Note

Synthesis and characterization of a dinuclear platinum complex with silsesquioxanate ligand

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ARTICLE INFO

ABSTRACT

The first dinuclear platinum complex with a silsesquioxanate ligand {[Pt(Ph)(PEt$_3$)$_2$]$_2$O$_{11}$Si$_7$(c-C$_5$H$_9$)$_7$(OH)} was synthesized by reaction of incompletely condensed silsesquioxane, (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OH)$_3$ with trans-PtI(Ph)(PEt$_3$)$_2$. Multinuclear (^{1}H, ^{13}C, ^{29}Si, and ^{31}P) NMR data clearly show two unequivalent platinum moieties (Pt(Ph)(PEt$_3$)$_2$) bridged by bulky silsesquioxanate ligand. DFT calculations were performed to analyse the molecular structure and NMR properties of the new platinum complex.

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1. Introduction

Metallasilsesquioxanes are structurally well-defined soluble compounds derived from numerous metal ions (early and late transition metals [1], lanthanides [2], earth-alkaline metals [3]) and incompletely condensed silsesquioxanes that mimic the surface of metal supported silica widely used in heterogeneous catalysis [4]. Understanding of mechanisms in surface chemistry attracts the attention of many scientists to investigate preparation, structure and reactivity of metallasilsesquioxanes. On the other side, metal complexes of silsesquioxanes show great structural diversity and therefore exploring structure-properties correlation is of current interest.

In the last years we have focused our research on investigation of coordination capability of incompletely condensed silsesquioxane trisilanol, R$_7$Si$_7$O$_9$(OH)$_3$ to organoplatinum and organopalladium complexes. Prior to our work, Abbenhuis [5] and Johnson [6] have reported platinum silsesquioxane complexes containing O,O-chelating bidentate silsesquioxanate ligands. A series of phenylplatinum and arylpalladium silsesquioxane complexes with auxiliary phosphine ligands, trans-[M{O$_{10}$Si$_7$(c-C$_5$H$_9$)$_7$(OH)$_2$}(Ar)(L)$_2$] (M = Pt, Pd, Ar = C$_6$H$_5$, C$_6$F$_5$, L = PMe$_3$, PEt$_3$, PMe$_2$Ph) were obtained and fully characterised [7,8]. Crystallographic results revealed that incompletely condensed silsesquioxane acts as a monodentate O-coordinated ligand with two intramolecular hydrogen bonds. The dynamic behavior in solution of the compounds mentioned above and of arylpalladium silsesquioxanate complexes with diamine ligands were studied by multinuclear NMR spectroscopy [9].

In this paper we report preparation, NMR and DFT studies of dinuclear platinum complex with bridging O,O-bonded silsesquioxane. In order to obtain additional information about the molecular structure of the dinuclear platinum complex we performed DFT calculations.
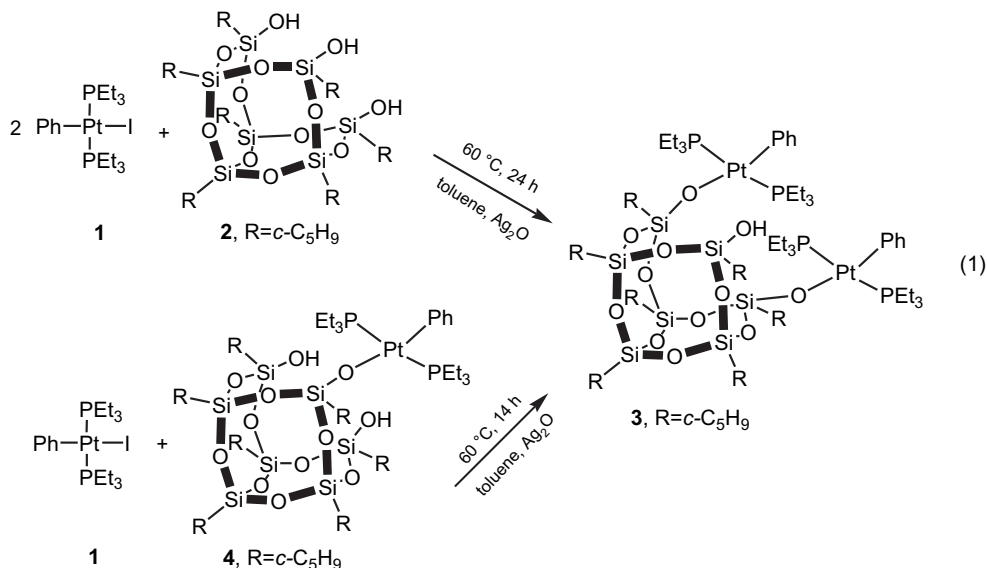
2. Results and discussion

2.1. Preparation of dinuclear Pt(II) complex

Two pathways were used to synthesize the dinuclear compound as shown in Eq. (1). Reaction of organoplatinum complex trans-PtI(Ph)(PEt$_3$)$_2$ (1) with incompletely condensed silsesquioxane (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OH)$_3$ (2) in a 2:1 molar ratio and in the presence of Ag$_2$O leads to the dinuclear platinum complex {[Pt(Ph)(PEt$_3$)$_2$]$_2$(μ-O)$_2$O$_9$Si$_7$(c-C$_5$H$_9$)$_7$(OH)} (3). The same product was achieved by coupling reaction of mononuclear platinum complex

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trans-[Pt{$O_{10}Si_7$(c-C_5H_9)$_7$(OH)$_2$}(Ph)(PEt$_3$)$_2$] (**4**) and trans-PtI(Ph)(PEt$_3$)$_2$ (**1**) in the presence of Ag$_2$O and in toluene medium at 60 °C.

optimization with DFT/ MPW1PW91/DZ method and it was used further for calculations of the NMR parameters.

(1)

2.2. Calculated structure of dinuclear Pt(II) complex

Attempts to synthesize a tricoordinated silsesquioxane complex with three organoplatinum (Pt(Ph)(PEt$_3$)$_2$) units bonded to silanol groups were unsuccessful, probably due to steric reasons. In addition, dinuclear platinum complex with PMe$_2$Ph ligands was not obtained either.

Complex **3** was isolated as a white solid in 46 % yield and was characterized by ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and ^{29}Si{^{1}H} NMR spectroscopy in solution. We performed attempts to determine the crystal structure of the newly synthesized compound. In spite of a good diffraction pattern, the final calculation was not converged well and lifted R-factors. Preliminary crystallographic data and details are summarized in Table 1. The structure of the dinuclear Pt(II) complex suggested by X-ray analysis was refined by means of geometry

The structure of Pt(II) complex optimized at MPWPW91/DZ level is shown in Fig. 1. Selected experimental and calculated structural data of **3** are collected in Table 2. Since the X-ray determination of the molecular structure of **3** was not completely successful, selected bond lengths and angles of **4** are also given in Table 2 for comparison. The crystallographic data of **4** were previously published [7].

The complex **3** contains two Pt atoms each bonded to a phenyl ring, two PEt$_3$ ligands and one bridging silsesquioxanate ligand (see Fig. 1). Similar coordination mode of silsesquioxane in osmium complex {[Os$_3$(CO)$_{10}$(μ-H)]$_2$(μ-O)$_2$Si$_7$O$_9$(OH)(c-C_6H_{11})$_7$} was suggested by Feher et al. [10]. The geometry around both platinum centers is square planar. Each phenyl ring is perpendicular to the corresponding coordination plane. The planes at the two Pt-centers are not coplanar and the calculated angle between them is about 46°. According to the experimental X-ray data of **3**, the Pt–L bond distances (L = C, O, P) are longer (up to 0.077 Å) than the corresponding Pt′–L′ bond lengths, with exception of Pt′–P2′ bond. The experimental Pt–C1 and Pt′–C1′ bonds (1.96(1) Å) are shorter than the Pt–C distance (2.014(4) Å) in mononuclear complex **4**. The Pt–O1 bond distance (2.122(8) Å) is similar to that of **4** (2.129(3) Å) and these are longer than the second Pt′–O1′ bond (2.046(7) Å) in the dinuclear complex. In comparison with the experiment, Pt–L bond lengths are overestimated with about 0.06 Å. The geometry differences observed are probably due to the comparison of a gas phase (obtained after optimization) with the solid state molecular geometry suggested by the X-ray analysis. The position of the H atom of the free silanol group is not determined by crystallographic data and it is completed by the geometry calculations of the dinuclear Pt(II) complex. The experimental O1···O2 distance of 2.626 Å is close to the sum of the van der Waals radii of H and O atoms (2.72 Å) [11]. The MPWPW91/DZ method shows distance of 2.578 Å for O1···O2 and 178.3 Å for O1···H2–O2 angle, indicating formation of hydrogen bond between the free OH group and the coordinated O atom of silsesquioxane. It was found that silanol

Table 1
Crystallographic data and details of refinement of **3**.

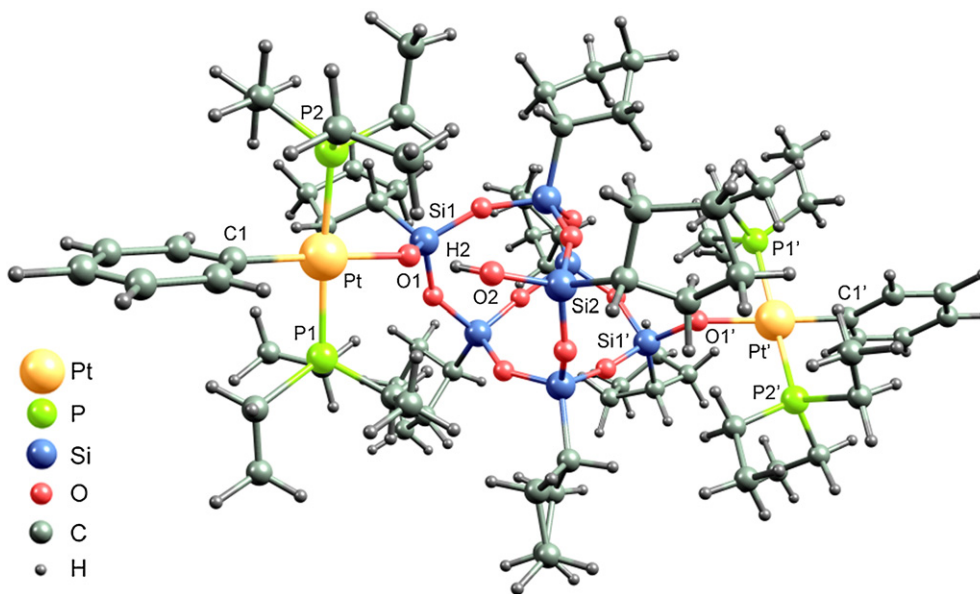|	Complex **3**
Empirical formula	$C_{71}H_{134}O_{12}P_4Si_7Pt_2$
Formula weight	1890.51
Crystal colour	Colorless
Crystal dimensions (mm)	$0.20 \times 0.20 \times 0.05$
Crystal system	Monoclinic
Space group	P2$_1$/n (No. 14)
a (Å)	22.490(9)
b (Å)	15.188(6)
c (Å)	28.199(12)
β (°)	106.961(5)
Volume (Å^3)	9213(7)
Z	4
Calculated density (g.cm^{-3})	1.363
F(000)	3880
μ/cm^{-1}	32.309
No. of reflections measured	54,936
No. of unique reflections	19,558
R_{int}	0.085
No. of variables	1029
R1 (I > 2.00σ(I))	0.1764
wR2 (I > 2.00σ(I))	0.1711
Goodness of fit	1.455

Fig. 1. MPWPW91/DZ optimized molecular structure of **3**.

groups in several mononuclear platinum silsesquioxane complexes are also engaged in hydrogen bonding [7–9]. It is worth mentioning that the calculated structural parameters at MPWPW91/DZ level confirm the available preliminary X-ray data and they complete and specify the structure of dinuclear Pt(II) complex with silsesquioxane.

Table 2
Selected experimental and calculated (at MPWPW91/DZ level) structural parameters of **3** and experimental bond lengths and angles of **4** [7].

	Exp. **3**	MPWPW91/DZ	Exp. **4** [7]
Bond lengths (Å)			
Pt–C1	1.96(1)	2.029	2.014(4)
Pt–O1	2.122(8)	2.144	2.129(3)
Pt–P1	2.311(3)	2.373	2.309(1)
Pt–P2	2.300(4)	2.376	2.309(1)
O1–Si1	1.59(1)	1.699	1.593(3)
Pt′–C1′	1.96(1)	2.032	
Pt′–O1′	2.046(7)	2.124	
Pt′–P1′	2.303(4)	2.372	
Pt′–P2′	2.325(4)	2.370	
O1′–Si1′	1.63(1)	1.686	
O1···O2	2.626[a]	2.578	2.558(4)
O2–H2	–	1.040	
O1···H2	–	1.539	1.84(6)
Bond angles (°)			
C1–Pt–O1	177.9(3)	176.67	177.9(1)
P1–Pt–P2	175.2(2)	173.59	173.2(4)
C1–Pt–P1	91.0(3)	91.59	88.5(1)
C1–Pt–P2	90.1(3)	89.76	86.6(1)
O1–Pt–P1	87.0(2)	86.90	92.02(8)
O1–Pt–P2	91.9(2)	91.41	92.70(9)
Pt–O1–Si1	137.5(5)	132.23	134.6(2)
C1′–Pt′–O1′	178.5(4)	178.31	
P1′–Pt′–P2′	169.8(2)	168.91	
C1′–Pt′–P1′	90.6(4)	93.87	
C1′–Pt′–P2′	89.4(4)	90.41	
O1′–Pt′–P1′	88.1(2)	84.90	
O1′–Pt′–P2′	91.9(2)	90.59	
Pt′–O1′–Si1′	135.8(6)	131.77	
O1···H2–O2	–	178.30	172(5)

[a] The value was taken from the visualized cif file containing the X-ray structure data.

2.3. Experimental and theoretical NMR study

Our calculations of Pt–silsesquioxane complexes in benzene have shown insignificant effect of the solvent on the geometry as well as on the NMR data. Therefore, we accept that the comparison of the calculated NMR data in gas phase with the experimental NMR data obtained in solution is reasonable and could help for reliable interpretation of the experimental NMR spectra. The list of theoretical chemical shifts of ^{1}H, ^{13}C, ^{31}P, ^{29}Si atoms with OPW91/6-31G(d,p) basis set and relevant experimental values are presented in Table S1 in Supplementary materials.

^{13}C NMR data show two sets of signals in the aromatic region at δ 139.29, 133.54, 122.04 and δ 138.23, 132.09, 121.49 ppm assigned, respectively, to C_{ortho}, C_{ipso}, C_{para} of the two unequivalent phenyl rings coordinated to the platinum centers. Similar chemical shifts were observed and assigned to the mononuclear platina silsesquioxane complexes [7]. The NMR calculations predicted six signals (1 C_{ipso}, 2 C_{ortho}, 2 C_{meta} and 1 C_{para}) in the range of 156.89–112.50 ppm for C atoms of each phenyl ring in the complex. According to the calculations, the chemical shifts for C_{ortho}, C_{meta}, C_{para} are in agreement with the previous suggestions. On the contrary to this interpretation, the C_{ipso} peak is calculated at low magnetic field (156.89 and 156.44 ppm) in line with the less negative charge on C_{ipso} atom (−0.190 a.u) as compared to the charges of the other phenyl carbon atoms (−0.259 ÷ −0.306 a.u). More experimental and theoretical data are required to solve the C_{ipso} peak interpretation.

Two pairs of signals are observed in the high magnetic field region at 7.74; 8.02 ppm and 13.20; 13.74 ppm and according to the calculations they are assigned to methyl and methylene carbon atoms of PEt$_3$, respectively. The doublets indicate two couples of PEt$_3$ ligands in *trans* position in the coordination plane of each metal ion. The carbon atoms of the PEt$_3$ ligands and the cyclopentyl groups produce well distinguished calculated signals, Table S1 in Supplementary materials. The chemical shifts of CH and CH$_2$ carbons of cyclopentyl substituents are calculated in the range of 32–26 ppm and their interpretation is not sufficiently reliable.

^{29}Si NMR spectrum displays seven signals at δ −58.47, −58.67, −64.14, −66.71, −66.75, −67.03 and −69.21 ppm and provides evidence for a different chemical environment of each silicon atom of silsesquioxane framework. We assigned the higher frequency

resonances (−58.47 and −58.67 ppm) to the coordinated Si atoms (Pt−O−Si) and the signal at −64.14 ppm to Si of Si−OH group engaged in hydrogen bonding. The next two peaks are positioned very closely to each other (−66.71 and −66.75 ppm) and together with the signals at −67.03 and −69.21 ppm correspond to Si atoms from internal silsesquioxane backbone. The low magnetic field shift of Si1, Si1' and Si2 could be explained with the lower electron density on the neighboring O atoms (−1.148, −1.170, −1.143 a.u), which are coordinated to the Pt or are included in O−H···O bonding, Fig. 1. For comparison the charges of O atoms from silsesquioxane backbone are approximately −1.25 a.u. According to the calculations, the NMR signals of Si atoms in silsesquioxane of dinuclear Pt(II) complex could be used for prediction of coordination mode to Pt as well as of hydrogen bonding of H−O−Si group.

In ^{1}H NMR spectrum of **3**, a sharp peak at 8.76 ppm is assigned to the hydrogen from the silanol group. The low magnetic field position of this signal indicates formation of a hydrogen bond between the OH group and the coordinated oxygen, in accord with our geometry calculations of **3**. The calculated ^{1}H chemical shift for OH hydrogen is obtained at 11.18 ppm. In the range 7.64–7.52 ppm, four peaks were calculated for the C_6H_5-*ortho* hydrogen atoms in the dinuclear complex **3**. The values obtained could be grouped and assigned to two observed ^{1}H NMR signals at 7.56 ppm (doublet) with $J_{HH} = 6.9$ Hz and at 7.45 ppm (broaden) corresponding to the two unequivalent phenyl rings in the dinuclear Pt(II) complex.

The ^{1}H signals of the cyclopentyl substituents (C*H* and C*H$_2$*) and of the PEt$_3$ groups (C*H$_2$* and C*H$_3$*) appear in the high magnetic field region at 3.6−0.8 ppm. The interpretation of the observed peaks is complicated because of the numerous C−H groups as well as because of overlapped signals. The upfield peaks at 1.3 ppm and 1.07 ppm are assigned to C*H*-pentyl and C*H$_3$* signals, respectively.

A ^{31}P NMR spectrum of **3** consists of two single peaks at δ 16.40 and δ 17.15 accompanied by platinum satellites with coupling constants J(PtP) = 2876 Hz and J(PtP) = 2905 Hz, respectively. Chemical shift and the value of the coupling constants are similar to the previously reported for the mononuclear complex *trans*-[Pt{O$_{10}$Si$_7$(*c*-C$_5$H$_9$)$_7$(OH)$_2$}(Ph)(PEt$_3$)$_2$] (**4**) [7]. These patterns clearly indicate the presence of two magnetically unequivalent platinum moieties (Pt(Ph)(PEt$_3$)$_2$) coordinated to silanol sites of silsesquioxane. Four ^{31}P NMR chemical shifts are calculated at 37.53 (P1), 36.93 (P2), 36.18 (P1'), 39.37 (P2') ppm. The ^{31}P signal of free PEt$_3$ is measured at −20 ppm [12]. When PEt$_3$ is bonded to Pt, the electron density on P atom decreases due to donor-acceptor P → Pt interaction with dominant σ-donation contribution and causes significant changes of the chemical shift. Taking into account the large range of ^{31}P chemical shift the differences observed between the calculated and the experimental values are reasonable.

2.4. IR data

The IR data of **3** show broad band at 3450 cm^{-1} due to stretching vibration of the OH group. Very similar peak position was observed in the IR spectrum of Pt−Ag heterobimetallic complex, [Pt{O$_{11}$Si$_7$(*c*-C$_5$H$_9$)$_7$(OH)(AgPPh$_3$)}(Ph)(PPh$_3$)] containing bidentate *O,O*-coordinated silsesquioxane and one free silanol group, whereas ν$_{OH}$ vibrations of the monodentate platinum silsesquioxanes were obtained at lower wavenumbers (3300–3200 cm^{-1}) [7]. New bands in the range 770−700 cm^{-1} appear in the spectrum of **3** in comparison with the free silsesquioxane ligand. Peaks at 739 and 733 cm^{-1} are assigned to the stretching vibration of Si−O bonds of the coordinated silanolate groups. This vibration was observed as a single peak at 739 cm^{-1} for monodentate platina silsesquioxane **4**.

3. Conclusion

The molecular structure of the newly obtained Pt(II) complex of silsesquioxane trisilanol was predicted by means of DFT calculations and X-ray analysis. Incompletely condensed silsesquioxane acts as (*μ-O,O*)-bridging ligand in a dinuclear platinum complex. The two platinum centers are magnetically unequivalent as revealed by the NMR data. The Si−OH group forms hydrogen bond with a coordinated oxygen atom. The calculated and experimental ^{1}H, ^{31}P, ^{13}C and ^{29}Si NMR spectra of the dinuclear platinum silsesquioxane complex are in good agreement and confirmed the suggested molecular structures.

4. Experimental section

The platinum complexes *trans*-[Pt{O$_{10}$Si$_7$(*c*-C$_5$H$_9$)$_7$(OH)$_2$}(Ph)(PEt$_3$)$_2$] (**4**), *trans*-[PtI(Ph)(PEt$_3$)$_2$] and its precursor [PtI(Ph)(cod)] were synthesized as described in [7,13,14], respectively. All manipulations of the complexes were carried out using standard Schlenk techniques under argon or nitrogen atmosphere. ^{1}H, ^{13}C {^{1}H}, ^{29}Si{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on Varian Mercury 300 or JEOL EX-400 spectrometers.

4.1. Preparation of [(Pt(Ph)(PEt$_3$)$_2$)$_2${O$_{11}$Si$_7$(c-C$_5$H$_9$)$_7$(OH)}] (3)

(*Cyclo*-C$_5$H$_9$)$_7$Si$_7$O$_9$(OH)$_3$ (71 mg, 0.08 mmol) and Ag$_2$O (46 mg, 0.20 mmol) were added to a toluene (10 mL) solution of *trans*-[PtI (Ph)(PEt$_3$)$_2$] (103 mg, 0.16 mmol). The mixture was heated at 60 °C for 24 h. After completion of the reaction, monitored with ^{31}P{^{1}H} NMR spectroscopy, a grey solid was removed by filtration under argon. The solvent was evaporated in vacuum, and then 0.5 ml hexane and 1 ml acetone were added. Cooling of the solution at −20 °C for several days afforded **3** as white crystals (70 mg, 46%). Anal. Calcd. for C$_{71}$H$_{134}$O$_{12}$P$_2$Si$_7$Pt$_2$ (1890.49): C, 45.11; H, 7.14. Found: C, 44.89; H, 7.06.

^{1}H NMR (300 MHz, benzene-d_6, room temperature): δ 1.07 (m, 36H, PCH$_2$C*H$_3$*), 1.3 (br m, 7H, C*H*-pentyl), 1.5−2.4 (br m, 56H, C*H$_2$*-pentyl and 24H, PC*H$_2$*CH$_3$), 7.00 (m, 6H, C$_6$*H$_5$* meta and para), 7.45 (br, 2H, C$_6$*H$_5$* ortho), 7.56 (d, 2H, C$_6$*H$_5$* ortho, J_{HH} = 6.9 Hz), 8.76 (s, 1H, O*H*). ^{13}C{^{1}H} NMR (100.4 MHz, benzene-d_6, room temperature): δ 7.74, 8.02 (s, PCH$_2$*C*H$_3$), 13.2 (br, P*C*H$_2$CH$_3$), 13.74 (vt, PCH$_2$*C*H$_3$, $^V J_{CP}$ = 15.5 Hz), 24.28, 24.45, 24.66, 24.67, 25.03, 26.82, 27.63, 27.73−27.97, 28.45−28.75, 29.81, 29.96, 30.09, 30.16 (7C, *C*H-pentyl and 28C, *C*H$_2$-pentyl), 121.49, 122.04 (*C$_6$*H$_5$ para), 132.09, 133.54 (*C$_6$*H$_5$ ipso), 138.23, 139.23 (*C$_6$*H$_5$ ortho). ^{29}Si{^{1}H} NMR (79.3 MHz, benzene-d_6, 0.02 M Cr(acac)$_3$, room temperature): δ −58.47, −58.67, −64.14, −66.71, −66.75, −67.03, −69.21. ^{31}P{^{1}H} NMR (122 MHz, benzene-d_6, room temperature): δ 16.40, J_{PtP} = 2876 Hz, 17.15, J_{PtP} = 2905 Hz. IR spectrum (KBr): 3450 (vw), 2949 (s), 2865 (s), 1572 (w), 1456 (w), 1242 (w), 1100 (vs), 990 (m), 900 (w), 766 (w), 739 (w), 733 (w), 704 (w), 633 (w), 500 (m) cm^{-1}.

4.2. Computational details

Geometry optimization of the dinuclear platinum(II) complex with bridging silsesquioxanate ligand was performed in gas phase at non-local DFT level of theory using ADF2008 program package [15]. A density functional, consisting of local density part (VWN) [16] and exchange-correlation gradient corrected parts (mPWx + PW91c) was used [17]. Scalar relativistic effects were considered by the Zero Order Regular Approximation (ZORA) [18]. A relativistic valence double zeta (DZ) basis set was applied for all the elements and thus the final level of calculations is MPW1PW91/ DZ. All electron ZORA/DZ calculations were used. The ^{1}H, ^{13}C, ^{29}Si,

[31]P isotropic shielding constants of the optimized dinuclear Pt(II) complex were calculated by using the gauge independent atomic orbital (GIAO) method [19] and OPW91 functional, implemented in Gaussian03 program package [20]. With a view to the large system studied (230 atoms), the 6−31G(d,p) basis set for Si, H, C, O, P atoms was chosen as a good compromise between reliability and computing time. The Pt atom was treated with quasi-relativistic effective core potential (RECP, MWB60), where $5s^2 5p^6 5d^9 6s^1$ are valence electrons and all other 60 electrons are included into the core. The absolute isotropic magnetic shielding constants (σ_i) were used to obtain the chemical shifts ($\delta_i = \sigma_{TMS} - \sigma_i$) by referring to the standard compounds, tetramethylsilane (TMS) (for Si, C and H atoms) and H_3PO_4 (for P atom). Both referred to compounds, TMS and H_3PO_4, were calculated at the same OPW91/6-31G(d,p) level of theory.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.03.033.

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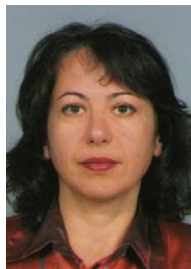
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