Inorganica Chimica Acta 363 (2010) 1979–1983

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis, structural characterization and catalytic activity of a palladium(II) complex bearing a new ditopic thiophene-*N*-heterocyclic carbene ligand

Han Vinh Huynh *, Ying Xia Chew

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

ARTICLE INFO

Article history:
Received 21 January 2009
Received in revised form 24 February 2009
Accepted 25 February 2009
Available online 9 March 2009

Dedicated to Prof. R.J. Puddephatt

Keywords:
N-Heterocyclic carbenes
Palladium
Thiophene
Suzuki–Miyaura reaction
Homogeneous catalysis

ABSTRACT

A new thiophene-functionalized benzimidazolium salt (**2**) has been prepared by reacting *N*-methylbenzimidazole with 2-bromomethylthiophene (**1**), which in turn was obtained by bromination of 2-thiophenemethanol with PBr_3. Subsequent reaction of salt **2** with $Pd(OAc)_2$ afforded the *cis*-configured bis(carbene) Pd(II) complex (*cis*-**3**), which in solution exists as an inseparable mixture of *cis–anti* and *cis–syn*-rotamers in a 3.5:1 ratio. All new compounds have been fully characterized by spectroscopic and spectrometric methods. A preliminary catalytic study shows that *cis*-**3** is highly active in the Suzuki–Miyaura coupling of aryl bromides with phenylboronic acid in/on water as environmentally benign reaction media.

1. Introduction

N-heterocyclic carbenes (NHCs) are nowadays common ligands in organometallic chemistry and catalysis mainly due to their strong donor-abilities surpassing those of classical phosphines and the ease of their preparation [1]. Moreover, additional functionalities can be easily introduced at the nitrogen atoms of the *N*-heterocyclic ring, and accordingly, various donor-functionalized NHCs and their complexes have been explored, and their use in catalysis has been recently reviewed [2]. To this point, *N*-functionalization with *N*-, *O*- and *P*-donor groups is relatively common, whereas carbene ligands bearing softer sulfur-donors are surprisingly rare, although some thiolate-NHCs [3–6], thioether-NHCs [7–10] and thiophene-NHCs [11,12] have been reported. Notably all these examples are based on an unsaturated imidazole or a saturated imidazoline *N*-heterocyclic scaffold. To the best of our knowledge, sulfur-functionalized NHCs as potentially hemilabile ligands based on benzimidazole are unknown, although benzannulated carbenes [13,14] are becoming increasingly popular. As part of our on-going research on complexes of benzannulated carbenes [15–21], we herein report the synthesis, structural characterization and catalytic activity of a palladium(II) complex bearing a new thiophene-functionalized benzimidazolin-2-ylidene ligand.

* Corresponding author. Tel.: +65 65162670; fax: +65 67791691.
E-mail address: chmhhv@nus.edu.sg (H.V. Huynh).

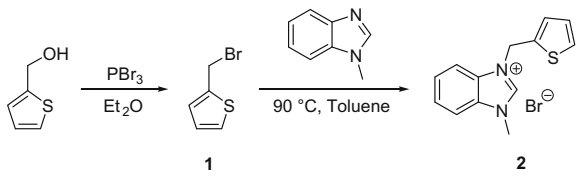
0020-1693/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2009.02.035

2. Results and discussion

2.1. Ligand precursor

The two-step synthesis of the new thiophene-functionalized benzimidazolium salt **2**, which serves as ligand precursor, is summarized in Scheme 1. The first step involves the bromination of commercially available 2-thiophenemethanol to afford 2-bromomethylthiophene (**1**). In contrast to a previous report [22], this can be easily accomplished with PBr_3, which furnishes 2-bromomethylthiophene (**1**) as a yellow liquid in 89% yield. Upon standing at ambient temperature in air, compound **1** slowly decomposes under formation of a dark brown solid with the evolution of fumes, possibly due to acid catalyzed polymerization [22,23]. However, bromide **1** can be stored under nitrogen and at low temperature in the dark for a few days without decomposition. Heating of **1** with *N*-methylbenzimidazole in toluene at 90 °C finally afforded the desired thiophene-functionalized benzimidazolium bromide **2** as an off-white powder in 78% yield.

A characteristic downfield resonance at 11.43 ppm corresponding to the NCHN (C2) proton in the ^1H NMR spectrum indicates the successful formation of salt **2**. The chemical shift of its C2 carbon at 142.9 ppm is in agreement with reported data for other benzimidazolium salts [24]. The ESI mass spectrum of the carbene precursor **2** is dominated by a base peak centered at $m/z = 229$ for the cation $[M-Br]^+$, which arises from loss of the bromide counter anion. For comparison purposes, we have also obtained single crys-



Scheme 1. Two-step synthesis of 1-(2-thienylmethyl)-3-methylbenzimidazolium bromide.

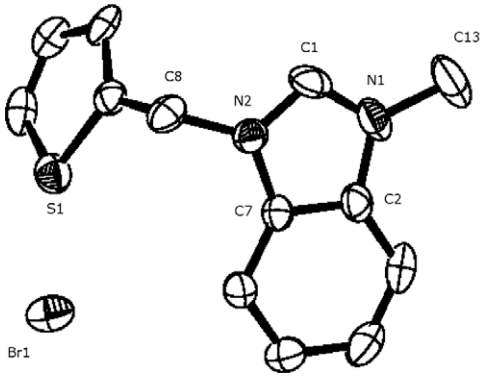
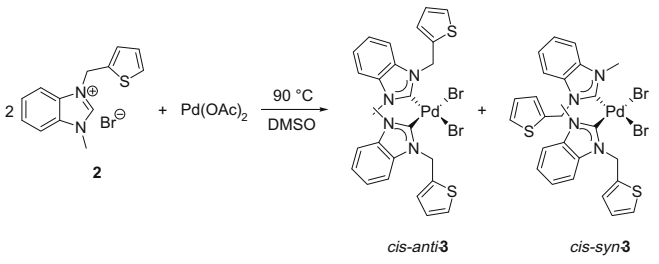


Fig. 1. Molecular structure of **2** · 1.5H_2O showing 50% probability ellipsoids. Water molecules and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): C1–N1 1.317(6), C1–N2 1.329(5), N1–C2 1.391(5), N1–C13 1.461(5), N2–C7 1.383(5), N2–C8 1.470(5), C2–C7 1.397(5); N1–C1–N2 111.0(4), C1–N1–C2 108.4(3), C1–N1–C13 126.4(4), C1–N2–C7 107.8(3), C1–N2–C8 125.2(4).

tals of the new thioether-functionalized benzimidazolium salt from a concentrated $CDCl_3$ solution as water solvate **2** · 1.5H_2O, which were subjected to X-ray diffraction analysis. The asymmetric unit contains two independent molecules, of which only one is shown in Fig. 1 along with the crystallographic numbering scheme.



Scheme 2. Preparation of Pd(II) bis(carbene) complex *cis*-**3**.

2.2. Synthesis and characterization of Pd–NHC complex

Reaction of two equiv of salt **2** with $Pd(OAc)_2$ under *in situ* deprotonation afforded the desired bis(carbene) complex *cis*-[$PdBr_2(NHC)_2$] (*cis*-**3**) (Scheme 2), which can be isolated as a light brown solid after washing of the crude reaction mixture with diethyl ether and THF. The formation of a carbene complex is indicated by the disappearance of the acidic C2 proton characteristic of **2** in the ^{1}H NMR spectrum of *cis*-**3**. Furthermore, two sets of closely spaced signals are observed indicating the existence of an inseparable isomeric mixture, the ratio of which was determined to be 3.5:1 through integration (vide infra).

Whereas the NCH_2 resonances of precursor **2** were detected as singlets, these protons become diastereotopic in the carbene complex *cis*-**3** giving rise to a doublet for each proton (AA′ spin system, Fig. 2). This observation is in agreement with a *cis*-arrangement of the two carbene ligands, in which a free rotation around the Pd–C bond is restricted due to steric repulsion of the bulky *N*-thienylmethyl substituents. As a consequence, the two isomers have been assigned to *cis–syn* and *cis–anti* rotamers, in which the unsymmetrical carbene ligands differ in the orientation of their *N*-substituents. Due to steric reasons, the major set of signals is assigned to the *cis–anti* rotamer. Correspondingly, two sets of signals are also observed in the ^{13}C NMR spectrum, and the assignment is further corroborated by two closely spaced carbene resonances at 174.5 and 174.2 ppm, which are in the typical range observed for *cis*-bis(benzimidazolin-2-ylidene)complexes of Pd(II). The corresponding *trans* isomers would exhibit more downfield carbene shifts of ~180 ppm [25,26]. Furthermore, rotamers in *trans*-bis(carbene) complexes are relatively common, and we have recently reported a detailed study on their isomerization behavior [27]. On the other hand, *cis*-bis(carbene) complexes bearing unsymmetrical ligands usually adopt a *cis–anti* arrangement due to steric constraints, and the existence of less favorable *cis–syn* rotamers have rarely been observed.

Single crystals of the rotamer *cis–anti*-**3** selectively crystallized as acetone solvate *cis–anti*-**3** · 1.5CH_3COCH_3 upon slow evaporation of a saturated acetone solution of **3**. The solid state molecular structure determined by X-ray diffraction studies is shown in Fig. 3. As anticipated for the major isomer in solution, the two carbene ligands are coordinating the metal center in the sterically more favorable *cis–anti* fashion, as it reduces the repulsion between the adjacent carbene ligands. The essentially square planar coordination sphere is completed by two bromo ligands. Due to a crystallographic symmetry, the pendant thienylmethyl groups are oriented *anti* to each other. The dihedral angle between the carbene ring planes and the coordination plane is 73.5°. Compared to its benzimidazolium salt precursor **2**, the $C_{carbene}$–N1/2 bonds have become elongated by Δd = 0.03 Å. Upon coordination, this bond elongation is further accompanied by a decrease in the N–C–N angle from 111.0(4)° in **2** to 105.4(6)° in *cis–anti*-**3**. Other structural parameters remain largely unchanged indicating that coordination to the Pd-centre only affects the carbene carbon and the neighboring nitrogen atoms.

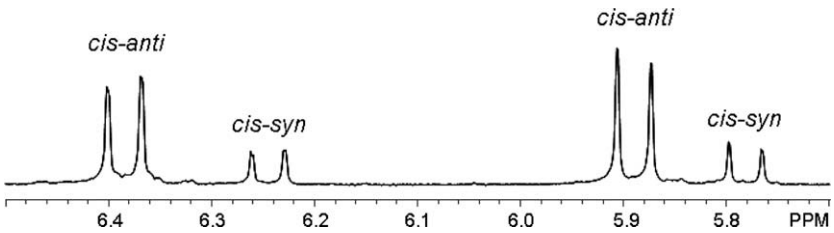


Fig. 2. Diastereotopic ^{1}H NMR signals of NCH_2 protons in *cis–anti* and *cis–syn* rotamers of *cis*-**3**.

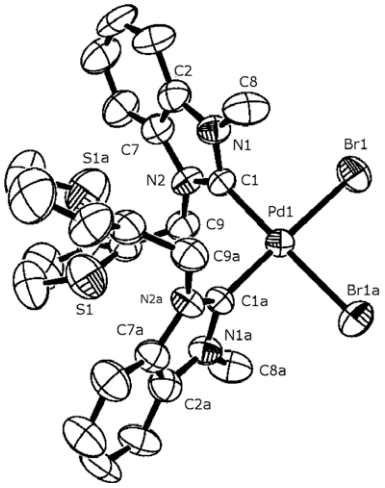


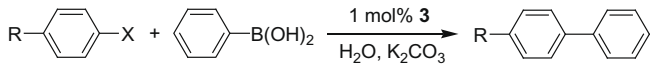
Fig. 3. Molecular structure of *cis–anti*-**3** · $1.5CH_3COCH_3$ showing 50% probability ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–C1 1.972(7), Pd1–Br1 2.4726(10), C1–N1 1.352(9), C1–N2 1.353(9), N1–C2 1.381(10), N1–C8 1.454(10), N2–C7 1.414(10), N2–C9 1.476(9), C2–C7 1.386(11); C1–Pd1–C1a 94.2(4), Br1–Pd1–Br1a 93.08(5), C1–Pd1–Br1 86.4(2), C1a–Pd1–Br1 178.3(2), C1–Pd1–Br1a 178.3(2), C1a–Pd1– Br1a 86.4(2), N1–C1–N2 105.4(6).

It is worth noting, that the dissolution of these single crystals led to the formation of a rotameric mixture of *cis–anti*-**3** and *cis–syn*-**3** as evidenced by ^{1}H NMR spectroscopy and confirming the facile interconversion of these rotamers in solution.

2.3. Suzuki–Miyaura catalysis

Complexes of *N*-heterocyclic carbene ligands have been applied in both homogeneous and heterogeneous catalysis. In particular, Pd–NHC complexes have been widely used in the making of C–C bonds often employing the Mizoroki–Heck [25,27,28] and Suzuki–Miyaura [29,30] coupling reactions. NHCs with additional donor-functions can potentially exhibit hemilabile behavior and thus offer additional stability for catalytically active intermediates. Thus, a preliminary study was carried out in this work to investigate the catalytic activities of the *N*-thienylmethyl-functionalized NHC complex *cis*-**3** in the Suzuki–Miyaura reaction. The coupling of aryl bromides and chlorides with phenylboronic acid to give the respective biaryls in/on water as environmentally benign media with 1 mol% catalyst loading was chosen as a standard test reaction. The results of these heterogeneous reactions summarized in Table 1 show that complex *cis*-**3** is highly efficient in the coupling of the activated aryl bromides at ambient temperature achieving yields of >85% (Entries 1/2). For deactivated aryl bromides addition of [N(n-C_4H_9)$_4$]Br, longer reaction times and a higher reaction temperature are required. Under these conditions, coupling occurs smoothly giving quantitative or near-quantitative yields (Entries 3/4). Disappointingly, the limitation of this catalytic system becomes apparent in the coupling of more challenging aryl chlorides resulting in low yields of only 9% and 14%, respectively (Entries 5/6). A comparison with previously reported Pd(II) catalysts bearing only one benzimidazolin-2-ylidene ligand shows that the current bis(carbene) system is less effective for coupling of aryl chlorides [21,24].

Table 1
Suzuki–Miyaura cross-coupling reactions catalyzed by *cis*-**3** in aqueous media.[a]



X = Br, Cl
R = $COCH_3$, CHO, OCH_3, CH_3

Entry	Aryl halide	t (h)	Temperature (°C)	Yield (%)[b]
1	4-Bromobenzaldehyde	8	RT	>99
2	4-Bromoacetophenone	8	RT	85
3	4-Bromoanisole	21	85	97[c]
4	4-Bromotoluene	21	85	>99[c]
5	4-Chlorobenzaldehyde	21	85	9[c]
6	4-Chloroacetophenone	21	85	14[c]

[a] Non-optimized reaction conditions: 1 mmol of aryl halide; 1.5 mmol of phenylboronic acid; 3 ml of water; 2 equiv. of K_2CO_3; 1 mol% of catalyst.
[b] Yields were determined by ^{1}H NMR spectroscopy for an average of two runs.
[c] With addition of 1.5 equiv. of [N(n-C_4H_9)$_4$]Br.

3. Conclusion

In summary, we have reported the facile synthesis of a new palladium(II) complex bearing two unsymmetrical, thienylmethyl-functionalized benzimidazolin-2-ylidene ligands. In solution, this complex exists as a mixture of *cis–anti* and *cis–syn* rotamers in a 3.5:1 ratio, from which the sterically more favorable *cis–anti* isomer crystallizes. A preliminary catalytic study shows that complex *cis*-**3** is highly active in the Suzuki–Miyaura coupling of activated and deactivated aryl bromides in/on water as green reaction media. The coupling of more challenging aryl chlorides, however, gave only low yields. Research in our lab is currently on-going to extend the coordination chemistry of thiophene-functionalized NHCs to other transition metals and to explore their potential applications in catalysis.

4. Experimental

4.1. General considerations

Unless otherwise noted all operations were performed without taking precautions to exclude air and moisture. All solvents and chemicals were used as received without any further treatment if not noted otherwise. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ACF 300 spectrometer or AMX 500 spectrophotometer and the chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (^{1}H, ^{13}C). ESI Mass spectra were measured using a Finnigan MAT LCQ spectrometer. Elemental analyses were performed on a Perkin–Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

4.2. Synthesis of 2-bromomethylthiophene (**1**)

PBr_3 (0.47 mL, 5.00 mmol) was added dropwise to a solution of 2-thiophenemethanol (0.95 mL, 10.0 mmol) in diethyl ether (10 mL) at 0 °C. The solution was stirred for 1 h at ambient temperature and methanol (1.5 mL) was then added. The mixture was diluted with deionised water (50 mL) and extracted with diethyl ether (1 × 50 mL, 3 × 30 mL). The combined organic layers were dried over Na_2SO_4 and filtered. Removal of the solvent *in vacuo* afforded the product as a yellow liquid (1.576 g, 8.90 mmol, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (d, ^3J(H,H) = 5.1 Hz, 1H, Ar-H), 7.16 (d, ^3J(H,H) = 3.2 Hz, 1H, Ar-H), 6.99 (m, 1H, Ar-H), 4.80 (s, 2H, CH_2).

4.3. Synthesis of 1-(2-thienylmethyl)-3-methylbenzimidazolium bromide (**2**)

Compound **1** (1.120 g, 6.33 mmol) was added to a solution of 1-methylbenzimidazole (0.905 g, 6.85 mmol) in toluene (5 mL). The reaction mixture was stirred overnight at 90 °C and a white precip-

itate was formed. The reaction mixture was filtered through a sintered funnel and the white precipitate was washed with toluene. The product was dried *in vacuo* to afford an off-white powder (1.522 g, 4.92 mmol, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.43 (s, 1H, NCHN), 7.77–7.75 (m, 1H, Ar-H), 7.70–7.61 (m, 3H, Ar-H), 7.51 (m, 1H, Ar-H), 7.31 (dd, ^3J(H,H) = 5.1 Hz, ^4J(H,H) = 1.2 Hz, 1H, Ar-H), 7.03–7.00 (m, 1H, Ar-H), 6.10 (s, 2H, CH_2), 4.26 (s, 3H, NCH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 142.9 (s, NCHN), 134.2, 132.0, 130.8, 129.9, 127.7, 127.3, 127.3, 113.5, 112.9 (s, Ar-C), 45.8 (s, CH_2), 33.9 (s, NCH_3). MS (ESI): m/z = 229 [M−Br]$^+$. *Anal.* Calc. for $C_{13}H_{13}BrN_2S$ (M = 309.22): C, 50.49; H, 4.24; N, 9.06. Found: C, 50.23; H, 4.51; N, 8.90%.

4.4. Synthesis of palladium complex cis-3

A mixture of salt **2** (0.343 g, 1.11 mmol) and $Pd(OAc)_2$ (0.120 g, 0.53 mmol) was dissolved in DMSO (12 mL) and stirred overnight at 90 °C. The yellow solution first turned green after a few hours and darkened after reacting overnight. The reaction mixture was filtered through a sintered funnel and the solvent of the filtrate was removed by vacuum distillation. The resulting residue was dissolved in CH_2Cl_2 (30 mL) and extracted with H_2O (5 × 20 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed *in vacuo*. The solid obtained was washed with diethyl ether and THF. Removal of the solvent *in vacuo* yielded a light brown powder (0.191 g, 0.26 mmol, 50%). Slow evaporation of a concentrated acetone solution afforded the *cis–anti* complex as crystals. *Cis–anti*-**3**: ^{1}H NMR (500 MHz, CD_2Cl_2): δ *7.20–7.12* (m, 4H, Ar-H), 7.05–7.00 (m, 1H, Ar-H) 6.70–6.66 (m, 2H, Ar-H), 4.16 (s, 3H, NCH_3). ^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2): δ 174.2 (s, NCN), 137.0, 135.7, 133.8, 127.3, 126.2, 125.7, 124.1, 124.0, 111.5, 110.9 (s, Ar-C), 48.6 (s, NCH_2), 36.1 (s, NCH_3). *Cis–syn*-**3**: ^{1}H NMR (500 MHz, CD_2Cl_2): δ *7.40–7.22* (m, 5H, Ar-H), 6.82–6.75 (m, 2H, Ar-H), 4.32 (s, 3H, NCH_3). ^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2): δ 174.4 (s, NCN), 136.9, 135.5, 133.9, 127.2, 126.1, 125.7, 124.1, 123.9, 112.0, 110.7 (s, Ar-C), 48.8 (s, NCH_2), 36.2 (s, NCH_3). MS (ESI): m/z = 643 [M−Br]$^+$. *Anal.* Calc. for $C_{26}H_{24}Br_2N_4PdS_2 \cdot CH_3COCH_3$ (M = 780.93): C, 44.60; H, 3.87; N, 7.17. Found: C, 44.46; H, 4.07; N, 6.89%.

4.5. General procedure for the Suzuki–Miyaura coupling

In a typical run, a test tube was charged with a mixture of aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), potassium carbonate (2 mmol), precatalyst *cis*-**3** (0.01 mmol) and [N(n-C_4H_9)$_4$]Br (1.5 mmol) (for entries 3–6 in the Table 1). To the mixture was added H_2O (3 mL). The reaction mixture was vigorously stirred at the appropriate temperature (RT or 85 °C). After the desired reaction time, the solution was allowed to cool. 10 ml of dichloromethane was added to the reaction mixture and the organic phase was extracted with water (6 × 5 mL) and dried over $MgSO_4$. The solvent was removed by evaporation to give a crude product, which was analyzed by ^{1}H NMR spectroscopy.

4.6. X-ray diffraction studies

X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation at 223 K (**2**) and 296 K (*cis–anti*-**3**), with the SMART suite of Programs [31]. Data were processed and corrected for Lorentz and polarisation effects with SAINT [32], and for absorption effect with SADABS [33]. Structural solution and refinement were carried out with the SHELXTL suite of programs [34]. The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All hydrogen atoms were put at calculated positions. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. A summary of the most important crystallographic data is given in Table 2.

Table 2
Selected crystallographic data for salt **2** and complex *cis–anti*-**3**.

	2 · 1.5H_2O	*cis–anti*-**3** · 1.5CH_3COCH_3
Empirical formula	$C_{13}H_{13}BrN_2S \cdot 1.5H_2O$	$C_{26}H_{24}Br_2N_4PdS_2 \cdot 1.5CH_3COCH_3$
Formula weight	336.25	809.95
Color, habit	colorless, block	colorless, needle
Crystal size (mm)	0.40 × 0.16 × 0.08	0.18 × 0.04 × 0.04
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	17.1632(14)	18.4228(13)
b (Å)	7.3363(6)	17.1467(14)
c (Å)	22.9362(17)	11.6450(7)
α (°)	90	90
β (°)	90.368(2)	102.643(2)
γ (°)	90	90
V (Å^3)	2887.9(4)	3589.3(4)
Z	8	4
D_{calcd} (g cm^{-3})	1.547	1.499
μ (mm^{-1})	2.986	2.889
θ range (°)	1.19–27.50	1.64–25.00
No. of unique data	12165	10375
Maximum, minimum transmition	0.7961, 0.3813	0.8932, 0.6244
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0485, wR_2 = 0.1242	R_1 = 0.0637, wR_2 = 0.1521
R indices (all data)	R_1 = 0.0737, wR_2 = 0.1368	R_1 = 0.0987, wR_2 = 0.1693
Goodness-of-fit (GOF) on F^2	1.030	1.046
Peak/hole (e Å^{-3})	0.728/−0.542	0.723/−0.599

Acknowledgements

The authors would like to thank the National University of Singapore for financial support (Grant No. R 143-000-327-133) and especially Ms. Geok Kheng Tan, Ms. Su Fen Woo and Prof. Lip Lin Koh for determining the X-ray molecular structures.

Appendix A. Supplementary material

CCDC 716610 and 716611 contain the supplementary crystallographic data for **2** · 1.5H_2O and *cis–anti*-**3** · 1.5CH_3COCH_3. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.02.035.

References

[1] F.E. Hahn, M.C. Jahnke, Angew. Chem., Int. Ed. 47 (2008) 3122.
[2] A.T. Normand, K.J. Cavell, Eur. J. Inorg. Chem. (2008) 2781.
[3] D. Sellmann, W. Prechtel, F. Knoch, M. Moll, Organometallics 11 (1992) 2346.
[4] D. Sellmann, W. Prechtel, F. Knoch, M. Moll, Inorg. Chem. 32 (1993) 538.
[5] D. Sellmann, C. Allmann, F. Heinemann, F. Knoch, J. Sutter, J. Organomet. Chem. 541 (1997) 291.
[6] J.A. Cabeza, I. del Rio, M.G. Sánchez-Vega, M. Suárez, Organometallics 25 (2006) 1831.
[7] H. Seo, H.-J. Park, B.Y. Kim, J.H. Lee, S.U. Son, Y.K. Chung, Organometallics 22 (2003) 618.
[8] J. Wolf, A. Labande, J.-C. Daran, R. Poli, Eur. J. Inorg. Chem. (2007) 5069.
[9] S.J. Roseblade, A. Ros, D. Monge, M. Alcarazo, E. Álvarez, J.M. Lassaletta, R. Fernández, Organometallics 26 (2007) 2570.
[10] H.V. Huynh, C.H. Yeo, G.K. Tan, Chem. Commun. (2006) 3833.
[11] D.J. Nielsen, K.J. Cavell, M.S. Viciu, S.P. Nolan, B.W. Skelton, A.H. White, J. Organomet. Chem. 690 (2005) 6133.
[12] D.S. McGuinness, J.A. Suttil, M.G. Gardiner, N.W. Davies, Organometallics 27 (2008) 4238.
[13] F.E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, Chem. Eur. J. 5 (1999) 1931.
[14] F.E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, Angew. Chem., Int. Ed. 39 (2000) 541.

[15] H.V. Huynh, C. Holtgrewe, T. Pape, L.L. Koh, E. Hahn, Organometallics 25 (2006) 245.
[16] Y. Han, H.V. Huynh, G.K. Tan, Organometallics 26 (2007) 4612.
[17] Y. Han, H.V. Huynh, G.K. Tan, Organometallics 26 (2007) 6447.
[18] H.V. Huynh, R. Jothibasu, L.L. Koh, Organometallics 26 (2007) 6852.
[19] H.V. Huynh, L.R. Wong, P.S. Ng, Organometallics 27 (2008) 2231.
[20] R. Jothibasu, H.V. Huynh, L.L. Koh, J. Organomet. Chem. 693 (2008) 374.
[21] Y. Han, Y.-T. Hong, H.V. Huynh, J. Organomet. Chem. 693 (2008) 3159.
[22] B.C. Ranu, R. Jana, Eur. J. Org. Chem. 4 (2005) 755.
[23] R.D. McCullough, Adv. Mater. 10 (1998) 93.
[24] H.V. Huynh, Y. Han, J.H.H. Ho, G.K. Tan, Organometallics 25 (2006) 3267.
[25] H.V. Huynh, J.H.H. Ho, T.C. Neo, L.L. Koh, J. Organomet. Chem. 690 (2005) 3854.
[26] Y. Han, H.V. Huynh, L.L. Koh, J. Organomet. Chem. 692 (2007) 3606.
[27] H.V. Huynh, J. Wu, J. Organomet. Chem. 694 (2009) 323.
[28] H.V. Huynh, T.C. Neo, G.K. Tan, Organometallics 25 (2006) 1298.
[29] N. Marion, O. Navarro, J. Mei, E.D. Stevens, N.M. Scott, S.P. Nolan, J. Am. Chem. Soc. 128 (2006) 4101.
[30] C. Fleckenstein, S. Roy, S. Leuthäußer, H. Plenio, Chem. Commun. (2007) 2870.
[31] SMART Version 5.628, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
[32] SAINT+ Version 6.22a, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
[33] G.W. Sheldrick, SADABS Version 2.10, University of Göttingen, 2001.
[34] SHELXTL version 6.14, Bruker AXS Inc., Madison, Wisconsin, USA, 2000.