Inorganica Chimica Acta 370 (2011) 292-296

Contents lists available at ScienceDirect

Inorganica Chimica Acta



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

Change of the coordination type for the phospholyl ligand under nucleophilic attack of H₂O on phosphorus atom in 2,5-diphenylphosphacymantrene promoted by aliphatic amines

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ARTICLE INFO

Article history: Received 27 April 2010 Received in revised form 21 January 2011 Accepted 24 January 2011 Available online 3 February 2011

Keywords: Manganese complexes Phosphacymantrenes Aliphatic amines Nucleophilic addition Phosphoryl rearrangement X-ray crystal structures

ABSTRACT

 $η^5$ -2,5-Diphenylphosphacymantrene (**1**) in benzene or CH₂Cl₂ solution does not react with amines. However, with amines NHEt₂, NEt₃, NEt(i-Pr)₂ in excess and in the presence of small amounts of water **1** reacts to form anionic complexes [(CO)₃Mn(η⁴-Ph₂H₂C₄P(=O)H]⁻ A⁺, where cation $A = H_2$ NEt₂⁺ (**2a**), HNEt₃⁺ (**2b**), HN(Et)(Prⁱ)₂⁺ (**2c**). Probably, first an unstable intermediate with P–OH bond is formed as a result of the attack by the activated H₂O molecule at the P atom. Afterwards, the rapid rearrangement occurs with migration of H from O to P which leads to the ligand 2,5-diphenyl-1-*H*-phosphol-1-oxide, Ph₂H₂C₄P(=O)H. Salts **2a–c** have been characterized by ¹H, ³¹P, ¹³C NMR- and IR-spectra and the structures of **2a** and **2c** established by single crystal X-ray diffraction analyses. The phosphoryl ligand in anions **2a** and **2c** has the "envelope" conformation and is η⁴-coordinated with Mn(CO)₃. The phosphorus atom is not involved in the coordination with Mn because the Mn–P distances (2.7670(4) and 2.7732(8) Å) are greater than the sum of covalent radii of P and Mn.

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1. Introduction

The chemistry of the transition metal phospholyl complexes including Fe, Mn, Rh and Co [1-3] has been intensely investigated in recent years (see reviews [4-7]). Among other η^5 -phospholyl complexes, the derivatives of manganese, phosphacymantrenes $(\eta$ -C₄R₄P)Mn(CO)₃ where R = H, Alk, Ph have been studied in more details. A P(III) atom and CH group are isolobal and the former can replace the latter in the Cp-ring until the complete replacement to form cyclo- P_5^- [6,7]. Ligands C_5R_5 and C_4R_4P are isolobal but not identical. In the properties of their manganese η^5 -complexes there are both analogies (electrophilic substitution in the phospholyl ring [8], exchange of CO ligands for phosphines) and differences (unlike cymantrene, for example, 3,4-dimethylphosphacymantrene is not metallated with BuLi in THF). Quantum-chemical calculations showed that in phosphacymantrenes LUMO is the anti-bonding combination of p_z (P) and d_{xz} (Mn) orbitals which is localized on the phosphorus atom [9,10]. Therefore one can expect that the nucleophilic attack will be directed to P atom.

Mathey et al. found that 3,4-dimethylphosphacymantrene reacted with PhLi or Bu^tLi to give the products of the addition of Ph or tert-Bu to P atom. Unstable anionic η^4 -intermediates were proposed for these reactions wherein the phospholyl ligand was bonded to Mn(CO)₃ through the diene system only; however, these species were not isolated [10,11]. Early it was supposed that the phospholyl ligand can be considered as a combination of two "subunits", namely, the planar η^4 -diene fragment and μ -phosphido atom P which could be coordinated separately or as a part of the whole ligand (in η^5 -phospholyl complexes) [12].

Previously, we found the novel reaction of solvopalladation of η^5 -2,5-diphenyl-phosphacymantrene (**1**) by means of Na₂PdCl₄ and NaOAc in alcoholic solutions (MeOH or EtOH). In this reaction, the binuclear complexes with Pd₂Cl₂ core which contain groups R = OMe or OEt bonded to phosphorus were formed [13]. In an attempt to use new nucleophiles in the reactions of complex **1** we studied its interaction with aliphatic amines under various conditions (see preliminary communication [14]).

In this paper, we report on the preparation of the first stable manganese anionic complexes with the ligand η^{4} -2,5-diphenyl-1-*H*-phosphol-1-oxide *via* the reaction of **1** with water and excess of aliphatic amines.

2. Results and discussion

Reactions of 1 with amines were not studied before. We have found that in benzene or CH_2Cl_2 1 does not react with aliphatic



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^{0020-1693/\$ -} see front matter \circledcirc 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2011.01.094

amines. However, if water is added and diethylamine or aliphatic tertiary amines with rather high basicity (triethylamine or ethyldiisopropylamine) are in excess, **1** adds OH⁻ to the phosphorus atom to give complexes **2a–c** of the general formula [(OC)₃Mn- η^4 -2,5-Ph₂H₂C₄P(=O)H]⁻ [HNR₃]⁺, where NR₃ = NHEt₂ (**2a**), NEt₃ (**2b**), N(Et)(i-Pr)₂ (**2c**) (Scheme 1). The crystalline products precipitate gradually for 1–2 days at ambient temperature. Under these conditions, the reaction has not gone to completion as shown by ³¹P NMR since in the spectra of mother liquid signals both from starting **1** (singlet at δ –30.6 ppm) and of products **2a–c** (downfield shifted doublets centered at δ –5 to –9 ppm with a characteristic large coupling constant ¹*J*(P–H) 536–549 Hz) were present. Under these conditions, **1** does not react with either NH₃ (gas) or a primary amine Ph₂CH–NH₂. According to ³¹P NMR when **2a** dissolves in DMSO it converts to starting **1**.

Thus the novel reaction has been observed wherein the role of diethylamine and other amines apparently is to activate a water molecule (probably through the formation of a hydrogen bond).

The formation of anionic complexes **2a–c** probably begins with the nucleophilic attack on the phosphorus atom by the H₂O molecule to primarily give a very unstable intermediate with fragment P–OH followed by fast rearrangement with the migration of H from O to P resulting in the final products **2a–c** with a phosphoryl fragment P(=O)H. Similar rearrangements are known in classical organophosphorus chemistry [15,16].

Complexes **2a–c** have the same anion $[(CO)_3Mn-\eta^4-2,5-Ph_2C_4H_2P(=O)H]^-$ and different cations HNR_3^+ . They are crystal-

line solids, stable on keeping in inert atmosphere at 0 °C, the most stable being **2c** and the least stable **2a**, respectively. Complexes **2ac** have been characterized by ¹H, ¹³C, ³¹P NMR and IR spectra. In ¹H–{³¹P} NMR spectra signals of H–P protons are observed as broad singlets around δ 7.8 ppm. In IR spectra, both v(CO) bands of Mn(CO)₃ undergo low-frequency shift by $\Delta v = 45-60 \text{ cm}^{-1}$ that is connected with the transfer from neutral molecule **1** to anionic complexes **2a–c**. For **1** v(CO) are 1955 cm⁻¹ (broad, E-mode) and 2025 cm⁻¹ (narrow, A₁-mode), for **2a–c** 1880–1890 cm⁻¹ (E) and 1980–1985 cm⁻¹ (A₁), respectively. Interrelation of the linewidths on the half-height of peaks characteristic of the Mn(CO)₃ fragment is retained. The structures of **2a** and **2c** have been established by single crystal X-ray diffraction.

The cation and the anion in **2a** occupy a general position. The structure of complex anion **2a** is presented in Fig. 1; the main geometric parameters are given in Table 1. In the anion **2a** heterocyclic fragment has the "envelope" conformation. The carbon moiety C(1)-C(4) is planar but the phosphorus atom P(1) is going out of the carbon mean plane by 0.622 Å at the opposite side from the manganese atom. The folding angle around C(1)-C(4) axis (the dihedral angle α between planes C(1)C(2)C(3)C(4) and C(1)-P-C(4)) is 29.9°. The phosphorus atom has the distorted tetrahedral environment of atoms C(1) and C(4) of the five-membered ring, O(P) and H(P) atoms. It is not involved in the coordination with Mn. The manganese atom is η^4 -coordinated with four carbon atoms C(1)-C(2)-C(3)-C(4) only. The distance Mn(1)-P(1) 2.7670(4) Å in the anion **2a** is greater than the sum of covalent ra-



Fig. 1. Structure of anion 2a. Thermal ellipsoids are drawn at 50% probability level.

Table I	
Selected bond lengths (Å) and	angles (°).

	Anion 2a	Anion 2c , molecule A	Anion 2c , molecule B
Mn(1)-C(1)	2.1733(14)	2.170(3)	2.160(3)
Mn(1)-C(2)	2.0859(14)	2.087(3)	2.087(3)
Mn(1)-C(3)	2.0872(14)	2.080(3)	2.079(3)
Mn(1)-C(4)	2.1603(14)	2.161(3)	2.177(3)
Mn(1)-C(5)	1.7996(16)	1.789(3)	1.781(4)
Mn(1)-C(6)	1.7978(16)	1.795(3)	1.799(4)
Mn(1)-C(7)	1.7839(16)	1.787(3)	1.788(3)
Mn(1) - P(1)	2.7670(4)	2.7732(8)	2.7773(8)
P(1)-C(1)	1.7710(15)	1.775(3)	1.770(3)
P(1)-C(4)	1.7683(15)	1.770(3)	1.764(3)
P(1) - O(1)	1.5224(11)	1.5053(19)	1.506(2)
P(1)-H(1P)	1.268(17)	1.29(3)	1.26(3)
C(1)-C(2)	1.452(2)	1.439(4)	1.443(4)
C(2) - C(3)	1.412(2)	1.414(4)	1.415(4)
C(3) - C(4)	1.439(2)	1.430(4)	1.445(4)
C(1)-P(1)-C(4)	90.47(7)	89.59(12)	90.32(13)
C(1)-C(2)-C(3)	112.25(13)	112.5(2)	112.0(2)
C(3)-C(4)-P(1)	107.24(11)	108.48(19)	107.4(2)
C(2)-C(1)-P(1)	106.94(11)	107.43(19)	107.16(19)
C(4)-C(3)-C(2)	112.51(13)	111.8(2)	112.4(2)
O(1P)-P(1)- H(1P)	107.1(8)	105.9(13)	106.8(13)

dii (r_{Mn} = 1.35–1.39 Å, r_P = 1.07–1.13 Å) [17,18]. The strong elongation of the distance Mn(1)–P(1) and the large dihedral angle α of "envelope" folding permits us to make the conclusion that the bond Mn–P in **2a** is absent. The anions **2a–c** have 18-electron configuration (electron count: 4e C(1)–C(4), 6e 3CO, 7e Mn and 1e negative charge).

The length of the P=O bond, 1.522(1) Å in **2a**, is greater than that in triphenylphosphine oxide (1.484 Å). The oxygen atom O(1P) in anion **2a** is involved in two strong H-bonds with H(1NA) and H(1NB) with the formation of the H-bonded centrosymmetric dimers (Fig. 2). This may be the reason for some elongation of the P=O bond.

The X-ray crystallographic study of **2c** (Fig. 3 and Table 1) showed that in an unit cell there are two crystallographically inde-

pendent molecules. Two anions have the identical structures close to that in **2a**. Distances Mn(1)–P(1) are equal to 2.7732(8) and 2.7773(8) Å. The atom of P is going out of the carbon plane C(1)C(2)C(3)C(4) by 0.611 Å in molecule **A** and 0.626 Å in molecule **B**, the dihedral angles α of the "envelope" are 29.1° and 30.2°, respectively. The oxygen atom P=O in the crystal **2c** involved in the formation of a strong hydrogen bond with one H atom H(1NS) of the cation (i-Pr)₂(Et)(H)N⁺. In this case, elongation of the bond P=O (1.505 Å) is not significant comparing to Ph₃PO, probably because of one hydrogen bond involved unlike two bonds for **2a**.

The geometric parameters of η^4 -anions **2a** and **2c** differ essentially from those of the geometry of η^5 -phosphacymantrenes. In the structurally characterized η^5 -phosphacymantrene derivatives the Mn–P bond distance is 2.332–2.390 Å that is less than the sum of covalent radii, the phospholyl ligand is only slightly folded around the C(1)–C(4) axis, the phosphorus atom is going out of the plane C(1)–C(4) by no more than ~0.05 Å [8,19–22]. For example, in 3,4-dimethyl-2-benzoylphosphacymantrene the dihedral angle α is 2.15°, the carbon moiety is planar and the phosphorus atom is going out of the carbon mean plane by 0.048(2) Å [8]. In binuclear complexes with the Pd₂Cl₂ core Mn–P bond lengths are greater (2.447(2)–2.475(2) Å) and close to the sum of the covalent radii of Mn and P, folding angle α is near to 2.5° and phosphorus atom is going out of the C(1)–C(4) plane away from the Mn atom by 0.055 Å [13].

Two related η^4 -zwitterionic complexes (CO)₃Mn⁻-[η^4 -3,4-Me₂C₄H₂P⁺(Ph)CH₂CH₂CO₂Et [10] and (CO)₃Mn⁻-[η^4 -1,2,3,4-(CO₂-Me)₄C₄P⁺Me₂] [23] for which the same structural characteristics were observed were reported previously. The non-bonding distances Mn–P are 2.765 [10] and 2.828 Å [23], the phosphorus atom is going out of the plane C(1)–C(4) by 0.66 and 0.64 Å, respectively. It is worth to note that the bonds Mn(1)–C(2) and Mn(1)–C(3) are shorter, than Mn(1)–C(1) and Mn(1)–C(4) bonds for all η^4 -complexes. Perhaps, these differences can be connected with the presence of two substituents at the phosphorus atom. The orientation of Mn(CO)₃ in all η^4 -complexes is such that one carbonyl group is located under the P atom, in the trans-position to the (C2)–(C3) bond.



Fig. 2. H-bonded centrosymmetric dimers in crystal 2a (N(1S)...O(1P) 2.804(7) Å, N(1S)-H(1NA)...O(1P) 165°; N(1S)...O(1PA)_{x+2,-y+1,-z} 2.751(7) Å, N(1S)-H(1NB)...O(1PA)_{-x+2,-y+1,-z} 162°).



Fig. 3. Structure for anion 2c. For two independent molecules the N(1S)...O(1P) distances are 2.713(3) and 2.669(3) Å, and the N(1S)-H(1NS)...O(1P) angles are 162 and 170°.

Probably, the steric hindrance of the bulky phosphoryl fragment causes the change in the geometry of η^4 -anionic complex as comparing with η^5 -neutral compounds, namely, large angle α on the "envelope" folding around the axis C(1)–C(4) and the significant exit of the P atom out of plane to the side opposite to the Mn atom. Consequently, the distance P–Mn becomes too lengthy for bonding and the change of hapticity occurs: from *hapto*-5 in starting **1** to *hapto*-4 in final **2**.

3. Conclusions

The new reaction of 2,5-diphenylphosphacymantrene with water and the aliphatic amines has been found. As a result of the cooperative process involving the nucleophilic attack of H₂O on the P atom followed by the migration of one H atom from H₂O to phosphorus atom and another one to amine, the η^4 -phosphoryl ligand 2,5-diphenyl-1-*H*-phosphol-1-oxide coordinated to Mn is formed. Salts **2a**-**c** with the cations H₂NEt₂⁺, HNEt₃⁺, HN(Et)(Prⁱ)₂⁺ have been prepared for the first time and characterized by ¹H, ³¹P, ¹³C NMR and IR-spectra, and the structures of **2a** and **2c** being established by the single crystal X-ray diffraction analysis.

4. Experimental

4.1. General

2,5-Diphenylphosphacymantrene (1) was prepared according to the procedure [24]. ¹H, ³¹P and ¹³C NMR spectra were recorded using spectrometer Bruker Avance-400 at 400.16 MHz for ¹H,

161.9 MHz for ³¹P and 100.6 MHz for ¹³C). The chemical shifts were measured relative to H_3PO_4 (³¹P) and TMS (¹H, ¹³C). All complexes were obtained and handled in argon atmosphere.

4.2. Synthesis of the complexes 2a-c

Complexes **2a**–**c** were obtained by the standard procedure: under inert atmosphere to 30-37.4 mg (0.08-0.1 mmol) of **1** in 3–4 ml of benzene was added 0.5–0.8 ml of the corresponding amine and 1–2 drops of water. After mixing and storage in the dark for 1–2 days yellow-gray crystals of **2a**–**c** precipitated. The solution was decanted, and 6–8 ml of pentane was added. The crystals formed were washed with pentane and dried *in vacuo*.

Complex **2a**: From 30.1 mg (0.08 mmol) **1** and 0.6 ml of NHEt₂ was obtained 20 mg (54%) **2a**. *Anal.* Calc. for $C_{23}H_{25}MnNO_4P$: C, 59.36; H, 5.41; N, 3.01. Found: C, 59.13; H, 5.45; N, 3.16%. ¹H- $\{^{31}P\}NMR$ (DMSO- d_6): δ , ppm: 7.83 (s, 1H, P–H); 7.31, 7.20, 7.01, 10H, *o*, *m*, *p* C₆H₅; 5.52 (d, 2H, ³*J*(H_{3,4}–P) = 12.7 Hz); 2.81 (k, 4H, N–CH₂, *J*(H–H) = 7.0 Hz); 1.09 (t, *J*(H–H) = 7.0 Hz, 6H, CH₃); from ¹H NMR-spectra ¹*J*(P–H) = 549 Hz. ³¹P NMR (CD₂Cl₂): δ –8.70 (dt, ¹*J*(P–H) = 549, ³*J*(P–H_{3,4}) = 12.7 Hz. IR-spectra (CH₂Cl₂): *v*(CO) 1895 cm⁻¹ (broad, E-mode), 1980 cm⁻¹ (A₁-mode).

Complex **2b**: From 37.4 mg (0.1 mmol) **1** and 0.8 ml of NEt₃ was obtained 25 mg (51%) of **2b**. *Anal.* Calc. for $C_{25}H_{29}MnNO_4P$: C, 60.86; H, 5.92; N, 2.84. Found: C, 60.83; H, 5.94; N, 2.78%. ¹H{³¹P}NMR(CD₂Cl₂), δ ppm: 7.98 (broad s, 1H, P–H); 7.36,7.32, 7.24, 10H, *o*, *m*, *p* C₆H₅; 5.45, d, 2H, ³J(H_{3,4}–P) = 14 Hz, H(3,4); 2.60, 6H, N–CH₂; 1.02, 9H, CH₃. ³¹P NMR (CD₂Cl₂): δ –5.11 (dt, ¹J(P–H) = 540 and ³J(P–H_{3,4}) = 14Hz). ¹³C NMR (CD₂Cl₂): δ 229.04, Mn(CO)₃; 139.54, key C-atoms of C₆H₅; 78.95, d, *J*(¹³C–³¹P) = 14 Hz,

Table 2

Crystal data, data collection and structure refinement parameters for 2a and 2c.

Complex	2a	2c
Formula Formula weight	(C ₁₉ H ₁₃ MnO ₄ P) ⁻ (C ₄ H ₁₂ N) ⁺ 465.35	(C ₁₉ H ₁₃ MnO ₄ P) ⁻ (C ₈ H ₂₀ N) ⁺ 521.45
Dimension (mm)	$0.30 \times 0.13 \times 0.12$	$0.35 \times 0.28 \times 0.15$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	P_{21}/c
Unit cell dimensions	1/	1/ -
a (Å)	10.6877(4)	12.076(7)
b (Å)	11.0570(5)	12.387(7)
c (Å)	19.2435(8)	34.9402(19)
α (°)	90.00	90.00
β (°)	94.6210(10)	93.360(10)
γ (°)	90.00	90.00
$V(Å^3)$	2266.69	5217.6
Z	4	8
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.364	1.328
Linear absorption	6.81	6.00
$(\mu) (cm^{-1})$		
$T_{\rm min}/T_{\rm max}$	0.821/0.925	0.81/0.908
$2\theta_{\max}$ (°)	58	54
No. unique refl. (R_{int})	6008(0.0304)	11,326(0.0531)
No. observed refl. $(I > 2\sigma(I))$	4985	8378
No. parameters	285	677
R_1 (on F for	0.0323	0.0513
observed refl.) ^a		
wR_2 (on F^2 for all	0.0828	0.1184
refl.) ^b		
Goodness-of-fit	1.036	1.014
(GOF)on F ²		

^a
$$R_1 = \sum ||F_0| - |F_c|| / \sum |F_c|$$

 $\label{eq:R1} \left. \begin{array}{l} ^{a} \;\; R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. \end{array} \right. \\ \left. \begin{array}{l} ^{b} \;\; wR_{2} = \left\{ \sum \left[w \left(F_{o}^{2} - F_{c}^{2}\right)^{2} \right] / \sum w (F_{o}^{2})^{2} \right\}^{1}. \end{array} \right.$

two C-atoms in β -positions to P; 64.12, d, $J({}^{13}C-{}^{31}P) = 90$ Hz, two Catoms in α-positions to P; 45.70, N-CH₂; 9.11, CH₃. IR-spectra (CH₂Cl₂): v(CO) 1890 (E-mode), 1980 cm⁻¹ (A₁-mode).IR-spectra in solid state (Nujol): 1870 (E-mode), 1965 cm^{-1} (A₁-mode).

Complex 2c: From 37.4 mg (0.1 mmol) 1 and 0.8 ml of N(Et)(i-Pr)₂ was obtained 35 mg (66%) of **2c**. Anal. Calc. for C₂₇H₃₃MnNPO₄: C, 62.19; H, 6.38; N, 2.69. Found: C, 62.21; H, 6.38; N, 2.61%. ¹H{³¹P}NMR (CD₂Cl₂), δ ppm: 7.94, broad s, 1H, P–H; 7.38, 7.23, 7.06, 10H, o, m, p C₆H₅; 5.44, d, 2H, ${}^{3}J(H_{3,4}-P) = 14$ Hz, H(3,4); 3.18, 2H, N-CH; 2.69, 2H, N-CH₂; 1.10, broad s, 15H, all Me-groups. ³¹P NMR (CD₂Cl₂): δ -4.95 (dt, ¹J(P-H) = 536 and ³J(P- $H_{3,4}$) = 14 Hz). ¹³C NMR (CD₂Cl₂): δ 228.26, Mn(CO)₃; 139.94, key C-atoms of C₆H₅; 128.49, 125.31 and 125.25, 124.52, C-atoms of *m*-, two types of *o*-, *p*-positions C_6H_5 ; 79.13,d, $J(^{13}C-^{31}P) = 21$ Hz, two C-atoms in β -positions to P; 65.10, d, $J({}^{13}C-{}^{31}P) = 87$ Hz, two C-atoms in α-positions to P; 41.69, N-CH₂; 17.72, CH₃; 12.36, N-CH. IR (CH₂Cl₂): v(CO) 1890 (E-mode) and 1980 cm⁻¹ (A₁-mode). IR-spectra in solid state (Nujol): 1885 (E-mode), 1970 cm⁻¹ (A₁mode).

4.3. X-ray crystal data for 2a and 2c

Single crystals of the complexes 2a and 2c were obtained by slow diffusion of pentane into the solutions of the complexes in CH₂Cl₂ or benzene in NMR-tubes at room temperature.

The crystal X-ray diffraction experiments for compound 2a and 2c were carried out with a Bruker SMART APEX II diffractometer (graphite monochromated Mo K α radiation, k = 0.71073 A, x-scan technique, T = 100 K). The APEX II software [25] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling and

absorption correction, and SHELXTL [26] for space group and structure determination, refinements, graphics, and structure reporting. The structures were solved by direct methods and refined by the full matrix least-squares technique against F^2 with the anisotropic thermal parameters for all non-hydrogen atoms. In the crystal 2c in independent part molecule **A**, one of the two independent cations $(HN(Et)(Pr^{i})_{2}^{+})$ is disordered over two positions with 0.75/0.25 occupancies. The hydrogen atoms at the N and P atoms in two compounds 2a and 2c were localized from different Fourier synthesis and involved in refining in isotropic approximation. All other hydrogen atoms of 2a and 2c were placed geometrically and refined in the riding motion approximation. The principal experimental and crystallographic parameters of 2a and 2c are presented in Table 2.

Acknowledgements

This work has been done under financial support of the Russian Foundation for Basic Research (Projects 08-03-00169, 11-03-00262 and 08-03-00631).

Appendix A. Supplementary material

CCDC 764036 and 764037 contains the supplementary crystallographic data for this paper. 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.2011.01.094.

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