and Technology, 130 MeiLong Road, Shanghai 200237, People's Republic of China

Received 17 October 2003; Accepted 28 May 2004

The Ir–NHC complex 6 was successfully synthesized from the reaction of axially chiral binaphthyl dibenzimidazolium salt 5 with $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) in tetrahydrofuran in the presence of KO^tBu base under reflux. Its unique crystal structure is unambiguously disclosed by X-ray diffraction. Complex 6 is orthorhombic, with space group $P2_12_12_1$, unit cell dimensions $a = 12.1406(16)$ Å, $b = 19.110(3)$ Å, $c = 20.312(3)$ Å, $\alpha = \beta = \gamma = 90°$ and volume $4712.6(11)$ Å^3, $Z = 4$, $D_{calc} = 1.930$ Mg m^{-3}.

KEYWORDS: Ir(I)–NHC complex; 1,1′-binaphthyl-2,2′-diamine; DPEphos–Pd; crystal structure; X-ray diffraction

INTRODUCTION

In 1968, Öfele[1] and Wanzlick and Schönherr concurrently prepared the first authentic metal complex of *N*-heterocyclic carbene. These two reports received little attention until Arduengo and co-workers[3,4] synthesized the stable free carbene. Herrmann's group made progress in this field by preparing numerous *N*-heterocyclic carbenes and their metal complexes, and further applied them in homogeneous catalysis; see Refs 4 and 5 for reviews. Numerous papers concerning this topic have appeared in the past few years. The complexes of *N*-heterocyclic carbenes have been applied to a broad spectrum of catalytic reactions.[5] On the other hand, although a few examples of good or excellent enantioselectivities have been made with the asymmetric catalytic process using chiral metal–NHC complexes,[7–11] to date this process not been investigated extensively.[12] The first axially chiral NHC chelated complexes of palladium(II) and nickel(II) derived from 2,2′-bis(bromomethyl)-[1,1′]binaphthalenyl were prepared by RajanBabu's group,[13] in which the two chelating *N*-heterocyclic carbenes orient in a trans-geometry, however, using them as catalysts has not appeared in asymmetric catalysis. For a similar case, a trans-geometry of the chelating *N*-heterocyclic carbene palladium(II) complex gave very poor chemical yields and enantioselectivities in an intramolecular Heck reaction.[14] Zhang and Trudell[15] also prepared similar diimidazolium salt bearing binaphthyl skeleton for the Pd-catalyzed Suzuki cross-coupling reaction. Two rhodium complexes derived from the axially chiral binaphthyl dibenzimidazolium salt **5** have been reported.[16] Hence, we report here on the synthesis of an axially chiral Ir–NHC complex derived from axially dissymmetric 1,1′-binaphthalenyl-2,2′-diamine (**1**; BINAM).

RESULTS AND DISCUSSION

Synthesis of axially chiral binaphthyl dibenzimidazolium salt 5 and its Ir–NHC complex 6

The preparation of the NHC complexes began with the bis(2-diphenylphosphinophenyl) ether (DPEphos)–Pd-catalyzed coupling reaction of 2-bromo-nitrobenzene with (*S*)-1,1′-binaphthalenyl-2,2′-diamine (**1**; BINAM) in toluene in the presence of Cs_2CO_3 to give compound **2** in quantitative yield.[17,18] Reduction of **2** by means of Pd/C–H_2 produced compound **3**. Subsequent cyclization with triethyl

---

*Correspondence to: Min Shi, State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, People's Republic of China.
E-mail: Mshi@pub.sioc.ac.cn

Contract/grant sponsor: State Key Project of Basic Research; Contract/grant number: G200004807.
Contract/grant sponsor: Shanghai Municipal Committee of Science and Technology.
Contract/grant sponsor: National Natural Science Foundation of China; Contract/grant numbers: 20025206; 203900502; 20272069.

orthoformate catalyzed by toluenesulfonic acid (TsOH) at 100 °C afforded product **4**; quaternization of the benzimidazole ring of **4** by methyl iodide then gave the dibenzimidazolium salt **5** in quantitative yield (Scheme 1). The desired compound **5** was treated with $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) without further purification in tetrahydrofuran (THF) in the presence of KO^{t}Bu base to give the iridium(I) complex **6** (effects at preparing the Ir(III)–NHC complex using Crabtree's method[19,20] were unsuccessful), which was separated by silica-gel column chromatography as a yellow solid (Scheme 2). This complex is stable under ambient atmosphere and its structure was determined by ^{1}H NMR spectroscopic data and X-ray diffraction.

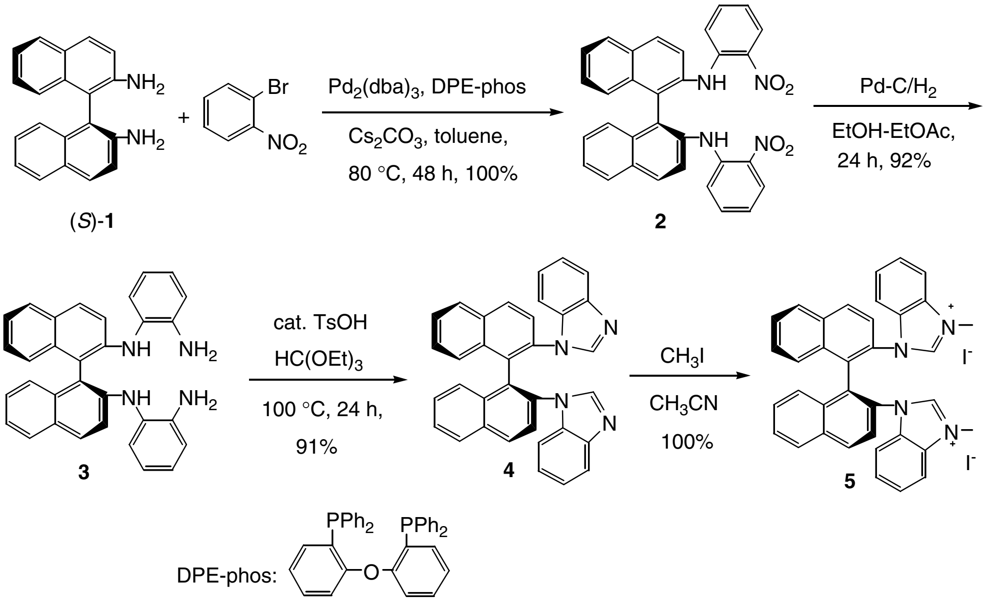
Molecular structures of complex 6

The single crystal of the Ir(I)–NHC complex **6** was obtained by careful recrystallization from CH_2Cl_2. Finally, its crystal structure was unambiguously disclosed by X-ray analysis (Figs 1 and 2). The crystal data are shown in Table 1. Selected bond lengths and bond angles are given in Tables 2 and 3 respectively.

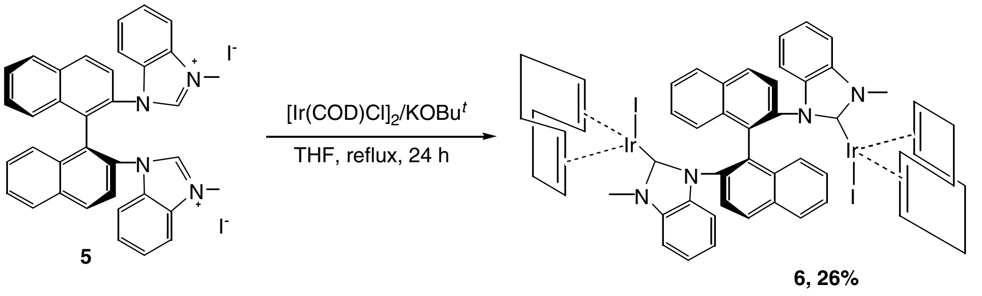
From Figure 1 it is very clear that the dibenzimidazolium precursor **5** binds two iridium atoms with two *N*-heterocyclic carbenes and the dihedral angle of the two naphthyl rings is 70.65°. The X-ray structure shows the iridium atom with a square-planar arrangement of the ligands and a bond angle I1–Ir1–C11(carbene) of 90.1(4)°. The Ir–C(carbene) distances, 2.059(12) and 1.924(19) Å, are normal for Ir–C σ bonds. The two iridium metal centers are far away from the axially chiral environment (Fig. 1). The study of the application of this axially chiral Ir–NHC complex in asymmetric catalysis is on going.

CONCLUSIONS

In conclusion, we have explored an Ir–NHC complex from the reaction of an axially chiral binaphthyl dibenzimidazolium salt **5** with $[Ir(COD)Cl]_2$ in THF in the presence of KO^{t}Bu base



Scheme 1. Synthesis of the axially chiral dibenzimidazolium salt.



Scheme 2. Synthesis of the axially chiral Ir–NHC complex.

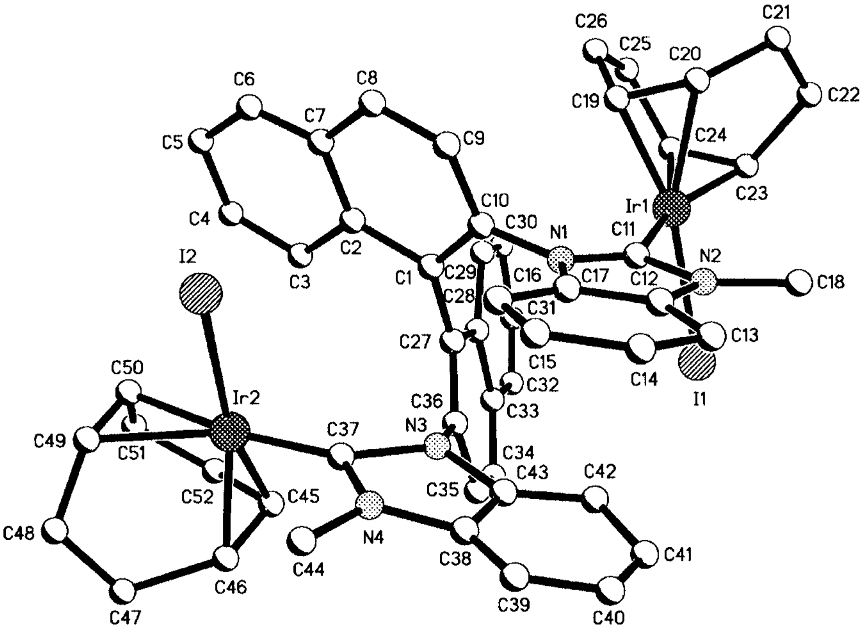


Figure 1. Crystal structure of complex **6**.

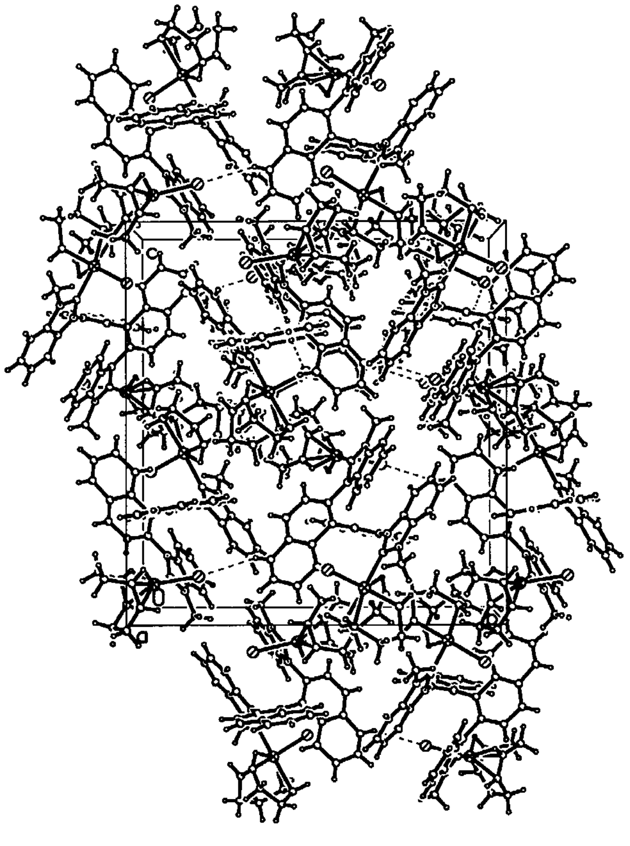


Figure 2. Crystal packing of complex **6**.

under reflux. Its unique crystal structure is unambiguously disclosed by X-ray analysis. We expect that our results will lead to the development of a new strategy on the synthesis of chiral metal–NHC complexes that can be used for asymmetric catalysis. Further studies in this area are in progress in our laboratory.

EXPERIMENTAL

General procedures

^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer in solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J*-values are in hertz. Mass spectra were recorded with an HP-5989 instrument. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin–Elmer-241 MC digital polarimeter; $[\alpha]$ D values are given in units of $10^{-1\circ}$ cm^2 g^{-1}. THF and toluene were distilled from sodium under anorgon atmosphere. All of the solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. $[Ir(COD)Cl]_2$ was prepared according to the literature.[21] Commercially obtained reagents were used without further purification. All reactions were monitored by thin-layer chromatography with Huanghai GF_{254} silica-gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

Preparation of chiral Ir–NHC complex 6

The preparation of the axially chiral binaphthyl dibenzimidazolium salt **5** has been reported in the supporting information of a previous publication.[16]

A mixture of **5** (77 mg, 0.10 mmol), $[Ir(COD)Cl]_2$ (33 mg, 0.05 mmol), KO^{t}Bu (25 mg, 0.20 mmol), and KI (33 mg,

Table 1. Crystal data and structure refinement of 6

Empirical formula	$C_{52}H_{50}N_4I_2Ir_2$
Formula weight	1369.16
Temperature (K)	293(2)
Crystal system	Orthorhombic
Lattice type	Primitive
Unit cell dimensions	
a (Å)	12.1406(16)
b (Å)	19.110(3)
c (Å)	20.312(3)
α (°)	90°
β (°)	90°
γ (°)	90°
V (Å^3)	4712.6(11)
Space group	$P2_12_12_1$
Z value	4
D_{calc}(Mg m^{-3})	1.930
$F_{(000)}$	2600
Θ range for data collection (°)	1.46 to 28.33
Reflections collected/unique	7301/5081 ($R_{int} = 0.0361$)
Completeness to $\theta = 25.50°$(%)	95.0%
Absorption correction	SADABS
Max. and min. transmission	1.0000 and 0.60169
Refinement method	Full-matrix least-squares on F^2
Data/restraints/ parameters	10 831/3/547
Goodness-of-fit on F^2	0.635
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0601, wR_2 = 0.1058$
R indices (all data)	$R_1 = 0.2241, wR_2 = 0.1354$
Largest diff. peak and hole (e$^-$ Å^{-3})	1.181 and −1.085

0.20 mmol) was stirred in THF (10 ml) under reflux for 24 h. After cooling, volatiles were removed under reduced pressure and the residue was purified by a silica-gel flash column chromatography (eluent: hexane/ethyl acetate, 8/1) to give the yellow solid iridium(I) complex **6**.

(S)-(−)-Diiodo-[1,1′-(1,1′-binaphthyl)-3,3′-dimethyldibenzimidazoline-2,2′-diylidene]bis-(η^4-1,5-cyclooctadiene)diiridium(I) (**6**). A crystal suitable for X-ray analysis was obtained by recrystallization from CH_2Cl_2. Yield: 18 mg (26%). M.p. >200 °C, ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.45–1.50 (m, 4H, COD-CH_2), 1.55–1.70 (m, 4H, COD-CH_2), 1.80–2.00 (m, 8H, COD-CH_2), 2.55–2.72 (m, 2H, COD-CH), 2.85–2.98 (m, 2H, COD-CH), 3.57–3.72 (m, 2H, COD-CH), 3.97 (s, 6H, CH_3), 4.50–4.68 (m, 2H, COD-CH), 6.60–6.68 (m, 4H, ArH), 6.78–6.84 (m, 2H, ArH), 6.96 (d, J = 8.4 Hz, 2H, ArH), 7.29–7.36 (m, 2H, ArH), 7.43–7.46 (d, 2H, J = 8.1 Hz, ArH), 7.56–7.63 (m, 4H, ArH), 7.92 (d, J = 9.0 Hz, 2H, ArH), 7.98 (d, J = 7.8 Hz, 2H, ArH).

Table 2. Selected bond lengths (Å) of complex **6**

Ir(1)–C(19)	1.99(4)
Ir(1)–C(11)	2.059(19)
Ir(1)–C(23)	2.11(2)
Ir(1)–C(20)	2.172(2)
Ir(1)–C(24)	2.27(2)
Ir(1)–I(1)	2.6691(17)
Ir(2)–C(37)	1.90(2)
Ir(2)–C(45)	1.99(3)
Ir(2)–C(46)	2.05(2)
Ir(2)–C(50)	2.14(3)
Ir(2)–C(49)	2.193(18)
Ir(2)–I(2)	2.6583(19)
Ir(2)–H(39)	2.1(3)

Table 3. Selected bond angles (°) of complex **6**

C(19)–Ir(1)–C(11)	87.6(10)
C(19)–Ir(1)–C(23)	99.0(10)
C(11)–Ir(1)–C(23)	158.9(11)
C(19)–Ir(1)–C(20)	36.5(10)
C(11)–Ir(1)–C(20)	91.4(8)
C(23)–Ir(1)–C(20)	82.5(8)
C(19)–Ir(1)–C(24)	81.1(12)
C(11)–Ir(1)–C(24)	163.9(11)
C(23)–Ir(1)–C(24)	36.3(7)
C(20)–Ir(1)–C(24)	86.4(9)
C(19)–Ir(1)–I(1)	163.4(8)
C(11)–Ir(1)–I(1)	89.0(6)
C(23)–Ir(1)–I(1)	89.9(5)
C(20)–Ir(1)–I(1)	160.0(9)
C(24)–Ir(1)–I(1)	98.5(8)

Crystallography

A suitable crystal was mounted on the top of a glass capillary. Crystal data and details of data collection and structure refinement are given in Table 1. Data were collected on a CCD area detector with graphite-monochromated Mo Kα radiation $\lambda = 0.710\,69$ Å using the ω–2θ technique at 20 °C. A total of 3887 unique reflections were collected. The data were corrected for Lorentz polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically by full-matrix least squares. All hydrogen atoms were included in calculated positions. All calculations were performed using the SHELXS-97 crystallographic software package. The crystal structure has been deposited at the Cambridge Crystallographic Data Center, deposition number CCDC 220628.

Acknowledgements

We thank the State Key Project of Basic Research (Project 973) (no. G2000048007), Shanghai Municipal Committee of Science and

Technology, and the National Natural Science Foundation of China (20025206, 203900502, and 20272069) for financial support.

REFERENCES

1. Öfele K. *J. Organometal. Chem.* 1968; **12**: 42.
2. Wanzlick HW, Schönherr HJ. *Angew. Chem. Int. Ed. Engl.* 1968; **7**: 141.
3. Arduengo III AJ, Harlow RL, Kline M. *J. Am. Chem. Soc.* 1991; **113**: 361.
4. Arduengo III AJ, Krafczyk R, Schmutzler R. *Tetrahedron* 1999; **55**: 14 523.
5. Herrmann WA. *Angew. Chem. Int. Ed. Engl.* 2002; **40**: 1290, and references cited therein.
6. Bourissou D, Guerret O, Gabba□ FP, Bertrand G. *Chem. Rev.* 2000; **100**: 39.
7. Seiders TJ, Ward DW, Grubbs RH. *Org. Lett.* 2001; **3**: 3225.
8. Powell MT, Hou DR, Perry MC, Cui XH, Burgess K. *J. Am. Chem. Soc.* 2001; **123**: 8878.
9. Perry MC, Cui XH, Powell MT, Hou DR, Reibenspies JH, Burgess K. *J. Am. Chem. Soc.* 2003; **125**: 113.
10. Van Veldhuizen JJ, Garber SB, Kingsbury JS, Hoveyda AH. *J. Am. Chem. Soc.* 2002; **124**: 4954.
11. Alexakis A, Winn CL, Guillen F, Pytkowicz J, Roland S, Mangeney P. *Adv. Synth. Catal.* 2003; **345**: 345.
12. Perry MC, Burgess K. *Tetrahedron: Asymm.* 2003; **14**: 951, and references cited therein.
13. Clyne DS, Jin J, Genest E, Gallucci JC, RajanBabu TV. *Org. Lett.* 2000; **2**: 1125.
14. Perry MC, Cui XH, Burgess K. *Tetrahedron: Asymm.* 2002; **13**: 1969.
15. Zhang CM, Trudell ML. *Tetrahedron Lett.* 2000; **41**: 595.
16. Duan W-L, Shi M, Rong G-B. *Chem. Commun.* 2003; 2916.
17. Yang BH, Buchwald SL. *J. Organometal. Chem.* 1999; **576**: 125.
18. Vyskočil Š, Jaracz J, Smrčina M, Šticha M, Hanuš V, Polášek M, Kočovsky P. *J. Org. Chem.* 1998; **63**: 7727.
19. Albrecht M, Crabtree RH, Mata J, Peris E. *Chem. Commun.* 2002; 32.
20. Albrecht M, Miecznikowski JR, Samuel A, Faller JW, Crabtree RH. *Organometallics* 2002; **21**: 3596.
21. Herde JL, Lambert JC, Senoff CV. *Inorg. Synth.* 1974; **15**: 18.