Inorganica Chimica Acta 365 (2011) 469–472

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Note

Synthesis, characterization and crystal structures of monocyclopalladated and biscyclopalladated 1,1′-bisferrocenylpyrimidine–monophosphine complexes

Chen Xu [a,*], Ya-Peng Zhang [b], Zhi-Qiang Wang [a], Ting Liang [b], Wei-Jun Fu [a,*], Xin-Qi Hao [b], Yan Xu [b], Bao-Ming Ji [a]

[a] College of Chemistry and Chemical Engineering, Luoyang Normal University, Longmen Road No. 71, Luoyang City, Henan Province 471022, PR China
[b] Department of Chemistry, Zhengzhou University, Zhengzhou, Henan 450052, PR China

ARTICLE INFO

Article history:
Received 9 March 2010
Received in revised form 18 July 2010
Accepted 23 August 2010
Available online 26 September 2010

Keywords:
Palladacycle
1,1′-Bisferrocenylpyrimidine
Monophosphine ligand
Crystal structure

ABSTRACT

A new 1,1′-bisferrocenylpyrimidine ligand [{(η^5-C_5H_4)–N_2C_4H–$2CH_3$}$_2$Fe] **1** was conveniently prepared via the coupling reaction of 1,1′-dichloromercuriferrocene and 4,6-dimethyl-2-iodopyrimidine, and its monophosphine–palladacycle complexes **2**–**3** were also readily obtained from the cyclopalladation reactions and bridge-splitting reactions. These compounds have been characterized by ^{1}H NMR, IR, ESI-MS, and elemental analysis. The complex **2** was found to be a biscyclopalladated complex, while the complex **3** was a monocyclopalladated complex. Additionally, their detailed structures have been determined by X-ray single-crystal diffraction. The most striking common feature of the structures of **2–3** is intermolecular C–H···Cl hydrogen bonds, which are attributed to construct the 1D chain structures.

1. Introduction

Palladacycles are one of the most developed and studied classes of organopalladium derivatives, which are widely applied in coupling reactions as effective catalysts precursors [1,2]. Usually, they are prepared in high yields through C–H activation, and most of them are thermally stable, not sensitive to air and moisture. Among them, cyclopalladated complexes containing N-donor ferrocenyl ligand have been studied extensively in the past two decades [3–7]. However, double cyclopalladation of disubstituted ferrocene is scarce, only a few biscyclopalladated complexes have been reported [8–10]. To our knowledge, there was only one report concerning the crystal structure of biscyclopalladated 1,1′-ferrocenyldiimine complex [11].

We have studied the double cyclopalladation of 1,1′-ferrocenyldiimine [{(η^5-C_5H_4)–CH=NCy}$_2$Fe] and found the corresponding tricyclohexylphosphine adduct is a monocyclopalladated complex (**A**, Scheme 1) [12]. Furthermore, we have recently studied the cyclopalladation of 4,6-dimethyl-2-pyrimidinylferrocene. Some of the obtained monophosphine-cyclopalladated complexes (**B**, Scheme 1) have been successfully used in palladium-catalyzed Buchwald–Hartwig amination [13]. These precatalysts combine the stability induced by the presence of a palladacycle framework with the high activity commonly associated with phosphine ligands, and were far more active than the corresponding dimeric palladacycles [14–17]. In view of these findings and our continuous interest in the cyclopalladation of ferrocenylpyrimidine, we synthesized a new 1,1′-di(4,6-dimethyl-2-pyrimidinyl)ferrocene **1** and its monophosphine-cyclopalladated complexes **2**–**3** (Scheme 2). Interestingly, **2** was a biscyclopalladated complex, while **3** was a monocyclopalladated complex.

2. Experimental

2.1. General procedures

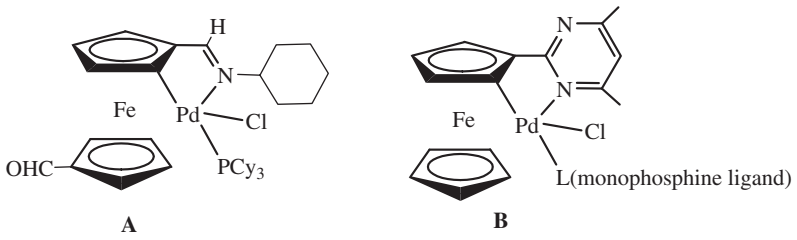
Solvents were dried and freshly distilled prior to use. All other chemicals were commercially available expect for 1,1′-dichloromercuriferrocene and 4,6-dimethyl-2-iodopyrimidine which were prepared according to the published procedures [18,19]. IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. ^{1}H NMR spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$ with TMS as an internal standard. Mass spectra were measured on a LC-MSD-Trap-XCT instrument. Elemental analyses were determined with a Carlo Erba 1160 Elemental Analyzer.

2.2. Synthesis of 1,1′-di(4,6-dimethyl-2-pyrimidinyl)ferrocene (1)

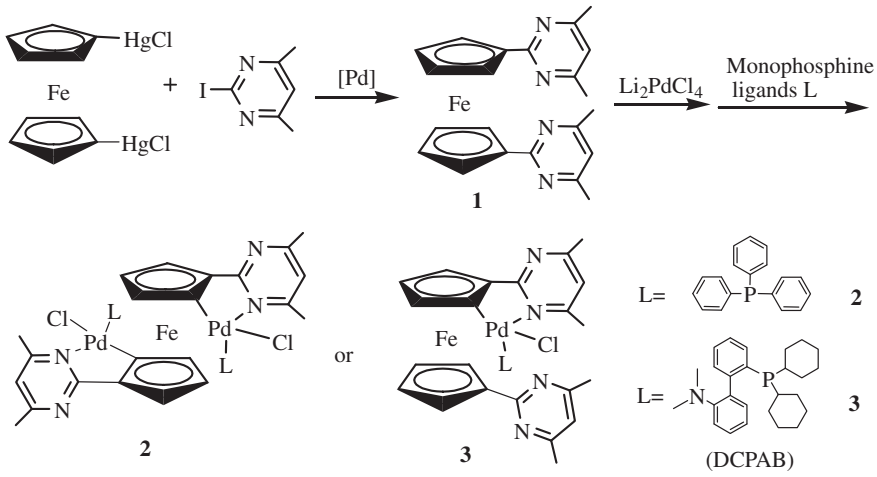
In a flask equipped with reflux condenser and gas inlet 1,1′-dichloromercuriferrocene (1 mmol), 4,6-dimethyl-2-iodopyrimidine (2.2 mmol), NaI (3 mmol) and $PdP(Ph_3)_4$ (0.05 mmol), 15 ml DMF were placed under N_2 atmosphere. The reaction mixture

* Corresponding authors. Tel./fax: +86 379 65523821.
E-mail address: xubohan@163.com (C. Xu).

0020-1693/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2010.08.046



Scheme 1. Examples of monophosphine-cyclopalladated complexes containing ferrocenyl ligand.



Scheme 2. Preparation of compounds **1–3**.

was then placed in an oil bath and heated at 130 °C for 8 h, cooled and quenched with water. The organic layer was separated and the aqueous layer was extracted with dichloromethane, then the combined organic layers were washed with water, dried over $MgSO_4$, filtered, and the solvent was removed on a rotary evaporator. The product was separated by passing through a short silica gel column with CH_2Cl_2 as eluent. The second band was collected and afforded the red solid **1**, yield 83%. IR (KBr, cm^{-1}): 3048, 2921, 2852, 1556, 1516, 1487, 1419, 1340, 1222, 1173, 1105, 1026. ^1H NMR (400 MHz, $CDCl_3$): δ 6.67 (s, 2H, Ar–H), 5.09 (s, 4H, C_5H_4), 4.33 (s, 4H, C_5H_4), 2.35 (s, 12H, $-CH_3$). MS-ESI$^+$: *m/z* 399.1 $[M+H]^+$. *Anal.* Calc. for $C_{22}H_{22}FeN_4$: C, 66.34; H, 5.57; N, 14.07. Found: C, 66.52; H, 5.43; N, 14.22%.

2.3. General procedure for the synthesis of the monophosphine-cyclopalladated ferrocenylpyrimidine complexes 2–3

A mixture of **1** (1 mmol), Li_2PdCl_4 (2.2 mmol) and NaOAc (2.2 mmol) in 40 ml of dry methanol was stirred for 48 h at room temperature. The red solids (yield: 88%) were collected by filtration and washed several times with methanol. Without further purification, it was treated with monophosphine ligands (2.2 mmol) in dry CH_2Cl_2 at room temperature for 1 h. The product was separated by passing through a short silica gel column with CH_2Cl_2 as eluent. The first band was collected and afforded the corresponding monophosphine-cyclopalladated ferrocenylpyrimidine complex.

2.3.1. $[Pd_2Cl_2\{(\eta^5\text{-}C_5H_3)\text{–}N_2C_4H\text{–}2CH_3\}_2Fe(PPh_3)_2]$ (**2**)

Red solid, yield 59%. IR (KBr, cm^{-1}): 3411, 2901, 1576, 1547, 1487, 1428, 1359, 1330, 1183, 1065, 1036. ^1H NMR (400 MHz, $CDCl_3$): δ 7.82–7.87 (m, 12H, Ph–H), 7.39–7.43 (m, 18H, Ph–H), 6.68(s, 2H, Ar–H), 5.10 (s, 2H, C_5H_3), 4.80 (b, 2H, C_5H_3), 4.34 (s, 2H, C_5H_3), 2.34 (s, 12H, $-CH_3$). MS-ESI$^+$: *m/z* 1132.1 $[M-2Cl]^+$. *Anal.* Calc. for $C_{58}H_{50}Cl_2FeN_4P_2Pd_2$: C, 57.83; H, 4.18; N, 4.65. Found: C, 57.97; H, 4.02; N, 4.46%.

2.3.2. $[PdCl\{[(\eta^5\text{-}C_5H_4)]Fe[(\eta^5\text{-}C_5H_3)\text{–}(N_2C_4H\text{–}2CH_3)_2]\}(DCPAB)]$ (**3**)

Red solid, yield 51%. IR (KBr, cm^{-1}): 2921, 2842, 1595, 1556, 1490, 1438, 1370, 1359, 1271, 1173, 1036. The ^1H NMR (400 MHz, $CDCl_3$): δ 7.50–7.54 (m, 2H, Ph–H), 7.01–7.11 (m, 6H, Ph–H), 6.71 (s, 1H, Ar–H), 6.67 (s, 1H, Ar–H), 5.09 (s, 1H, C_5H_3), 4.31 (s, 2H, C_5H_3), 3.69–3.75 (m, 4H, C_5H_4), 2.53 (s, 6H, $-NMe_2$), 2.36 (s, 6H, $-CH_3$), 2.32 (s, 6H, $-CH_3$), 1.25–1.72 (m, 22H, PCy_3). MS-ESI$^+$: *m/z* 897.3 $[M-Cl]^+$. *Anal.* Calc. for $C_{48}H_{57}ClFeN_5PPd$: C, 61.81; H, 6.16; N, 7.51. Found: C, 61.96; H, 6.05; N, 7.62%.

2.4. X-ray diffraction studies

Crystallographic data for **1–3** were collected on a Bruker SMART APEX-II CCD diffractometer with Mo Kα radiation (λ = 0.071073 Å). The data were corrected for Lorentz-polarization factors as well as for absorption. Structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 with the SHELX-97 program [20]. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions. **CCDC** reference numbers 762578–762580 for compounds **1–3**, respectively.

3. Results and discussion

3.1. Synthesis and characterization of compounds 1–3

The synthetic route of **1** and monophosphine-cyclopalladated complexes **2–3** is demonstrated in Scheme 2. The palladium-catalyzed cross-coupling reactions of organomercury compounds as a source of ferrocenyl group with aryl halides were shown to be easy

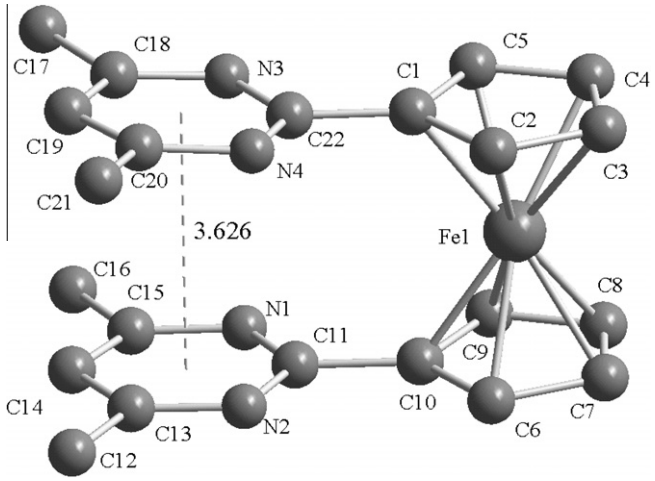


Fig. 1. Molecular structure of compound **1** showing the intramolecular π–π stacking interaction. H atoms are omitted for clarity.

and convenient for the synthesis of monoarylsubstituted ferrocenes [13,21]. In most case THF-acetone has been used as solvent, while 1,1′-dichloromercuriferrocene was highly insoluble. So, we have chosen DMF as solvent, in the present of $PdP(Ph_3)_4$ provided coupled product **1** in good yield in the reaction of 1,1′-dichloromercuriferrocene and 4,6-dimethyl-2-iodopyrimidine.

The following double cyclopalladation reaction was carried out with **1** and 2.2 equivalents of Li_2PdCl_4 and NaOAc in methanol at room temperature for 24 h. The formed red solids (yield: 88%) were collected by filtration and washed several times with methanol. Because of its poor solubility in all common organic solvents, it was characterized only by IR and assigned to be polymeric or dimeric biscyclopalladated derivatives [12]. Compared with **1**, the C=N absorption (1527 cm^{-1}) of its pyrimidine ring shifted to lower energy, indicating the coordination of nitrogen to palladium [12–16]. Without further purification, it was directly subjected to bridge-splitting reaction with monophosphine ligands to produce the monophosphine-cyclopalladated complexes **2**–**3**.

Compounds **1** and **2–3** were fully characterized by elemental analysis, IR, ^1H NMR, and ESI-MS. In the IR spectra of **2–3**, the C=N absorptions of the pyrimidine rings also shifted to lower energy. However, band at 1556 cm^{-1} is still detected in the IR spectrum of **3** and the absorption is the same as free ligand **1**. The ^1H NMR spectra of **1**–**3** are consistent with the proposed structures, **2** exhibits three peaks for Cp ring with the proton ratio of 2:2:2, clearly showing that it was *ortho*-biscyclopalladated product, while **3** exhibits three peaks with the proton ratio of 1:2:4. The above results indicate that **3** is a monocyclopalladated complex.

The IR spectrum of the bridge-splitting reaction with monophosphine ligands were also determined and band at 1556 cm^{-1} was only observed in the reaction with DCPAB ligand. This suggested that monocyclopalladated complex **3** was formed during the reaction. This process would significantly reduce the steric hindrance around the coordinative nitrogen and the palladium due to the steric bulk of the DCPAB ligand [11,12]. The expected DCPAB-biscyclopalladated complex was not isolated. In order to further investigate the structures of these compounds, their detailed structures have been determined by X-ray single-crystal diffraction.

3.2. Molecular structures of compounds 1–3

All the crystals were obtained by recrystallization from CH_2Cl_2–petroleum ether solution at room temperature. The molecules are shown in Figs. 1–3 (displacement ellipsoids are drawn at the 50% probability level). The Cp ring of **1** are approximately coplanar with the pyrimidine ring because of smaller steric hindrance [22–24], the dihedral angels between them are 3.9° and 6.5°. The molecules adopt a synperiplanar eclipsed conformation, with the two pyrimidine rings arranged in parallel fashion (Fig. 1). There are strong intramolecular π–π stacking interactions between the pyrimidine rings (the interplane distances are about 3.626 Å) [25].

The single-crystal X-ray analysis further confirms that **2–3** are biscyclopalladated and monocyclopalladated complexes, respectively. The Pd atom in each complex is in a slightly distorted square-planar environment bonded to the phosphorus atom, the chloride atom, the pyrimidinyl nitrogen atom and the carbon atom of the ferrocenyl moiety. In these complexes, the ferrocenylpyrimidine metallacycle is essentially flat. The Pd–N [2.230(3) and 2.247(5) Å] and Pd–P [2.2457(10)–2.2653(16) Å] bond lengths of **2–3** are obviously longer than those of the corresponding **B** [2.2006(18)–2.240(3) Å and 2.2382(7)–2.2602(8) Å] [13]. In

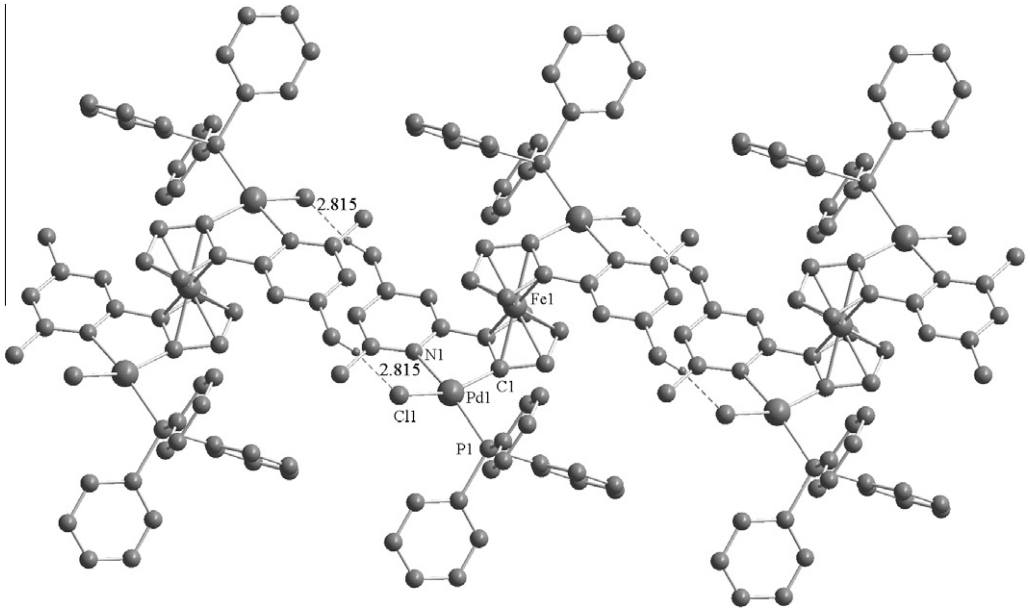


Fig. 2. One-dimensional chain structure of **2** showing the intermolecular C–H···Cl hydrogen bonds. Non-hydrogen-bonding H atoms are omitted for clarity.

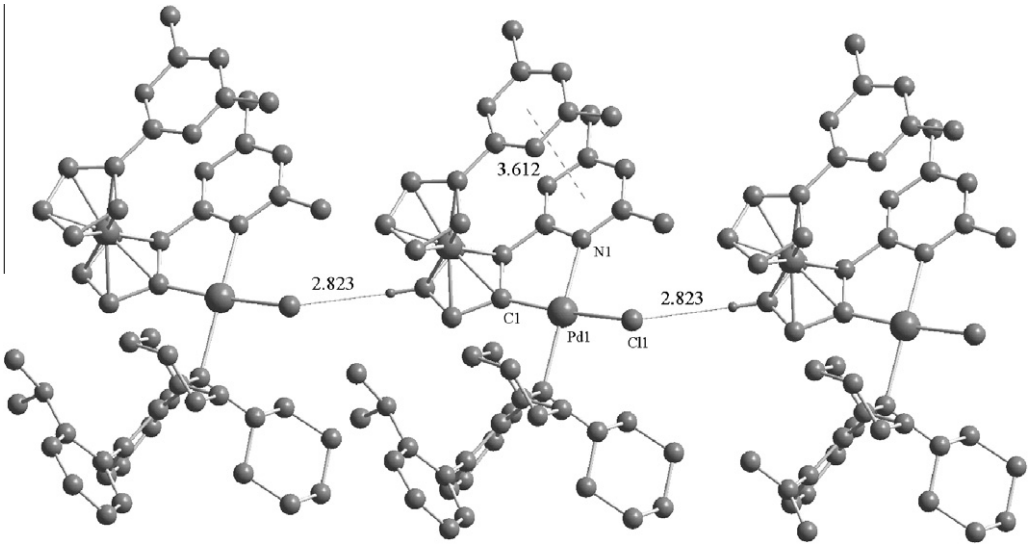


Fig. 3. One-dimensional chain structure of **3** showing intramolecular π–π stacking interactions and the intermolecular C–H···Cl hydrogen bonds. Non-hydrogen-bonding H atoms and H_2O are omitted for clarity.

addition, the above bond lengths in **3** also are longer than those of **2** possibly due to the steric bulk of the DCPAB ligand [12,13].

In complex **2**, the Fe^{II} ion lying on a center of symmetry, the two Cp rings adopt an antiperiplanar staggered conformation, with the two pyrimidine rings pointing in the opposite directions (Fig. 2). However, like **1**, **3** adopts a synperiplanar conformation, with the two pyrimidine rings arranged in parallel fashion (the interplane distances are about 3.612 Å) (Fig. 3). The most striking common feature of the structures of **2–3** is intermolecular C–H···Cl hydrogen bonds [13,14,26], their lengths are 2.815 Å [(CH_3)C–H···Cl] and 2.823 Å [(Cp)C–H···Cl], respectively, which are attributed to construct the 1D chain structures.

Acknowledgments

We are grateful to the National Natural Science Foundation of China (Nos. 20902043 and 20902042) and the Natural Science Foundation of Henan Education Department, China (No. 2009B150019) for financial support of this work.

Appendix A. Supplementary material

CCDC 762578, 762579 and 762580 contain the supplementary crystallographic data for compounds **1**–**3**, respectively. 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.2010.08.046.

References

[1] R.B. Bedford, Chem. Commun. (2003) 1787.
[2] J. Dupont, M. Pfeffer, Palladacycles, Wiley–VCH, Weinheim, Germany, 2008.
[3] R. Bosque, C. López, J. Sales, Inorg. Chim. Acta 244 (1996) 141.
[4] Y.J. Wu, S.Q. Huo, J.F. Gong, X.L. Cui, L. Ding, K.L. Ding, C.X. Du, Y.H. Liu, M.P. Song, J. Organomet. Chem. 637–639 (2001) 27.
[5] L.L. Troitskaya, Z.A. Starikova, T.V. Demeshchik, S.T. Ovseenko, E.V. Vorontsov, V.I. Sokolov, J. Organomet. Chem. 690 (2005) 3976.
[6] X.M. Zhao, X.Q. Hao, B. Liu, M.L. Zhang, M.P. Song, Y.J. Wu, J. Organomet. Chem. 691 (2006) 255.
[7] M.E. Günay, C.J. Richards, Organometallics 28 (2009) 5833.
[8] R. Bosque, C. López, J. Sales, X. Solans, J. Silver, Dalton Trans. (1996) 3195.
[9] C. López, R. Bosque, J. Organomet. Chem. 524 (1996) 247.
[10] Y.J. Wu, Y.H. Liu, Polyhedron 16 (1996) 335.
[11] R. Bosque, C. López, X. Solans, M. Font-Bardia, Organometallics 18 (1999) 1267.
[12] C. Xu, J.F. Gong, Y.H. Zhang, Y. Zhu, C.X. Du, Y.J. Wu, Inorg. Chem. Commun. 9 (2006) 456.
[13] C. Xu, Z.Q. Wang, W.J. Fu, X.H. Lou, Y.F. Li, F.F. Cen, H.J. Ma, B.M. Ji, Organometallics 28 (2009) 1909.
[14] C. Xu, J.F. Gong, S.F. Yue, Y. Zhu, Y.J. Wu, Dalton Trans. (2006) 4730.
[15] C. Xu, J.F. Gong, Y.J. Wu, Tetrahedron Lett. 48 (2007) 1619.
[16] C. Xu, J.F. Gong, G. Tao, Y.H. Zhang, Y.J. Wu, J. Mol. Catal. 279 (2008) 69.
[17] M.R. Biscoe, B.P. Fors, S.L. Buchwald, J. Am. Chem. Soc. 130 (2008) 6686.
[18] M. Rausch, M. Vogel, H. Rosenberg, J. Org. Chem. 22 (1957) 900.
[19] G.M. Kosolapoff, C.H. Roy, J. Org. Chem. 26 (1961) 1895.
[20] G.M. Sheldrick, SHELXL-97, Program for refinement of crystal structure, University of Göttingen, Germany, 1997.
[21] I.P. Beletskaya, A.V. Tsvetkov, G.V. Latyshev, V.A. Tafeenko, N.V. Lukashev, J. Organomet. Chem. 637–639 (2001) 653.
[22] M. Enders, G. Kohl, H. Pritzkow, J. Organomet. Chem. 622 (2001) 66.
[23] D. Braga, M. Polito, M. Bracaccini, D. D'Addario, E. Tagliavini, L. Sturba, F. Grepioni, Organometallics 22 (2003) 2142.
[24] T. Mochida, K. Okazawa, R. Horikoshi, Dalton Trans. (2006) 693.
[25] S.M. Malathy Sony, M.N. Ponnuswamy, Cryst. Growth Des. 6 (2006) 736.
[26] L. Brammer, E.A. Bruton, P. Sherwood, Cryst. Growth Des. 1 (2001) 277.