Journal of Organometallic Chemistry 743 (2013) 156–162

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

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

Opening of the azastibol heterocycle with various acids: Isolation of novel *N*,*C*-chelated organoantimony(III) compounds

Iva Urbanová [a], Milan Erben [a], Roman Jambor [a], Aleš Růžička [a], Robert Jirásko [b], Libor Dostál [a,*]

[a] Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-532 10 Pardubice, Czech Republic

[b] Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-532 10 Pardubice, Czech Republic

ARTICLE INFO

Article history:
Received 24 April 2013
Received in revised form
17 June 2013
Accepted 20 June 2013

Keywords:
Antimony
Azastiboles
Chelating ligands
X-ray structures
NMR

ABSTRACT

The reaction of *N*,*C*-intramolecularly coordinated organoantimony(III) compound L_2SbCl (**1**) (where L is [2-(2′,6′-*i*-$Pr_2C_6H_3$)N=CHC_6H_4]) with one molar equivalent of the K-selectride (K[B(*s*-Bu)$_3$H]) gave compound LSb{2-[CH_2N(2′,6′-*i*-$Pr_2C_6H_3$)]C_6H_4} (**2**) containing five membered aza-stiba heterocycle. On the contrary, analogical reaction between the organobismuth(III) compound L_2BiCl (**3**) and K-selectride gave only inseparable mixture of products. Reactions of **2** with selected acids HX resulted in the cleavage of the present Sb–N bond and formation of novel *N*,*C*-chelated compounds LSb(X){2-[CH_2NH(2′,6′-*i*-$Pr_2C_6H_3$)]C_6H_4} (where X = Cl (**4**), CH_3COO (**5**), CF_3COO (**6**), CF_3SO_3 (**7**) or FcCOO (**8**); Fc = ferrocenyl). Compounds **4**–**8** were characterized by the help of elemental analysis, electrospray ionization (ESI) mass spectrometry, multinuclear NMR spectroscopy, IR spectroscopy and in the case of **5** by the single-crystal X-ray diffraction analysis. The molecular structures of compounds LSb(X){2-[CH_2NH(2′,6′-*i*-$Pr_2C_6H_3$)]C_6H_4}·HX (where X = CF_3COO (**6a**), CF_3SO_3 (**7a**)) were determined by the single-crystal X-ray diffraction analysis as well. Compounds **6a** and **7a** are most probably products of partial hydrolysis of compounds **6** and **7**.

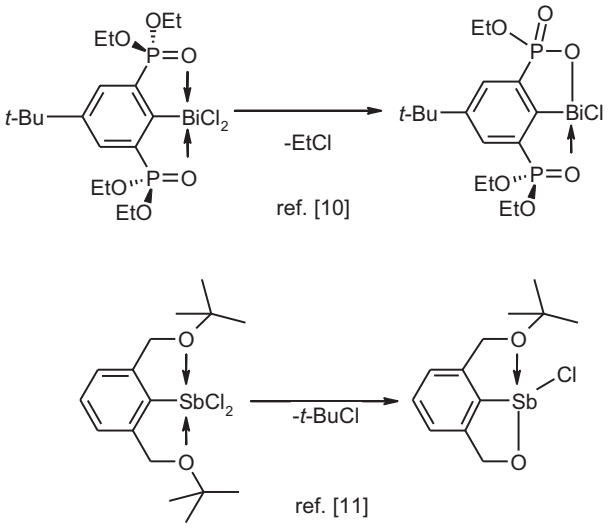
1. Introduction

The utilization of various types of *Y*,*C*- or *Y*,*C*,*Y*-chelating ligands (*Y* designates a donor atom such as N or O) for stabilization of organoantimony(III) and organobismuth(III) compounds is well known phenomenon in the chemistry of heavier group 15 elements [1]. In this regard, the pioneer works of Cowley [2], Silvestru and Breunig [3], and later on by our group and others [4] are noteworthy. The majority of compounds contain chelating ligands with nitrogen atom as in-built donor functionality. The initial efforts in the field were mainly focused on the description of strength of N → Sb(Bi) interactions and their influence on the coordination numbers of the central atom and(or) structures of studied compounds. Later on, it turned out that the stabilization of the central antimony or bismuth atoms by *N*,*C*,*N*-chelating ligands is not pointless, but allowed isolation of many, before elusive, antimony and bismuth compounds. The monomeric stibinidine and bismuthinide [5], compounds containing terminal M=E (E = S, Se, Te) bonds [6], highly Lewis acidic antimony and bismuth cations [7], and many mixed oxido-compounds [8] may serve as representative examples of this research. Reports describing compounds containing related *O*,*C*,*O*-chelating ligands were published by Jurkschat et al. and our group [9]. The common feature of these *O*,*C*,*O*-chelated antimony and bismuth compounds is their tendency to form oxa-stiba heterocycles (Scheme 1), thus, changing the former O → Sb donor–acceptor interaction into a Sb–O bond [9,10]. On the contrary, such cyclization procedure was, to the best of our knowledge, unknown for related *N*,*C*-chelated compounds.

New type of *N*,*C*-chelating ligand [2-(2′,6′-*i*-$Pr_2C_6H_3$)N=CHC_6H_4], designated as L hereafter, has been recently introduced by Mehring and us to the field of antimony and bismuth chemistry [11,12]. Besides the excellent donor ability of the imino-nitrogen donor centre and significant sterical shielding of the metal atom by bulky aromatic group attached to the imino-nitrogen atom, this ligand carries a C=N functionality. The presence of this functional group is not of marginal importance for main group element compounds as demonstrated in the field of boron chemistry, where the benzazaboroles were obtained by the reaction of the *N*,*C*-chelated chloroboranes by ligand L with lithium anilides. This procedure involves a nucleophilic addition across the C=N double

* Corresponding author.
E-mail address: libor.dostal@upce.cz (L. Dostál).

0022-328X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jorganchem.2013.06.023



Scheme 1. Syntheses of known oxastiboles based on O,C,O-chelating ligands.

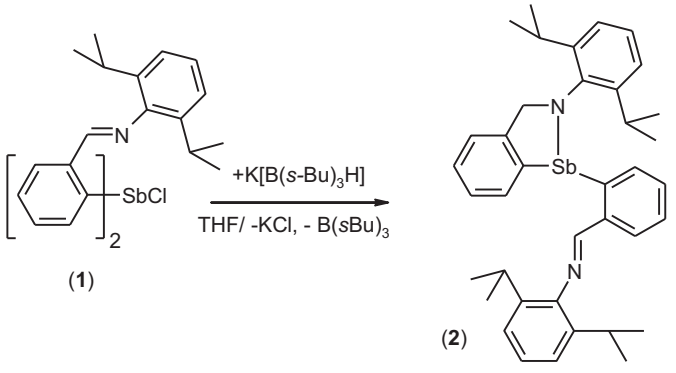
bond of the ligand L and closure of benzazaborole rings [13]. By an analogy, we have recently discovered that the reaction between compound L_2SbCl (**1**) and one molar equivalent of the K-selectride ($K[B(s\text{-}Bu)_3H]$) gave compound $LSb\{2\text{-}[CH_2N(2',6'\text{-}i\text{-}Pr_2C_6H_3)]C_6H_4\}$ (**2**) as a result of hydrogen atom migration and formation of the Sb–N bond (Scheme 2). This procedure also led to the saturation of the C=N double bond of the ligand L [11a].

Herein, we report on the reaction of compound **2** with various HX acids with the aim to open the azastibol heterocycle *via* cleavage of the present Sb–N bond. The synthesis and characterization of compound L_2BiCl (**3**) as a possible precursor for formation bismuth analogue of compound **2** are also included.

2. Results and discussion

The reaction of **1** with one molar equivalent of the K-selectride gave **2** according to Scheme 2 [11].

In order to test similar reaction with the bismuth analogue, compound L_2BiCl (**3**) was prepared by the reaction of LLi with $BiCl_3$ in molar ratio of 2:1. Compound **3** could be isolated in rather low yield of 11% in the form of bright yellow air-stable crystals. Compound **3** was characterized by the help of elemental analysis, ESI mass spectrometry. The ^1H NMR spectrum of **3** revealed one set of broaden signals for both ligands L at 294 K and upon cooling of the sample in $CDCl_3$ to 220 K the splitting of these resonances into two set of independent signals for two non-equivalent ligands L was



Scheme 2. Synthesis of compound **2**.

observed most probably indicating that N → Bi interaction is rigid on the ^1H NMR time scale and the two ligands are non-equivalent at this temperature. The molecular structure of **3** was unambiguously established by the help of single-crystal X-ray diffraction analysis (Fig. 1). Both nitrogen atoms N(1) and N(2) are coordinated to the central atom Bi(1), but the bond distances point to a different strength of these contacts Bi(1)–N(1) 2.614(3) *vs.* Bi(1)–N(2) 2.916(3) Å, as suggested already in solution *vide supra*. Nevertheless, if weaker interaction with the N(2) atom and the lone pair of the central atom are taken into account, the resulting coordination polyhedron of the central atom may be described as strongly distorted octahedron, where the central bismuth atom is [4 + 1] coordinated. Unfortunately, all reactions of **3** with K-selectride produced only mixtures of products and, thus, formation of bismuth analogue of **2** failed.

2.1. Reactions of HX with 2

The treatment of **2** with selected acids HX resulted in the cleavage of the Sb–N bond and formation of novel *N,C*-chelated compounds $LSb(X)\{2\text{-}[CH_2NH(2',6'\text{-}i\text{-}Pr_2C_6H_3)]C_6H_4\}$ (where X = Cl (**4**), CH_3COO (**5**), CF_3COO (**6**), CF_3SO_3 (**7**) or FcCOO (**8**); Fc = ferrocenyl, Scheme 3).

Compounds **4**–**8** were characterized by the help of elemental analysis and ESI mass spectroscopy. In the mass spectra, the observation of ions $[M - X]^+$ (X = Cl for **4**, CH_3COO for **5**, CF_3COO for **6**, CF_3SO_3 for **7** and FcCOO for **8**) as well as of other ions (see Experimental) proved the identity of studied compounds [14]. Infrared spectroscopy unambiguously proved the presence of the NH group by the observation of the characteristic weak-to-medium bands in the range of 3344–3357 cm^{-1} for **4**–**8**. Furthermore, the presence of carbonyl functionalities in **5**, **6** and **8** was evidenced by the detection of bands corresponding to the $\nu_a(CO_2)$ vibration at 1636, 1702 and 1628 cm^{-1} for **5**, **6** and **8**, respectively. Triflate anion in **7** gives characteristic strong bands of S–O and C–F stretch at 1306, 1023, 1231 and 1213 cm^{-1} [15].

The ^1H NMR spectra of **4**–**8** clearly established the proposed structure in solution (Fig. 2).

The ^1H NMR spectra of **4**–**8** revealed typical AX pattern for the CH_2NH group, one broad signal for N*H* proton and the signal for

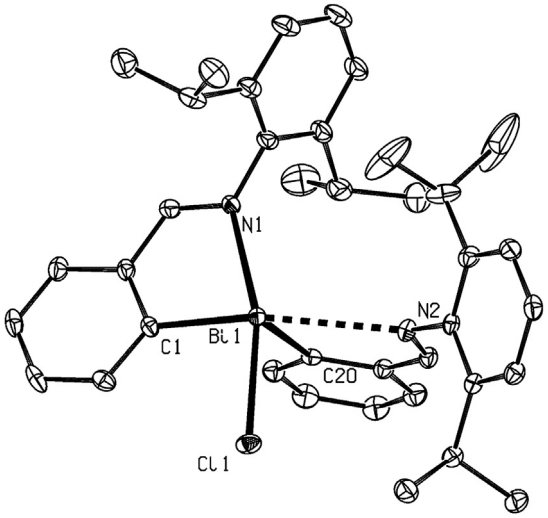
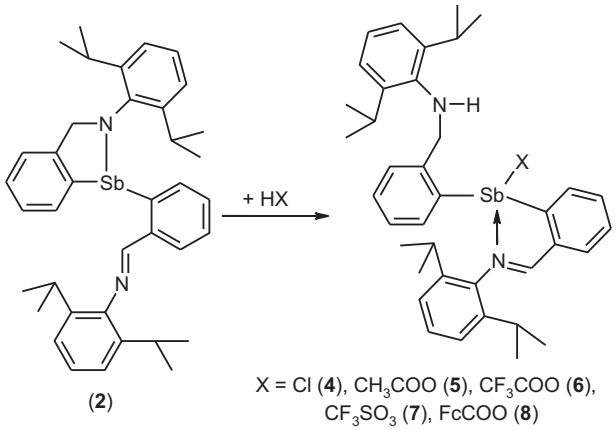


Fig. 1. ORTEP view of **3**. The thermal ellipsoids are drawn with 40% probability. Hydrogen atoms are omitted for clarity. Only one position of one of the disordered *i*-Pr groups is shown. Selected bond distances (Å) and angles (°): Bi(1)–C(1) 2.275(4), Bi(1)–C(20) 2.268(4), Bi(1)–N(1) 2.614(3), Bi(1)–N(2) 2.916(3), Bi(1)–Cl(1) 2.6086(9), N(1)–Bi(1)–Cl(1) 160.52(8), C(1)–Bi(1)–N(2) 159.71(11).



Scheme 3. Syntheses of compound **4**–**8**.

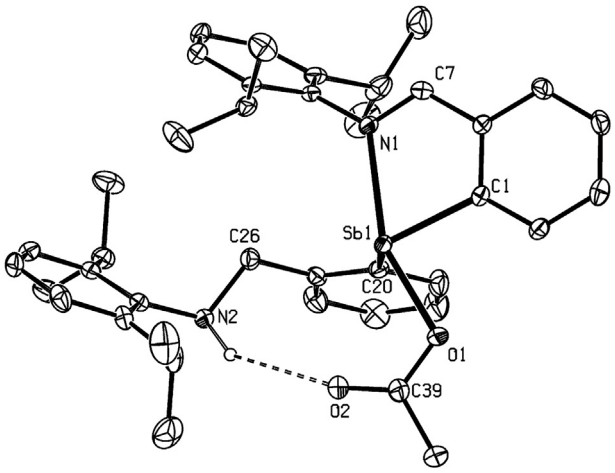


Fig. 3. ORTEP view of **5**. The thermal ellipsoids are drawn with 40% probability. Hydrogen atoms except the NH group are omitted for clarity. Selected bond distances (Å) and angles (°): Sb(1)–C(1) 2.145(4), Sb(1)–C(20) 2.149(3), Bi(1)–N(1) 2.614(3), Bi(1)–O(1) 2.484(3), Bi(1)–O(2) 2.944(3), C(7)–N(1) 1.290(5), C(26)–N(2) 1.480(5), N(2)–O(2) 3.596(4), N(1)–Sb(1)–O(1) 154.89(9), C(1)–Sb(1)–C(20) 100.88(12), N(2)–H–O(2) 147.

C*H*=N group in mutual integral ration of 2:1:1. One set of sharp signals was observed for the *i*-Pr groups of the coordinated CH=N(Dipp) (Dipp = diisopropylphenyl) group. On the contrary, signals of the *i*-Pr groups belonging to the non-coordinated CH_2NH(Dipp) were obtained as broaden set of signals most probably reflecting hindered rotation of this group. This may be caused either by a steric hindrance or by the presence of hydrogen bond between the NH group and polar atoms of the group X as observed in the solid state (*vide infra*). The ^{13}C NMR spectra revealed the presence of one *C*H=N group (signals in the range of 168.4 and 170.5 ppm in **4**–**8**) and one *C*H_2NH group (signals between 58.7 and 59.1 ppm in **4**–**8**), thus, proving the proposed structure of **4**–**8**.

The molecular structure of **5** was unambiguously determined by the help of single-crystal X-ray diffraction analysis (Fig. 3).

The central atom Sb(1) is four coordinated and the bond distance Sb(1)–N(1) of 2.484(3) Å indicates the presence of strong intramolecular N → Sb interaction. The nitrogen atom N(2) with the bond distance Sb(1)–N(2) of 4.322(3) Å is out of the coordination sphere of the central atom. The difference between the bond distances C(7)–N(1) 1.290(5) Å and C(26)–N(2) 1.480(5) Å clearly proves the presence of CH=N and CH_2–NH bonds, respectively. The acetate group is bonded to the central atom in a monodentate fashion as demonstrated by the fairly different bond distances Sb(1)–O(1) and Sb(1)–O(2) being 2.484(3) and 2.944(3) Å, respectively. The coordination polyhedron of the central atom in **5** may be described as pseudo-trigonal bipyramid with the lone pair, C(1) and C(20) located in equatorial positions, while N(1) and O(1) atoms occupy the axial positions as demonstrated by the bonding angle N(1)–Sb(1)–O(1) 154.89(9)°. The oxygen atom O(2) of the acetate group is involved in a weak hydrogen bond with the hydrogen atom of the NH group, that is characterized by the bond distance O(2)–N(1) of 3.596 Å and the bonding angle O(2)–H–N(1) of 147°.

Unfortunately, all other attempts to grow single-crystals of **4** or **6**–**8** failed. After slow evaporation of solutions of **6** and **7** a tiny amount of single-crystals was found in both mixtures and their

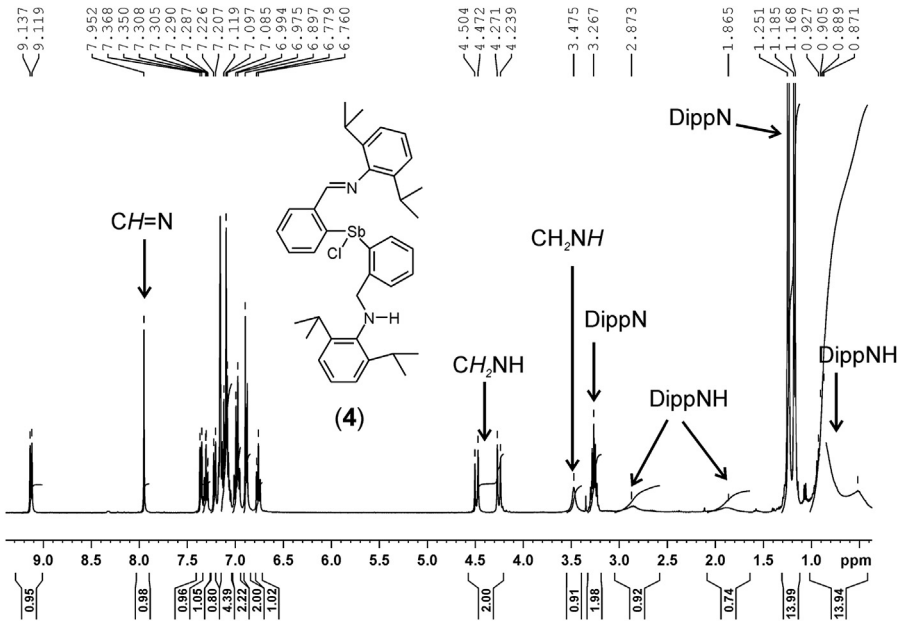


Fig. 2. Typical ^1H NMR spectrum of compounds **4**–**8** illustrated on the example of the spectrum of **4**.

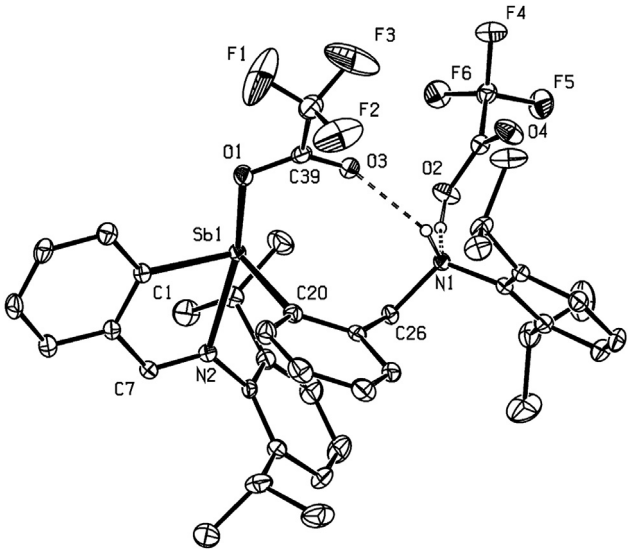


Fig. 4. ORTEP view of **6a**. The thermal ellipsoids are drawn with 40% probability. Hydrogen atoms except the NH group are omitted for clarity.

molecular structures were determined by the single-crystal X-ray diffraction analysis. It turned out that the revealed structures correspond to the adducts between one molecule of the corresponding acid and expected products **6**·(CF_3COOH) (**6a**) and **7**·(CF_3SO_3H) (**7a**). The attempts to prepare **6a** or **7a** in high yield *via* reaction of **2** with two molar equivalents of corresponding acids were unsuccessful. The lack of sufficient amount of pure material of **6a** and **7a** hampered complex analytical studies and only IR spectra of manually separated single-crystals of **6a** and **7a** were recorded. In the IR spectrum of single-crystals of **6a**, broad medium absorption at 3196 cm^{-1} and twinned band of carbonyl vibration (1705 and 1678 cm^{-1}) were observed. Band at 3196 cm^{-1} could be assigned to ν(OH) of CF_3COOH molecule involved in strong hydrogen bond towards secondary amine function [16]. Infrared spectrum of **7a** also contained band significantly broadened over the region 3600–3200 cm^{-1} attributable to the presence of free triflic acid in the sample. IR bands characteristic for the presence of triflate anion were also broadened but not twinned.

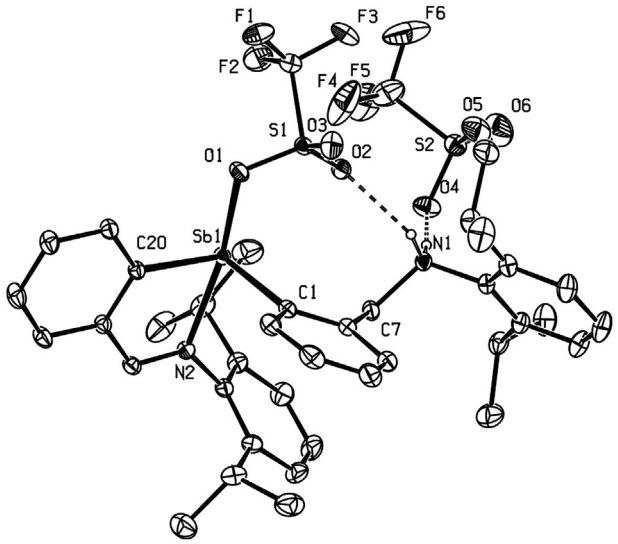


Fig. 5. ORTEP view of **7a**. The thermal ellipsoids are drawn with 40% probability. Hydrogen atoms except the NH group are omitted for clarity.

The molecular structures of **6a** and **7a** are depicted together with selected structural parameters in Figs. 4 and 5.

The molecular structure of **6a** and **7a** is closely related to that found for **5**. The central antimony atom is *N,C*-chelated by the ligand L (the bond distances Sb(1)–N(2) 2.346(3) and 2.259(3) for **6a** and **7a**, respectively), while the second ligand is bonded only *via ipso* Sb–C bond. The coordination polyhedron of the antimony atom in **6a** and **7a** is again a pseudo-trigonal bipyramid with the O(1) and N(2) placed in axial positions, similarly to **5**. The oxygen atoms O(3) in the case of **6a** and O(2) in **7a** are involved in a hydrogen bond with the amino-group as demonstrated by the bond distances O(3)–N(1) of 2.908(4) for **6a** (the bonding angle O(3)–H–N(1) is 150°) and O(2)–N(1) of 2.841(3) for **7a** (the bonding angle O(2)–H–N(1) is 155°). In contrast to **5**, there is another molecule of the acid coordinated to the nitrogen atom N(1) in **6a** and **7a**. The bond distances and bonding angles describing these hydrogen atoms are O(2)–N(1) 2.619(5) for **6a** (O(2)–H–N(1) 153°) and O(4)–N(1) 2.774(4) for **7a** (O(4)–H–N(1) 174°).

3. Conclusion

It was demonstrated that compound **2** containing central azastibole five-membered heterocycle is an excellent precursor for preparation of a variety of substituted organoantimony(III) compounds using simple and high-yield procedure. These compounds carry NH functionality in their structures, which may be interesting for further reactivity studies. Investigation dealing with the preparation of similar azametal heterocycles based on the ligand L is currently in progress in our labs.

4. Experimental

4.1. General methods

The starting compounds **1** and **2** [11a] and precursor of the ligand LBr [16] were prepared according to the literature procedures. All solvents were dried by standard procedures. Starting acids were obtained from commercial suppliers and used as delivered. The ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer at room temperature in $CDCl_3$ or in the temperature range 220–294 K in $CDCl_3$ in the case of **3**. The ^1H, ^{13}C NMR chemical shifts δ are given in ppm and referenced to the central peaks of residual signal of the $CDCl_3$ ($\delta(^1H) = 7.27$ ppm, $\delta(^{13}C) = 77.23$ ppm). Elemental analyses were performed on an LECO-CHNS-932 analyzer. Positive-ion and negative-ion electrospray ionization (ESI) mass spectra were measured on an Esquire 3000 ion trap analyzer (Bruker Daltonics, Bremen, Germany) in the range m/z 50–1500. Samples were dissolved in acetonitrile and analyzed by direct infusion at a flow rate of 5 μL/min. The ion-source temperature was 300 °C, the tuning parameter compound stability was 100%, and the flow rate and the pressure of nitrogen were 4 L/min and 10 psi, respectively. Infrared spectra were recorded in 4000–350 cm^{-1} region on a Nicolet 6700 FTIR spectrometer using diamond ATR technique.

4.2. Synthesis of compound *3*

4.2.1. {2-[CH=N(2′,6′-i-Pr$_2$C$_6$H$_3$)]C$_6$H$_4$}$_2$BiCl (*3*)

n-Buli (2.5 mL, 4.03 mmol, 1.6 M solution in hexane) was added to a solution *o*-C_6H_4(CH=NC_6H_3*i*Pr_2-2,6)Br (1.39 g, 4.03 mmol) in diethyl ether (50 mL) at −70 °C and stirred for 1 h. The resulting yellow suspension of lithium compound was added to a solution of $BiCl_3$ (0.634, 2.01 mmol) in diethyl ether (25 mL) precooled to 0 °C. The resulting mixture was allowed to reach room temperature and

stirred for an additional 20 h. The volume of the reaction was reduced to around 25 mL. The insoluble material was filtered off and washed with hexane (10 mL). The remaining yellowish solid was extracted by dichloromethane (30 mL) and 10 mL of hexane was added to the extract. This solution was slowly evaporated to obtain single-crystals of **3** suitable for X-ray studies. Yield 0.16 g, 11%; m.p. 190 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.47 (s (broad), 3H, CH(CH_3)$_2$), 1.06 (m (broad), 21H, CH(CH_3)$_2$), 1.97 (sept (broad), 1H, CH(CH$_3$)$_2$), 2.82 (m (broad), 3H, CH(CH$_3$)$_2$), 7.13 (m (broad), 6H, CH=N(2,6-*i*-Pr$_2$C$_6$H$_3$)), 7.74 (m (broad), 6H, C$_6H_4$), 8.37 (m (broad), 2H, C$_6H_4$ and CH=N(2,6-*i*-Pr$_2$C$_6$H$_3$)), 8.98 (m (broad), 1H, CH=N), 9.25 (m (broad), 1H, C$_6H_4$). Anal. calcd for $C_{38}H_{44}N_2BiCl$ (773.27 g mol^{-1}): C 44.9, H 4.4; Found C 45.2, H 4.7. ESI–MS: Positive mode – *m*/*z* 737 [M–Cl]$^+$ (100%). Negative mode – *m*/*z* 578 [LBiCl$_3$]$^-$ (100%).

4.3. Synthesis of compounds **4**–**8**

4.3.1. {2-[CH=N(2′,6′-*i*-Pr$_2$C$_6$H$_3$)]C$_6$H$_4$}Sb(Cl){2-[CH$_2$NH(2′,6′-*i*-Pr$_2$C$_6$H$_3$)]C$_6$H$_4$} (**4**)

HCl (20 μL, 0.08 mmol, 4 M solution in dioxane) was added to a suspension of compound **3** (0.05 g, 0.08 mmol) in hexane (10 mL). The resulting mixture was stirred for an additional 1 h at room temperature. Evaporation of the mixture gave yellow powder, which was washed with hexane (5 mL), dried *in vacuo* and characterized **4**. Yield 0.05 g, 85%; m.p. 123–124 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.52 (d (broad), 3H, CH(CH_3)$_2$), 0.90 (d (broad), 9H, CH(CH_3)$_2$), 1.18 (d, 6H, CH(CH_3)$_2$), 1.24 (d, 6H, CH(CH_3)$_2$), 1.88 (sept (broad), 1H, CH(CH$_3$)$_2$–NH(2,6-*i*-Pr$_2$C$_6$H$_3$)), 2.85 (sept (broad), 1H, CH(CH$_3$)$_2$–NH(2,6-*i*-Pr$_2$C$_6$H$_3$)), 3.27 (sept, 2H, CH(CH$_3$)$_2$–CH=N(2,6-*i*-Pr$_2$C$_6$H$_3$)), 3.48 (s (broad), 1H, NH(2,6-*i*-Pr$_2$C$_6$H$_3$)), 4.25 and 4.48 (AX system, 2H, NCH_2), 6.77 (t, 1H, (2,6-*i*-Pr$_2$C$_6$H$_3$)), 6.88 (d, 2H, (2,6-*i*-Pr$_2$C$_6$H$_3$)), 6.98 (m, 2H, C$_6H_4$ and NH(2,6-*i*-Pr$_2$C$_6$H$_3$)), 7.10 (m, 5H, C$_6H_4$ and NH(2,6-*i*-Pr$_2$C$_6$H$_3$)), 7.21 (d, 1H, C$_6H_4$), 7.31 (dd, 1H, C$_6H_4$), 7.36 (d, 1H, C$_6H_4$), 7.95 (s, 1H, CH=N(2,6-*i*-Pr$_2$C$_6$H$_3$)), 9.13 (d, 1H, C$_6H_4$) ppm. ^{13}C NMR (100.61 MHz, C_6D_6, 25 °C): δ = 25.0, 25.1, 28.6 (s, CH(*C*H$_3$)$_2$ and *C*H(CH$_3$)$_2$), 58.9 (s, NCH$_2$), 124.2, 124.3, 124.7, 127.5, 128.9, 129.8, 129.9, 130.0, 133.2, 133.9, 135.5, 138.3, 140.1, 140.7, 142.7, 144.0, 144.3, 144.9, 147.9, 152.3 (s, *C*$_6$H$_4$), 169.4 (s, *C*H=N(2,6-*i*-Pr$_2$C$_6$H$_3$)). Anal. calcd for $C_{38}H_{46}N_2SbCl$ (688.05 g mol^{-1}) 66.3, H 6.7; Found C 66.6, H 6.9. ESI–MS: Positive mode – *m*/*z* 651 [M–Cl]$^+$ (100%); *m*/*z* 649 [M–Cl–H$_2$]$^+$ (29%). IR (cm^{-1}): 3354w ν(NH).

4.3.2. {2-[CH=N(2′,6′-*i*-Pr$_2$C$_6$H$_3$)]C$_6$H$_4$}Sb(CH$_3$COO)[{2-[CH$_2$NH(2′,6′-*i*-Pr$_2$C$_6$H$_3$)]C$_6$H$_4$} (**5**)

Compound **5** was prepared analogously to compound **4**. CH_3COOH (21 μL, 0.37 mmol); compound **3** (0.239 g, 0.37 mmol). Yield of **5** 0.227 g, 87%; m.p. 182–183 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.72 (d (broad), 6H, CH(CH_3)$_2$), 0.91 (d, 6H, CH(CH_3)$_2$), 1.23 (d, 6H, CH(CH_3)$_2$), 1.33 (d, 6H, CH(CH_3)$_2$), 1.92 (s, 3H, CH_3CO$_2$), 3.48 (sept, 2H, CH(CH$_3$)$_2$), 4.12 (s (broad), 1H, NH(2,6-*i*-Pr$_2$C$_6$H$_3$)), 4.13 and 4.65 (AX system, 2H, NCH_2), 6.83–7.12 (m, 10H, C$_6H_4$, NH(2,6-*i*-Pr$_2$C$_6$H$_3$) and (2,6-*i*-Pr$_2$C$_6$H$_3$)), 7.37 (m, 2H, C$_6H_4$), 7.49 (dd, 1H, C$_6H_4$), 7.96 (s, 1H, CH=N(2,6-*i*-Pr$_2$C$_6$H$_3$)), 8.70 (d, 1H, C$_6H_4$). ^{13}C NMR (100.61 MHz, C_6D_6, 25 °C): δ = 22.9, 24.9, 25.2, 28.8 (s, CH(*C*H$_3$)$_2$ and *C*H(CH$_3$)$_2$), 28.5 (s, *C*H$_3$CO), 58.7 (s, NCH$_2$), 124.1, 124.2, 124.4, 127.2, 128.5, 129.5, 129.6, 129.7, 133.2, 133.3, 135.0, 137.5, 140.0, 140.4, 143.3, 144.5, 144.9, 146.1, 147.9, 152.7 (s, *C*$_6$H$_4$), 168.4 (s, *C*H=N(2,6-*i*-Pr$_2$C$_6$H$_3$)), 176.3 (s, CH$_3$*C*=O). Anal. calcd for $C_{40}H_{49}N_2SbO_2$ (711.65 g mol^{-1}) C 67.5, H 6.9; Found C 67.5, H 7.2. ESI–MS: Positive mode – *m*/*z* 749 [M + K]$^+$ (17%); *m*/*z* 733 [M + Na]$^+$ (7%); *m*/*z* 651 [M-CH$_3$COO]$^+$ (100%); *m*/*z* 649 [M–CH$_3$COO–H$_2$]$^+$ (45%). IR (cm^{-1}): 3344w ν(NH), 1636s ν_a(CO$_2$).

4.3.3. {2-[CH=N(2′,6′-*i*-Pr$_2$C$_6$H$_3$)]C$_6$H$_4$}Sb(CF$_3$COO)[{2-[CH$_2$NH(2′,6′-*i*-Pr$_2$C$_6$H$_3$)]C$_6$H$_4$} (**6**)

Compound **6** was prepared analogously to compound **4**. CF_3COOH (8 μL, 0.11 mmol); compound **3** (0.067 g, 0.11 mmol). Yield of **6** 0.064 g, 80%; m.p. 190 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.40 (d (broad), 3H, CH(CH_3)$_2$), 0.69 (d (broad), 3H, CH(CH_3)$_2$), 0.81 (d (broad), 3H, CH(CH_3)$_2$), 0.97 (d (broad), 3H, CH(CH_3)$_2$), 1.21 (d, 6H, CH(CH_3)$_2$), 1.28 (d, 6H, CH(CH_3)$_2$), 1.60 (sept (broad), 1H, CH(CH$_3$)$_2$–NH(2,6-*i*-Pr$_2$C$_6$H$_3$)), 2.93 (sept (broad), 1H, CH(CH$_3$)$_2$–NH(2,6-*i*-Pr$_2$C$_6$H$_3$)), 3.26 (sept, 2H, CH(CH$_3$)$_2$–CH=N(2,6-*i*-Pr$_2$C$_6$H$_3$)), 4.16 (t (broad), 1H, NH(2,6-*i*-Pr$_2$C$_6$H$_3$)), 3.69 a 4.30 (AX system, 2H, NCH_2), 6.73–7.14 (m, 10H, Ar-*H*, NH(2,6-*i*-Pr$_2$C$_6$H$_3$) and CH=N(2,6-*i*-Pr$_2$C$_6$H$_3$)) 7.24 (m, 2H, C$_6H_4$), 7.36 (d, 1H, C$_6H_4$), 7.87 (s, 1H, CH=N(2,6-*i*-Pr$_2$C$_6$H$_3$)), 8.65 (d, 1H, C$_6H_4$). ^{13}C NMR (100.61 MHz, C_6D_6, 25 °C): δ = 25.0, 25.1 a 28.4 (s, CH(*C*H$_3$)$_2$ and *C*H(CH$_3$)$_2$), 58.9 (s, NCH$_2$), 116.7 (q, *C*F$_3$C=O, ^{1}J(^{19}F,^{13}C) = 290 Hz), 124.3, 124.4, 124.6, 128.1, 129.1, 129.9, 130.0, 130.5, 133.4, 135.1, 135.5, 137.4, 139.6, 141.0, 142.8, 143.3, 144.2, 145.9, 146.0, 153.1 (s, *C*$_6$H$_4$), 161.6 (q, CF$_3$*C*=O, ^{2}J(^{19}F,^{13}C) = 38 Hz), 170.5 (s, *C*H=N(2,6-*i*-Pr$_2$C$_6$H$_3$)). Anal. calcd for $C_{40}H_{46}N_2SbO_2F_3$ (765.07 g mol^{-1}) C 62.8, H 6.1; Found C 62.9, H 6.4. ESI–MS: Positive mode – *m*/*z* 803 [M + K]$^+$ (5%); *m*/*z* 651 [M-CF$_3$COO]$^+$ (100%); *m*/*z* 649 [M–CF$_3$COO–H$_2$]$^+$ (6%). Negative mode – (clusters of CF$_3$COONa): *m*/*z* 1065(CF$_3$COONa)$_7$ + CF$_3$COO]$^-$ (2%); *m*/*z* 929 [(CF$_3$COONa)$_6$ + CF$_3$COO]$^-$ (4%); *m*/*z* 793 [(CF$_3$COONa)$_5$ + CF$_3$COO]$^-$ (11%); *m*/*z* 657 [(CF$_3$COONa)$_4$ + CF$_3$COO]$^-$ (29%); *m*/*z* 521 [(CF$_3$COONa)$_3$ + CF$_3$COO]$^-$ (100%); *m*/*z* 385 [(CF$_3$COONa)$_2$ + CF$_3$COO]$^-$ (29%); *m*/*z* 249 [CF$_3$COONa + CF$_3$COO]$^-$ (89%); *m*/*z* 113 [CF$_3$COO]$^-$ (8%); *m*/*z* 69 [CF$_3$]$^-$ (4%). IR (cm^{-1}): 3356m ν(NH), 1703s ν_a(CO$_2$), 1191vs, 1143s ν(CF). IR spectrum of single-crystals of **6a**: 3357w ν(NH), 3196m ν(OH), 1705m, 1678s ν_{as}(CO$_2$), 1192s, 1148s ν(CF).

4.3.4. {2-[CH=N(2′,6′-*i*-Pr$_2$C$_6$H$_3$)]C$_6$H$_4$}Sb(CF$_3$SO$_3$)[{2-[CH$_2$NH(2′,6′-*i*-Pr$_2$C$_6$H$_3$)]C$_6$H$_4$} (**7**)

Compound **7** was prepared analogously to compound **4**. CF_3SO_3H (17 μL, 0.20 mmol); compound **3** (0.130 g, 0.20 mmol). Yield of **7** 0.122 g, 77%; m.p. 191–192 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.38 (d (broad), 3H, CH(CH_3)$_2$), 0.93 (d (broad), 3H, CH(CH_3)$_2$), 1.00 (d (broad), 6H, CH(CH_3)$_2$), 1.11 (d (broad), 12H, CH(CH_3)$_2$), 1.84 (sept, 1H, CH(CH$_3$)$_2$–NH(2,6-*i*-Pr$_2$C$_6$H$_3$)), 2.72 (sept, 2H, CH(CH$_3$)$_2$–CH=N(2,6-*i*-Pr$_2$C$_6$H$_3$)), 2.99 (sept, 1H, CH(CH$_3$)$_2$–NH(2,6-i-Pr$_2$C$_6$H$_3$)), 4.23 and 4.40 (AX system, 2H, NCH_2), 7.06–7.26 (m, 10H, C$_6H_4$, NH(2,6-*i*-Pr$_2$C$_6$H$_3$) and (2,6-*i*-Pr$_2$C$_6$H$_3$)), 7.73 (dd, 1H, C$_6H_4$), 7.74 (dd, 1H, C$_6H_4$), 7.90 (dd, 1H, C$_6H_4$), 7.99 (d, 1H, C$_6H_4$), 8.53 (d, 1H, C$_6H_4$), 8.61 (s, 1H, CH=N(2,6-*i*-Pr$_2$C$_6$H$_3$)). Anal. calcd for $C_{39}H_{46}N_2SbO_3SF_3$ (801.68 g mol^{-1}) C 58.4, H 5.8; Found C 58.7, H 5.9. ESI–MS: Positive mode – *m*/*z* 651 [M-CF$_3$SO$_3$]$^+$ (100%). Negative mode – *m*/*z* 149 [CF$_3$SO$_3$]$^-$ (100%). ESI–MS: Positive mode – *m*/*z* 651 [M-CF$_3$SO$_3$]$^+$ (100%). Negative mode – *m*/*z* 149 [CF$_3$SO$_3$]$^-$ (100%). IR (cm^{-1}): 3354w ν(NH), 1306vs ν_a(SO$_3$), 1231s, 1212vs ν(CF), 1023s ν_s(SO$_3$).

4.3.5. {2-[CH=N(2′,6′-*i*-Pr$_2$C$_6$H$_3$)]C$_6$H$_4$}Sb(FcCOO)[{2-[CH$_2$NH(2′,6′-*i*-Pr$_2$C$_6$H$_3$)]C$_6$H$_4$} (**8**)

The suspension of compound **3** (0.235 g, 0.36 mmol) in hexane (15 mL) was added to the suspension of FcCOOH (0.083 g, 0.36 mmol) in hexane (10 mL). The resulting mixture was stirred for an additional 1 h at room temperature. Evaporation of mixture gave **8**. The resulting orange powder was washed with hexane (5 mL) to give **8**. Yield 0.259 g, 82%; m.p. 168–169 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.75 (m (broad), 12H, CH(CH_3)$_2$), 1.30 (d, 6H, CH(CH_3)$_2$), 1.39 (d, 6H, CH(CH_3)$_2$), 1.85 (sept (broad), 1H, CH(CH$_3$)$_2$–NH(2,6-*i*-Pr$_2$C$_6$H$_3$)), 3.13 (sept (broad), 1H, CH(CH$_3$)$_2$–NH(2,6-*i*-Pr$_2$C$_6$H$_3$)), 3.62 (sept, 2H, CH(CH$_3$)$_2$–CH=N(2,6-*i*-Pr$_2$C$_6$H$_3$)), 3.91 (s, 5H, Cp), 3.98 and 4.79 (AX system, 2H, NCH_2), 4.02 (s, 1H, NH(2,6-*i*-

Table 1
Crystallographic data for **3**, **5**, **6a** and **7a**.

	3	**5**	**6a**	**7a**
Empirical formula	$C_{38}H_{44}BiClN_2$	$C_{40}H_{49}N_2O_2Sb$	$C_{40}H_{46}F_3N_2O_2Sb.C_2HF_3O_2$	$C_{39}H_{47}F_3N_2O_3SSb.CF_3O_3S$ $0.5(C_6H_6)$
Cryst syst	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	P − 1	Cc	P − 1	P − 1
a [Å]	11.6330(9)	9.9333(5)	10.8670(12)	10.6460(9)
b [Å]	12.5511(11)	22.7440(3)	11.9320(7)	12.2800(9)
c [Å]	13.1690(9)	16.8212(4)	17.3081(14)	20.1551(12)
α [°]	90.218(6)	90	71.076(5)	80.908(5)
β [°]	109.429(6)	105.861(3)	85.882(6)	75.679(6)
γ [°]	103.405(5)	90	77.799(6)	64.477(6)
Z	2	4	2	2
μ [mm^{-1}]	5.120	0.789	0.734	0.761
D_x [Mg m^{-3}]	1.461	1.293	1.408	1.431
Cryst size [mm]	0.35 × 0.34 × 0.23	0.25 × 0.25 × 0.18	0.40 × 0.13 × 0.08	0.30 × 0.21 × 0.15
θ range, [°]	1–27.5	1–27.5	1–27.5	1–27.5
T_{min}, T_{max}	0.869, 0.912	0.869, 0.912	0.846, 0.957	0.875, 0.946
No. of reflections measured	33 109	26 002	37 192	48 248
No. of unique reflns, R_{int}[a]	8055, 0.045	7901, 0.050	9390, 0.060	10 478, 0.043
No. of observed reflns [$I > 2\sigma(I)$]	7121	6938	7483	8734
No. of parameters	398	406	496	518
S[b] all data	1.118	1.110	1.090	1.112
Final R[b] indices [$I > 2\sigma(I)$]	0.030	0.036	0.049	0.045
$wR2$[b] indices (all data)	0.061	0.058	0.090	0.083
$\Delta\rho$, max., min. [e Å^{-3}]	1.519, −1.173	0.532, −0.340	1.223, −0.788	0.490, −0.504

[a] $R_{int} = \sum\left|F_o^2 - F_{o,mean}^2\right| / \sum F_o^2$.

[b] $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$, $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$.

$Pr_2C_6H_3$)), 4.05 (m, 1H, Cp(COO)Fe), 4.09 (m, 1H, Cp(COO)), 4.93 (m, 1H, Cp(COO)Fe), 4.96 (m, 1H, Cp(COO)Fe), 6.86–7.02 (m, 8H, C_6H_4, NH(2,6-*i*-$Pr_2C_6H_3$) and CH=N(2,6-*i*-$Pr_2C_6H_3$)), 7.20 (m, 2H, C_6H_4), 7.52 (m, 2H, C_6H_4), 7.58 (d, 1H, C_6H_4), 7.98 (s, 1H, *CH*=N(2,6-*i*-$Pr_2C_6H_3$)), 8.99 (d, 1H, C_6H_4). ^{13}C NMR (100.61 MHz, C_6D_6, 25 °C): δ = 25.3 and 28.2 (s, $CH(CH_3)_2$ and $CH(CH_3)_2$), 59.1 (s, NCH_2), 70.2, 70.9, 71.1, 71.2, 71.4 (s, Cp and Cp(COO)), 75.8 (s, Cp(COO)-*ipso*), 124.1, 124.2, 124.3, 127.2, 128.8, 129.6, 129.8, 129.9, 133.2, 133.4, 134.7, 137.6, 140.0, 140.4, 143.2, 144.8, 145.0, 146.5, 148.0, 153.1 (s, C_6H_4), 168.4 (s, *C*H=N(2,6-*i*-$Pr_2C_6H_3$)), 175.8 (s, *C*=O). Anal. calcd for $C_{49}H_{55}N_2SbO_2Fe$ (881.65 g mol^{-1}) C 66.8, H 6.3; Found C 66.9, H 6.5. ESI/MS: Positive mode – *m*/*z* 919 $[M + K]^+$ (56%); *m*/*z* 651 $[M\text{-}Fe(Cp)_2COO]^+$ (100%). IR (cm^{-1}): 3357mν(NH), 1626s $\nu_{as}(CO_2)$.

4.4. X-ray structure determination

4.4.1. Crystallography

The X-ray data for colourless crystals of **3**, **5**, **6a** and **7a** were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K_α radiation (λ = 0.71073 Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN [17]. The absorption was corrected by integration methods [18]. Structures were solved by direct methods (Sir92) [19] and refined by full matrix least-square based on F^2 (SHELXL97) [20]. Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2U_{eq}$(pivot atom) or of $1.5U_{eq}$ for the methyl moiety with C–H = 0.96, 0.97, 0.98 and 0.93 Å for methyl, methylene, methine and hydrogen atoms in aromatic ring, respectively. The N–H and O–H hydrogen atoms are placed according to Fourier difference map. One of the isopropyl groups in **3** is disordered and the disorder was treated by standard constraints and restraints from SHELXL97 program [21]. There is disordered solvent (benzene) in the structure of **7a**. Attempts were made to model this disorder or split it into two positions, but were unsuccessful. The Squeeze routine of the program Platon [22] was used to correct the data for the presence of disordered solvent. A potential solvent volume of 194 Å^3 was found. 40 electrons per unit cell worth of scattering were located in the void. The calculated stoichiometry of solvent was calculated to be one molecule of benzene per unit cell which results in 42 electrons per unit cell. The crystallographic data are summarized in Table 1.

Acknowledgements

The authors wish to thank the Faculty of Chemical Technology of the University of Pardubice for continuous financial support.

Appendix A. Supplementary material

CCDC 932689, 932690, 932691 and 932692 contain 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.

References

[1] C.I. Rat, C. Silvestru, H.J. Breunig, Coord. Chem. Rev. 257 (2013) 818.
[2] (a) D.A. Atwood, A.H. Cowley, J. Ruiz, Inorg. Chim. Acta 198–200 (1992) 271;
(b) C.J. Carmalt, A.H. Cowley, R.D. Culp, R.A. Jones, S. Kamepalli, N.C. Norman, Inorg. Chem. 36 (1997) 2770;
(c) C.J. Carmalt, D. Walsh, A.H. Cowley, N.C. Norman, Organometallics 16 (1997) 3597;
(d) S. Kamepalli, C.J. Carmalt, R.D. Culp, A.H. Cowley, R.A. Jones, N.C. Norman, Inorg. Chem. 35 (1996) 6179.
[3] For example see: (a) L.M. Opris, A. Silvestru, C. Silvestru, H.J. Breunig, E. Lork, Dalton Trans. (2003) 4367;
(b) L.M. Opris, A. Silvestru, C. Silvestru, H.J. Breunig, E. Lork, Dalton Trans. (2004) 3575;
(c) L.M. Opris, A.M. Preda, R.A. Varga, H.J. Breunig, C. Silvestru, Eur. J. Inorg. Chem. (2009) 1187;
(d) L. Balazs, H.J. Breunig, E. Lork, A. Soran, C. Silvestru, Inorg. Chem. 45 (2006) 2341.
[4] For example see: (a) I.J. Casely, J.W. Ziller, M. Fang, F. Furche, W.J. Evans, J. Am. Chem. Soc. 133 (2011) 5244;
(b) I.J. Casely, J.W. Ziller, B.J. Mincher, W.J. Evans, Inorg. Chem. 50 (2011) 1513;
(c) S.F. Yin, J. Muruyama, T. Yamashita, S. Shimada, Angew. Chem. Int. Ed. 47 (2008) 6590;
(d) M. Bao, T. Hayashi, S. Shimada, Organometallics 26 (2007) 1816;

(e) A. Fridrichová, T. Svoboda, R. Jambor, Z. Padělková, A. Růžička, M. Erben, R. Jirásko, L. Dostál, Organometallics 28 (2009) 5522;
(f) L. Dostál, R. Jambor, A. Růžička, J. Holeček, Organometallics 27 (2008) 2169;
(g) L. Dostál, R. Jambor, A. Růžička, M. Erben, R. Jirásko, Z. Černošková, J. Holeček, Organometallics 28 (2009) 2633.
[5] P. Šimon, F. de Proft, R. Jambor, A. Růžička, L. Dostál, Angew. Chem. Int. Ed. 49 (2010) 5468.
[6] (a) L. Dostál, R. Jambor, A. Růžička, R. Jirásko, V. Lochař, L. Beneš, F. de Proft, Inorg. Chem. 48 (2009) 10495;
(b) L. Dostál, R. Jambor, A. Růžička, A. Lyčka, J. Brus, F. de Proft, Organometallics 27 (2008) 6059;
(c) P. Šimon, R. Jambor, A. Růžička, A. Lyčka, F. de Proft, L. Dostál, Dalton Trans. 41 (2012) 5140;
(d) L. Dostál, R. Jambor, A. Růžička, R. Jirásko, E. Černošková, L. Beneš, F. de Proft, Organometallics 29 (2010) 4486.
[7] (a) L. Dostál, R. Jambor, R. Jirásko, Z. Padělková, Aleš Růžička, Jaroslav Holeček, J. Organomet. Chem. 695 (2010) 392;
(b) L. Dostál, P. Novák, R. Jambor, A. Růžička, I. Císařová, R. Jirásko, J. Holeček, Organometallics 26 (2007) 2911.
[8] (a) T. Svoboda, R. Jambor, A. Růžička, Z. Padělková, M. Erben, R. Jirásko, L. Dostál, Eur. J. Inorg. Chem. (2010) 1663;
(b) T. Svoboda, L. Dostál, R. Jambor, A. Růžička, R. Jirásko, A. Lyčka, Inorg. Chem. 50 (2011) 6411;
(c) T. Svoboda, R. Jambor, A. Růžička, R. Jirásko, A. Lyčka, F. De Proft, L. Dostál, Organometallics 31 (2012) 1725;
(d) Mairychová, T. Svoboda, M. Erben, A. Růžička, L. Dostál, R. Jambor, Organometallics 35 (2013) 157;
(e) H.J. Breunig, M.G. Nema, C. Silvestru, A.P. Soran, R.A. Varga, Dalton Trans. 39 (2010) 11277.
[9] (a) L. Dostál, I. Císařová, R. Jambor, A. Růžička, R. Jirásko, J. Holeček, Organometallics 25 (2006) 4366;
(b) K. Peveling, M. Schurmann, S. Herres-Pawlis, C. Silvestru, K. Jurkschat, Organometallics 30 (2011) 5181.
[10] (a) L. Dostál, R. Jambor, A. Růžička, R. Jirásko, J. Holeček, F. De Proft, Dalton Trans. 40 (2011) 8922;
(b) M. Chovancová, R. Jambor, A. Růžička, R. Jirásko, I. Císařová, L. Dostál, Organometallics 28 (2009) 1934.
[11] (a) L. Dostál, R. Jambor, A. Růžička, P. Šimon, Eur. J. Inorg. Chem. (2011) 2380;
(b) P. Šimon, R. Jambor, A. Růžička, L. Dostál, Organometallics 32 (2013) 239.
[12] A.M. Preda, C.I. Rat, C. Silvestru, H.J. Breunig, H. Lang, T. Ruffer, M. Mehring, Dalton Trans. 42 (2013) 1144.
[13] M. Hejda, A. Lyčka, R. Jambor, A. Růžička, L. Dostál, Dalton Trans. 42 (2013) 6417.
[14] R. Jirásko, M. Holčapek, Mass Spectrom. Rev. 30 (2011) 1013.
[15] S.P. Gejji, K. Hermansson, J. Lindgren, J. Phys. Chem. 97 (1997) 3712.
[16] J.W. Keller, J. Phys. Chem. A 108 (2004) 4610.
[17] D. Zhao, W. Gao, Y. Mu, L. Ye, Chem. Eur. J. 16 (2010) 4394.
[18] Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307.
[19] P. Coppens, in: F.R. Ahmed, S.R. Hall, C.P. Huber (Eds.), Crystallographic Computing, Munksgaard, Copenhagen, 1970, p. 255.
[20] A. Altomare, G. Cascarone, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M.J. Camalli, Appl. Crystallogr. 27 (1994) 1045.
[21] G.M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, 2008.
[22] P. van der Sluis, A.L. Spek, Acta Crystallogr. A 46 (1990) 194.