Synthesis and Spectroscopic Structural Elucidation of Some Novel Heterobimetallic Complexes of Monoorganotin(IV)

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ABSTRACT

Novel heterobimetallic organotin(IV) derivatives of the types $R'N(CH_2CH_2O)_2Sn(R)\{(OCH_2CH_2)NR'(OCH_2CH_2O)M(OCH_2CH_2)_2NR'\}$, and $[RSn(OGO)\{OV(OGO)\}_2]_2$ (where R = Bu, R′ = H, M = Al **1**; R = Bu, R′ = Me, M = Al **2**; R = Bu, R′ = Bu, M = Al **3**; R = Bu, R′ = Ph, M = Al **4**; R = Bu, R′ = Me, M = OV **5**; R = Bu, R′ = Ph, M = OV **6**; R = Ph, R′ = Me, M = OV **7**; R = Ph, R′ = Ph, M = OV **8**; R = Bu, G = $CHMeCH_2CMe_2$ **9**; R = Bu, G = $CMe_2CH_2CH_2CMe_2$ **10**; R = Ph, G = $CHMeCH_2CMe_2$ **11**; R = Ph, G = $CMe_2CH_2CH_2CMe_2$ **12**) have been prepared and characterised by elemental analyses, molecular weight measurements, IR and NMR (^1H, ^{27}Al, ^{51}V and ^{119}Sn) studies. Cryoscopic molecular weight determinations show that complexes **1-8** are monomeric, whereas **9-12** are dimeric.

INTRODUCTION

Although there has been considerable development during the past two decades in the heterometallic alkoxides chemistry /1-6/. heterobimetallic derivatives involving glycolate/diethanolaminate/ triethanolaminate moieties are of only recent origin /7/. Surprisingly, known examples of heterobimetallic derivatives involving organotin(IV) moieties are limited in number /4,5,7/. In continuation of our recent studies on organotin(IV) heterometallic coordination complexes based on di- and tri- hydroxy ligands /8/, we report in this paper the synthesis and characterisation of new types of heterobimetallic monoorganotin(IV) complexes.

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EXPERIMENTAL

All preparations and subsequent manipulations were carried out under moisture-free environment. All glassware was carefully dried prior to use. Reagent grade benzene and *n*-hexane were dried by refluxing over sodium benzophenone ketyl, while dichloromethane was dried by refluxing over phosphorous pentoxide and distilled immediately prior to use.

The literature procedures were used for the preparations of $Al(OPr^i)_3$ /9/, $BuSn(OPr^i)_3$ /10/, $OV(OPr^i)_3$ /11/, $PhSn(OPr^i)_3$ /4/, $R'N(CH_2CH_2O)_2Sn(R)(OPr^i)$ /8(b)/, $R'N(CH_2CH_2O)_2Al(OCH_2CH_2NR'CH_2CH_2OH)$ /12/, $R'N(CH_2CH_2O)V(O)$ $(OCH_2\text{-}CH_2NR'CH_2CH_2OH)$ /13/, $RSn(OGO)(OPr^i)$ /14/, and $OV(OGO)(OGOH)$ /13/. Isopropyl alcohol in the azeotrope was determined by an oxidimetric method. Vanadium was determined by redox- titration method, using N-phenyl anthranilic acid as an indicator. Tin was determined as oxide, aluminium as oxinate and nitrogen by Kjeldahl's method.

NMR spectra were recorded using a JEOL AL 300MHz spectrometer : ^1H (300.40MHz), ^{27}Al (78.18 MHz), ^{51}V (78.90 MHz), and ^{119}Sn (111.95 MHz), IR spectra (4000-400 cm^{-1}) were recorded as Nujol mulls using CsI optics on a Nicolet Magna-550 spectrophotometer. Microanalysis (C, H, and N) were carried out on a Perkin-Elmer 2400 II CHNS/O analyser of this department. Molecular weights were determined cryoscopically in benzene solution.

Preparation of new heterobimetallic butyltin(IV) derivatives

$[HN(CH_2CH_2O)_2SnBu(OCH_2CH_2)NH(CH_2CH_2O)Al(OCH_2CH_2)_2NH]$, 1

The reaction mixture containing equimolar amounts of $BuSn\{(OCH_2CH_2)_2NH\}(OPr^i)$ (3.11 g, 9.19 mmol) and $NH(OCH_2CH_2)_2Al$ $\{(OCH_2CH_2NHCH_2CH_2OH)\}$ (2.15 g, 9.17 mmol) in benzene (~0.60 mL) was refluxed for 6 h, during which the liberated isopropyl alcohol was azeotropically distilled out and determined periodically to monitor the progress and completion of the reaction. After completion of the reaction (as was evident by the amount of isopropyl alcohol collected, 0.54 g), the refluxing was stopped and the system allowed to cool to room temperature. The volatiles from the solution were removed under reduced pressure to obtain the title compound as a light yellow solid, which was purified by recrystallisation from 1:2 mixture of dichloromethane and *n*-hexane at –20°C. Yield 3.53 g (75%).

The procedure similar to **1** was used for the synthesis of **2** - **8**. The quantities of the reactants used in each case are given below:

2: $MeN\{(CH_2CH_2O)_2Sn(Bu)\}(OPr^i)$ (2.52 g, 7.15 mmol) and $MeN(CH_2\text{-}CH_2O)_2Al(OCH_2CH_2NMeCH_2CH_2OH)$ (1.88 g, 7.16 mmol).

3: $BuN\{(CH_2CH_2O)_2Sn(Bu)\}(OPr^i)$ (3.17 g, 8.04 mmol) and $BuN(CH_2\text{-}CH_2O)_2Al(OCH_2CH_2NBuCH_2CH_2OH)$ (2.78 g, 8.02 mmol).

4: $PhN\{(CH_2CH_2O)_2Sn(Bu)\}(OPr^i)$ (2.78 g, 6.71 mmol) and $PhN(CH_2\text{-}CH_2O)_2Al(OCH_2CH_2NPhCH_2CH_2OH)$ (2.59 g, 6.70 mmol).

5: $MeN\{(CH_2CH_2O)_2Sn(Bu)\}(OPr^i)$ (1.72 g, 4.88 mmol) and $MeN(CH_2CH_2O)_2V(O)(OCH_2CH_2NMeCH_2CH_2OH)$ (1.48 g, 4.89 mmol).

6: $PhN\{(CH_2CH_2O)_2Sn(Bu)\}(OPr^i)$ (1.94 g, 4.68 mmol) and $PhN(CH_2CH_2O)_2V(O)(OCH_2CH_2NPhCH_2CH_2OH)$ (2.00 g, 4.69 mmol).

7: $MeN\{(CH_2CH_2O)_2Sn(Ph)\}(OPr^i)$ (1.82 g, 4.89 mmol) and $MeN(CH_2CH_2O)_2V(O)(OCH_2CH_2NMeCH_2CH_2OH)$ (1.48 g, 4.89 mmol).

8: $PhN\{(CH_2CH_2O)_2Sn(Ph)\}(OPr^i)$ (1.75 g, 4.03 mmol) and $PhN(CH_2CH_2O)_2V(O)(OCH_2CH_2NPhCH_2CH_2OH)$ (1.72 g, 4.03 mmol).

***$[BuSn(OCHMeCH_2CMe_2O)OV(OCHMeCH_2CMe_2O)_2]_2$*, 9**

A benzene (~ 40 mL) solution containing $BuSn(OCHMeCH_2CMe_2O)(OPr^i)$ (2.02 g, 5.75 mmol) and $OV(OCHMeCH_2CMe_2O)(OCHMeCH_2\text{-}CMe_2OH)$ (1.73 g, 5.76 mmol) was refluxed with continuous azeotropic removal of the liberated isopropyl alcohol till the distillate showed only negligible presence of an oxidizable material. After completion of the reaction, refluxing was stopped and volatiles from the solution were removed under reduced pressure to obtain the title compound, which was dissolved in dichloromethane (10 mL) and *n*-hexane (4 mL) and the resulting solution was kept at –20°C for 7 days to afford analytically pure product **9** as a viscous liquid 3.38 g.

Complexes **10** - **12** were also prepared and purified by the procedure similar to that described for **9**. The quantities of reactants used in each case are given below :

10: $BuSn(OCMe_2CH_2CH_2CMe_2O)(OPr^i)$ (1.89 g, 4.98 mmol) and $OV(OCMe_2CH_2CH_2CMe_2O)(OCMe_2CH_2CH_2CMe_2OH)$ (1.77 g, 4.96 mmol).

11: $PhSn(OCHMeCH_2CMe_2O)(OPr^i)$ (1.01 g, 2.72 mmol) and $OV(OCHMeCH_2CMe_2O)(OCHMeCH_2CMe_2OH)$ (0.82 g, 2.73 mmol).

12: $PhSn(OCMe_2CH_2CH_2CMe_2O)(OPr^i)$ (1.41 g, 3.53 mmol) and $OV(OCMe_2CH_2CH_2CMe_2O)(OCMe_2CH_2CH_2CMe_2OH)$ (1.25 g, 3.50 mmol).

Analytical and some physical data for the new complexes are listed in Table 1.

RESULTS AND DISCUSSION

Reactions of $[RSn\{OCH_2CH_2\}_2NR'(OPr^i)]_2$/$[RSn(OGO)(OPr^i)]_2$ with $R'N(CH_2CH_2O)_2M\{OCH_2CH_2\}NR'(CH_2CH_2OH)\}$ (M = Al and OV) or $[OV(OGO)(OGOH)_2]_2$ afford novel heterobimetallic organic(IV) complexes **1** - **12** according to the reactions as illustrated in equations 1 and 2 :

Table 1. Some analytical and physical data for **(1)-(12)**

Emperical formula Yield Colour and state	Liberated Pr^iOH Found (Calcd.)	% Analysis Found (Calcd.) Sn	Al/V	C	H	N	Mol. Wt. Found (Calcd.)
$C_{16}H_{36}N_3AlO_6Sn$ **1** 3.53 Light yellow solid	0.54 (0.55)	23.1 (23.2)	5.2 (5.2)	37.48 (37.52)	7.06 (7.08)	8.19 (8.20)	532 (512)
$C_{19}H_{42}N_3AlO_6Sn$ **2** 3.96 White solid	0.43 (0.43)	21.4 (21.4)	4.8 (4.9)	41.41 (41.13)	7.80 (7.63)	7.30 (7.59)	578 (554)
$C_{28}H_{60}N_3AlO_6Sn$ **3** 5.47 Orange viscous liquid	0.48 (0.48)	17.4 (17.4)	3.9 (3.9)	49.76 (49.37)	9.51 (8.88)	6.10 (6.17)	690 (681)
$C_{34}H_{48}N_3AlO_6Sn$ **4** 4.96 White solid	0.40 (0.40)	16.0 (16.0)	3.6 (3.6)	54.94 (55.09)	6.58 (6.53)	5.28 (5.67)	756 (741)
$C_{19}H_{42}N_3O_7SnV$ **5** 2.90 Yellow viscous solid	0.28 (0.29)	19.9 (19.9)	8.5 (8.6)	38.16 (38.36)	7.12 (7.12)	7:00 (7.06)	612 (594)
$C_{34}H_{48}N_3O_7SnV$ **6** 3.65 Brown sticky solid	0.28 (0.28)	15.1 (15.2)	6.6 (6.5)	51.67 (52.27)	5.99 (6.19)	5.35 (5.38)	809 (797)

$C_{[illegible]}H_{38}N_3O_7SnV$ 2.99 Orange floppy solid	**7**	0.29 (0.29)	19.3 (19.3)	8.2 (8.3)	40.74 (41.02)	6.65 (6.23)	6.08 (6.83)	622 (614)
$C_{36}H_{44}N_3O_7SnV$ 3.22 Brown solid	**8**	0.24 (0.24)	14.8 (14.8)	6.3 (6.4)	54.11 (54.01)	5.50 (5.54)	5.19 (5.24)	842 (800)
$C_{22}H_{45}O_7SnV$ 3.38 Red brown viscous liquid	**9**	0.34 (0.34)	20.0 (20.1)	8.6 (8.6)	44.67 (44.68)	7.61 (7.67)	-	12[illegible] (591)
$C_{28}H_{57}O_7SnV$ 2.62 White yellow solid	**10**	0.30 (0.30)	17.6 (17.6)	7.5 (7.6)	49.72 (49.78)	8.48 (8.50)	-	1365 (675)
$C_{24}H_{41}O_7SnV$ 1.16 Brown semi-solid	**11**	0.16 (0.16)	19.4 (19.4)	8.3 (8.3)	47.11 (47.15)	6.74 (6.76)	-	1240 (611)
$C_{30}H_{53}O_7SnV$ 1.76 White solid	**12**	0.21 (0.21)	17.0 (17.1)	7.3 (7.3)	51.78 (51.80)	6.60 (7.68)	-	1410 (695)

$$[RSn(OCH_2CH_2)_2NR']\{(OPr^i)]_2 + R'N(CH_2CH_2O)_2M\{(OCH_2CH_2)NR'(CH_2CH_2OH)\} \xrightarrow[\text{reflux}]{\text{benzene,}}$$

$$R'N(CH_2CH_2O)Sn(R)\{(OCH_2CH_2)NR'(CH_2CH_2O)M(OCH_2CH_2)_2NR'\} + Pr^iOH \quad (1)$$

1: R = Bu, R′ = H, M = Al; **2**: R = Bu, R′ = Me, M = Al; **3**: R = Bu, R′ = Bu, M = Al; **4**: R = Bu, R′ = Ph, M = Al; **5**: R = Bu, R′ = Me, M = OV; **6**: R = Bu, R′ = Ph, M = OV; **7**: R = Ph, R′ = Me, M = OV; **8**: R = Ph, R′ = Ph, M = OV

$$2\,RSn(OGO)(OPr^i) + [OV(OGO)(OGOH)]_2 \xrightarrow[\text{reflux}]{\text{benzene}} [RSn(OGO)OV(OGO)_2]_2 + Pr^iOH\uparrow \quad (2)$$

9: R = Bu, G = $CHMeCH_2CMe_2$; **10**: R = Bu, G = $CMe_2CH_2CH_2CMe_2$; **11**: R = Ph, G = $CHMeCH_2CMe_2$; **12**: R = Ph, G = $CMe_2CH_2CH_2CMe_2$

These heterobimetallic complexes **1** - **12** are viscous liquids or solids (Table 1) soluble in organic solvents and, when freshly prepared, exhibit monomeric nature for **1** - **8** and dimeric nature for **9** - **12**. On ageing complexes **1** - **8** show lower solubility in organic solvents possibly due to oligomerization, which precluded molecular weight determinations of aged samples.

Spectroscopic studies

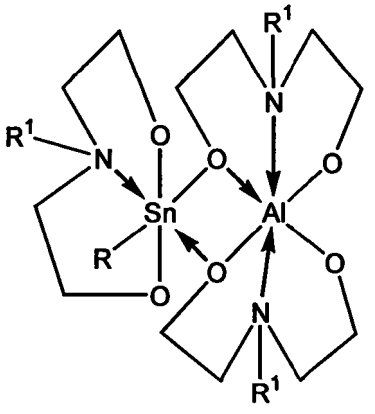
Infrared spectra of **1** - **8** *exhibit characteristic absorptions of organic moieties* /13-15/ such as diethanolaminates, glycolates, and butyl/phenyl group bonded to tin(IV) present in the new complexes (Table 2) at : 3128 ν(N-H), 1452-1420 ν(CH_2). 1370-1338 ν(C-N), 969-960 ν(V=O); 669-653 ν(Al-O), 592-576 ν(Sn-C), 550-546 ν(Sn-O), 465-458 ν(V-O) and 452-435 ν(M←N) (M = Sn, OV, Al). Lowering by ~ 10 cm^{-1} in the ν(C-N) vibrational frequency for amino group in **2** - **8** compared to these found in free diethanolamines may be ascribed to the formation of M←N dative bond. The characteristic bands for glycolate /16/ moieties in derivatives **9** - **12** appear at 1365-1354 cm^{-1} due to δ (C-H) vibrations for CMe_2 or CHMe group, 766-693 cm^{-1} for ρ (CH_2) rocking, 1100-1050 for ν(C-O), 965-960 for ν(V=O) and 669-465 cm^{-1} for ν(M-O) (M = Sn, OV) stretching vibrations.

^{1}H NMR spectra of **1** - **8** exhibit signals (Table 2) characteristic of diethanolaminate moieties attached to tin(IV)/Al/V=O in the δ 2.65-3.59 (NCH_2), 3.72-3.85 (OCH_2), 2.35-2.41 (NMe), and 6 61-7.15 (NPh) ppm regions. Signals for glycolate moieties in **9** - **12** appear at δ 1.16–1.18 (CHMe), 1.24 (CMe), 1.51–1.58 (CH_2) and 4.35-4.37 (CHMe). Signals due to butyltin(IV) protons in complexes **1** - **6** and **9** - **10** appears as complex multiplets in the δ 0.80-1.68 ppm region.

The appearance of ^{27}Al NMR signals in the δ 0.7 - 9 ppm region for the complexes **1** - **4**, is consistent with the chemical shifts reported in literature /17/ for six-coordinate aluminium (Structure I).

The ^{51}V NMR signals (Table 2) for the complexes **5 - 8** in the δ -438 to -534 region are consistent with the chemical shifts reported in literature for six-coordinate vanadium(V) having VNO_5 core (Structure II) /11,18/. However, the complexes **9 - 12** display signals in the δ -560 to -681 region, which are characteristic of hexacoordinated oxovanadium(V) complexes featuring a VO_6 core /19/ (Structure III).

The ^{119} Sn NMR spectra for complexes **1 - 8** and **9 - 12** display signals in the δ -549 to -591 and δ -417 to -467 regions, which are in agreement with six- and five-coordinate tin(IV) /20/ (Structures I and II as well as III), respectively.



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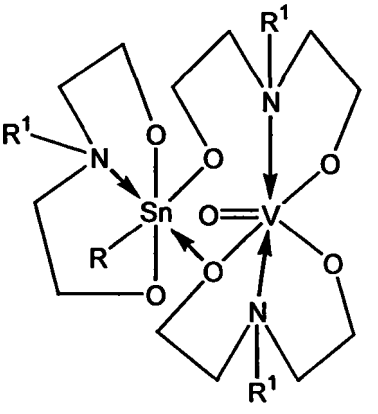
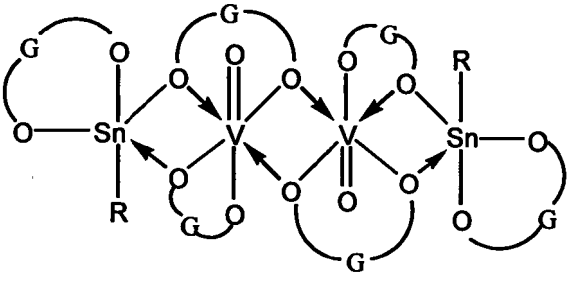


II



III

Table 2

IR (cm^{-1}) and NMR data (δ. ppm) for complexes (1)-(12)

Compound	IR	^1H	$^{27}Al/^{51}V$	^{119}Sn
1	1452, 1440ν(CH_2); 3120ν(N-H); 660ν(Al-O); 590ν (Sn-C); 552ν(Sn-O); 450ν(Sn←N); 442ν(Al←N)	0.92 (t, 3H, $Me(CH_2)_3Sn$); 1.16 (m, 2H, Me CH_2 $(CH_2)_2Sn$); 1.33 (m, 2H, $MeCH_2CH_2CH_2Sn$); 1.64 (t, 2H, $Me(CH_2)_2CH_2Sn$); 2.86 (m, 12H, NCH_2); 3.80 (m, 15H, OCH_2+NH)	7	-582
2	1454, 1438ν(CH_2); 1361, 1348ν(C-N); 669ν(Al-O); 592ν (Sn-C); 546ν(Sn-O); 449ν(Sn←N); 438ν(Al←N)	0.83 (t, 3H, $Me(CH_2)_3Sn$); 1.17 (m, 2H, $MeCH_2$ $(CH_2)_2Sn$); 1.28 (m, 2H, $MeCH_2CH_2CH_2Sn$); 1.61 (t, 2H, $Me(CH_2)_2CH_2Sn$); 2.38 (s, 9H, NMe); 2.63 (m, 12H, NCH_2); 3.71 (m, 12H, OCH_2)	0.7	-586
3	1446, 1438ν(CH_2); 1359, 1342ν(C-N); 654ν(Al-O); 590ν (Sn-C); 546ν(Sn-O); 445ν(Sn←N); 435ν(Al←N)	0.91 (t, 12H, $Me(CH_2)_3Sn$+ $Me(CH_2)_3N$); 1.21 (m, 8H, $MeCH_2(CH_2)_2Sn$+ $MeCH_2(CH_2)_2N$); 1.45 (m, 8H, $MeCH_2CH_2CH_2Sn$+ $MeCH_2CH_2CH_2N$); 1.65 (m, 8H, $Me(CH_2)_2CH_2Sn$+ $Me(CH_2)_2CH_2N$); 2.67 (m, 12H, NCH_2); 3.77 (m, 12H, OCH_2)	7	-582
4	1452, 1446ν(CH_2); 1353, 1338ν(C-N); 653ν(Al-O); 576ν (Sn-C); 546ν(Sn-O); 448ν(Sn←N); 438ν(Al←N)	0.91 (t, 3H, $Me(CH_2)_3Sn$); 1.16-1.68 (m, 6H, Me $(CH_2)_3Sn$); 3.25 (m, 12H, NCH_2); 3.85 (m, 12H, OCH_2); 6.72-7.15 (m, 15H, C_6H_5N)	9	-591
5	1430, 1420ν(CH_2); 1362, 1345ν(C-N); 960ν(V=O); 572ν (Sn-C); 550ν(Sn-O); 465ν(V–O); 448n(V←N); 440ν(Sn←N)	0.89 (t, 3H, $Me(CH_2)_3Sn$); 1.35-1.62 (m, 6H, Me $(CH_2)_3Sn$); 2.36, 2.41 (s, 9H, NCH_2); 2.74 (m, 12H, NCH_2); 3.90 (m, 12H, OCH_2)	-438	-549

6	1432, 1425ν(CH_2); 1370, 1355ν(C-N); 962ν(V=O); 578ν (Sn-C); 553ν(Sn-O); 460ν(V-O); 448ν(V←N); 445ν(Sn←N)	0.80 (t, 3H, $Me(CH_2)_3Sn$); 1.13-1.64 (m, 6H, Me $(CH_2)_3Sn$); 3.59 (m, 12H, NCH_2); 3.87 (m, 12H, OCH_2); 6.73-7.10 (m, 15H, C_6H_5N)	-534	-591
7	1452, 1440ν(CH_2); 1362, 1340ν(C-N); 960ν(V=O); 578ν (Sn-C); 555ν(Sn-O); 467ν(V-O); 450ν(V←N); 445ν(Sn←N)	2.37,2.45 (s, 9H, NMe); 2.82 (m, 12H, NCH_2); 3.85 (m, 12H, OCH_2); 6.80-7.15 (m, 5H, C_6H_5N+PhSn)	-465	-575
8	1440, 1438ν(CH_2); 1368, 1358ν(C-N); 960ν(V=O); 576ν (Sn-C); 554ν(Sn-O); 459ν(V-O); 446ν(V←N); 448ν(Sn←N)	3.59 (br, 12H, NCH_2); 3.82 (br, 12H, OCH_2); 6.62, 7.10 (m, 20H, C_6H_5N+PhSn)	-534	-595
9	1360, 1350ν(CMe_2); 1090, 1060ν(C-O); 959ν(V=O); 729 p(CH_2); 578ν(Sn-C); 560ν(Sn-O); 462ν(V-O)	0.94 (t, 3H, $Me(CH_2)_3Sn$); 1.18-1.67 (m, 39H, Me $(CH_2)_3Sn$+CMe_2+CHMe +CH_2); 4.23 (m, 3H, CHMe)	-560	-417
10	1362, 1352ν(CMe_2); 1090, 1058ν(C-O); 960ν(V=O); 720 p(CH_2); 578ν(Sn-C); 556ν(Sn-O); 465ν(V-O)	0.96 (t, 3H, $Me(CH_2)_3Sn$); 1.24-1.78 (m, 54H, Me $(CH_2)_3Sn$+CMe_2+CH_2)	-680	-435
11	1365, 1355ν(CMe_2); 1100, 1070ν(C-O); 960ν(V=O); 720 p(CH_2); 580ν(Sn-C); 558ν(Sn-O); 465ν(V-O)	0.19 (s, 9H, CMe_2); 1.26 (s, 9H, CMe_2); 1.32 (s, 9H, CHMe); 1.52 (m, 6H, CH_2); 4.25 (m, 3H, CHMeN); 7.26-7.40(m, 5H, PhSn)	-560	-449
12	1365, 1360ν(CMe_2); 1150, 1135ν(C-O); 962ν(V=O); 735 p(CH_2); 585ν(Sn-C); 565ν(Sn-O); 468ν(V-O)	1.26 (s, 36H, CMe_2); 1.65 (s, 12H, CH_2); 7.10-7.43 (m, 5H, PhSn)	-681	-440

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