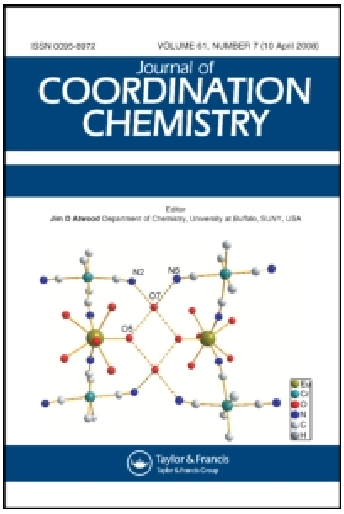


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses of (η^6-*p*-cymene)ruthenium(II) piano-stool amine complexes: molecular structure of [(η^6-$C_{10}H_{14}$)$RuCl_2$(H_2N-C_6H_4-*p*-Cl)]

Padavattan Govindaswamy[a]; Mohan Rao Kollipara[a]
[a] Department of Chemistry, North Eastern Hill University, Shillong - 793022, India

To cite this Article Govindaswamy, Padavattan and Kollipara, Mohan Rao(2006) 'Syntheses of (η^6-*p*-cymene)ruthenium(II) piano-stool amine complexes: molecular structure of [(η^6-$C_{10}H_{14}$)$RuCl_2$(H_2N-C_6H_4-*p*-Cl)]', Journal of Coordination Chemistry, 59: 2, 131 — 136

To link to this Article: DOI: 10.1080/00958970500266040

URL: http://dx.doi.org/10.1080/00958970500266040

Journal of Coordination Chemistry
Vol. 59, No. 2, January 2006, 131–136

Syntheses of (η^6-*p*-cymene)ruthenium(II) piano-stool amine complexes: molecular structure of [(η^6-$C_{10}H_{14}$)$RuCl_2$(H_2N-C_6H_4-*p*-Cl)]

PADAVATTAN GOVINDASWAMY and MOHAN RAO KOLLIPARA*

Department of Chemistry, North Eastern Hill University, Shillong – 793022, India

(*Received 2 June 2005*)

The dimeric complex [{(η^6-*p*-cymene)Ru(μ-Cl)Cl}$_2$] (**1**) reacts with S,N-donor Schiff base ligands, *para*-substituted *S*-(thiophen-2-ylmethylene)phenylamines in methanol to give mononuclear amine complexes of the type [(η^6-*p*-cymene)$RuCl_2$(NH_2–C_6H_4–*p*-X)] {X = H (**2a**); X = CH_3 (**2b**); X = OCH_3 (**2c**); X = Cl (**2d**); Br (**2e**) X = NO_2 (**2f**), respectively} by hydrolysis of the imine group of the ligand after coordination to the metal. The complexes were characterized by analysis and IR and NMR spectroscopy. The molecular structure of [(η^6-$C_{10}H_{14}$)$RuCl_2$(H_2N–C_6H_4–*p*-Cl)] (**2d**) was established by a single-crystal X-ray diffraction study.

Keywords: S,N′-Schiff base ligands; *p*-Cymene; Thiophene-2-carboxaldehyde; Amine complexes; Ruthenium; Crystal structure

1. Introduction

The well-developed synthetic chemistry of ruthenium, particularly with ammine, amine and imine ligands, provides many approaches to innovative new metallopharmaceuticals. Arene ruthenium(II) complexes have been the subject of intense research in the fields of bioorganometallic and organometallic chemistry during recent years [1, 2] and anti-tumor activity exhibited by some water-soluble arene ruthenium(II) complexes has evoked interest [3]. Recent advances in catalytic amination have been based on the use of early transition metal and f block complexes [4]. However, catalytic addition of amines H-NR_2 to non-activated double or triple bonds mediated by late transition metal complexes are rare [4]. We report here the syntheses and characterization of arene-ruthenium(II) amine complexes through hydrolysis of S,N′-donor Schiff base ligands, *para*-substituted *S*-(thiophen-2-ylmethylene)phenylamines. The molecular structure of [(η^6–$C_{10}H_{14}$)$RuCl_2$(H_2N–C_6H_4–*p*-Cl)] is reported as well.

---

*Corresponding author. Email: kmrao@nehu.ac.in

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500266040

2. Experimental

2.1. *Physical measurements*

Elemental analyses were performed using a Perkin-Elmer-2400 CHN/O instrument. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer (KBr pellets). ^{1}H NMR spectra were recorded on Bruker AMX-400 (400 MHz) and Bruker ACF-300 (300 MHz) spectrometers ($CDCl_3$ with tetramethylsilane as internal standard).

2.2. *Materials and methods*

All chemicals used were of reagent grade. Ruthenium trichloride trihydrate was purchased from Arora Matthey Ltd and thiophene-2-carboxaldehyde (Fluka) were used as received. All liquid aromatic amines of reagent grade were distilled prior to use, while solid aromatic amines were used as such. The ligands C_4H_3S–2–CH=NC_6H_4–*p*-X (X = H, CH_3, OCH_3, Cl, Br, NO_2), were prepared by condensation of thiophene-2-carboxaldehyde and aromatic amines, and the precursor complex [{(η^6-*p*-cymene)Ru(μ–Cl)Cl}$_2$] was prepared by known methods [5].

2.3. *[(η^6-p-Cymene)$RuCl_2$(NH_2–C_6H_4–p-X)] {X = H (2a), CH_3 (2b), OCH_3 (2c), Cl (2d), Br (2e), NO_2 (2f)}*

The following general procedure was used for preparation of the complexes. A mixture of [{(η^6-*p*-cymene)Ru(μ-Cl)Cl}$_2$] (**1**) (100 mg, 0.163 mmol) and an excess of *para*-substituted *S*-(thiophen-2-ylmethylene)phenylamine (2-TP) (0.41 mmol) in methanol was stirred for 6 h. The yellow product precipitated from solution was filtered off, washed with diethylether and dried *in vacuo* to give [(η^6-$C_{10}H_{14}$)Ru($NH_2C_6H_4$–*p*-X)Cl_2] in quantitative yield. Complex **2a**: IR: $\nu_{(N–H)}$ 3329 (s), 3236 (s); ^{1}H NMR (δ): 1.29 (d, 6H, $J_{H–H}$ = 7.04 Hz, CH_3), 2.21 (s, 3H, CH_3), 2.79 (sep, 1H, CH), 3.37 (s, 2H, NH_2), 5.32 (d, 2H, $J_{H–H}$ = 4.88 Hz, cymene), 5.48 (d, 2H, $J_{H–H}$ = 4.88 Hz, cymene), 7.29–7.35 (m, 5H, Ph). Anal. Calcd for $C_{16}H_{21}Cl_2NRu$ (%): C, 48.12; H, 5.30; N, 3.50. Found: C, 48.35; H, 5.42; N, 3.46. Complex **2b**: IR: $\nu_{(N–H)}$ 3406 (s), 3188 (s); ^{1}H NMR: 1.32 (d, 6H, $J_{H–H}$ = 5.88 Hz, CH_3), 2.15 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.82 (sep, 1H, CH), 3.31 (s, 2H, NH_2), 5.24 (d, 2H, $J_{H–H}$ = 5.84 Hz, cymene), 5.36 (d, 2H, $J_{H–H}$ = 5.80 Hz, cymene), 7.23 (d, 2H, $J_{H–H}$ = 6.24 Hz, Ph), 7.62 (d, 2H, $J_{H–H}$ = 8.18 Hz, Ph). Anal. Calcd For $C_{17}H_{23}Cl_2NRu$ (%): C, 49.39; H, 5.61; N, 3.39. Found: C, 49.44; H, 5.18; N, 3.10. Complex **2c**: IR: $\nu_{(N–H)}$ 3368 (s), 3192 (s); ^{1}H NMR: 1.26 (d, 6H, $J_{H–H}$ = 4.52 Hz, CH_3), 2.23 (s, 3H, CH_3), 2.92 (sep, 1H, CH), 3.29 (s, 2H, NH_2), 3.67 (s, 3H, CH_3), 5.08 (d, 2H, $J_{H–H}$ = 4.26 Hz, cymene), 5.32 (d, 2H, $J_{H–H}$ = 4.32 Hz, cymene), 7.26 (d, 2H, $J_{H–H}$ = 5.82 Hz, Ph), 7.74 (d, 2H, $J_{H–H}$ = 7.12 Hz, Ph). Anal. Calcd for $C_{17}H_{23}Cl_2NORu$ (%): C, 47.55; H, 5.40; N, 3.26. Found: C, 47.11; H, 5.68; N, 3.46. Complex **2d**: IR: $\nu_{(N–H)}$ 3323 (s), 3192 (s); ^{1}H NMR: 1.23 (d, 6H, $J_{H–H}$ = 7.01 Hz, CH_3, cymene), 2.12 (s, 3H, CH_3, cymene), 2.82 (septet, 1H, cymene), 3.32 (s, 2H, NH_2), 5.02 (d, 2H, $J_{H–H}$ = 6.00 Hz, cymene), 5.10 (d, 2H, $J_{H–H}$ = 6.01 Hz, cymene), 7.36 (d, 2H, $J_{H–H}$ = 7.85 Hz, Ph), 7.51 (d, 2H, $J_{H–H}$ = 14.19 Hz, Ph). Anal. Calcd for $C_{16}H_{18}Cl_3NRu$ (%): C, 44.51; H, 4.20; N, 3.24. Found: C, 44.26; H, 4.65; N, 3.04. Complex **2e**: IR: $\nu_{(N–H)}$ 3403 (s), 3088 (s); ^{1}H NMR: 1.31 (d, 6H, $J_{H–H}$ = 6.22 Hz, CH_3, cymene), 2.15 (s, 3H, CH_3, cymene), 2.92 (septet, 1H, cymene), 3.41 (s, 2H, NH_2), 5.23 (d, 2H, $J_{H\text{–}H} = 5.48$ Hz, cymene), 5.58 (d, 2H, $J_{H\text{–}H} = 6.01$ Hz, cymene), 7.23 (d, 2H, $J_{H\text{–}H} = 6.32$ Hz, Ph), 7.53 (d, 2H, $J_{H\text{–}H} = 8.42$ Hz, Ph). Anal. Calcd for $C_{16}H_{18}Cl_2NBrRu$ (%): C, 40.35; H, 3.81; N, 2.94. Found: C, 40.46; H, 3.23; N, 2.45. Complex **2f**: IR: $\nu_{(N\text{–}H)}$ 3416 (s), 3208 (s), $\nu_{(NO_2,\,\text{asymmetric})}$ 1533 (s), $\nu_{(NO_2,\,\text{symmetric})}$ 1345 (s); ^{1}H NMR: 1.28 (d, 6H, $J_{H\text{–}H} = 8.62$ Hz, CH_3), 2.09 (s, 3H, CH_3), 2.73 (sep, 1H, CH), 3.52 (s, 2H, NH_2), 5.37 (d, 2H, $J_{H\text{–}H} = 4.38$ Hz, cymene), 5.83 (d, 2H, $J_{H\text{–}H} = 4.38$ Hz, cymene), 7.08 (d, 2H, $J_{H\text{–}H} = 5.82$ Hz, Ph), 7.59 (d, 2H, $J_{H\text{–}H} = 6.04$ Hz, Ph). Anal. Calcd for $C_{16}H_{20}Cl_2N_2O_2Ru$ (%): C, 43.25; H, 4.53; N, 6.30. Found: C, 43.42; H, 4.83; N, 6.14.

2.4. *Crystallography*

Crystals of **2d** suitable for X-ray diffraction were grown by slow diffusion of hexane into a dichloromethane solution. An orange crystal was mounted on a Bruker Apex CCD diffractometer equipped with a CCD detector. Intensity data were collected with graphite-monochromated Mo-Kα radiation (0.71073 Å) at 293(2) K, with a 0.3° ω scan mode and 10 s per frame. Intensity data were corrected for Lorentz and polarization effects [6]. A summary of crystal data, data collection parameters and convergence results is compiled in table 1. An empirical absorption correction was made by modeling a transmission surface by spherical harmonics employing equivalent reflections with $I > 2\sigma(I)$ [7]. The structure was solved by direct methods [8]. All non-hydrogen atoms were refined anisotropically using full-matrix, least-squares techniques on F^2 using SHELXL-97 software [9]. All hydrogen atoms were found from difference Fourier syntheses after four cycles of an isotropic refinement and

Table 1. Summary of crystal data for $[(\eta^6\text{-}C_{10}H_{14})Ru(H_2N\text{–}C_6H_4\text{–}p\text{-}Cl)Cl_2]$.

Formula	$C_{16}H_{20}Cl_3NRu$
Formula weight	433.75
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	8.7904(4)
b (Å)	12.4019(6)
c (Å)	15.4041(8)
β (°)	91.034(6)
V (Å^3)	1679.05(14)
Z	4
D_{Calcd} (g cm^{-3})	1.716
$F(000)$	872
θ range for data collection (°)	2.11–28.30
Index ranges	$-11 \le h \le 7$, $-16 \le k \le 16$, $-19 \le l \le 20$
Reflections collected	11018
Independent reflections	4138 [$R_{\text{int}} = 0.0205$]
Absorption coefficient (mm^{-1})	1.403
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4138/0/199
Goodness-of-fit on F^2	1.065
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0253$, $wR_2 = 0.0629$
R indices (all data)	$R_1 = 0.0273$, $wR_2 = 0.0640$
Largest different peak and hole (e Å^{-3})	0.639 and −0.758

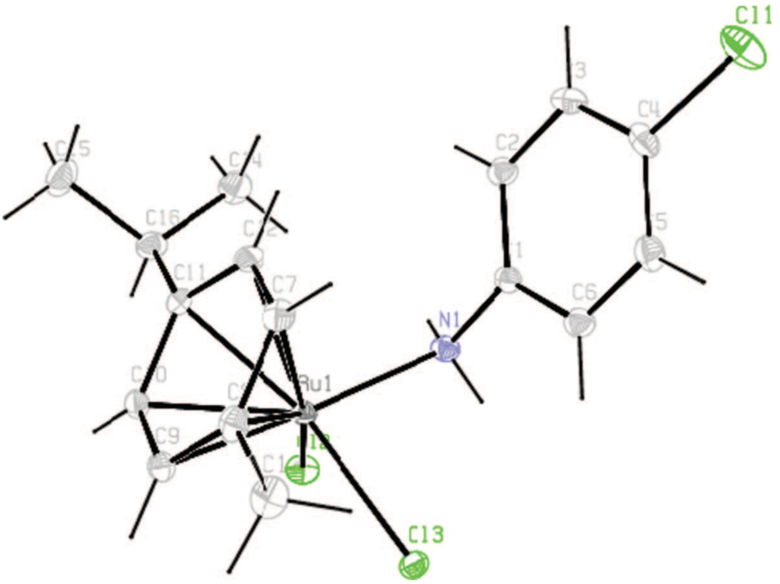


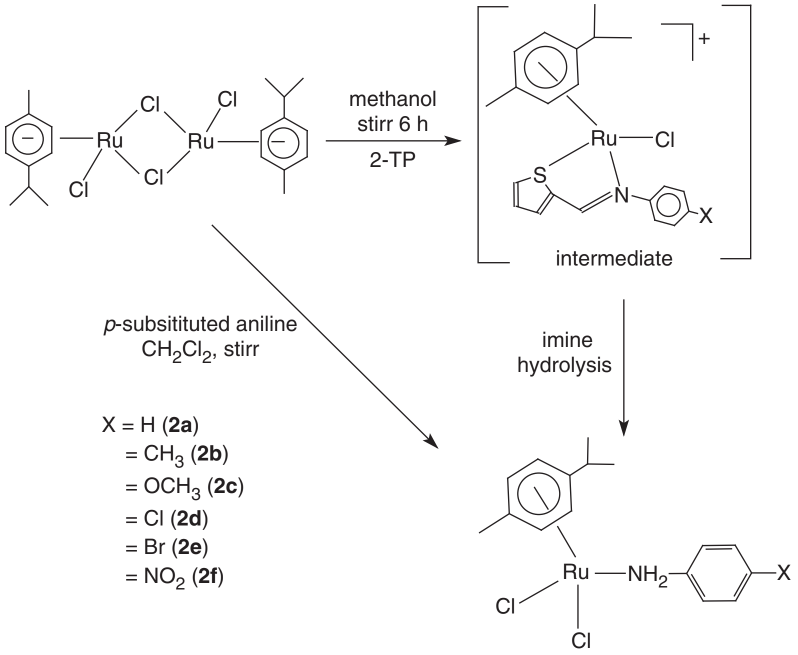
Figure 1. ORTEP diagram of the complex $[(\eta^6\text{-}C_{10}H_{14})RuCl_2(H_2N\text{–}C_6H_4\text{–}p\text{-}Cl)]$ showing the atom numbering scheme.

were included in subsequent calculations as per the "riding" model. Figure 1 displays an ORTEP [10] representation of the molecule. Refinement converged final R_1 of 0.0253 (for observed F).

3. Results and discussion

The dinuclear complex $[\{(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}Cl)Cl\}_2]$ (**1**) undergoes bridge cleavage with S,N′-donor Schiff bases in methanol (scheme 1). Thee complexes $[(\eta^6\text{-}p\text{-cymene})RuCl_2(NH_2\text{–}C_6H_4\text{–}p\text{-}X)]$, **2a**–**2e**, (scheme 1) are formed by hydrolysis of the Schiff base after formation of complex [11] in the reaction medium. The complexes can be isolated directly by reaction of **1** with substituted aniline in the presence of dichloromethane under mild conditions. However, the same reaction in methanol formed complexes of the type $[RuCl_2(NH_2\text{–}C_6H_4\text{–}p\text{-}X)_4]$. The orange-yellow complexes are air-stable microcrystalline solids, soluble in dichloromethane and acetone, and insoluble in hexane, petroleum ether and diethylether.

The complexes were completely characterized by elemental analysis and spectroscopic methods. IR spectra show a strong band in the range 3416–3188 cm^{-1} due to $\nu_{N\text{–}H}$ of the amine ligand. IR spectra of **2f** exhibit characteristic bands for ν_{NO_2} at 1533 and 1345 cm^{-1}. ^1H NMR spectra exhibit a doublet in the range 1.23–1.32 ppm for methyl protons of the isopropyl group, a singlet at 2–2.5 ppm for the methyl group and a septet in the range 2.5–3.0 ppm for the isopropyl CH proton of the p-cymene ligand, while the arene ring protons appear as two doublets around 5–6 ppm. Ligand aniline protons are observed at 3.0–3.5 ppm for NH_2 group and the phenyl protons appear as two doublets in the aromatic region [12].



Scheme 1. Reaction scheme for syntheses of compounds.

Table 2. Selected bond lengths (Å) and angles (°) for the complex.

Ru(1)–N(1)	2.1735(18)	Ru(1)–Cl(2)	2.4183(5)
Ru(1)–Cl(3)	2.4230(5)	Ru(1)–C(8)	2.199(2)
Ru(1)–C(7)	2.174(2)	Ru(1)–C(9)	2.187(2)
Ru(1)–C(10)	2.168(2)	Ru(1)–C(11)	2.1879(19)
Ru(1)–C(12)	2.1562(19)	N(1)–C(1)	1.4183(3)
N(1)–Ru(1)–Cl(2)	80.22(5)	N(1)–Ru(1)–Cl(3)	82.90(5)
Cl(2)–Ru(1)–Cl(3)	89.227(18)		

3.1. *Molecular structure*

In order to confirm the structure suggested by the spectroscopic data, the molecular structure of complex **2d** was determined using single-crystal X-ray diffraction. The structure of complex **2d** consists of a ruthenium atom η^6-coordinated to a *p*-cymene molecule, two chlorine atoms and one *p*-chloro aniline ligand (bonded through the N atom) leading to the formation of a "three-legged piano stool" structure. The average Ru–C bond distance is 2.178 Å (table 2). These bond lengths are close to those in other related complexes [13]. The Ru–N bond length involving *p*-chloro aniline is 2.1735 Å, within the usual range of Ru–N bond distances [14]. The Ru–Cl bond lengths are 2.4183 and 2.4230 Å, well in accord with literature values [12, 15]. The geometry of the complex is octahedral and is marked by near 90° values for the angles Cl(2)–Ru(1)–Cl(3) (89.227(18)°), N(1)–Ru(1)–Cl(2) (80.22(5)°) and N(1)–Ru(1)–Cl(3) (82.90(5)°).

Supplementary material

Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication CCDC 269430. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code +(44) 1223/336033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] (a) M.J. Clarke. *Coord. Chem. Rev.*, **236**, 209 (2003); (b) F.C. Pigge, J.J. Coniglio. *Curr. Org. Chem.*, **5**, 757 (2001).

[2] H.L. Bozec, D. Touchard, P.H. Dixneuf. *Adv. Organomet. Chem.*, **29**, 163 (1989).

[3] (a) C.S. Allardyce, P.J. Dyson, D.J. Ellis, S.L. Heath. *J. Chem. Soc., Chem. Commun.*, 1396 (2001); (b) H. Chen, J.A. Parkinson, S. Parsons, R.A. Coxall, R.O. Gould, P.J. Sadler. *J. Am. Chem. Soc.*, **124**, 3064 (2003); (c) R.E. Aird, J. Cummings, A.A. Ritchie, M. Muir, R.E. Morris, H. Chen, P.J. Sadler, D.I. Jodrell. *Brit. J. Cancer*, **86**, 1652 (2002); (d) R.E. Morris, R.E. Aird, P.D.S. Murdoch, H. Chen, J. Cummings, N.D. Hughes, S. Parsons, A. Parkin, G. Boyd, D.I. Jodrell, P.J. Sadler. *J. Med. Chem.*, **44**, 3616 (2001).

[4] C.J. Schaverien. *Adv. Organomet. Chem.*, **36**, 283 (1994).

[5] (a) M.A. Bennett, A.K. Smith. *J. Chem. Soc., Dalton Trans.*, 233 (1974); (b) M.A. Bennett, T.N. Huang, T.W. Matheson, A.K. Smith. *Inorg. Synth.*, **21**, 74 (1982); (c) M.A. Bennett, T.W. Matheson, G.B. Robertson, A.K. Smith, P.A. Tucker. *Inorg. Chem.*, **19**, 1014 (1980).

[6] D. Becke. *J. Chem. Phys.*, **98**, 5648 (1993).

[7] *XRD Single Crystal Software*, Bruker Analytical X-ray Systems, Madison, WI, USA (2002).

[8] G.M. Sheldrick. *SHELXS86, Program for Crystal Structure Solution*, University of Göttingen, Germany (1986).

[9] G.M. Sheldrick. *SHELXS97, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).

[10] C.K. Johnson. *ORTEPII: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*, ORNL – 5138 (1976).

[11] (a) D.L Davies, O. Al-Duaij, J. Fawcett, M. Giardiello, S.T. Hilton, D.R. Russell. *J. Chem. Soc., Dalton Trans.*, 4132 (2003); (b) R.M. Hartshorn. *J. Chem. Soc., Dalton Trans.*, 3214 (2002).

[12] P. Govindaswamy, Y.A. Mozharivskyj, M.R. Kollipara. *Polyhedron*, **23**, 3115 (2004).

[13] R. Baldwin, M.A. Bennett, D.C.R. Hockless, P. Pertici, A. Verrazzani, G.U. Barretta, F. Marchetti, P. Salvadori. *J. Chem. Soc., Dalton Trans.*, 4488 (2002).

[14] (a) D. Zuccaccia, E. Clot, A. Macchioni. *New J. Chem.*, **29**, 430 (2005); (b) J.A. Cabeza, I.D. Rio, M.E. Navarro, S.G. Granda. *Acta Cryst.*, **E57**, m162 (2001).

[15] Y. Yamamoto, H. Nakamura, J.F. Ma. *J. Organomet. Chem.*, **640**, 10 (2001).