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Polyhedron 23 (2004) 219–223

POLYHEDRON

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Complexes of heteroscorpionate trispyrazolylborate ligands. Part XII. Variable hapticity of hydrobis (3-phenyl-5-isopropylpyrazolyl)(3,5-dimethylpyrazolyl) borate in its rhodium(I) complexes with COD and NBD

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Received 11 May 2003; accepted 14 August 2003

Abstract

The structure of Tp″Rh(NBD) complex was determined by X-ray crystallography (Tp″ = hydrobis(3-phenyl-5-isopropylpyrazolyl)(3,5-dimethylpyrazolyl)borate, NBD = 2,5-norbornadiene). The Tp″ was found to be κ^3 coordinated to rhodium(I). Two independent molecules of Tp″Rh(NBD) were found in triclinic crystals with Rh–N(pz) distances in the region of 2.113(3)–2.307(3) Å. On the other hand the same Tp″ ligand was demonstrated to be coordinated in κ^2 fashion in Tp″Rh(COD) (COD = 1,5-cyclooctadiene) by variable temperature 1-D and 2-D ^{1}H NMR measurements. The intramolecular exchange between coordinated and uncoordinated 3-phenyl-5-isopropylpyrazolyl residues occurs with $\Delta G^{\neq} = 42.2$ kJ/mol as it was calculated from the ^{1}H NMR studies.

Keywords: Polypyrazolylborate; Rhodium(I); Cyclooctadiene; Norbornadiene; Structure; NMR

1. Introduction

Heteroscorpionate trispyrazolylborates (Tp″) are tripodal anionic ligands of potentially C_s symmetry [1]. The symmetry of the ligands can be preserved in their metal ion complexes, when Tp″s are coordinated in κ^3 fashion. The κ^3 hapticity resulting in effective C_s symmetry of the complexes was observed in the series of high-spin cobalt(II) complexes of the general formula Tp″Co(NCS) [2–8].

In case of Tp″Rh(LL) complexes (where LL = $(CO)_2$ or COD), the Tp″ ligands are coordinated in κ^2 fashion [9]. Fluxional behavior of those complexes was studied in detail by variable-temperature ^{1}H NMR spectroscopy. The homoscorpionate Tp″ ligands are in most cases κ^2-bonded in their Tp″Rh(LL) complexes ([9] and references [6–16] cited therein). However, there are three examples of κ^3 hapticity in rhodium complexes with trispyrazolylborates and ancillary ligands (LL) other than mentioned: $Tp^{Me}Rh(NBD)$ [10], $Tp^{Me2}Rh(PEt_3)(C_2H_4)$ [11], $TpRh(PPh_3)[(CCOOCH_3)_2]$ [12], and $Tp^{iPr2}Rh(NBD)$ [13], in which the N(pz)–Rh bond lengths fall into the region of 2.12–2.27 Å. Here we report on the structure of another complex, in which the Tp″ ligand bearing two sterically demanding 3-phenyl substituents is coordinated in κ^3 fashion in Tp″Rh(NBD), while κ^2 hapticity is found in Tp″Rh(COD) analogue as can be concluded on the basis of variable temperature 1-D and 2-D ^{1}H NMR experiments.

2. Experimental

2.1. Syntheses

The sodium salt of hydrobis(3-phenyl-5-isopropylpyrazolyl)(3,5-dimethylpyrazolyl)borate (NaTp″) was synthesized as before [7]. The Tp″Rh(NBD) (**1**) and Tp″Rh(COD) (**2**) complexes were synthesized upon

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doi:10.1016/j.poly.2003.11.010

addition of 120 mg of NaTp″ dissolved in toluene into the equimolar amounts of $[(COD)RhCl)]_2$ [14] or $[(NBD)RhCl)]_2$ [15] in toluene. The reaction mixtures were stirred at room temperature for 4 h under atmosphere of nitrogen, filtrated by passing through short bed of celite, the solvent was partially removed, the solutions layered with heptane and allowed to stand at 4 °C until formation of yellow crystals of **1** (yield 85%) or **2** (yield 80%).

2.2. Analytical data

1: Elemental analysis: Calc. for $C_{36}H_{42}N_6BRh$ (MW 672.48): C, 64.30; H, 6.29; N, 12.50. Found: C, 64.55; H, 6.16; N, 12.43%.

^{1}H NMR (toluene-d_8, 298 K): 8.01 (4H, m, *o*-H(3-Ph)); 7.25 (4H, m, *m*-H(3-Ph)); 7.16 (2H, m, *p*-H(3-Ph)); 6.31 (2H, s, 4-H(3-Ph,5-*i*Prpz)); 5.58 (1H, s, 4-H(3,5-diMepz)); 3.33 (6H, septet + broad singlet, C*H*(5-*i*Pr) + 2′, 3′, 5′, 6′-H(NBD)); 2.94 (2H, s, 1′, 4′ –H(NBD)); 2.31 (3H, s, 3(5)-CH_3); 2.14 (3H, s, 5(3)-CH_3); 1.29 (6H, d, $J_{(CH_3–CH)} = 6.6$ Hz, 2×CH_3(5-*i*Pr)); 1.21(6H, d, $J_{(CH_3–CH)} = 6.6$ Hz, 2×CH_3(5-*i*Pr)); 0.59 (2H, s, 7′-H(NBD)).

IR (KBr): ν(BH) 2534, 2474 cm^{-1}.

2: Elemental analysis: Calc. for $C_{37}H_{46}N_6BRh$ (MW 688.53): C, 64.54; H, 6.73; N, 12.21. Found: C, 64.62; H, 6.86; N, 12.13%.

^{1}H NMR (toluene-d_8, 273 K): 8.10 (4H, m, *o*-H(3-Ph)); 7.25 (4H, m, *m*-H(3-Ph)); 7.10 (2H, m, *p*-H(3-Ph)); 6.45 (2H, s, 4-H(3-Ph,5-*i*Prpz)); 5.56 (1H, s, 4-H(3,5-diMepz)); 4.10 (4H, s, 1′, 2′, 5′, 6′-H(COD)); 3.19 (2H, septet, C*H*(5-*i*Pr)), 2.34 (3H, s, 5-CH_3); 2.22 (3H, s, 3-CH_3); 1.87 (4H, s, 3′, 4′, 7′, 8′-H_{exo} (COD)); 1.39 (6H, d, $J_{(CH_3–CH)}) = 6.6$ Hz, 2×CH_3(5-*i*Pr)); 1.20 (10H, d, $J_{(CH_3–CH)}) = 6.6$ Hz, 2×CH_3(5-*i*Pr) + overlapped s, 3′, 4′, 7′, 8′-H_{endo} (COD)).

IR (KBr): ν(BH) 2478 cm^{-1}.

2.3. Methods

The ^{1}H NMR spectra were recorded with Bruker AMX 300 spectrometer. Standard COSY and NOESY experiments were performed with repetition time 1.0 and mixing time 0.3 s (NOESY).

Crystal data are given in Table 1, together with refinement details. All measurements of crystal were performed at low temperature using an Oxford Cryosystem device on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation. The crystal was positioned 65 mm from the CCD camera. 612 frames were measured at 0.75° intervals with a counting time of 20 s. Accurate cell parameters were determined and refined by least-squares fit of 5950 of the strongest reflections. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Oxford Diffraction (Poland) Sp. z o.o (formerly Kuma Diffraction Wrocław, Poland) programs. The structure was solved by direct methods (program SHELXS-97 [17]) and refined by the full-matrix least-squares method on all F^2 data using the SHELXL-97 [17] programs. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were included from geometry of molecules and $\Delta\rho$ maps. During refinement they were fixed.

Table 1
Crystal data and structure refinement

Empirical formula	$C_{36}H_{42}BN_6Rh$
Formula weight	672.48
T (K)	100(2)
λ (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	12.197(2)
b (Å)	15.876(3)
c (Å)	17.120(3)
α (°)	102.42(3)
β (°)	102.73(3)
γ (°)	90.88(3)
V (Å^3)	3151.1(10)
Z	4
D_{calc} (Mg m^{-3})	1.418
μ (mm^{-1})	0.578
F(000)	1400
Crystal size (mm)	0.17 × 0.15 × 0.15
θ Range for data collection (°)	3.43–28.41
Ranges of h, k, l	−15 to 16, −20 to 20, −22 to 21
Reflections collected	21 925
Independent reflections	13 848 (0.0561)
Data/parameters	13 848/806
Goodness-of-fit (F^2)	0.952
Final R_1/wR_2 indices ($I > 2\sigma(I)$)	0.0549/0.0738
Extinction coefficient	0.00015(10)
Largest diffraction peak/hole (e Å^{-3})	0.569/−0.734

3. Results and discussion

The heteroscorpionate ligand used in these studies, composed of two 3-phenyl-5-isopropylpyrazolyl and 3,5-dimethylpyrazolyl residues ($[HB(3\text{-}Ph,5\text{-}iPrpz)_2(3,5\text{-}diMepz)]^-$) is more sterically demanding in comparison with homoscorpionates Tp^{Me} [10], Tp [11], or Tp^{Me2} [12], which coordinate in κ^3 fashion to the rhodium(I) metal ion in their Tp′Rh(LL) complexes. On the other hand it is probably slightly less demanding than Tp^{iPr2}, which forms Tp″Rh(diene) complexes with κ^3 hapticity, when dien = NBD and κ^2 hapticity in case of diene = COD [13]. Other sterically demanding Tp′ ligands, like Tp^{Ph} [18] and Tp$^{4\text{-}OMePh}$ [19], as well as $[HB(pz)_4]^-$ [20] coordinate in κ^2 fashion in their Tp′Rh(diene) complexes. We have synthesized two compounds: $[HB(3\text{-}Ph,5\text{-}iPrpz)_2(3,5\text{-}diMepz)]Rh(NBD)$ (**1**) and $[HB(3\text{-}Ph,5\text{-}iPrpz)_2(3,5\text{-}$

diMepz)]Rh(COD) (**2**) in which the coordination mode of Tp″ ligand is κ^3 and κ^2, respectively.

The structure of **1** was elucidated crystallographically. There are two independent molecules of **1**. The views of the molecules are shown in Fig. 1 together with relevant bond lengths and angles around metal ion. The Rh–N(pz) distances fall into the region of 2.113(3)–2.307(3) Å (average value 2.24 Å), which is typical for other κ^3-Tp″Rh(NBD) complexes [10–13] and apparently longer in comparison with those for κ^2-Tp″Rh(NBD) ones (average value of Rh–N(pz) is equal 2.08 Å) [18–20].

The ^{1}H NMR spectrum of **1** (Fig. 1(b)) is composed of two 4-H(pz) resonances of relative 2:1 intensity ratio throughout broad range of temperature (down to 193 K) indicating the effective C_s symmetry of the molecule. Thus, the ligand remains coordinated in κ^3 fashion in solution or is in fast exchange between κ^2 and κ^3 mode. The resonances from methyl groups of 5-ispopropyl substituents are diastereotopically split into two doublets due to local chirality in **1**. The mutual rotation of Tp″ and NBD ligands in **1** is fast at the time-scale of the ^{1}H NMR even at the lowest temperature available in toluene-d_8 solvent as can be concluded from the presence of three resonances from NBD throughout the studied temperature range.

The crystals of **2** suitable for X-ray analysis could not be obtained. Therefore, the detailed analysis of the

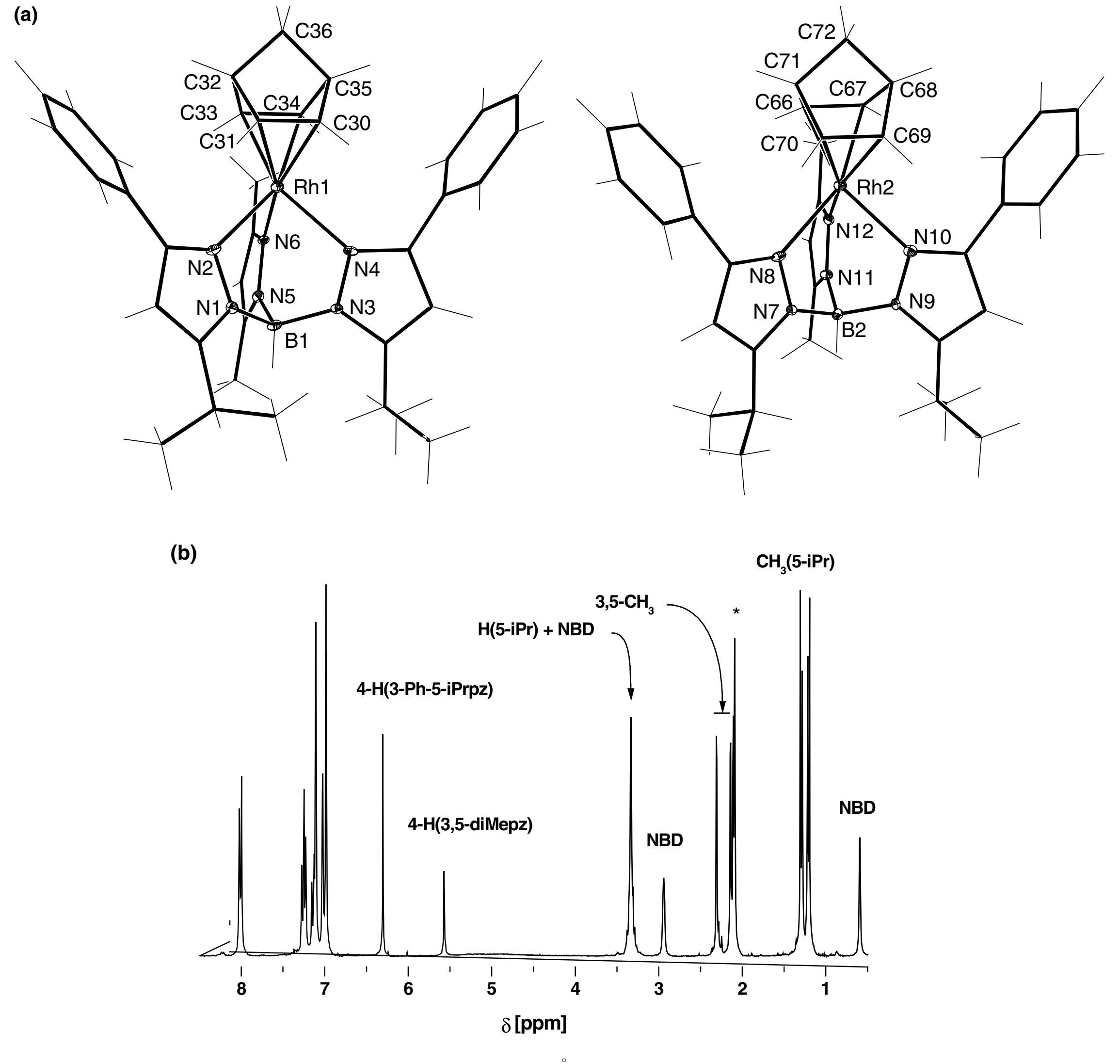

Fig. 1. (a) View of two independent molecules of **1**. Selected bond lengths (Å) and angles (°): Rh(1)–N(2), 2.299(3); Rh(1)–N(4), 2.290(3); Rh(1)–N(6), 2.113(3); Rh(1)–C(30), 2.169(4); Rh(1)–C(31), 2.157(4); Rh(1)–C(33), 2.078(4); Rh(1)–C(34), 2.069(4); N(4)–Rh(1)–N(2), 88.15(12); N(6)–Rh(1)–N(4), 83.26(13); N(6)–Rh(1)–N(2), 83.59(12); C(34)–Rh(1)–C(31), 79.34(16); C(33)–Rh(1)–C(30), 79.55(17) and Rh(2)–N(8), 2.307(3); Rh(2)–N(10), 2.282(4); Rh(2)–N(12), 2.136(3); Rh(2)–C(66), 2.087(4); Rh(2)–C(67), 2.082(4); Rh(2)–C(69), 2.166(4); Rh(2)–C(70), 2.177(4); N(10)–Rh(2)–N(8), 87.26(12); N(12)–Rh(2)–N(8), 85.07(12); N(12)–Rh(2)–N(10), 83.35(13); C(67)–Rh(2)–C(70), 79.44(17); C(66)–Rh(2)–C(69), 79.85(17). (b) ^{1}H NMR spectrum of **1** in toluene-d_8 at 298 K. The residual peak from solvent (q, C*H*D$_2$) is labeled with asterisk. The peaks from norbornadiene are labeled as NBD.

variable temperature ^{1}H NMR experiments was performed for **2** in toluene-d$_8$. The spectrum of **2** at ambient temperature reflects the effective C_s symmetry of **2**. However, the spectrum changes dramatically upon decrease of temperature; the coalescence point observed at 223 K clearly indicates that a chemical exchange between coordinated and uncoordinated pyrazolyl residues becomes slow at the time-scale of the method. Further decrease of temperature results in decrease of symmetry of the spectrum consistent with slow exchange between coordinated and uncoordinated 3-Ph-5-*i*Prpz residues. Three resonances of 4-H(pz) and four resonances from olefinic COD hydrogens are observed at 193 K (resonances a–d at lower trace at Fig. 2).

These features were already observed in case of other heteroscorpionate complexes: [HB(3-Ph,5-Mepz)$_2$(3-Me,5-Phpz)]Rh(COD) and [HB(3-Ph,5-Mepz)$_2$(3,5-diEtpz)]Rh(COD) [9], in which the Tp″ ligands are coordinated in κ^2 fashion, and attributed to slow exchange between coordinated and uncoordinated 3-Ph,5-Mepz moiety. The ^{1}H-^{1}H COSY and NOESY experiments showed the cross-peaks within a $\Longleftrightarrow$ b and c $\Longleftrightarrow$ d pairs of olefinic protons of COD, similarly as it was found for [HB(3-Ph,5-Mepz)$_2$(3-Me,5-Phpz)]Rh(COD) and [HB(3-Ph,5-Mepz)$_2$(3,5-diEtpz)]Rh(COD) [9]. Thus, the scalar coupling within a $\Longleftrightarrow$ b and c $\Longleftrightarrow$ d pairs of signals in COSY spectrum and concomitant EXSY cross-peaks between the same diagonal peaks in NOESY spectrum clearly confirm that effective C_1 symmetry of the ^{1}H NMR spectrum of **2** at 193 K is consistent with slow exchange between coordinated and uncoordinated 3-Ph,5-*i*Prpz residues. For this interconversion the $\Delta G^{\neq} = 42.2$ kJ/mol has been calculated. The obtained value of energy of activation is very close to those found in other similar systems, in which the coordinated and uncoordinated 3-Ph,5-Mepz residues interchanged with $\Delta G^{\neq} = 41.1$ kJ/mol in case when third, slowly exchanging pyrazolyl residue was 3,5-diEtpz and $\Delta G^{\neq} = 43.2$ kJ/mol in case of 3-Me,5-Phpz as third, coordinated pyrazolyl moiety [9].

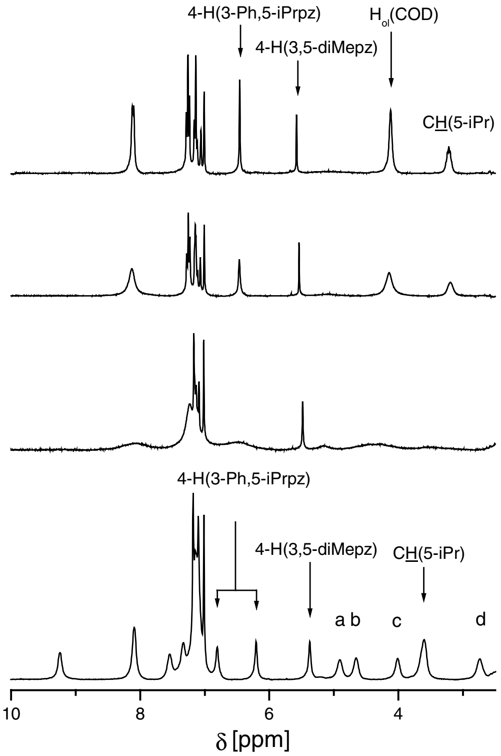

Fig. 2. The relevant fragments of ^{1}H NMR spectra of **2** in toluene-d$_8$ taken at temperature (from top to bottom): 273, 253, 223, and 193 K, respectively. The resonances labeled with H$_{ol}$(COD) (top trace) and a, b, c, d (bottom trace) belong to 1′, 2′, 5′, and 6′ H(COD).

The heteroscorpionate [HB(3-Ph,5-*i*Prpz)$_2$(3,5-diMepz)]$^-$ ligand serves a borderline example of steric demand towards the Rh(diene) counterpart, similar to homoscorpionate Tp^{iPr2} [13]. The hapticity of Tp″ depends on the rhodium-centered diene cone angle. Tp″ coordinates in κ^2 fashion in case of diene = COD (average value of α for Tp″Rh(COD) complexes is 93.4° [9]), while κ^3 coordination mode occurs for diene = NBD ($\alpha = 79.5°$ in **1**) in solid state at 100 K. However, it should be emphasized that according to the IR spectral criterion proposed by Akita et al. [21] based on the position of ν(BH) the presence of two distinct bands at 2534 and 2474 cm^{-1} (of relative intensity about 2:1 both in KBr and in chloroform solution) for **1** suggests that at ambient temperature the [HB(3-Ph,5-*i*Prpz)$_2$(3,5-diMepz)]$^-$ ligand is coordinated in two ways: κ^3 and κ^2 mode, while in case of **2** (one ν(BH) band at 2478 cm^{-1}) the ligand remains coordinated in κ^2 mode both in solid state and in solution throughout the entire range of temperatures.

4. Supplementary data

Crystallographic data for the structures reported in this paper (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 209564. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge 1EZ, UK (fax: +44-1223-336033; deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Acknowledgements

The authors thank KBN (Poland) for the Grant No. 3 T09A 05219.

References

[1] S. Trofimenko, Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands, Imperial College Press, London, UK, 1999.

[2] M. Łukasiewicz, Z. Ciunik, S. Wołowiec, Polyhedron 19 (2000) 2119.
[3] M. Łukasiewicz, Z Ciunik, T. Ruman, M. Skóra, S. Wołowiec, Polyhedron 20 (2001) 237.
[4] T. Ruman, M. Łukasiewicz, Z. Ciunik, S. Wołowiec, Polyhedron 20 (2001) 2551.
[5] T. Ruman, Z. Ciunik, A. Goclan, M. Łukasiewicz, S. Wołowiec, Polyhedron 20 (2001) 2965.
[6] T. Ruman, Z. Ciunik, S. Wołowiec, Eur. J. Inorg. Chem. (2003) 89.
[7] T. Ruman, Z. Ciunik, S. Wołowiec, Eur. J. Inorg. Chem. (2003) 2475.
[8] T. Ruman, Z. Ciunik, S. Wołowiec, Polyhedron 22 (2003) 581.
[9] T. Ruman, Z. Ciunik, A.M. Trzeciak, S. Wołowiec, J.J. Ziółkowski, Organometallics 22 (2003) 1072.
[10] U.E. Bucher, A. Currao, R. Nesper, H. Rüegger, L.M. Venanzi, E. Younger, Inorg. Chem. 34 (1995) 66.
[11] M.C. Nikasio, M. Paneque, P.J. Perez, A. Pizzano, M.L. Poveda, M. Rey, S. Sirol, S. Taboada, M. Trujillo, A. Monge, C. Ruiz, E. Carmona, Inorg. Chem. 39 (2000) 180.
[12] A.F. Hill, A.J.P. White, D.J. Williams, J.D.E.T. Wilton-Ely, Organometallics 17 (1998) 3152.
[13] M. Akita, Y. Takahashi, S. Hikichi, U. Moro-oka, Organometallics 16 (1997) 4121.
[14] G. Giordano, R.H. Crabtree, Inorg. Synth. 28 (1990) 88.
[15] E.W. Abel, M.A. Bennet, G. Wilkinson, J. Chem. Soc. (1959) 3178.
[16] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.
[17] G.M. Sheldrick, SHELXL-97: Program for Crystal Structure Refinement, University of Göttingen, Göttingen, 1997.
[18] D. Sanz, M.D. Santa Maria, R.M. Claramunt, M. Cano, J.V. Heras, J.A. Campo, F.A. Ruiz, E. Penilla, A. Monge, J. Organomet. Chem. 526 (1996) 341.
[19] M.D. Santa Maria, R.M. Claramunt, J.A. Campo, M. Cano, R. Criado, J.V. Heras, P. Ovejero, E. Pinilla, M.R. Torres, J. Organomet. Chem. 605 (2000) 117.
[20] M. Cocivera, C. Ferguson, B. Kaitner, F.J. Lalor, D.J. O'Sullivan, M. Parvez, B. Ruhl, Organometallics 1 (1982) 1132.
[21] M. Akita, K. Ohta, Y. Takahashi, S. Hikichi, Y. Moro-oka, Organometallics 16 (1997) 4121.