ESI for:

## N-donor Stabilized Tin(II) Cations as Efficient ROP Catalysts for Synthesis of Linear and Star-Shaped PLAs via Activated Monomer Mechanism

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## Table of contents:

Crystallographic data for 2, 7 and 8 THF	<b>S2-S4</b>
Theoretical studies	<b>S5-S11</b>
TG-GCMS of PLA prepared by using 1	S12
NMR spectra of studied compounds and NMR tests	S13-S42
References	S43

Crystal data	
Chemical formula	$C_{31}H_{24}Cl_4N_2Sn$
$M_{ m r}$	685.01
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.0630 (7), 21.331 (3), 13.7750 (15)
β (°)	104.481 (7)
$V(Å^3)$	2862.9 (5)
Ζ	4
Radiation type	Μο Κα
$\mu (mm^{-1})$	1.29
Crystal size (mm)	0.29  imes 0.15  imes 0.15
•	
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
	Multi-scan
Absorption correction	SADABS2016/2 - Bruker AXS area detector scaling and
	absorption correction
$T_{\min}, T_{\max}$	0.644, 0.746
No. of measured, independent	
and	22412 6428 4074
observed $[I > 2\sigma(I)]$	23412, 0438, 4974
reflections	
R <sub>int</sub>	0.026
$(\sin \theta / \lambda)_{max} (Å^{-1})$	0.650
Retinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.025, 0.060, 1.05
No. of reflections	6438
No. of parameters	343
H-atom treatment	H-atom parameters constrained
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	0.52, -0.43

 Table S1. Crystallographic data for 2

Computer programs: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997), *COLLECT* and *DENZO*, *SIR92* (Altomare *et al.*, 1994), *SHELXL2017*/1 (Sheldrick, 2017), *PLATON* (Spek, 2003), *SHELXL97* (Sheldrick, 2008).

Crystal data	
Chemical formula	$C_{14}H_{14}Cl_4N_4Sn_2$
$M_{ m r}$	617.47
Crystal system, space group	Triclinic, P-1
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.5798 (3), 15.3141 (5), 15.8858 (6)
α, β, γ (°)	115.173 (2), 95.224 (2), 106.201 (2)
$V(Å^3)$	1965.58 (12)
Ζ	4
Radiation type	Μο Κα
$\mu (mm^{-1})$	3.09
Crystal size (mm)	0.42  imes 0.28  imes 0.07
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction Multi-scan	
	SADABS2016/2 - Bruker AXS area detector scaling and
	absorption correction
$T_{\min}, T_{\max}$	0.435, 0.746
No. of measured, independent	66961, 9078, 6655
and	
observed $[I > 2\sigma(I)]$	
reflections	
$R_{\rm int}$	0.124
$(\sin \theta / \lambda)_{\text{max}} (\text{\AA}^{-1})$	0.652
Refinement	
$\overline{R[F^2 > 2\sigma(F^2)]}, wR(F^2), S$	0.034, 0.057, 1.00
No. of reflections	9078
No. of parameters	433
H-atom treatment	H-atom parameters constrained
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	0.79, -0.96

 Table S2. Crystallographic data for 7

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.9-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2017*/1 (Sheldrick, 2017), Bruker *SHELXTL*.

Crystal data	
Chemical formula	$C_{20}H_{24}F_6N_4O_8S_2Sn$
$M_{ m r}$	745.24
Crystal system, space group	Triclinic, P-1
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.4888 (4), 13.3072 (6), 13.3311 (6)
α, β, γ (°)	103.695 (2), 105.950 (2), 110.086 (2)
$V(Å^3)$	1414.18 (11)
Ζ	2
Radiation type	Μο Κα
$\mu (mm^{-1})$	1.14
Crystal size (mm)	0.59  imes 0.19  imes 0.19
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction Multi-scan	
	SADABS2016/2 - Bruker AXS area detector scaling and
	absorption correction
$T_{\min}, T_{\max}$	0.578, 0.746
No. of measured,	42712, 6535, 5623
independent and	
observed $[I > 2\sigma(I)]$	
reflections	
R <sub>int</sub>	0.068
$(\sin \theta / \lambda)_{\max} (A^{-1})$	0.652
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.042, 0.117, 1.09
No. of reflections	6535
No. of parameters	401
No. of restraints	393
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}}$ (e Å <sup>-3</sup> )	1.34, -1.57

Table S3. Crystallographic data for  $8^{\cdot}\text{THF}$ 

Computer programs: Bruker Instrument Service vV6.2.3, APEX3 v2016.9-0 (Bruker AXS), SAINT V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, SHELXL2017/1 (Sheldrick, 2017), Bruker SHELXTL.

## **Theoretical studies**

A DFT computational study was carried out in order to gain more insight on the formation of the studied complexes and their steric and electronic properties. All calculations were performed both for the neutral complexes (1', 2, 3 and 7') and for the ionic complexes (1, 4-8), where 1' is [L<sup>0</sup> $\rightarrow$ SnCl<sub>2</sub>] (L<sup>0</sup> = 2-((CH<sub>3</sub>)C=N(C<sub>6</sub>H<sub>3</sub>-2,6-iPr<sub>2</sub>))-6-CH<sub>3</sub>O-C<sub>5</sub>H<sub>3</sub>N) and 7' is [L<sup>3</sup> $\rightarrow$ SnCl<sub>2</sub>].



Figure S1. Optimized geometries of the neutral complexes 2 and 3 as well as the neutral analogues of 1 and 7 (1' and 7')

Majumdar and Raut described dicationic complexes  $[\{1,2-(C_5H_4N-2-C(CH_3)=N)_2CH_2CH_2\}Sn][OTf]_2$  and  $[\{1,2-(C_5H_4N-2-C(CH_3)=N)_2C_6H_{10}\}Sn][OTf]_2$  analogous to **8**.<sup>1,2</sup> However, the molecular structure of an aqua complex **8** resembles more the structure of **7**, where the Cl ligand is replaced by the O atom of H<sub>2</sub>O. Nevertheless, geometry optimization of **8**' without the coordinated water molecule reveals a molecular structure almost identical to the previously published dicationic compounds (Figure S2, Table S5).



Figure S2. Optimized geometries of the cationic part of the complex 8 and its analogue without the coordinated water molecule (8') along with selected bond distances (in Å). Hydrogen atoms are omitted for clarity.

	$\Delta G(\mathrm{DZ})^{[a]}$	$\Delta G(\mathrm{TZ})^{[b]}$	$\Delta G^{\rm solv}({\rm TZ})^{[c]}$
$L^0 + SnCl_2 \rightarrow L^0SnCl_2 (1')^{[d]}$	-23.9	-19.7	-17.1
$L^1 + SnCl_2 \rightarrow L^1SnCl_2$ (2)	-24.6	-20.8	-18.3
$L^2 + SnCl_2 \rightarrow L^2SnCl_2 (3)$	-19.8	-17.2	-16.3
$L^3 + SnCl_2 \rightarrow L^3SnCl_2$ (7')	-30.3	-23.7	-22.9
$L^{0}SnCl_{2} + SnCl_{2} \rightarrow [L^{0}SnCl_{2}][SnCl_{3}] (1)$	55.4	54.1	-8.2
$L^{1}SnCl_{2} + SnCl_{2} \rightarrow [L^{1}SnCl_{2}][SnCl_{3}] (4)$	57.4	56.3	-3.9
$L^{1}SnCl_{2} + GaCl_{3} \rightarrow [L^{1}SnCl_{2}][GaCl_{4}] $ (5)	41.4	41.0	-19.9
$L^2SnCl_2 + SnCl_2 \rightarrow [L^2SnCl_2][SnCl_3]$	68.4	67.3	2.4
$L^{2}SnCl_{2} + GaCl_{3} \rightarrow [L^{2}SnCl_{2}][GaCl_{4}]$ (6)	52.3	52.0	-13.6
$L^{3}SnCl_{2} + SnCl_{2} \rightarrow [L^{3}SnCl_{2}][SnCl_{3}](7)$	45.5	44.1	-15.2
$L^0 + 2 \operatorname{SnCl}_2 \rightarrow [L^0 \operatorname{SnCl}_2][\operatorname{SnCl}_3](1)$	31.5	34.4	-25.3
$L^3 + 2 \operatorname{SnCl}_2 \rightarrow [L^3 \operatorname{SnCl}_2][\operatorname{SnCl}_3](7)$	15.3	20.4	-38.1
$L^3 + Sn(OTf)_2 + H_2O \rightarrow [L^3Sn(H_2O)][OTf]_2$ (8)	202.7	187.5	-15.0

**Table S4.** Gibbs free energy differences ( $\Delta G$ ; in kcal mol<sup>-1</sup>) for the formation of the studied complexes 1 - 8.

	$d_{\text{Sn-N(Im)}}$	WBI <sub>Sn-N(Im)</sub>	$d_{\text{Sn-N(Py)}}$	WBI <sub>Sn-N(Py)</sub>	$q_{ m Sn}$
1'	2.534	0.210	2.760	0.125	1.13
2	2.843	0.085	2.536	0.194	1.18
3	2.965	0.070	2.550	0.188	1.15
7'	2.823 2.828	$0.090 \\ 0.087$	2.714 2.723	0.129 0.125	1.16
1+	2.347	0.265	2.346	0.264	1.25
<b>4</b> <sup>+</sup> / <b>5</b> <sup>+</sup>	2.403	0.237	2.418	0.221	1.28
<b>6</b> <sup>+</sup>	2.346	0.275	2.393	0.247	1.26
<b>7</b> +	2.490 2.497	0.216 0.215	2.740 2.758	0.123 0.119	1.21
<b>8</b> <sup>2+</sup>	2.394 2.423	0.252 0.253	2.695 2.727	0.155 0.139	1.42
<b>8'</b> <sup>2+</sup>	2.360 2.387	0.263 0.271	2.431 2.439	$0.270 \\ 0.261$	1.36

**Table S5.** Selected bond lengths (*d*; in Å), Wiberg bond indices (WBI), and NPA atomic charges (*q*; in *e*) for all neutral and cationic complexes 1 - 8.

	$\Delta E_{\rm int}$	$\Delta E_{ m Pauli}$	$\Delta E_{ m oi}$	$\Delta V_{ m elstat}$	$E_{disp}$
1'	-33.0	90.8	-38.6 (31)	-67.5 (55)	-17.8 (14)
2	-35.8	89.4	-39.1 (31)	-69.9 (56)	-16.2 (13)
3	-29.0	78.2	-33.6 (31)	-59.2 (55)	-14.4 (13)
7'	-49.1	110.7	-47.5 (30)	-95.0 (59)	-17.3 (11)
1+	-96.2	155.2	-101.6 (40)	-135.3 (54)	-14.4 (6)
$4^{+}/5^{+}$	-97.3	141.7	-99.1 (41)	-123.6 (52)	-16.3 (7)
6+	-87.0	151.0	-99.5 (42)	-123.9 (52)	-14.5 (6)
<b>7</b> <sup>+</sup>	-119.9	139.6	-97.4 (38)	-147.7 (57)	-14.4 (6)
<b>8</b> <sup>2+</sup>	-216.3	147.5	-159.1 (44)	-191.2 (53)	-13.5 (4)
<b>8'</b> <sup>2+</sup>	-266.0	196.6	-221.4 (48)	-230.6 (50)	-10.7 (2)

**Table S6.** Energy decomposition analysis (EDA) for all neutral and cationic complexes 1 - 8 (All energies are in kcal mol<sup>-1</sup>).<sup>[a]</sup>

<sup>[a]</sup>Values written in parentheses represent the relative contribution (in %) of the orbital interaction energy, the electrostatic energy, and the dispersion energy with respect to the total stabilization component of the interaction energy.

The interaction of 1, 4 - 8 with L-LA was further examined using EDA (Table S7). Not surprisingly, the highest value of  $\Delta E_{int}$  was observed for the L-LA adduct with the complex 8 (-39.3 kcal mol<sup>-1</sup>), which has the shortest O $\rightarrow$ Sn bond. In contrast, the interaction energy of the monocationic complexes (1 and 4 - 7) is significantly smaller (*ca.* -22.0 kcal mol<sup>-1</sup>) with electrostatic interactions (*ca.* 50 %) clearly dominating orbital interactions (*ca.* 25 %).

**Table S7.** Energy decomposition analysis (EDA) for the L-LA adducts [LSnCl]<sup>+</sup>[L-LA]. (All energies are in kcal mol<sup>-1</sup>).<sup>[a]</sup>

	$\Delta E_{\rm int}$	$\Delta E_{\mathrm{Pauli}}$	$\Delta E_{ m oi}$	$\Delta V_{ m elstat}$	$E_{\rm disp}$
[ <b>1</b> ] <sup>+</sup> [L-LA]	-21.0	43.4	-16.4 (25)	-32.6 (51)	-15.5 (24)
[ <b>4</b> / <b>5</b> ] <sup>+</sup> [L-LA]	-24.8	45.2	-16.5 (24)	-34.0 (48)	-19.6 (28)
[ <b>6</b> ] <sup>+</sup> [L-LA]	-26.1	55.8	-21.8 (27)	-41.6 (51)	-18.4 (22)
[ <b>7</b> ] <sup>+</sup> [L-LA]	-16.4	27.5	-10.6 (24)	-21.6 (49)	-11.7 (27)
[ <b>8</b> ] <sup>2+</sup> [L-LA]	-39.3	55.3	-32.5 (34)	-50.1 (53)	-12.0 (13)

<sup>[a]</sup>Values written in parentheses represent the relative contribution (in %) of the orbital interaction energy, the electrostatic energy, and the dispersion energy with respect to the total stabilization component of the interaction energy.

**Table S8.** Computed FIA (in kJ mol<sup>-1</sup>) for cationic complexes 1, 4 - 8 along with the FIA<br/>value of SbF<sub>5</sub> as a reference.

	1+	<b>4</b> / <b>5</b> <sup>+</sup>	6+	7+	<b>8</b> <sup>2+</sup>	SbF <sub>5</sub>
FIA <sup>[a]</sup>	595	610	651	547	955	502

<sup>[a]</sup>calculated at the B3LYP-D3BJ/cc-pVDZ-PP//PW6B95-D3BJ/def2-QZVPP level of theory.



Figure S3. TG-GCMS of PLA prepared by using 1





Figure S5.  ${}^{13}C{}^{1}H$  APT NMR spectrum of 2 in THF-d<sub>8</sub>



Figure S6.  $^{13}C{^{1}H}$  NMR spectrum of 2 in THF-d<sub>8</sub>



Figure S7. <sup>119</sup>Sn NMR spectrum of 2 in THF-d<sub>8</sub>



**Figure S8.** <sup>1</sup>H NMR spectrum of **3** in THF-d<sub>8</sub> (\* residual signal of THF)



**Figure S9.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **3** in THF-d<sub>8</sub> (\* residual signal of THF)



Figure S10. <sup>119</sup>Sn NMR spectrum of 3 in THF-d<sub>8</sub>



**Figure S11.** <sup>1</sup>H NMR spectrum of **3** in THF-d<sub>8</sub> (\* residual signal of THF)



Figure S12.  $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$  NMR spectrum of 4 in THF-d\_8







**Figure S14.** <sup>119</sup>Sn NMR spectrum of **4** in THF-d<sub>8</sub> at -50 °C



**Figure S15.** <sup>1</sup>H NMR spectrum of **5** in THF-d<sub>8</sub> (\* residual signal of THF)







**Figure S18.** <sup>1</sup>H NMR spectrum of **6** in THF-d<sub>8</sub> (\* residual signal of THF)



**Figure S19.** <sup>13</sup>C{<sup>1</sup>H} APT NMR spectrum of **6** in THF-d<sub>8</sub> (\* residual signal of THF)



Figure S20. <sup>119</sup>Sn NMR spectrum of 6 in THF-d<sub>8</sub>



Figure S21. <sup>1</sup>H NMR spectrum of 7 in CD<sub>3</sub>CN (\* residual signal of CH<sub>3</sub>CN)



Figure S22. <sup>13</sup>C{<sup>1</sup>H} APT NMR spectrum of 7 in CD<sub>3</sub>CN (\* residual signal of CH<sub>3</sub>CN)



Figure S23. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 7 in CD<sub>3</sub>CN (\* residual signal of CH<sub>3</sub>CN)



Figure S24. <sup>119</sup>Sn NMR spectrum of 7 in CD<sub>3</sub>CN



Figure S25. <sup>1</sup>H NMR spectrum of 8 · THF in CD<sub>3</sub>CN (\* residual signal of CH<sub>3</sub>CN)



Figure S26. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 8 · THF in CD<sub>3</sub>CN (\* residual signal of CH<sub>3</sub>CN)



Figure S27. <sup>19</sup>F NMR spectrum of 8 THF in CD<sub>3</sub>CN



S37



Figure S29. Comparison of <sup>31</sup>P NMR chemical shifts of 1[Ph<sub>3</sub>P=O], 6-8[Ph<sub>3</sub>P=O] adducts with starting Ph<sub>3</sub>P=O



Figure S30. <sup>1</sup>H NMR spectrum of 6[L-LA] in THF-d<sub>8</sub> (\* residual signal of THF)



Figure S31. <sup>119</sup>Sn NMR spectrum of 6[L-LA] in THF-d<sub>8</sub>

![](_page_40_Figure_0.jpeg)

Figure S32. <sup>1</sup>H NMR spectrum of 8[L-LA] in CD<sub>3</sub>CN (\* residual signal of CH<sub>3</sub>CN)

![](_page_41_Figure_0.jpeg)

Figure S33. <sup>119</sup>Sn NMR spectrum of 8[L-LA] in CD<sub>3</sub>CN

## References

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