

(Acetonitrile){2,6-bis[1-(2-ethyl-6-methylphenylimino)ethyl]pyridine}-dichlororuthenium(II) dichloromethane hemisolvate: a chain of edge-fused $R_6^6(24)$ ringsNamık Özdemir,^{a*} Muharrem Dinçer,^a Osman Dayan^b
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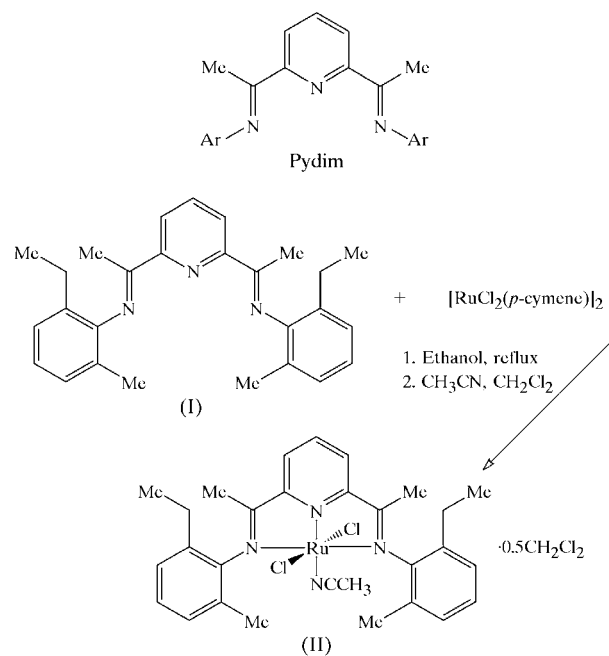
In the title compound, $[\text{RuCl}_2(\text{C}_2\text{H}_3\text{N})(\text{C}_{27}\text{H}_{31}\text{N}_3)] \cdot 0.5\text{CH}_2\text{Cl}_2$, the Ru^{II} ion is six-coordinated in a distorted octahedral arrangement, with the two Cl atoms located in the apical positions, and the pyridine (py) N atom, the two imino N atoms and the acetonitrile N atom located in the basal plane. The dichloromethane solvent molecule lies on a twofold axis. The two equatorial $\text{Ru}-\text{N}_{\text{imino}}$ distances are almost equal (mean 2.089 Å) and are substantially longer than the equatorial $\text{Ru}-\text{N}_{\text{py}}$ bond [1.914 (4) Å]. It is observed that the $\text{N}_{\text{imino}}-\text{M}-\text{N}_{\text{py}}$ bond angle for the five-membered chelate rings of pyridine-2,6-diimine complexes is inversely related to the magnitude of the $\text{M}-\text{N}_{\text{py}}$ bond. The title structure is stabilized by intra- and intermolecular $\text{C}-\text{H} \cdots \text{Cl}$ hydrogen bonds. The intermolecular hydrogen bonds form an $R_6^6(24)$ ring and a chain of edge-fused rings running parallel to the [001] direction.

Comment

Although many pydim-based transition metal complexes have been reported (pydim is pyridine-2,6-diimine; Small & Brookhart, 1998, 1999; Britovsek *et al.*, 1999; Gibson & Spitzmesser, 2003; Nakayama *et al.*, 2005; Humphries *et al.*, 2005, and references therein), examples of the related Ru complexes are scarce (Çetinkaya *et al.*, 1999; Bianchini & Lee, 2000; Dias *et al.*, 2000; Seçkin *et al.*, 2004; Dayan & Çetinkaya, 2005). The structural feature of five-coordination results in the formation of coordinatively unsaturated Ru^{II} complexes containing the pydim ligand and makes these complexes interesting from the viewpoint of potential application in homogeneously Ru^{II} -catalyzed reactions. The presence of a labile ligand makes these complexes potentially interesting as precursors for the synthesis of a variety of Ru^{II} complexes of

the type $[\text{RuCl}_2(\text{pydim})L]$, where L is a neutral ligand. For example, $[\text{RuCl}_2(\text{pydim})(\text{CH}_3\text{CN})]$ compounds ($\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) exhibit efficient activity for the epoxidation of cyclohexane (Çetinkaya *et al.*, 1999).

In the present study, the title compound, (II), was synthesized in good yield (70%) by the reaction sequences depicted in the scheme below. The composition of this complex has been confirmed by CHN elemental and IR and NMR spectroscopic analyses. In order to establish the coordination geometry about the metal atom and to examine the structural parameters in this case, we present here the synthesis and crystal structure of complex (II).



The molecular structure of complex (II) and the atom-labelling scheme are shown in Fig. 1. Selected geometric parameters are summarized in Table 1. The mononuclear pydim molecule contains an ($N,N'E,N,N'E$)- N,N' -[1,1'-(pyridine-2,6-diyl)bis(ethan-1-yl-1-ylidene)]bis(2-ethyl-6-methyl-aniline) ligand, (I), with an Ru^{II} metal centre, one acetonitrile ligand and two Cl ligands. Complex (II) crystallizes with one-half of a dichloromethane solvent molecule in the asymmetric unit and the ligand, (I), with its two imine groups in *ortho* positions with respect to the pyridine (py) N atom, behaves as a symmetrical N,N',N' -tridentate chelate. The Ru^{II} ion is six-coordinated by two imine N atoms, one pyridine N atom, one acetonitrile N atom and two Cl atoms (Fig. 1). The five-membered chelate rings formed by atoms $\text{Ru1}/\text{N1}/\text{C1}/\text{C8}/\text{N3}$ and atoms $\text{Ru1}/\text{N1}/\text{C5}/\text{C6}/\text{N2}$ are planar and the maximum deviations from their planes are 0.054 (3) and 0.076 (3) Å, respectively, for atom N1. These two chelate rings make a small dihedral angle of 1.59 (8)° with one another, indicating that they are nearly coplanar.

The asymmetric unit of (II) comprises one mononuclear pydim molecule and one-half of a dichloromethane solvent molecule lying on a twofold axis. The local structure around the Ru^{II} ion is that of an octahedron, of which the equatorial

plane (N1/N2/N3/N4) is formed by three N atoms from ligand (I) (N1, N2 and N3) and one N atom of the acetonitrile ligand (N4). The axial positions in the octahedron are occupied by two Cl atoms (Cl1 and Cl2). As can be seen from the *trans* angles, which vary from 156.99 (19) to 176.65 (6)°, and the *cis* angles, which vary from 78.73 (18) to 103.73 (18)°, the coordination octahedra around the Ru^{II} ion can be visualized as being distorted, with the major distortion arising *via* the N2—Ru1—N3 angle, at 156.96 (19)°. This angle is considerably smaller than the ideal angle of 180° and there is no steric barrier to coordination of a fourth ligand in the equatorial plane *trans* to the pyridine moiety. The N1—Ru—N4 angle, involving the acetonitrile and pyridine N atoms, is normal at 171.93 (19)°. The Ru—N2 and Ru—N3 bond lengths are comparable with the reported values for [RuCl₂(pybox-dihydro)(C₂H₄)] [pybox is bis(hydrooxazolyl)pyridine; Nishiyama *et al.*, 1995]. However, the *M*—N_{py} bond [1.914 (4) Å] is somewhat shorter than the *M*—N_{imino} and *M*—N_{MeCN} bonds, with the formal double-bond character of the imino linkages N2—C6 and N3—C8 having been retained [C=N = 1.311 (7) and 1.299 (8) Å, respectively]. This coordination environment is similar to that observed in [RuCl₂(pydim)(CH₃CN)] (Ar = 4-MeOC₆H₄; Çetinkaya *et al.*, 1999).

The title complex possesses approximate non-crystallographic C_s symmetry about a plane bisecting the central pyridine ring and containing the metal atom, the acetonitrile N atom and the two halogen atoms. The planes of the benzene rings substituted on the bis(imino)pyridine ligand backbone are, as usual for bis(imino)pyridine ligands, inclined almost orthogonally to the plane of the backbone [77.75 (18) and 77.3 (2)° for rings C10—C15 and C19—C24, respectively], while the dihedral angle between the two benzene planes are 84.64 (18)°. The geometries at the imino N-atom centres are all trigonal planar, the sums of the three bond angles around these centres being 359.6 and 359.7°, and none is more than *ca* 0.04 Å out of its associated RuC₂ plane.

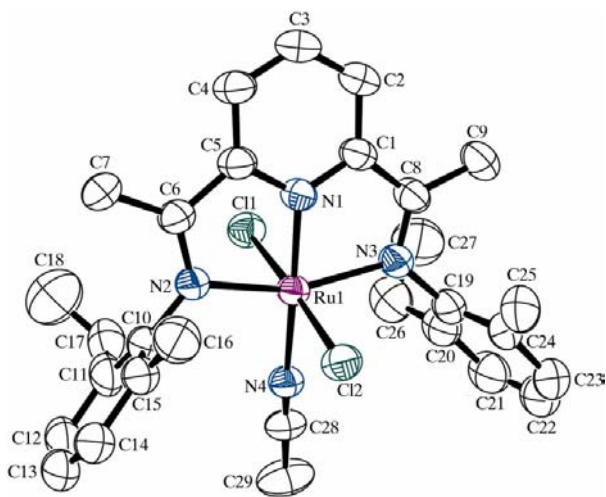


Figure 1
A view of (II), showing 30% probability displacement ellipsoids and the atom-numbering scheme. The dichloromethane solvent molecule and H atoms have been omitted for clarity.

There are several structures reported in the literature containing various transition metal complexes of pydim-based ligands (Britovsek *et al.*, 1999; Dias *et al.*, 2000; Nakayama *et al.*, 2005; Humphries *et al.*, 2005). Inspection of the the *M*—N bond distances in (II) and in these examples indicates that the two *M*—N_{imino} bonds are *ca* 0.1–0.2 Å longer than the corresponding *M*—N_{py} bond within each metal–tridentate chelate unit. Furthermore, it is observed that the N_{imino}—*M*—N_{py} bond angle for the five-membered chelate rings of pydim complexes is inversely related to the magnitude of the *M*—N_{py} bond. As the *M*—N_{py} distance increases from 1.833 (3) Å for [CoMe(pydim)] (Ar = 2,6-*i*-Pr₂C₆H₃; Humphries *et al.*, 2005) to 1.911 (3) Å for [RhMe(pydim)](OTf)₂ (Ar = 2,6-*i*-Pr₂C₆H₃; OTf is triflate; Dias *et al.*, 2000) to 1.914 (4) Å for (II) to 2.001 (3) Å for [CrCl₃(pydim)] (Ar = C₆F₅; Nakayama *et al.*, 2005) to 2.110 (6) Å for [FeCl₂(pydim)] (Ar = 2,4,6-Me₃C₆H₂; Britovsek *et al.*, 1999), the corresponding inner ‘bite’ angle decreases continuously from 81.17 (average) to 79.8 (average) to 78.76 (average) to 76.6 (average) to 72.8° (average), respectively.

The Ru—N_{MeCN} distance is 2.076 (5) Å and this is noticeably longer than the Ru—N_{MeCN} distances in [Ru(C₅H₈)(C₁₀H₁₅)(C₂H₃N)]CF₃SO₃ [2.059 (3) Å; Gemel *et al.*, 1999], [Ru(C₅H₅)(C₂H₃N)(C₁₈H₁₅P)₂]BF₄ [2.040 (3) Å; Carreón *et al.*, 1997] and [RuCl₂(C₂H₃N)₄] [2.021 (3) and 2.020 (3) Å; Bown & Hockless, 1996]. This enlargement can be attributed to the different coordination environments of the metal atoms. As expected, the acetonitrile ligand is in an almost perfectly linear configuration [N4—C28—C29 = 178.9 (8)°], but with a slightly bent coordination to the Ru^{II} ion [Ru1—N4—C28 = 172.1 (5)°]. Such coordination has been observed in [RuCl₂(pydim)(CH₃CN)] [Ar = 4-MeOC₆H₄; 173.3 (9)°; Çetinkaya *et al.*, 1999]. A bent metal–acetonitrile coordination is indeed quite common, with angles from 145.2 to 176.9°, and an average of 167°, having been reported (Agterberg *et al.*, 1998; Begley *et al.*, 1985; Chisholm *et al.*, 1996; Holligan *et al.*, 1992; Libby *et al.*, 1993). This average is somewhat lowered by the two extremely low values for Ni^{II} (145.2°; Holligan *et al.*, 1992) and Mn^{III} (149.1°; Libby *et al.*, 1993) complexes, which have

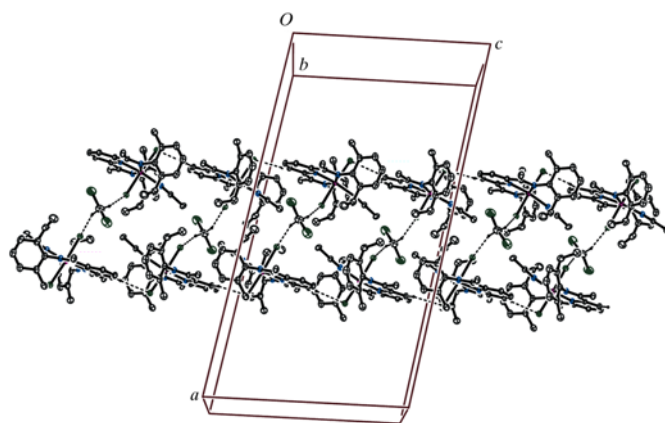


Figure 2
Part of the crystal structure of (II), showing the formation of a chain of edge-fused R₆⁶(24) rings along [001]. For clarity, only H atoms involved in hydrogen bonding have been included.

been attributed to hydrogen-bonding and steric effects, respectively.

In the molecular structure of (II), two intramolecular interactions are observed between the methylene H atom substituted on the benzene rings and the Cl atom coordinated to the metal atom (Table 2), which lead to the formation of seven-membered rings with graph-set descriptor $S(7)$ (Bernstein *et al.*, 1995). Each of these intramolecular hydrogen bonds is fused with both the benzene ring and the five-membered chelate ring. Examination of the structure with *PLATON* (Spek, 2003) reveals that there are intermolecular interactions between atom Cl1 coordinated to the metal atom and atom H30 of the dichloromethane solvent molecule. These interactions are probably responsible for stabilizing the dichloromethane molecule in the observed position. Another interaction is observed between atom Cl2 coordinated to the metal atom and atom H2 on atom C2 of the pyridine ring. Together, these intermolecular interactions form an $R_6^6(24)$ ring. Propagation of this hydrogen-bonding motif generates a chain of edge-fused rings running parallel to the [001] direction (Fig. 2). The full geometry of the intra- and intermolecular interactions is given in Table 2.

Experimental

All manipulations were performed under argon using standard Schlenk techniques. Melting points were determined in open capillary tubes on a digital Electrothermal 9100 melting-point apparatus. IR spectra (KBr pellets) were recorded in the range 400–4000 cm^{-1} on an ATI UNICAM 2000 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained on a Varian AS 400 MHz spectrometer operating at 399.883 and 100.561 MHz, respectively. Elemental analyses were carried out by the analytical service of TÜBİTAK (the Scientific and Technical Research Council of Turkey) using a Carlo Erba 1106 apparatus. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Johnson Matthey), α -phellandrene (Acros), diacetylpyridine (Fluka) and 2-ethyl-6-methylaniline (Avacado) were used as received. $[\text{RuCl}_2(p\text{-cymene})]_2$ was synthesized according to the procedure of Bennett & Smith (1974).

Compound (I) was prepared using a modification of Çetinkaya's method (Çetinkaya *et al.*, 1999; Dayan & Çetinkaya; 2005). Solvents were of analytical grade and were distilled after drying. An ethanolic solution (15 ml) of 1.10 equivalents of (I) (437 mg, 1.10 mmol) was mixed with $[\text{RuCl}_2(p\text{-cymene})]_2$ (306 mg, 0.5 mmol). The reaction mixture was heated under reflux for 10 h. The resulting deep-purple solution was cooled to room temperature. The ethanol was removed by distillation. The residue was dissolved in dichloromethane (15 ml) with acetonitrile (1 ml, excess mmol) and precipitated by the addition of diethyl ether (30 ml). The microcrystalline solid was then washed with diethyl ether (30 ml) and pentane (30 ml). The desired product was dried in a vacuum at 323 K for 1 h. X-ray quality crystals were grown from $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ (30 ml, 1:2 v/v) [yield 425 mg, 70%; m.p. 421 K (decomposition)]. Analysis calculated for $\text{C}_{29}\text{H}_{34}\text{Cl}_2\text{N}_4\text{Ru}$: C 57.05, H 5.61, N 9.18%; found: C 57.45, H 5.34, N 8.76%. ^1H NMR (CDCl_3): δ 1.09 [*t*, 6H, $J = 7.2$ Hz, 2-Me-6-(CH_2Me)-Ph], 2.24 [*s*, 6H, 2-Me-6-(CH_2Me)-Ph], 2.30 [*s*, 3H, MeCN], 2.65 [*s*, 6H, N=CMe], 2.72 [*m*, 4H, 2-Me-6-(CH_2Me)-Ph], 5.28 [*s*, 1H, CH_2Cl_2], 7.13 [*m*, 6H, Ph-H], 7.62 [*t*, 1H, $J = 7.8$ Hz, py-Hp], 7.87 [*d*, 2H, $J = 7.6$ Hz, py-Hm]; ^{13}C NMR (CDCl_3): δ 11.14, 11.52, 14.68, 17.20, 21.82, 119.83, 122.23, 122.64, 124.67, 127.85, 133.91, 134.22, 142.00, 143.23, 159.29, 169.16; IR (KBr): $\nu(\text{C}=\text{N})$ 1601 cm^{-1} .

Crystal data

$[\text{RuCl}_2(\text{C}_2\text{H}_3\text{N})(\text{C}_{27}\text{H}_{31}\text{N}_3)] \cdot 0.5\text{CH}_2\text{Cl}_2$	$V = 6360.2$ (7) \AA^3
$M_r = 653.04$	$Z = 8$
Monoclinic, $C2/c$	$D_x = 1.364$ Mg m^{-3}
$a = 31.385$ (2) \AA	Mo $K\alpha$ radiation
$b = 12.4151$ (7) \AA	$\mu = 0.77$ mm^{-1}
$c = 16.5874$ (11) \AA	$T = 296$ K
$\beta = 100.246$ (6) $^\circ$	Prism, black
	$0.73 \times 0.47 \times 0.24$ mm

Data collection

Stoe IPDS-II diffractometer	43963 measured reflections
ω scans	6268 independent reflections
Absorption correction: integration (<i>X-RED32</i> ; Stoe & Cie, 2002)	3804 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.691$, $T_{\max} = 0.865$	$R_{\text{int}} = 0.091$
	$\theta_{\max} = 26.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0844P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.053$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.159$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.03$	$\Delta\rho_{\max} = 0.77$ e \AA^{-3}
6268 reflections	$\Delta\rho_{\min} = -0.48$ e \AA^{-3}
347 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	(Sheldrick, 1997)
	Extinction coefficient: 0.000167 (7)

Table 1

Selected geometric parameters (\AA , $^\circ$).

Ru1–N2	2.088 (4)	Ru1–Cl2	2.3833 (17)
Ru1–N3	2.090 (4)	Ru1–Cl1	2.3967 (17)
N1–Ru1–N2	78.73 (18)	N3–Ru1–Cl2	89.49 (15)
N4–Ru1–N2	103.73 (18)	N1–Ru1–Cl1	83.10 (14)
N1–Ru1–N3	78.78 (19)	N4–Ru1–Cl1	89.17 (14)
N4–Ru1–N3	99.23 (19)	N2–Ru1–Cl1	90.23 (14)
N1–Ru1–Cl2	100.13 (14)	N3–Ru1–Cl1	92.01 (15)
N4–Ru1–Cl2	87.63 (14)	Cl2–Ru1–Cl1	176.65 (6)
N2–Ru1–Cl2	89.55 (14)		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
C26–H26A \cdots Cl1	0.97	2.57	3.523 (9)	168
C17–H17A \cdots Cl1	0.97	2.62	3.563 (9)	165
C30–H30 \cdots Cl1	0.97	2.76	3.684 (12)	160
C2–H2 \cdots Cl2 i	0.93	2.75	3.593 (6)	152

Symmetry code: (i) $x, -y + 2, z + \frac{1}{2}$.

H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.96, 0.97 and 0.93 \AA for CH_3 , CH_2 and aromatic CH groups, respectively. The displacement parameters of the H atoms were constrained at $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, or $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms. Riding methyl H atoms were allowed to rotate freely during refinement using the AFIX 137 command of *SHELXL97* (Sheldrick, 1997). Examination of the refined structure using *PLATON* (Spek, 2003) revealed the presence of void spaces having a total volume of 224.6 \AA^3 (3.5%) per unit cell, the volume of the individual voids being 28 \AA^3 . The maximum peak in the final difference Fourier map is 0.42 \AA from atom H16C and the minimum peak is 0.82 \AA from atom Ru1. Even though the structure contains solvent-accessible voids, both the minimum and maximum residual electron-density peaks are smaller than 1 e \AA^{-3} , indicating that no molecular fragments remain unaccounted for.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3081). Services for accessing these data are described at the back of the journal.

References

- Agterberg, F. P. W., Provo Kluit, H. A. J., Driessen, W. L., Reedijk, J., Oevering, H., Buijs, W., Veldman, N., Lakin, M. T. & Spek, A. L. (1998). *Inorg. Chim. Acta*, **267**, 183–192.
- Begley, M. J., Dove, M. F. A., Hibbert, R. C., Logan, N., Nunn, M. & Sowerby, D. B. (1985). *J. Chem. Soc. Dalton Trans.* pp. 2433–2436.
- Bennett, M. A. & Smith, A. K. (1974). *J. Chem. Soc. Dalton Trans.* pp. 233–241.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bianchini, C. & Lee, H. M. (2000). *Organometallics*, **19**, 1833–1840.
- Bown, M. & Hockless, D. C. R. (1996). *Acta Cryst.* **C52**, 1105–1106.
- Britovsek, G. J. P., Gibson, V. C., Kimberley, B. S., Maddox, P. J., MacTavish, S. J., Solan, G. A., White, A. J. P. & Williams, D. J. (1999). *J. Am. Chem. Soc.* **121**, 8728–8740.
- Carreón, O. Y., Leyva, M. A., Fernández-G, J. M. & Pénicaud, A. (1997). *Acta Cryst.* **C53**, 301–302.
- Çetinkaya, B., Çetinkaya, E., Brookhart, M. & White, P. S. (1999). *J. Mol. Catal. A*, **142**, 101–112.
- Chisholm, M. H., Christou, G., Folting, K., Huffman, J. C., James, C. A., Samuels, J. A., Wesemann, J. L. & Woodruff, W. H. (1996). *Inorg. Chem.* **35**, 3643–3658.
- Dayan, O. & Çetinkaya, B. (2005). XIXth National Chemistry Congress, Kuşadası, Turkey, 30 September–4 October 2005, Abstracts, p. 133.
- Dias, E. L., Brookhart, M. & White, P. S. (2000). *Organometallics*, **19**, 4995–5004.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Gemel, C., Kirchner, K., Schmid, R. & Mereiter, K. (1999). *Acta Cryst.* **C55**, 2053–2055.
- Gibson, V. C. & Spitzmesser, S. K. (2003). *Chem. Rev.* **103**, 283–316.
- Holligan, B. M., Jeffery, J. C. & Ward, M. D. (1992). *J. Chem. Soc. Dalton Trans.* pp. 3337–3344.
- Humphries, M. J., Tellmann, K. P., Gibson, V. C., White, A. J. P. & Williams, D. J. (2005). *Organometallics*, **24**, 2039–2050.
- Libby, E., Folting, K., Huffman, C. J., Huffman, J. C. & Christou, G. (1993). *Inorg. Chem.* **32**, 2549–2556.
- Nakayama, Y., Sogo, K., Yasuda, H. & Shiono, T. (2005). *J. Polym. Sci. Polym. Chem.* **43**, 3368–3375.
- Nishiyama, H., Itoh, Y., Suguwara, Y., Matsumoto, H., Aoki, K. & Itoh, K. (1995). *Bull. Chem. Soc. Jpn*, **68**, 1247–1262.
- Seçkin, T., Köytepe, S. & Çetinkaya, E. (2004). *J. Polym. Res.* **11**, 119–125.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Small, B. L. & Brookhart, M. (1998). *J. Am. Chem. Soc.* **120**, 7143–7144.
- Small, B. L. & Brookhart, M. (1999). *Macromolecules*, **32**, 2110–2119.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.