Communication

Synthesis of 1,3-bis-(5-ferrocenylisoxazole-3-yl) benzene-derived palladium(II) acetate complex and its application in Mizoroki–Heck reaction in an aqueous solution

Yong-jia Shang *, Jian-wei Wu, Chen-li Fan, Jin-song Hu, Ben-ye Lu

Anhui Key Laboratory of Functional Molecular Solids, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, PR China

A R T I C L E   I N F O

A B S T R A C T

The first synthesis and characterization of 1,3-bis-(5-ferrocenylisoxazole-3-yl) benzene-derived palladium(II) acetate complex were described and its application in Heck coupling reactions in an aqueous solution was studied. Complex **5** had been demonstrated to be a highly stable, active and efficient catalyst for Mizoroki–Heck coupling reactions.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Palladium catalyzed aryl or vinyl halides with alkenes, known as the Mizoroki–Heck reaction, has been recognized as a powerful tool in multiple organic transformations [1]. Mostly palladium complexes are used to catalyze these couplings reactions as they offer high product yields, high regioselectivity, high stereoselectivity and compatibility with many functional moieties. Palladium complexes containing phosphine, phosphate, and phosphine oxides are widely used as catalysts in Mizoroki–Heck coupling reactions. Important examples of the use of phosphines are found in the group of Fu [2], Beller [3], and Harttwig [4] who have made use of sterically demanding and electron-rich tertiary phosphines as catalyst modifiers in the Mizoroki–Heck reactions. Despite their effectiveness in controlling reactivity and selectivity, phosphine catalysts require air-free handling to prevent the oxidation of the ligand and are subject to P–C activation at elevated temperatures [5–7]. Furthermore, the difficulties involved in the removal of these by-products from organic products and high price of phosphine ligands led chemists to discover phosphine-free ligands. There has been increasing interest in the development of new phosphorus free palladium catalysts involving the use of N-, O-, S-donor ligands in recent years [8]. Especially N, N-type ligand have shown excellent properties for palladium complexation and

also as catalysts for cross-coupling reactions compared to P, P-type ligands, due to the stronger σ-donation which favors both oxidative addition and slow reductive elimination steps in the catalytic cycle [9].

Our continuing interest in the synthesis and applications of isoxazol(in)es and ferrocene derivatives in organic synthesis [10] also prompted us to use them as ligands [11] in metal-catalyzed reactions. To the best of our knowledge, there had been no example of any transition metal complexes of benzene-1,3-isoxazole ligands. Thus, benzene-1,3-bis(isoxazole) has attracted our attention as a possible alternative for the widely used phosphine ligands in the catalysis. In order to obtain highly stable and efficient palladium catalyst, we chose to build a benzene-bis(isoxazole) on the robust ferrocenic backbones [12] to obtain the ligand **4**, in which there were four potential co-ordination sites (two N and two O). The multidentate ligand can offer certain advantages that an additional co-ordination site in the ligand as a stabilizing group during the course of a Pd-mediated reaction can improve the catalytic efficiency of the complex [13]. The isoxazole ring has proven to be a suitable system for metal co-ordination to form pincer type metal complex which is testified by our experiment.

The use of water as solvent represents one of the safest and most advantageous alternatives economically and environmentally to organic solvents for metal-catalyzed reactions [14]. In addition, the use of water may have positive effects such as increasing selectivity and catalytic efficiency [15]. Herein, we report the first synthesis and characterization of 1,3-bis-(5-ferrocenylisoxazole-3-yl)

---

* Corresponding author. Fax: +86 0553 3883517.
  E-mail address: shyj@mail.ahnu.edu.cn (Y.-j. Shang).

benzene-derived palladium(II) acetate complex and its application in Mizoroki–Heck coupling reactions in an aqueous solution. The results showed that the complex was highly effective for Mizoroki–Heck coupling reactions.

## 2. Results and discussion

2.1. Complex

The preparation of 1,3-bis-(5-ferrocenylisoxazole-3-yl) benzene-derived palladium(II) acetate complex **5** was shown in Scheme 1. The ligand **4** was obtained in 87% yield via 1,3-dipolar cycloaddition reaction of ethynylferrocene **3** with the isophthald-nitrile oxides in situ generated from isophthaldehyde. The structure of ligand **4** was unambiguously confirmed by X-ray diffraction analysis [16], which was in accordance with ^{1}H NMR, ^{13}C NMR, and EIMS spectra [16] (Fig. 1).

Complex **5,** which was synthesized according to the method described by Hartshorn and Steel [17] was thermally stable and not sensitive to air and moisture. Complex **5** was determined by spectroscopic analysis. The ligand **4** is bound to palladium in a tridentate fashion forming two five-membered chelate rings. The C=N bands of complex **5** were shifted to lower frequency in the IR spectrum compared to that of the free ligand **4**. Moreover, the ^{1}H NMR spectrum of **4** shows a singlet at 8.33 ppm for the phenyl ring proton which is adjacent to both the isoxazole heterocycles. In the ^{1}H NMR spectrum of complex **5**, the signal of the phenyl ring proton at 8.33 ppm disappears and all the protons were observed to appear a downfield shift. The signal of the acetyl proton in the ^{1}H NMR at 2.32 ppm and the signal of carbonyl in the ^{13}C NMR at 172.2 ppm were also observed.

2.2. Catalytic activity of the complex

We next investigated this novel palladium complex as a catalyst for Mizoroki–Heck reaction. We applied the coupling of 4-iodotoluene and styrene as substrates to determine the optimum reaction conditions. Firstly, a variety of bases were essayed for the coupling between styrene and 4-iodotoluene to give desired product in the presence of 1 mol% complex **5** as catalyst and 1 equiv. tetra-*n*-butylammonium bromide (TBAB) as the reagent for activation and stabilization of palladium(0) species in an aqueous solution (DMF:H$_2$O = 1:1) at 80 °C under an argon atmosphere. Using NaO-Ac as a base in the presence of TBAB, the reaction had proceeded in high yield. The reaction carried out in the absence of TBAB was in a relative low yield. TBAB probably strengthened the stabilizations of
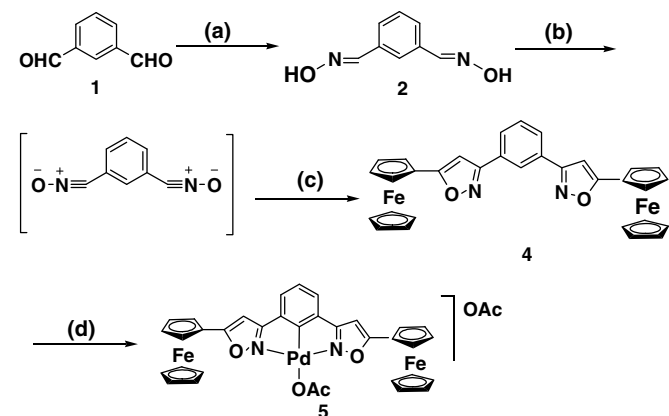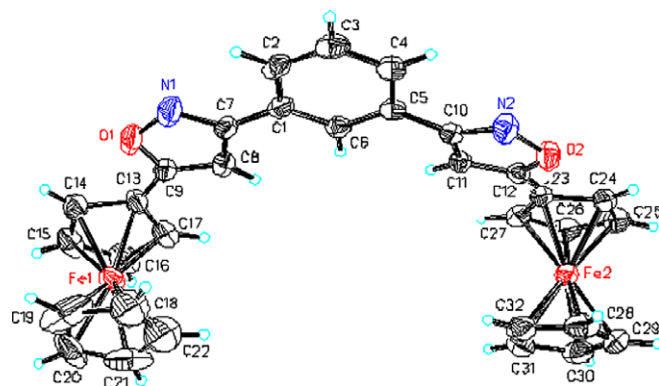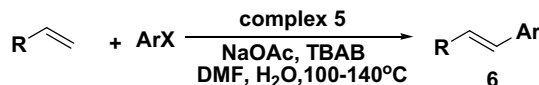

Fig. 1. The single-crystal X-ray structure of 1,3-bis-(5-ferrocenylisoxazole-3-yl) benzene **4**.

low co-ordinated Pd(0) species, and it was also as the phase transfer catalyst for the inorganic base/polar solvent/organic substrates/product phases [17]. The survey of aqueous solutions revealed that *N*,*N*-dimethyl formamide (DMF) with H$_2$O was much better than others. We also studied the reaction temperature in the presence of TBAB with NaOAc as a base using 1 mol% complex **5** as a catalyst in an aqueous solution under an argon atmosphere. We found 100 °C was the optimal reaction temperature for coupling of styrene and 4-iodotoluene. Instead of 1 mol%, it was found that the loading of complex **5** could be reduced to 0.01 mol% with similar yields under the same reaction conditions. However, the relatively long reaction time would be needed. We found the following optimized conditions: using complex **5** as a catalyst, the reaction proceeded in 88% yield with NaOAc as a base in the presence of TBAB in an aqueous solution (DMF:H$_2$O = 1:1) at 100 °C for 6 h under an argon atmosphere.

These optimized reaction conditions were then applied to cross-coupling reactions between olefins and electron-poor or electron-rich aryl iodides or bromides or chlorides to give internal alkenes **6** (Scheme 2 and Table 1). Couplings of 4-nitrophenyl iodide with a variety of olefins proceeded in short times and with excellent yields in the presence of 1 mol% complex **5** (Table 1, entries 1–3). The deactivated 4-methoxyphenyl iodide was coupled with different olefins. These results were similar to those obtained with the activated aryl iodides (Table 1, entries 4–7). The acrylonitrile gave a relative low yields because the desired *E*-isomeric product was obtained accompanied with *Z*-isomeric, according to ^{1}H NMR analysis (Table 1, entry 7). The stereo-hindered 2-nitrophenyl iodide gave the cross-coupled product in excellent yield in comparison with 4-nitrophenyl iodide (Table 1, entries 2 and 9). The heterocyclic compound of 2-chloro-5-iodopyridine also afforded high yield when it reacted with acrylic acid *n*-butyl ester (Table 1, entry 11).

We then studied the cross-coupling reaction with aryl bromides, using 2 mol% palladium complex **5** to provide alkenes **6m–t** (Table 1, entries 13–23) [18]. In general these coupling reactions proceeded with lower rates and yields than those with aryl iodides. Therefore we elevated the reaction temperature and the loading of catalyst and prolonged the reaction time and added an excess of olefin in order to increase the yields of the expected product **6**. The stereo-hindered 2-bromotoluene gave the cross-coupled product in modest yields in comparison with 4-bromotoluene and

Scheme 1. Synthesis of 1,3-bis-(5-ferrocenylisoxazole-3-yl) benzene-derived palladium(II) acetate complex **5**. Reagents and conditions: (a) NH$_2$OH · HCl, Na$_2$CO$_3$; (b) NCS, CH$_2$Cl$_2$; (c) ethynylferrocene (**3**), Et$_3$N; (d) Pd (OAc)$_2$, CH$_3$COOH.

Scheme 2. Cross-coupling reaction between olefins and aryl halides in an aqueous solution.

Table 1
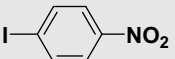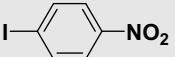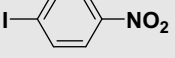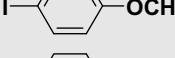The results of cross-coupling reaction between olefins and aryl halides in an aqueous solution[a]
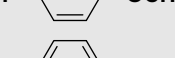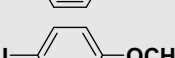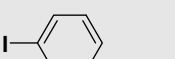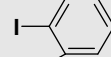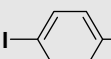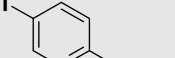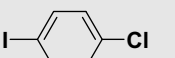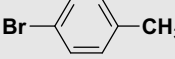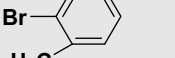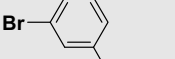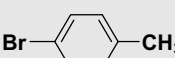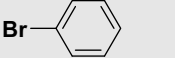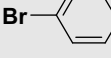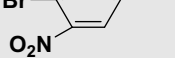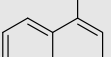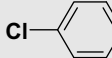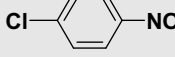
Entry	R	Aryl halides	Products	Yield[b] (%)
1	$CO_2CH_2CH_3$	I–C6H4–NO2	6a	93
2	$CO_2(CH_2)_3CH_3$	I–C6H4–NO2	6b	94
3	Phenyl	I–C6H4–NO2	6c	93
4	Phenyl	I–C6H4–OCH3	6d	85
5	$CO_2CH_2CH_3$	I–C6H4–OCH3	6e	80
6	$CO_2(CH_2)_3CH_3$	I–C6H4–OCH3	6f	89
7	CN	I–C6H4–OCH3	6g	78[c]
8	$CO_2(CH_2)_3CH_3$	I–C6H5	6h	93
9	$CO_2(CH_2)_3CH_3$	I–C6H4(o-NO2)	6i	92
10	$CO_2(CH_2)_3CH_3$	I–C6H4–CH3	6j	78
11	$CO_2(CH_2)_3CH_3$	5-iodo-2-chloropyridine	6k	90
12	$CO_2(CH_2)_3CH_3$	I–C6H4–Cl	6l	90
13	$CO_2(CH_2)_3CH_3$	Br–C6H4–CH3	6m	65
14	$CO_2(CH_2)_3CH_3$	Br–C6H4(o-CH3)	6n	67
15	$CO_2(CH_2)_3CH_3$	Br–C6H4(m-CH3)	6o	73
16	$CO_2CH_2CH_3$	Br–C6H4–CH3	6p	60
17	$CO_2(CH_2)_3CH_3$	Br–C6H5	6q	80
18	$CO_2(CH_2)_3CH_3$	Br–C6H4–NO2	6r	90
19	$CO_2(CH_2)_3CH_3$	Br–C6H4(o-NO2)	6s	93
20	$CO_2(CH_2)_3CH_3$	1-bromonaphthalene	6t	89

Table 1 (continued)

Entry	R	Aryl halides	Products	Yield[b] (%)
21	$CO_2(CH_2)_3CH_3$	Cl–C6H5	6u	Trace
22	$CO_2(CH_2)_3CH_3$	Cl–C6H4–NO2	6v	58
23	$CO_2(CH_2)_3CH_3$	Cl–C6H4–COCH3	6w	78

[a] General reaction conditions for coupling reaction between olefins and aryl halides: olefin (1.5 mmol), aryl halides (1 mmol), NaOAc (2 mmol), TBAB (1 mmol), complex **5** (1–5 mol%), aqueous solution (4 mL) under an argon atmosphere.
[b] Isolated yields after column chromatography.
[c] $E/Z = 4:1$.

3-bromotoluene (Table 1, entries 13–15). We unexpectedly found that the aryl bromide with nitro group gave excellent results with catalyst loading 2 mol% and the reactions performed in short times. The above findings were similar to activated aryl iodides (Table 1, entries 18 and 19). Bromonaphthalene could also perform the cross-coupling reaction smoothly under the same reaction conditions to afford the cross-coupling product in good yield (Table 1, entry 20). As for non-activated aryl chlorides, complex **5** shows relative low activities under the similar reaction conditions. We found that even aryl chlorides with nitro group gave modest results with catalyst loading 5 mol% and the reaction proceeded in long times (Table 1, entry 21–23). It is worth noting that in all the reactions no Pd black was observed and complex **5** was easily removed in the extraction step after the reaction because of its low solubility in most of solvents.

In conclusion, 1,3-bis-(5-ferrocenylisoxazole-3-yl) benzene-derived palladium(II) acetate complex **5** had been demonstrated to be a highly active and efficient catalyst for Mizoroki–Heck coupling reactions in an aqueous solution. A variety of functional groups such as methoxy and nitro were well tolerated under the present catalytic system. Complex **5** showed very high stability in an aqueous solution at reflux and no Pd black was observed. Moreover, it is easy to recovery and re-use of the catalyst because of its low solubility in most of solvents. Further work is in progress to broaden the scope of this catalytic system for aryl chlorides and other organic transformations.

3. Experimental

3.1. General

All reagents and solvents were obtained from commercial suppliers and used without further purification. Melting points were measured using a WC-1 microscopic apparatus. IR spectra were recorded on a Perkin–Elmer 983 FT-IR spectrometer. ^{1}H NMR spectra were recorded on a Bruker Avance DMX 300 instrument (300 MHz). Chemical shifts are reported in ppm with tetramethylsilane (TMS, 0.00 ppm) as internal standard. GC–MS analyses were performed on a HP-5973 spectrometer. Elemental analyses were carried out on an EA-1110 elemental analyzer. X-ray crystallographic data were made on a Rigaku Mercury CCDC X-ray diffractometer (3 kV, sealed tube) at 193 K by using graphite monochromated Mo Kα (k = 0.71070 AX).

3.2. Preparation of 1,3-bis-(5-ferrocenylisoxazole-3-yl) benzene **4**

Hydroxylamine hydrochloride (1.2 mmol) and sodium bicarbonate (1.5 mmol) were added to the solution of 1,3-benzenedialdehyde (1.0 mmol) in 10 mL ethanol. The mixture was stirred at

room temperature over night. The precipitate was removed by filtration and washed with water. After dried, the aldoxime was obtained in 98% yield.

Aldoxime (1 mmol) and chlorosuccinimide (NCS, 1 mmol) were stirred in flask containing dry dichloromethane (5 mL). The reaction mixture was refluxed at 30 °C for 40 min. The ethynylferrocene (1 mmol) was added. Triethylamine (1.4 mL in 3 mL of CH$_2$Cl$_2$) was added dropwise over about 1.5 h and the mixture was stirred overnight at room temperature. The complete consumption of starting materials was judged by TLC analysis. After stirring overnight, the residue was extracted with dichloromethane (3 × 3 mL) and washed with water for three times. The combined organic layers were dried with anhydrous magnesium sulfate. The solution was filtered and the solvents were removed in vacuo. The residue was purified by flash column chromatography on alumina gel to afford red crystals in 87% yield. M.p. 200–202 °C. IR (KBr): 1612 (C=N), 1560 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.33 (s, 1H, C$_6$H$_4$), 8.06 (dd, J = 6.3, 7.7 Hz, 2H, C$_6$H$_4$), 7.66 (t, J = 7.8 Hz, 1H, C$_6$H$_4$), 6.67 (s, 2H, C$_3$HON), 4.85 (s, 4H, C$_5$H$_4$), 4.49 (s, 4H, C$_5$H$_4$), 4.22 (s, 10H, C$_5$H$_5$). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 162.0, 137.1, 133.6, 128.9, 127.8, 127.5, 124.3, 95.0, 69.3, 65.5. EIMS: m/z = 580.1 (M$^+$). Anal. Calc. for C$_{32}$H$_{24}$Fe$_2$N$_2$O$_2$: C, 66.20; H, 4.14; N, 4.82. Found: C, 66.18; H, 4.12; N, 4.80%.

3.3. Preparation of 1,3-bis-(5-ferrocenylisoxazole-3-yl) benzene-derived palladium(II) acetate complex 5

Compound **5** was synthesized according to the method described by Hartshorn and Steel. A solution of 1,3-bis-(5-ferrocenylisoxazole-3-yl) benzene **4** (1.5 mmol) and palladium acetate (1.5 mmol) in acetic acid (15 mL) was heated under reflux for 16 h in a round-bottomed flask. The precipitate was removed by filtration and washed with water. After dried, complex **5** was obtained in 85% yield. IR (KBr): 1601 (C=N), 1523 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, DMF-d_6): δ = 8.68 (dd, J = 6.3, 7.7 Hz, C$_6$H$_4$), 7.98 (t, J = 7.8 Hz, 1H, C$_6$H$_4$), 7.47 (s, 2H, C$_3$HON), 5.14 (s, 4H, C$_5$H$_4$), 4.73 (s, 4H, C$_5$H$_4$), 4.40 (s, 10H, C$_5$H$_5$), 3.09 (s, 3H, CH$_3$CO), 2.92 (s, 3H, CH$_3$CO). ^{13}C NMR (75 MHz, DMF-d_6): δ = 172.2, 171.7, 162.1, 134.2, 129.9, 129.7, 127.4, 124.1, 96.5, 69.9, 66.8. EIMS: 804.2 ([M+H]$^+$). Anal. Calc. for C$_{36}$H$_{29}$O$_6$N$_2$Fe$_2$Pd: C, 53.77; H, 3.61; N, 3.48. Found: C, 53.75; H, 3.59; N, 3.47%.

3.4. General procedure for the Heck coupling reaction in an aqueous solution

Under an argon atmosphere, a 10 mL round-bottomed flask was charged with palladium complex **5** (1–5 mol%), aryl halide (1 mmol), olefin (1.5 mmol), NaOAc (2 mmol), tetrabutylammonium bromide (1 mmol) and aqueous solutions (4 mL). The mixture was stirred at 100–140 °C for the 6–24 h. The reaction progress was analysed by GLC. The mixture was extracted with EtOAc (3 × 15 mL), dried over MgSO$_4$, concentrated in vacuo and purified by flash chromatography on silica gel. All the prepared products except 6 K had been reported previously and were characterized by comparison with their reported data. Physical, analytical and spectroscopic data of newly synesized compound followed:

(E)-2-chloro-5-(acrylic acid n-Butyl ester) pyridine (**6k**): m.p. 53–54 °C. IR (KBr): 1713 (C=O), 1640 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 8.51 (s, 1H, C$_5$H$_3$N), 7.82–7.78 (dd, J = 2.5, 8.4 Hz, 1H, C$_5$H$_3$N), 7.65 (d, J = 16.11 Hz, 1H, CH=CH), 7.37 (d, J = 8.37 Hz, 1H, C$_5$H$_3$N), 6.51 (d, J = 15.57 Hz, 1H, CH=CH), 4.22 (t, 2H, COCH$_2$CH$_2$CH$_2$CH$_3$), 1.73–1.64 (m, 2H, COCH$_2$CH$_2$CH$_2$CH$_3$), 1.49–1.42 (m, 2H, COCH$_2$CH$_2$CH$_2$CH$_3$), 0.98–0.94 (t, 3H, COCH$_2$CH$_2$CH$_2$CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$) δ: 166.1, 152.7, 149.5, 139.2, 136.5, 129.3, 124.5, 121.2, 64.8, 30.7, 19.1, 13.7.

HRMS (ESI): 239.07 ([M]$^+$). Anal. Calc. for C$_{12}$H$_{14}$ClNO$_4$: C, 60.13; H, 5. 89; N, 5.84. Found: C, 60.10; H, 5.86; N, 5.82%.

4. Supplementary material

CCDC 292945 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] (a) R.F. Heck, Acc. Chem. Res. 12 (1972) 139;
(b) R.F. Heck, Org. React. 27 (1982) 345;
(c) G.D. Davis Jr., A. Hallberg, Chem. Rev. 89 (1989) 1433;
(d) C.H. Oh, S.H. Jung, S.Y. Bang, D.I. Park, Org. Lett. 4 (2002) 3325;
(e) A. Salcedo, L. Neuville, C. Rondot, P. Retailleau, Org. Lett. 10 (2008) 857;
(f) R. Abu-Reziq, D. Wang, M. Post, H. Alper, Chem. Mater. 20 (2008) 2544;
(g) K.E. Plass, X. Liu, B.S. Brunschwig, N.S. Lewis, Chem. Mater. 20 (2008) 2228;
(h) J.L. Henderson, A.S. Edwards, M.F. Greaney, Org. Lett. 9 (2007) 5589.
[2] (a) A.F. Littke, G.C. Fu, J. Org. Chem. 64 (1999) 10;
(b) A.F. Littke, G.C. Fu, J. Am. Chem. Soc. 123 (2001) 6989.
[3] A. Ehrentraut, A. Zopf, M. Beller, Synlett 11 (2000) 1589.
[4] M. Jorgensen, S. Lee, X. Liu, J.P. Wolkowski, J.F. Hartwig, J. Am. Chem. Soc. 124 (2002) 12557.
[5] N.A. Bumagin, V.V. Bykov, Tetrahedron 53 (1997) 14437.
[6] M. Beller, H. Fischer, W.A. Herrmann, K. Ofele, C. Brossmer, Angew. Chem., Int. Ed. 34 (1995) 1848.
[7] M. Feuerstein, D. Laurenti, H. Doucet, M. Santelli, Synthesis 15 (2001) 2320.
[8] (a) R. Bernini, S. Cacchi, G. Fabrizi, G. Forte, S. Niembro, F. Petrucci, Org. Lett. 10 (2008) 561;
(b) B.M. Suijkerbuijk, J.M. Herreras, S.D. Martínez, G. van Koten, Organometallics 27 (2008) 534;
(c) V. Montoya, J. Pons, V. Branchadell, J. Garcia-Antón, M. Font-Bardia, J. Ros, Organometallics 27 (2008) 1084;
(d) B. Punji, J.T. Mague, M.S. Balakrishna, Inorg. Chem. 46 (2007) 11316;
(e) S. Haneda, Z. Gan, K. Eda, M. Hayashi, Organometallics 26 (2007) 6551.
[9] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organometallic Chemistry, 2nd ed., University Science Books, Mill Valley, CA, 1987.
[10] (a) Y.J. Shang, C.L. Fan, M.G. Li, C.Y. Zheng, Appl. Organomet. Chem. 20 (2006) 626;
(b) Y.J. Shang, Y.G. Wang, Tetrahedron Lett. 43 (2002) 2247;
(c) Y.J. Shang, W.G. Shou, Y.G. Wang, Synlett 7 (2003) 1064;
(d) Y.J. Shang, Y.G. Wang, Synthesis 12 (2002) 1663.
[11] (a) M.A. Arai, T. Arai, H. Sasai, Org. Lett. 1 (1999) 1795;
(b) M.A. Arai, M. Kuraishi, T. Arai, H. Sasai, J. Am. Chem. Soc. 123 (2001) 2907;
(c) T. Shinohara, M.A. Arai, K. Wakita, T. Arai, H. Sasai, Tetrahedron Lett. 44 (2003) 711;
(d) C. Muthiah, M.A. Arai, T. Shinohara, S. Takizawa, H. Sasai, Tetrahedron Lett. 44 (2003) 5201;
(e) K. Wakita, G.B. Bajracharya, M.A. Arai, S. Takizawa, T. Suzuki, H. Sasai, Tetrahedron: Asymmetry 18 (2007) 372.
[12] (a) R.M. Moreno, A. Bueno, A. Moyano, J. Organomet. Chem. 660 (2002) 62;
(b) A. Eds. Meijera, F. Diederich, Metal-Catalyzed Cross-coupling Reactions, Wiley-VCH, Weinheim, 2004.
[13] (a) M.T. Reetz, S.R. Waldvogel, R. Goddard, Tetrahedron Lett. 38 (1997) 5967;
(b) I.G. Jung, S.U. Son, K.H. Park, Y.K. Chung, Organometallics 22 (2003) 4715;
(c) I.D. Kostas, B.R. Steele, S.V. Amosova, Tetrahedron 59 (2003) 3467.
[14] (a) B.H. Lipshutz, B.R. Taft, Org. Lett. 10 (2008) 1329;
(b) B.H. Lipshutz, T.B. Petersen, A.R. Abela, Org. Lett. 10 (2008) 1333;
(c) B.H. Lipshutz, G.T. Aguinaldo, S. Ghorai, K. Voigtritter, Org. Lett. 10 (2008) 1325;
(d) Z. Zhang, Z. Zha, C. Gan, C. Pan, Y. Zhou, Z. Wang, M.M. Zhou, J. Org. Chem. 71 (2006) 4339;
(e) B. Liang, M. Dai, J. Chen, Z. Yang, J. Org. Chem. 70 (2005) 391.
[15] J.P. Genet, M. Savignac, J. Organomet. Chem. 576 (1999) 305.
[16] Crystallographic data for **4**: space group P1̄, a = 11.8066(3) Å, b = 21.3730(18) Å, c = 11.2852(9) Å, α = 90.00(2)°, β = 116.79(2)°, γ = 90.00(2)°, V = 2542.2(2) Å^3, T = 293(2) K, Z = 4.
[17] C.M. Hartshorn, P.J. Steel, Organometallics 17 (1998) 3487.
[18] G.A. Grase, R. Singh, E.D. Stevens, S.P. Nolan, J. Organomet. Chem. 687 (2003) 269.