

Available online at www.sciencedirect.com





Inorganica Chimica Acta 359 (2006) 4179-4190

www.elsevier.com/locate/ica

Self-assembled diorganotin(IV) moieties with 2,3,4,5-tetrafluorobenzoic acid: Syntheses, characterizations and crystal structures

Chunlin Ma^{a,b,*}, Junshan Sun^a, Rufen Zhang^a, Dagi Wang^a

^a Department of Chemistry, Liaocheng University, Wenhua Road 34, Liaocheng, Shandong 252059, PR China ^b Taishan University, Taian 271021, PR China

> Received 20 May 2006; received in revised form 2 July 2006; accepted 3 July 2006 Available online 11 July 2006

Abstract

A series of new organotin(IV) derivatives with 2,3,4,5-tetrafluorobenzoic acid: $\{[(2,3,4,5-F_4C_6HCO_2)R_2Sn]_2O\}_2$ (R = Et 1, *n*-Bu 2, Ph 3), $[R_2Sn(O_2CC_6F_4H)_2]_n$ (R = n-Bu 4, Et 5, Ph 6), and $Sn_2R_4(O_2CC_6F_4H)_3$ (OH) (R = Et 7, n-Bu 8, Ph 9), were synthesized by the reaction of diorganotin oxide and 2,3,4,5-tetrafluorobenzoic acid. All the complexes 1-9 have been characterized by elemental analysis, IR, ¹H, ¹³C, ¹¹⁹Sn NMR spectra. Among them complexes 2, 4, 8 were also characterized by X-ray crystallography diffraction analyses. The crystal structure of complex 2 exhibited a tetra-nuclear geometry with the Sn₂O₂ symmetry core. Complex 4 formed a 1D helical doublechain structure through intermolecular $O \rightarrow Sn$ coordinating and completed a DNA-like assembly. Complex 8 revealed that the both Sn atoms were held together by hydroxide and acetate bridges, forming a chair-like six-membered ring. Moreover, the supramolecular structures of dimer, 1D chain or 2D network have been found in complexes 4 and 8 by intermolecular C-H···F weak hydrogen bond and non-bonded $F \cdots F$ or $F \cdots Sn$ interaction, which were highly effective in the assembly of supramolecular structures and could lead to the formation of complexes with fascinating topologies properties.

© 2006 Elsevier B.V. All rights reserved.

Keywords: 2,3,4,5-Tetrafluorobenzoic acid; Double-chain structure; Diorganotin; Self-assembly; Supramolecular structure

1. Introduction

Organotin carboxylates have been the subjects of interest for some time owing to their biochemical properties and commercial applications [1]. These complexes may adopt a variety of structural modes depending on the nature of organic ligand and the ratio of the reactant [2]. Especially the presence of much higher electro-negativity of fluorine atom in the ligand strongly affected the electronic-density in the molecular. Moreover, the substitution of hydrogen on the aromatic carboxylic acid by fluorine influenced markedly the biological activity of organic molecule [3]. In recent years, there have been a series of reports about organotin complexes of fluorinated aromatic carboxylic acids containing mono- or polyfluorophenyl groups,

which have been synthesized by Marcel [4], and these complexes exhibited different anti-tumor activities when the number of fluorine atoms on the benzoate moiety was increased [5]. Moreover, owing to the presence of fluorine atom, these ligands presented a number of opportunities for creating supramolecular arrangement via weak intermolecular contacts. In recent literatures, evidences have been provided for the property of the formation of interactions such as C-H···F-C and C-F··· π [6]. So one of our research interests has now focused on the study of the fluorinated complexes.

In this work, we selected 2,3,4,5-tetrafluorobenzoic acid as ligand and successfully obtained several new complexes { $[(2,3,4,5-F_4C_6HCO_2)R_2Sn]_2O$ }, (R = Et 1, *n*-Bu 2, Ph 3), $[R_2Sn(O_2CC_6F_4H)_2]_n$ (R = *n*-Bu 4, Et 5, Ph 6), and $Sn_2R_4(O_2CC_6F_4H)_3(OH)$ (R = Et 7, *n*-Bu 8, Ph 9) through controlling the ratios of reactants. It is worthwhile to note that these complexes were synthesized by different molar

Corresponding author. Tel.: +86 635 8230660; fax: +86 538 6715521. E-mail address: macl@lctu.edu.cn (C. Ma).

^{0020-1693/\$ -} see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2006.07.001



Scheme 1. Different coordination modes of the carboxylate group.

ratios of 1:1, 1:2, and 2:3 in the same solvent of benzene. Moreover, the COO group shows different coordination to the center tin(IV) atom. All complexes were characterized by elemental, IR, ¹H, ¹³C, and ¹¹⁹Sn NMR spectroscopy analysis and the structures of **2**, **4**, **8** were also determined by X-ray crystallography. Different coordination modes of the carboxylate group were shown in Scheme 1.

2. Experimental

2.1. Materials and measurements

Di-*n*-butyltin oxide, diphenyltin oxide, diethyltin oxide and 2,3,4,5-tetrafluorobenzoic acid were commercially available, and they are used without further purification. The melting points were obtained on a Kofler micro-melting point apparatus and were uncorrected. Infrared-spectra were recorded on a Nicolet–460 spectrophotometer using KBr discs and sodium chloride optics. ¹H, ¹³C, ¹⁹F and ¹¹⁹Sn NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer operating at 400, 100.6 and 149.2 MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified; ¹³C spectra are broadband proton decoupled. The chemical shifts are reported in ppm relative to Me₄Si in CDCl₃ as solvent. Elemental analyses (C, H) were performed with a PE-2400II apparatus.

2.2. Syntheses

2.2.1. { $[(2,3,4,5-F_4C_6HCO_2)Et_2Sn]_2O$ }₂ (1)

The reaction was carried out under nitrogen atmosphere. The diethyltin oxide (0.250 g, 1 mmol) and 2,3,4,5-tetrafluorobenzoic acid (0.19 4 g, 1 mmol) were added to a solution of dry benzene (30 ml) in a Schlenk flash and stirred refluxing 16 h at 80 °C. The solvent was removed by evaporation under vacuum until solid product was obtained. Recrystallized from ether-petroleum. Yield: 75%, m.p. 128-130 °C. Anal. Calc. for C44H44O10F16Sn4: C, 34.96; H, 2.93. Found: C, 35.03; H, 2.98%. IR (KBr, cm⁻¹): v(C=O) 1740; v(COO_{asym}) 1693; v(COO), 1448, 1420; v(C-F) 1874; v(Sn-O-Sn) 632; v(Sn-O) 476. ¹H NMR (CDCl₃, ppm): δ 7.70–7.77 (d, 1H, Ph-H), 1.46 (m, 2H, CH₂); 0.89 (t, CH₃). ¹³C NMR (CDCl₃): δ 168 (COO), 154, 150, 148, 146, 142, 118. 29.9 (α-CH₂, $^{1}J(^{119}\text{Sn}-^{13}\text{C})$, 980.4 Hz), 26.9 (β-CH₂), 26.5 and 26.0 (γ-CH₂), 13.7 (CH₃). ¹¹⁹Sn NMR (CDCl₃, 298 K): -192.7, -170.2 ppm.

2.2.2. $\{[(2,3,4,5-F_4C_6HCO_2)Bu_2Sn]_2O\}_2$ (2)

The synthesis procedure was the same as **1**, recrystallized from ether–petroleum. Yield: 68%, m.p. 134– 136 °C. *Anal.* Calc. for C₆₀H₇₆F₁₆O₁₀Sn₄: C, 41.51; H, 4.41. Found: C, 41.55; H, 4.43%. IR (KBr, cm⁻¹): v(C=O) 1695; v(COO_{asym}) 1617; v(COO_{sym}) 1472, 1352; v(C–F) 1995; v(Sn–O–Sn) 631; v(Sn–O) 473 cm⁻¹. ¹H NMR (CDCl₃, ppm): δ 0.910 (t, 12H, 4CH₃); 1.464 (m, 8H, 4CH₂); 1.892 (m, 16H, 4CH₂CH₂), 7.70–7.77 (m, 3H, 3Ph-H). ¹³C NMR (CDCl₃): δ 168 (COO), 42.8 and 41.2 (α -CH₂, ¹J(¹¹⁹Sn–¹³C), 986.8 Hz), 30.6 (β -CH₂), 27.8 and 27.2 (γ -CH₂), 13.7 (CH₃). ¹¹⁹Sn NMR (CDCl₃, 298 K): –192.8, –168.6 ppm,

2.2.3. $\{[(2,3,4,5-F_4C_6HCO_2)Ph_2Sn]_2O\}_2$ (3)

The synthesis procedure was the same as 1, recrystallized from ether-petroleum. Yield: 75%, m.p. 128– 130 °C. Anal. Calc. for $C_{36}H_{28}O_{10}F_{16}Sn_4$: C, 30.90; H, 2.02. Found: C, 30.88; H, 2.18%. IR (KBr, cm⁻¹): v(C=O) 1698s; $v(COO_{asym})$ 1619s; $v(COO_{sym})$ 1475s, 1446s; v(C-F) 1997s; v(Sn-O-Sn) 635 m; v(Sn-O) 472 m. ¹H NMR (CDCl₃, ppm): δ 7.70–7.77 (m, 1H, 1Ph-H); 6.80–7.67 (m,10H, Ph-H); 1.78 (m, α -CH₂); 1.46 (m, β -CH₂); 1.34 (tq, γ -CH₂); 0.88 (t, CH₃). ¹³C NMR (CDCl₃): δ 164.6 (COO), 152, 148, 146, 143, 141, 114 (Ph-C). ¹¹⁹Sn NMR (CDCl₃, 298 K): -196.6, -172.1 ppm.

2.2.4. $[Bu_2Sn(O_2CC_6F_4H)_2]_n$ (4)

The synthesis procedure was the same as **1**. Recrystallized from hexane. Yield: 72%, m.p. 102–104 °C. *Anal.* Calc. for C₂₂H₂₀O₄F₈Sn: C, 42.68; H, 3.26. Found: C, 42.92; H, 2.96%. IR (KBr, cm⁻¹): $v(COO_{asym})$, 1611; $v(COO_{sym})$, 1379; v(Sn-O-Sn), 694; v(Sn-C), 588; v(Sn-O), 532, 461. ¹H NMR (CDCl₃): δ 0.910 (t, 12H, 4CH₃); 1.464 (m, 8H, 4CH₂); 1.892 (m, 16H, 4CH₂CH₂); 7.70– 7.76 (m, 1H, 3Ph-H). ¹³C NMR (CDCl₃): δ 170 (COO), 150, 147, 145, 142, 140, 114(Ph-C). 29.9 (α -CH₂, $^{1}J(^{119}Sn^{-13}C)$, 992.6 Hz); 26.9 (β -CH₂); 26.5 and 26.0 (γ -CH₂); 13.7 (CH₃). ¹¹⁹Sn NMR (CDCl₃, 298 K): –216.6 ppm.

2.2.5. $[Et_2Sn(O_2CC_6F_4H)_2]_n$ (5)

The synthesis procedure was the same as **1**. Recrystallized from hexane. Yield: 72%, m.p. 102–104 °C. *Anal.* Calc. for C₁₈H₁₂O₄F₈Sn: C, 38.40; H, 2.15. Found: C, 38.52; H, 2.04%. IR (KBr, cm⁻¹): ν (COO_{asym}), 1613; ν (COO_{sym}), 1380; ν (Sn–O–Sn), 689; ν (Sn–C), 586; ν (Sn–O), 532, 461. ¹H NMR (CDCl₃): δ 0.912 (t, 6H, 2CH₃); 1.886 (m, 4H, 2CH₂); 7.71–7.79 (m, 1H, 3Ph-H). ¹³C NMR (CDCl₃): δ 172 (COO), 148, 145, 143, 140, 138, 118 (Ph-C). 29.6 (α -CH₂, ¹J(¹¹⁹Sn–¹³C), 982.2 Hz); 13.8 (CH₃). ¹¹⁹Sn NMR (CDCl₃, 298 K): –215.8 ppm.

2.2.6. $[Ph_2Sn(O_2CC_6F_4H)_2]_n$ (6)

The synthesis procedure was the same as 1. Recrystallized from hexane. Yield: 72%, m.p. 102–104 °C. *Anal.* Calc. for $C_{26}H_{12}O_4F_8Sn$: C, 47.38; H, 1.84. Found: C, 47.52; H, 1. 72%. IR (KBr, cm⁻¹): $v(COO_{asym})$, 1611; v (COO_{sym}), 1379; v(Sn-O-Sn), 694; v(Sn-C), 582; v(Sn-O), 531, 464 cm⁻¹ ¹H NMR (CDCl₃): δ 0.912 (t, 12H, 4CH₃); 1.460 (m, 8H, 4CH₂); 1.891 (m, 16H, 4CH₂CH₂); 7.70–7.77 (m, 1H, 3Ph-H). ¹³C NMR (CDCl₃): δ 172 (COO), 152, 149, 147, 144, 142, 135, 126, 124, 116 (Ph-C). ¹¹⁹Sn NMR (CDCl₃, 298 K): -217.8 ppm.

2.2.7. $[Et_4Sn_2(O_2CC_6F_4H)_3(OH)]$ (7)

The synthesis procedure was the same as **1**. Recrystallized from dichloromethane. Yield: 68%, m.p. 156– 158 °C. Anal. Calc. for C₂₉H₂₄O₇F₁₂Sn₂: C, 36.67; H, 2.55. Found: C, 36.63; H, 2.50%. IR (KBr, cm⁻¹): $v(COO_{asym})$, 1698, 1656; $v(COO_{sym})$, 1368, 1334; v(Sn-O-Sn), 689; v(Sn-C), 572; v(Sn-O), 512, 487. ¹H NMR (CDCl₃): δ 6.80–7.67 (m, 10H, Ph-H); 7.70–7.77 (m, 1H, Ph-H). ¹³C NMR (CDCl₃): δ 165 (COO), 150, 147, 145, 142, 140, 115 (Ph-C). 24.9 (α -CH₂, ¹J(¹¹⁹Sn-¹³C), 986.6 Hz); 22.9 (β -CH₂); ¹¹⁹Sn NMR (CDCl₃, 298 K): -164.8 ppm.

2.2.8. $[Bu_4Sn_2(O_2CC_6F_4H)_3(OH)]$ (8)

The synthesis procedure was the same as **1**. Recrystallized from dichloromethane. Yield: 76%, m.p. 168–170. °C. *Anal.* Calc. for $C_{37}H_{40}F_{12}O_7Sn_2$: C, 41.86; H, 3.80. Found: C, 41.83; H, 3.76%. IR (KBr, cm⁻¹): ν (COO_{asym}), 1696, 1653; ν (COO_{sym}), 1369, 1336; ν (Sn–O–Sn), 686; ν (Sn–C), 578; ν (Sn–O), 512, 487. ¹H NMR (CDCl₃): δ 0.90 (t, 12H, 4CH₃); 1.45 (m, 8H, 4CH₂); 1.86 (m, 16H, 4CH₂CH₂); 1.20 (m, 3H, 3Ph-H). ¹³C NMR (CDCl₃): δ ¹³C NMR (CDCl₃): δ 170 (COO), 150, 147, 145, 142, 140, 116(Ph-C); 29.9 (α -CH₂, ¹J(¹¹⁹Sn–¹³C), 988.7 Hz); 26.9 (β -CH₂); 26.5 and 26.0 (γ -CH₂); 13.7 (CH₃); ¹¹⁹Sn NMR (CDCl₃, 298 K): –160.8 ppm.

2.2.9. $[Ph_4Sn_2(O_2CC_6F_4H)_3(OH)]$ (9)

The synthesis procedure was the same as **1**. Recrystallized from dichloromethane. Yield: 68%, m.p. 156– 158 °C. *Anal.* Calc. for C₄₅H₂₄O₇F₁₂Sn₂: C, 47.32; H, 2.12. Found: C, 47.38; H, 2.14%. IR (KBr, cm⁻¹): $v(COO_{asym})$, 1698, 1656; $v(COO_{sym})$, 1368, 1334; v(Sn-O-Sn), 689; v(Sn-C), 572; v(Sn-O), 512, 487. ¹H NMR (CDCl₃): δ 6.80–7.67 (m, 10H, Ph-H); 7.70–7.77 (m, 1H, Ph-H). ¹³C NMR (CDCl₃): δ 165 (COO), 152, 148, 146, 143, 138,136, 126, 112 (Ph-C). ¹¹⁹Sn NMR (CDCl₃, 298 K): -170.2 ppm.

2.3. X-ray structures determination

Crystals were mounted in Lindemann capillaries under nitrogen. All X-ray crystallographic data were collected on a Bruker SMART CCD 1000 diffractometer with graphite monochromated Mo K α radiation ($\lambda =$ 0.71073 Å). A semi-empirical absorption correction was applied to the data. The structure was solved by directmethods using SHELXLS-97 and refined against F^2 by fullmatrix least squares using SHELXL-97. The positions of hydrogen atoms were calculated, and their contributions in structure factor calculations were included. Crystal data and experimental details of the structure determinations are listed in Table 4.

3. Results and discussion

3.1. Synthesis

The new diorganotin carboxylates containing the 2,3,4,5-tetrafluorophenyl moiety are {[(2,3,4,5-F₄C₆HCO₂)- $R_2Sn_{2}O$ }₂ (R = Et 1, *n*-Bu 2, Ph 3), as obtained from a 1:1 condensation, [R₂Sn(O₂CC₆F₄H)₂]_{*n*} (R = *n*-Bu 4, Et 5, Ph 6), as obtained from 2:1 condensation, and $R_4Sn_2(O_2CC_6F_4H)_3(OH)$ (R = Et 7, *n*-Bu 8, Ph 9), as obtained from a 3:2 condensation of the appropriate carboxylic acid with diorganotin(IV) oxide, which exhibit strongly structural orderliness. The synthetic procedures are shown in Scheme 2.

3.2. Spectroscopic studies

3.2.1. IR spectra

The stretching frequencies of interest are those associated with the C(O)O, Sn–C and Sn–O and Sn–O–Sn groups. The strong absorption appears in the region of $568-596 \text{ cm}^{-1}$ in the respective spectra of **1**–**9**, which is absent in the spectra of the free ligand, is assigned to the Sn–O stretching mode of vibration. All these values are consistent with that detected in number of organotin(IV)oxygen derivatives [7,8].

In organotin(IV) carboxylate complexes, the IR spectroscopy can provide useful information concerning the coordinate formation of the carboxylate. Based on the previous reports, it is possible to distinguish the coordination mode of the COO⁻ group [9]. The IR spectrums of 1-3 shows characteristic bands of carboxylate groups occur at near 1697 and 1619 cm⁻¹ for asymmetric stretching and at near 1513 and 1279 cm^{-1} , which are higher than that for non-fluorinated carboxylates [10]. For complexes 7–9, the characteristic bands of carboxylate groups at near 1684 and 1640 cm^{-1} for asymmetric stretching and at near 1355 and 1320 cm^{-1} for symmetric stretching. Owing to the presence higher electro-negativity of fluorine atoms, these data are higher than that observed for non-fluorinated carboxylates [10]. The magnitude of $\Delta v (v(COO_{asym})$ $v(COO_{sym})$) about 185 and 350 cm⁻¹, respectively, which suggest that the coordinate formation for complexes 1-3 e acid (480 cm^{-1}) and comparable with that of the sodium salt of the acid (275 cm^{-1}) . A strong band in the 662– 685 cm^{-1} region for complexes 1-3, 7-9 and is assigned to v(Sn–O–Sn), indicating and 7–9 are both bidentate mode and monodentate mode under the conditions employed [11]. In complexes 4–6, the $\Delta v (v(COO_{asym}) - v(COO_{sym}))$ is near 272 cm^{-1} , which is lower than that observed in the spectrum of the fre a Sn-O-Sn bridged structure [12]. The absorption bands at 581 cm^{-1} are attributed to



Scheme 2.

v(Sn-C) and v(Sn-O), respectively [13]. This is also consistent with the X-ray diffraction study.

3.2.2. NMR spectra

The ¹H NMR spectra show the expected integration and peak multiplicities. In the spectrum of the free ligand, the resonance observed at about $\delta = 10.114$ ppm, which is absent in the spectra of the complexes, indicates the replacement of the carboxylic acid proton on complex formation. The chemical shifts of the signals for the butyl group exhibit resonance in the 0.87–1.89 ppm region. Signals for the other groups, such as phenyl H appear at the same as in the ligand. In the spectrum of the complexes, the absence of the signal ($\delta = 9.6$ ppm) in the spectrum of the complex indicates the replacement of the carboxyl proton by organotin (IV) on complexation.

The ¹³C NMR spectra of all complexes show a significant downfield shift of all carbon resonance, compared with the free ligand. The shift is a consequence of an electron density transfer from the ligand to the acceptor. Although at least two different types of carboxyl groups are present, only single resonance are observed for the COO group in the ¹³C spectra. The possible reason is that either accidental magnetic equivalence of the carbonyl carbon atoms or the separation between the two sets of resonance is small to be resolved. Complementary information is given by the values of the coupling constant. The ¹J_{Sn-C} value for **4** is 902.6 Hz, similar to that of the hexa-coordinate complex, and the calculated θ (C–Sn–C) by the Holeček and Lyčka equation [14] is 165.4°, which is close to the angles observed in the solid state for complex **4**.

The ¹¹⁹Sn NMR chemical shifts of tin complexes appear to depend not only on coordination number, but also on the type of donor atoms bonds to the metal ion [15]. The ¹¹⁹Sn NMR data show only signal at -216.8 ppm for complexes **4–6**, typical of a six-coordination species, and has been found in accordance with the solid state structure [16]. However, the chemical shift of complexes **1–3** present at -193.0 ppm. Though $\delta(^{119}Sn)$ is influenced by several factors, including the aromatic or aliphatic of the R group bound to the tin atom (and possibly the type of donor atoms of the ligand), it may be used with a cation to infer the coordination number of the tin atom [17]. As for complexes **7–9**, the ¹¹⁹Sn NMR spectra shows a single resonance at $\delta - 165.3$ ppm, indicating the presence of only signal of five-coordination tin atom in solution.

4. Crystal structures

4.1. Crystal structure of $\{Bu_2Sn(O_2CC_6HF_4)_2O\}_2$ (2)

The molecular structure and cell packing of complex 2 are shown in Figs. 1 and 2, selected bond lengths and angles are given in Table 1. The structure is centrosymmetric about a $Bu_4Sn_2O_2$ core. Attached to each bridging oxygen atom is an exocyclic Bu_2Sn unit leading to a three-coordinate O(5) atom. Further connections between the tin atoms arise as a result of bridging carboxylate



Fig. 1. ORTEP view of tetraorganodistannoxane of the molecular structure **2** (the fluorine atoms of phenyl ring is somewhat disordered).



Fig. 2. Unit cell packing of complex 2.

ligands which form almost equal Sn–O bond distances to the endo- and exo-cyclic tin atoms, i.e. [Sn(1)-O(1)]2.272(7) and [Sn(2A)-O(2)] 2.277(7) Å. The remaining independent carboxylate ligand coordinates in the monodentate mode to the exocyclic tin atom exclusively with Sn–O 2.195(5) Å. This configuration leads to two five-coordinate tin centers, each existing in a distorted trigonal bipyramidal geometry. Distortion from ideal geometries may be traced, in part, to the presence of close intramolecular Sn···O interactions. Thus, the centrosymmetrically related O(3) atom forms a contact of 2.844(6) Å with the Sn(1),

| Table 1 | |
|---|--|
| Selected bond lengths (Å) and angles (°) of complex 2 | |
| Bond lengths (\mathring{A}) | |

| Bond lengths (A) | | | |
|-------------------------|----------|------------------------|-----------|
| $Sn(1)-O(5)^{a}$ | 2.049(5) | Sn(1)-C(15) | 2.125(10) |
| Sn(1) - C(19) | 2.126(9) | Sn(1)–O(5) | 2.182(5) |
| Sn(1) - O(1) | 2.271(6) | $Sn(2)-O(2)^{a}$ | 2.280(6) |
| Sn(2)–O(5) | 2.023(5) | Sn(2)–O(4) | 2.845(7) |
| O(2)–Sn(2)CC | 2.280(6) | | |
| Bond angles (°) | | | |
| C(15)-Sn(1)-C(19) | 142.0(4) | C(23)-Sn(2)-C(27) | 140.2(5) |
| $O(5)^{a}$ -Sn(1)-C(15) | 107.9(4) | $O(5)^{a}$ -Sn(1)-O(5) | 77.6(2) |
| $O(5)^{a}$ -Sn(1)-O(1) | 142.8(2) | $O(5)^{a}$ -Sn(1)-O(1) | 90.6(3) |
| C(19) - Sn(1) - O(5) | 97.4(4) | C(15)-Sn(1)-O(1) | 87.2(5) |
| C(19)-Sn(1)-O(1) | 85.9(4) | C(19)-Sn(1)-O(3) | 76.8(4) |
| | | | |

Symmetry transformations used to generate equivalent atoms: a - x + 1/2, -y + 1/2, -z + 1.

which has the effect of opening up the C(15)-Sn(1)-C(19) angle to 141.8(5)°. Similarly, a contact of 2.838(8) Å between the Sn(2) and O(4) atoms results in the expansion of the C(23)–Sn(2)–C(27) angle to $140.6(6)^{\circ}$. Whereas the intramolecular Sn...O contacts are well within the van der Waals distance for these atoms, the relatively large separations and the minor perturbations from the ideal trigonal bipyramidal geometries indicate that these interactions must be considered much weaker. The dihedral angles of 118.8° and 62.0° between the O(1)-C(1)-O(2)/C(2)-C(7)and the O(4)-C(8)-O(3)/C(9)-C(14) planes, respectively, indicate little conjugation between the carboxylate and C₆F₄H groups. Other parameters associated with the carboxylate residues are as expected. In the lattice, there is a close intermolecular contact between each Sn(2) atom and a centrosymmetrically related O(4) atom, i.e. a noncoordinating atom, of 3.204(5) Å. This loose association between Sn(2) and O(4) atoms leads to chains of weakly connected dimers of distannoxanes running parallel to the *c*-axis, as shown in Fig. 1. Similar chains, involving the equivalent Sn and O atoms, are observed in the crystal lattice of $\{[(MeCOO)Me_2Sn]_2O\}_2$ [18], however, in this structure the intermolecular contacts were significantly closer at 2.56(1) Å. A further difference arises between the two as a result of the presence of three bidentate, bridging carboxylate ligands rather than two as in the present of determination. In this structure, the non-coordinating atom of the carboxylate ligand, O(4), is orientated so that it is directed away from the rest of the molecule but nevertheless does form weak intramolecular interactions with the Sn(2) atom. In the case of three of the R = n-Bu derivatives, the O(4) also forms weak intermolecular interactions with the Sn(2) atoms of neighboring molecules such that $Sn(2) \cdots O(4')$ contacts of >3.0 Å are found [19]. The presence of bulkier R groups residing on the Sn atoms (and/ or on the carboxylate ligands) in the remaining structures apparently precludes close intermolecular contacts of this type. The molecular structure for $\{[(F_4HCOO)Bu_2Sn]_2O\}_2$ conforms with the common structural motif found for complexes with the general formula $\{[(R'COO)R_2Sn]_2O\}_2$ [20].



Fig. 3. Molecular structure of complex 4.



Fig. 4. Unit cell packing of complex 4.

4.2. Crystal structure of $\{Bu_2Sn(O_2C_6F_4H)_2\}_n$ (4)

The representative X-ray structure and cell packing for complex **4** are shown in Figs. 3 and 4, selected band distances and angles are summarized in Table 2. The Sn atom exists in a square planar geometry defined by two ipso-C atoms [C(15) and C(19)] of the butyl groups and oxygen atoms [O(1) and O(3)] of two carboxyl groups. The major departure from the ideal plane geometry is found in the Bu–Sn–Bu angle of 172.1(8)° and the angle of O(1)– Sn(1)–O(3) is 174.1°(6), which is slightly departure of the ideal plane, out of which the Sn atom lies 0.0293 Å. The distances of the Sn–O are 2.236(14) Å [O(1)–Sn(1)], 2.247(14) [O(3)–Sn(1)] and the Sn–C are 2.115(17) Å [C(15)–Sn(1)], 2.096(18) Å [C(15)–Sn(1)], respectively. The

| Table 2 | | | |
|---------------------------|-------------------|-------------------------------------|-----------|
| Selected bond length | is (Å) and angles | s (°) of complex 4 | |
| Bond lengths (Å) | | | |
| Sn(1)–C(19) | 2.096(18) | Sn(1)–O(1) | 2.236(14) |
| Sn(1)–C(15) | 2.115 (17) | $Sn(1)-O(4)^{a}$ | 2.246(17) |
| Sn(1)–O(3) | 2.246(17) | Sn(1)-O(2) | 4.060(12) |
| $Sn(1) - O(2)^{b}$ | 2.250(15) | $O(2) - Sn(1)^{a}$ | 2.250(15) |
| $O(4)-Sn(1)^b$ | 2.246(17) | | |
| Bond angles (°) | | | |
| C(19)-Sn(1)-C(15) | 172.1(8) | C(19) - Sn(1) - O(1) | 90.2(6) |
| C(15)–Sn(1)–O(1) | 89.3(6) | C(19)-Sn(1)-O(4) ^a | 96.4(6) |
| $C(15)-Sn(1)-O(4)^{a}$ | 91.6(7) | $O(1)-Sn(1)-O(4)^{a}$ | 96.9(5) |
| C(19)–Sn(1)–O(3) | 93.3(5) | C(15)-Sn(1)-O(3) | 86.6(6) |
| O(3)-Sn(1)-O(1) | 174.1(6) | $C(19)-Sn(1)-O(2)^{b}$ | 81.0(6) |
| $C(15)-Sn(1)-O(2)^{b}$ | 91.1(6) | $O(4)^{a}$ -Sn(1)-O(2) ^b | 173.3(7) |
| $O(1) - Sn(1) - O(2)^{b}$ | 89.3(5) | $O(3) - Sn(1) - O(2)^{b}$ | 86.6(5) |
| C(19)–Sn(1)–O(2) | 68.4(5) | C(15)-Sn(1)-O(2) | 112.9(5) |
| O(1)-Sn(1)-O(2) | 26.1(4) | O(3)-Sn(1)-O(2) | 159.3(4) |
| $O(4)^{a}$ -Sn(1)-O(2) | 85.1(4) | $O(2)^{b}-Sn(1)-O(2)$ | 99.5(4) |
| $Sn(1)^{a}-O(2)-Sn(1)$ | 99.5(4) | C(1)–O(1)–Sn(1) | 134.0(15) |
| $C(1)-O(2)-Sn(1)^{a}$ | 134.4(14) | C(1)-O(2)-Sn(1) | 43.5(11) |
| C(8)-O(3)-Sn(1) | 139.7(15) | $C(8) - O(4) - Sn(1)^{b}$ | 128.2(13) |
| - | | | |

Symmetry transformations used to generate equivalent atoms: ${}^{a}x + 1, y, z$; ${}^{b}x - 1, y, z$.

bond angles of C(15)–Sn(1)–O(1) and C(19)–Sn(1)–O(1) are 89.3(6)° and 90.2(6)°, respectively, which illustrates the Sn atom with two O atoms of carboxyl groups and two *trans-n*-butyl groups exhibit a similarly square geometry. Moreover, the bond distance of O(2)–Sn(1) is 4.060(12) Å, larger than the van der Waals' sum of Sn and O (3.68 Å) [21], but the bond distance of O-Sn^b (symmetry operations x + 1, y, z) is (2.250(15)) Å, close to the covalent sum of Sn and O (2.13 Å) [21], which illustrates the bidentate coordination mode of carboxyl group. The molecular structure of **4** corresponds to a centrosymmetric dimer based on an eight-membered ring containing two five-coordinate tin atoms which exhibits distorted tetragonal pyramid environment with the O(4)A atom in apical position, and the equatorial planar position is occupied by two O atoms from two carboxyl groups and two *trans-n*-butyl groups (Fig. 5). The distortion lies the angle of O(1)–Sn(1)– $O(4)^a$ [96.9(5)°] (symmetry operation



Fig. 5. The dimer grid unit of structure of complex 4 via $O \rightarrow Sn$ coordination (the butyl groups have been omitted for clarity).

x + 1, y, z). Two carboxyl groups form a non-symmetrical bridging (C(1)–O(1) = 1.29(2) and C(1)–O(2) = 1.25(2), O(1)–Sn(1) = 2.236(14) and O(2)–Sn(1)^a = 2.250(14)). Further, the link of the dimer unit through intermolecular C=O→Sn coordination interaction leads to infinite 1D helical double-chain structure along *a* axis (Fig. 6), which is similar to another organotin complex that has been reported [22]. In this structure, the tin atom displays a six-coordinated distorted octahedron geometry with four O atoms from four carboxyl groups and two C atoms from *trans-n*-butyl groups (it may alternately be described as a bicapped tetrahedron with oxygens), The deviation from



Fig. 6. Perspective view shows the 1D helical double-chain polymeric structure of complex **4** (the butyl groups have been omitted for clarity).



Fig. 7. Perspective view showing 1D chain structure of complex 4 connected by intermolecular $C-H\cdots F$ weak hydrogen bond (a) and non-bonded $F\cdots F$ interaction (b) (the butyl groups have been omitted for clarity).

the standard octahedron environment is also confirmed by the value of the C(15)-Sn(1)-C(19) angle, 172.1(8)° and two C atoms of the butyl groups occupied the axial apical position. This monoorganotin oxo clusters based on doubly bridging carboxyl oxo derivatives and hexa-coordinated tin atoms have been reported by Holmes and co-workers [23,24].

Worth mentioning here is that supramolecular structure of complex 4 is shown in Figs. 7 and 8, owing to intermolecular C–H···F and F···F weak interaction, which are 2.350 and 2.725 Å, respectively, smaller than the sum of van der Waals radii (2.67 and 2.94 Å) [21]. These contacts form a infinite 1D chain structure, respectively.

The supramolecular structure of **4**, as shown in Fig. 8(b), exhibits a 2D network structure unit, in which the corner of this structure is composed of weak C– $H\cdots F$ and $F\cdots F$ contact (2.350 and 2.725 Å, respectively),

nevertheless smaller than the sum of van der Waals radii (2.67 and 2.94 Å) [22]. These contacts assemble the complex **4** into 2D planar structure through C–H···F and F···F along the *ab* axis. The network structure extended along *c* axis and formed a infinite 3D metal-organic framework, showing a channel-like supramolecular structure, whose structure unit is shown in Fig. 8(c).

4.3. Crystal structure of $\{Bu_2Sn_2(O_2CC_6HF_4)_3(OH)\}$ (8)

The molecular structure and unit cell of the complex **8** depicted in Figs. 9 and 10, selected bond lengths and angles are given in Table 3. Both of Sn atoms exist in distorted trigonal bipyramidal geometries with two carboxylate O atoms at an axial position and the bridging OH atom and two butyl groups from decreases in O(2)-Sn(2)-O(5) and O(1)-Sn(1)-O(3) axial angles to $175.0(5)^{\circ}$ and



Fig. 8. (a) Perspective view shows grid unit of supramolecular structure 4. (b) Perspective view shows the 2D grid diagram of intermolecular structure of complex 4 weak C-H···F hydrogen bond and non-bonded F···F interaction. (c) A 3D metal-organic framework, showing the infinite channel-like structure unit of complex 4.

Table 3



Fig. 9. Molecular structure of complex 6.



Fig. 10. Unit cell of complex 8.

162.0(5)°, respectively, which is coupled with severe angular distortion in the equatorial planes. Angular distortion in the equatorial planes seem to be only an effect on the adjustment of bond angles according to the electronegativity of the attached groups [25]. The mutual repulsions between the two butyl groups which are less electronegative than the *O*-hydroxy result in expanding of the C–Sn–C angle from 120° to 135.4(9)° in C(30)–Sn(2)–C(34) and to

| Selected bond lengths (Å) and angles (°) of complex ${\boldsymbol 8}$ | | | |
|---|-----------|------------------|-----------|
| Bond lengths (Å) | | | |
| Sn(1)-C(22) | 2.006(17) | Sn(2)-C(30) | 2.12(2) |
| Sn(1)-C(26) | 1.986(17) | Sn(2)–O(7) | 2.028(11) |
| Sn(1)–O(7) | 2.123(11) | Sn(2)-C(34) | 2.07(2) |
| Sn(1)–O(3) | 2.183(11) | Sn(2)–O(5) | 2.153(12) |
| Sn(1) - O(1) | 2.275(12) | O(2) - C(1) | 1.21(2) |
| Sn(2)-O(2) | 2.235(14) | O(1)–C(1) | 1.22(2) |
| Bond angles (°) | | | |
| C(22)-Sn(1)-C(26) | 151.6(8) | C(22)-Sn(1)-O(3) | 97.4(7) |
| C(26)-Sn(1)-O(7) | 100.0(6) | C(22)-Sn(1)-O(1) | 85.7(7) |
| C(26)-Sn(1)-O(3) | 97.2(6) | C(22)-Sn(1)-O(7) | 106.8(7) |
| C(34)-Sn(2)-O(5) | 99.1(7) | C(26)-Sn(1)-O(1) | 87.7(7) |
| C(34)-Sn(2)-O(2) | 83.2(7) | O(3)-Sn(1)-O(1) | 160.0(5) |
| C(34)-Sn(2)-C(30) | 135.4(9) | O(7)-Sn(1)-O(1) | 84.4(4) |
| C(30)-Sn(2)-O(2) | 88.5(7) | O(7)-Sn(1)-O(3) | 77.8(4) |
| O(7)-Sn(2)-O(5) | 87.6(5) | O(5)-Sn(2)-O(2) | 175.0(5) |
| O(7)-Sn(2)-O(2) | 87.4(5) | O(5)-Sn(2)-C(30) | 92.9(7) |
| O(7)-Sn(2)-C(34) | 111.5(8) | O(7)-Sn(2)-C(30) | 111.9(7) |
| C(1)–O(1)–Sn(1) | 142.8(12) | C(1)-O(2)-Sn(2) | 138.0(13) |
| C(8)–O(3)–Sn(1) | 122.2(12) | C(15)-O(5)-Sn(2) | 132.7(13) |
| Sn(2)-O(7)-Sn(1) | 140.2(6) | | |

151.6(8)° in C(22)–Sn(1)–C(26), whereas for the C–Sn–O(7), the mean value is only 100.0°.

Although the Sn atom environments are similar, there are two distinct carboxylate groups in the structure. There is a total of three 2,3,4,5-tetrafluorobenzoic acid ions in the title complex. One of these is bidentate bridging and bridges both the Sn atoms via O(1) and O(2) atoms. These Sn-O bond distances, [Sn(1)-O(1) 2.275(12) and Sn(2)-O(2) 2.235(14) Å] and the C-O bond distances [C(1)-O(1) 1.22(2), C(1)-O(2) 1.21(2) Å] are dissimilar, so that the bonds bridges the Sn atoms in an asymmetric fashion. The other two carboxyl ligands coordinate to each Sn atom in the monodentate mode via the O(3)and O(5) atoms, respectively. The non-coordinating atoms of these second carboxylate ligands, O(4) and O(6), are orientated so that they are directed away from the rest of the molecule. The hydroxy bridge is almost symmetrical, the difference between Sn(1)-O(7) and Sn(2)-O(7)bond distances being only 0.095 Å. The Sn-O and C-O bond distances are non-equivalent between the bidentate and the monodentate ligands. The Sn-O bond lengths for the bidentate coordinating (2.235(14))and 2.275(12) Å) are both longer than those for Sn–O in the monodentate coordinating (2.153(12) and 2.183(11) Å). The difference in the C-O bond length in the bidentate 2,3,4,5-tetrafluorobenzoate is small, only 0.01 Å, indicating delocalization of the double bond, whereas for the monodentate 2,3,4,5-tetrafluorobenzoate the significant difference of C-O bond character of one C-O at the expense of the other C-O bond of the carboxylate. The tin-carbon distances (mean value 2.12(2) Å) appear to be normal [25].

As shown in Fig. 11, the intermolecular $C=O \rightarrow Sn$ coordination bonds are recognized, which associate the discrete molecule into a eight-membered ring dimer structure, in

Table 4 Crystal data and structure refinement parameters for complexes **2**, **4**, **8**

| Complex | 2 | 4 | 8 |
|---|--------------------------------|--------------------------------|--------------------------------|
| Empirical formula | $C_{60}H_{76}F_{16}O_{10}Sn_4$ | $C_{22}H_{20}F_8O_4Sn$ | $C_{37}H_{40}F_{12}O_7Sn_2$ |
| Formula weight | 1735.97 | 619.07 | 1062.07 |
| Crystal system | monoclinic | triclinic | triclinic |
| Space group | C2/c | <i>P</i> 1 | $P\overline{1}$ |
| a (Å) | 18.174(6) | 4.955(2) | 11.763(3) |
| b (Å) | 18.913(6) | 9.904(4) | 12.196(3) |
| c (Å) | 20.921(7) | 12.252(5) | 15.782(4) |
| α (°) | 90 | 99.657(6) | 107.520(4) |
| β (°) | 97.242(5) | 97.299(6) | 91.652(4) |
| γ (°) | 90 | 97.077(5) | 91.264(4) |
| Ζ | 4 | 1 | 2 |
| Absorption coefficient (mm^{-1}) | 1.476 | 1.190 | 1.253 |
| Crystal size (mm) | $0.50 \times 0.48 \times 0.47$ | $0.42 \times 0.36 \times 0.28$ | $0.62 \times 0.55 \times 0.36$ |
| $D_{\rm c} ({\rm g}{\rm cm}^{-3})$ | 1.616 | 1.768 | 1.635 |
| θ Range for data collection (°) | 2.37-25.01 | 2.95-24.99 | 2.42-25.01 |
| Reflections collected | 18316 | 2973 | 11 289 |
| Unique reflections (R_{int}) | 6267 (0.0435) | 2568 (0.0213) | 7457 (0.0449) |
| Data/restraints/parameters | 6267/21/416 | 2433/25/316 | 7457/38/527 |
| Goodness-of-fit on F^2 | 1.007 | 1.005 | 0.994 |
| Final <i>R</i> indices $[I > 2\sigma(I)]$ | $R_1 = 0.0495,$ | $R_1 = 0.0435,$ | $R_1 = 0.0672,$ |
| | $Wr_2 = 0.1262$ | $Wr_2 = 0.1184$ | $Wr_2 = 0.1512$ |
| R indices (all data) | $R_1 = 0.0981,$ | $R_1 = 0.0436,$ | $R_1 = 0.1774,$ |
| | $Wr_2 = 0.1720$ | $Wr_2 = 0.1185$ | $Wr_2 = 0.2147$ |

which O–Sn distances are 2.183 and 2.636 Å, respectively. The O···O, O–H···O distances and the O–H···O angle are 2.634 Å, 1.798 Å and 149.19°, respectively. In the dimerization, there are two tin environments: the Sn(2) atom geometry is distorted octahedral with the two *transn*-butyl groups and four O atoms from two carboxyl groups, and two *n*-butyl C occupy apical axis positions.

In contrast, the geometry about the Sn(1) atom is based on a trigonal bipyramid with the two butyl groups and the hydroxyl group defining the trigonal plane and two O (carboxyl) atoms occupying apical axial positions.

In Fig. 12(a), the 1D chain of ring structure is connected via intermolecular non-bonded $F \cdots Sn$ and $F \cdots F$ weak interaction, forming a centrosymmetric macrocycle with a



Fig. 11. The dimer structure via $O \rightarrow Sn$ coordination. The intramolecular $O-H \cdots O$ hydrogen bonds distance and the $O-H \cdots O$ angle are 2.648 Å and 1.819 Å and 147.17°, respectively. (For clarity, the butyl groups are omitted.)



Fig. 12. The supramolecular structure of complex **8**. (a) 1D chain structure connected by intermolecular C–H \cdots F interaction and non-bonded F \cdots Sn and F \cdots F interaction. (For clarity, the butyl groups are omitted.) (b) 1D chain structure connected by the intermolecular C–H \cdots F hydrogen bonds. (The excessive hydrogen atoms are omitted for clarity.)

head-to-tail arrangement [26]. The distances are 3.600 and 2.949 Å, respectively, which are significantly considerably smaller than the corresponding sum of van der Waals radii (3.70 and 2.98 Å) [21]. The dimer of the complex **8** are further linked by intermolecular C–H···F weak hydrogen bonds and formed a infinite 1D infinite chain structure [Fig. 12(b)]. The C–H···F distances are 2.539, 2.665, and 2.613 Å, respectively, which are smaller than the sum of van der Waals radii (2.67 Å) [21]. The corresponding angles are 159.51°, 164.50° and 155.82°, respectively, which are consistent with those reported by Dautel [27]. Despite these weak C–H···F, F···Sn and F···F interaction often being neglected, they clearly govern these self-assembly of the molecules into 1D chain structure.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper (2, 4, and 8) have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC – 600208 (for 2), 600207 (for 4), 600206 (for 8). Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgement

We thank the National Natural Science Foundation of China (20271025) for financial support.

References

- C.J. Evans, S. Karpel, Organotin compounds in modern technology, J. Organomet. Chem. Library, 16, Elsevier, Amsterdam, 1985.
- [2] (a) E.R.T. Tiekink, Appl. Organomet. Chem. 1 (1991) 5;
- (b) S.G. Teoh, E.S. Looi, S.B. Teo, S.W. Ng, J. Organomet. Chem. 50 (1996) 957.
- [3] J.T. Welch, Tetrahedron 43 (1987) 3123.
- [4] (a) M. Gielen, A. El Khloufi, M. Biesemans, R. Willem, Appl. Organomet. Chem. 7 (1993) 119;
 (b) M. Gielen, M. Biesemans, A. El. Khloufi, J. Meunier-Piret, F. Kayser, R. Willem, J. Fluorine Chem. 64 (1993) 279;
 (c) M. Gielen, A. El Khloufi, D. de Vos, H.J. Kolker, J.H.M. Schellens, R. Willem, Bull. Soc. Chim. Belg. 102 (1993) 761;
 (d) M. Gielen, A. El Khloufi, M. Biesemans, F. Kayser, R. Willem, Appl. Organomet. Chem. 7 (1993) 201;
 (e) M. Gielen, M. Boualam, A. Meriem, B. Mahieu, M. Biesemans, R. Willem, Heteroatom. Chem. 3 (1992) 449.
- [5] Siang-Guan Teoh, Show-Hing Ang, Eng-Seng Looi, Chye-Aun Keok, J. Organomet. Chem. 523 (1996) 75.
- [6] Vadapalli Chandrasekhar, Selvarajan Nagendran, Chem. Commun. (2003) 862.
- [7] R.R. Holmes, C.G. Schmid, V. Chandrasekhar, R.O. Day, J.M. Homels, J. Am. Chem. Soc. 109 (1987) 1048.
- [8] G.K. Sandhu, R. Hundal, J. Organomet. Chem. 412 (1991) 31.

- [9] M. Gielen, M. Melotte, G. Atassi, R. Willem, Tetrahedron 45 (1989) 1219.
- [10] C.L. Ma, Y.F. Han, R.F. Zhang, D.Q. Wang, Eur. J. Inorg. Chem. (2005) 3024.
- [11] G.K. Sandhu, R. Gupta, S.S. Sandhu, R.V. Parish, Polyhedron 4 (1985) 81.
- [12] G.K. Sandhu, N. Sharma, E.R.T. Tiekink, J. Organomet. Chem. 403 (1991) 119.
- [13] V. Peruzzo, G. Plazzogna, G. Tagliavini, J. Organomet. Chem. 40 (1972) 121.
- [14] (a) J. Holeček, A. Lyčka, Inorg. Chim. Acta 118 (1986) L15;
 (b) T.P. Lockhart, F. Davidson, Organometallics 6 (1987) 2471;
 (c) T.P. Lockhart, W. Manders, J. Am. Chem. Soc. 109 (1987) 7015.
- [15] C.H. Yoder, L.A. Margolis, J.M. Horne, J. Organomet. Chem. 633 (2001) 33.
- [16] J. Otera, J. Organomet. Chem. 221 (1981) 57.
- [17] J. Holeček, A. Lyčka, K. Handlír, M. Nádvomík, Collect. Czech. Chem. Commun. 55 (1990) 1193.
- [18] T.P. Lockhart, W.F. Manders, E.M. Holt, J. Am. Chem. Soc. 108 (1986) 6611.

- [19] (a) R. Faggiani, J.P. Johnson, I.D. Brown, T. Birchall, Acta Crystallogr. B 34 (1978) 3743;
 (b) G. Valle, V. Peruzzo, G. Tagliavini, P. Ganis, J. Organomet. Chem. 276 (1984) 325;
 (c) T. Birchall, C.S. Frampton, J.P. Johnson, Acta Crystallogr. C 43 (1987) 1492.
- [20] E.R.T. Tiekink, Appl. Organomet. Chem. 5 (1991) 1.
- [21] A. Bondi, J. Phys. Chem. 68 (1964) 441.
- [22] Vadapalli Chandrasekhar, Selvarajan Nagendran, Viswanathan Baskar, Coord. Chem. Rev. 235 (2002) 1.
- [23] K.C.K. Swamy, C.G. Schmid, R.O. Day, R.R.J. Holmes, Am. Chem. Soc. 112 (1990) 223.
- [24] (a) R.R. Holmes, Acc. Chem. Res 22 (1989) 190;
 (b) R.O. Day, J.M. Holmes, V. Chandrasekhar, R.R. Holmes, J. Am. Chem. Soc 109 (1987) 940.
- [25] R. Graziani, G. Bombieri, E. Forsellini, P. Furlan, V. Peruzzo, G. Tagliavini, J. Organomet. Chem. 125 (1977) 43.
- [26] D.L. Reger, J.R. Gardinier, R.R. Semeniuc, M.D. Smith, Dalton Trans. (2003) 1712.
- [27] O.J. Dautel, M.F. Ourmigue, J. Org. Chem. 65 (2000) 6479.