Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary Materials

Homoleptic aminophenolates of Ca, Mg and Zn. Synthesis, structure, DFT studies and polymerization activity in ROP of lactides

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(*) Though **8'** has structure close to crystallographic one (or rather its mirror image form), we found two lower energy conformers: **8** and **8".** In the lowest energy conformation both dioxolane groups are arranged in such way that methine protons are directed toward phenyl oxygen atoms. The difference between ZPE corrected TPSS-D3/def2-TZVPPD energies of the lowest energy forms **8** and **8"** is slightly over 1.3 kcal/mol.

(*) Table 1S presents geometrical parameters calculated for Ca-, Mg-, and two conformers (I, and II) of Zn-complexes. Experimentally found conformers I and II correspond to the structures **1** and to the mirror image form of molecule **8'**, respectively. In round parentheses are values for conformer with geometric parameters closer to experimental ones but slightly higher in energy (**8'**). The lower energy form corresponds to **8''**.

Tabela 1S. Geometric parameters (in Å and degrees) for the Ca-, Mg-, and Zn-complexes computed at diferent levels of theory, along with experimental data from X-ray diffraction. For the atom numbering see Figure 1. All calculated structures have C_2 symmetry. For explanation of values in round parentheses see text.

	TPSS-D3		MP2-SCS	Exp.	TPSS-D3		MP2-SCS	Exp.
	SVPD	**TZVPPD**	**SVPD**		**SVPD**	**TZVPPD**	**SVPD**	
		[Ca(L^{tBu})$_2$]				**[Mg(L^{tBu})$_2$]**		
r(M-O44) [r(M-O89)]	2.397	2.408	2.377	2.405 [2.373]	2.156	2.172	2.143	2.164 [2.190]
r(M-O2) [r(M-O46)]	2.205	2.204	2.227	2.187 [2.210]	1.976	1.970	1.976	1.943 [1.954]
r(M-N28) [r(M-N72)]	2.670	2.683	2.639	2.609 [2.663]	2.301	2.300	2.294	2.272 [2.283]
r(C3-C47)	5.530	5.587	5.478	5.783	5.994	6.015	5.933	6.023
r(C20-C64)	10.694	10.729	10.625	11.114	11.191	11.212	11.073	11.086
r(C5-C49)	5.833	5.947	5.703	6.308	8.874	8.983	8.751	9.167
a(O44-M-O89)	145.5	144.8	145.9	144.3	87.3	86.5	88.0	90.3
a(O2-M-O46)	104.1	105.6	105.6	103.2	176.0	175.5	175.4	176.5
a(N28-M-N72)	101.1	100.2	100.1	100.0	117.2	117.9	117.0	112.9
d(M-N28-C33-C36) [d(M-N72-C77-C80)]	35.3	35.3	34.1	45.5 [39.1]	26.8	29.3	22.6	34.2 [40.3]
d(N28-C33-C36-H45) [d(N72-C77-C80-H81)]	54.7	55.5	54.0	73.8 [72.5]	64.2	63.3	67.3	67.8 [61.6]
		[Zn(L^{tBu})$_2$] (I)				**[Zn(L^{tBu})$_2$] (II)**		
r(M-O44) [r(M-O89)]	2.537	2.675	2.454	2.726 [2.726]	4.045 (3.157)	4.094 (3.261)	4.047	3.011 [3.011]
r(M-O2) [r(M-O46)]	1.960	1.952	1.958	1.934 [1.934]	1.914 (1.927)	1.912 (1.924)	1.911	1.924 [1.924]
r(M-N28) [r(M-N72)]	2.170	2.153	2.169	2.101 [2.101]	2.111 (2.130)	2.117 (2.126)	2.103	2.094 [2.094]
r(C3-C47)	4.294	4.387	4.202	4.827	5.201 (5.065)	5.212 (5.093)	5.135	4.989
r(C20-C64)	7.880	8.156	7.690	9.414	10.007 (9.588)	10.025 (9.675)	9.856	9.648
r(C5-C49)	5.246	5.379	5.175	6.386	6.409 (6.306)	6.448 (6.356)	6.296	6.416
a(O44-M-O89)	76.7	77.1	74.9	80.6	62.8 (66.8)	62.9 (65.7)	61.6	68.2
a(O2-M-O46)	115.3	117.4	114.7	117.0	136.1 (134.1)	135.9 (133.8)	137.7	123.9
a(N28-M-N72)	154.0	150.6	155.1	148.6	126.6 (146.1)	126.3 (143.3)	126.1	147.5

d(M-N28-C33-C36)	-54.4	-56.8	-52.1	-59.5	55.0	56.0	54.4	53.1
[d(M-N72-C77-C80)]				[-59.5]	(48.2)	(49.0)		[53.1]
d(N28-C33-C36-H45)	158.6	160.9	156.0	164.3	-17.9	-18.6	-19.2	34.2
[d(N72-C77-C80-H81)]				[164.3]	(30.0)	(27.9)		[34.2]

(*)

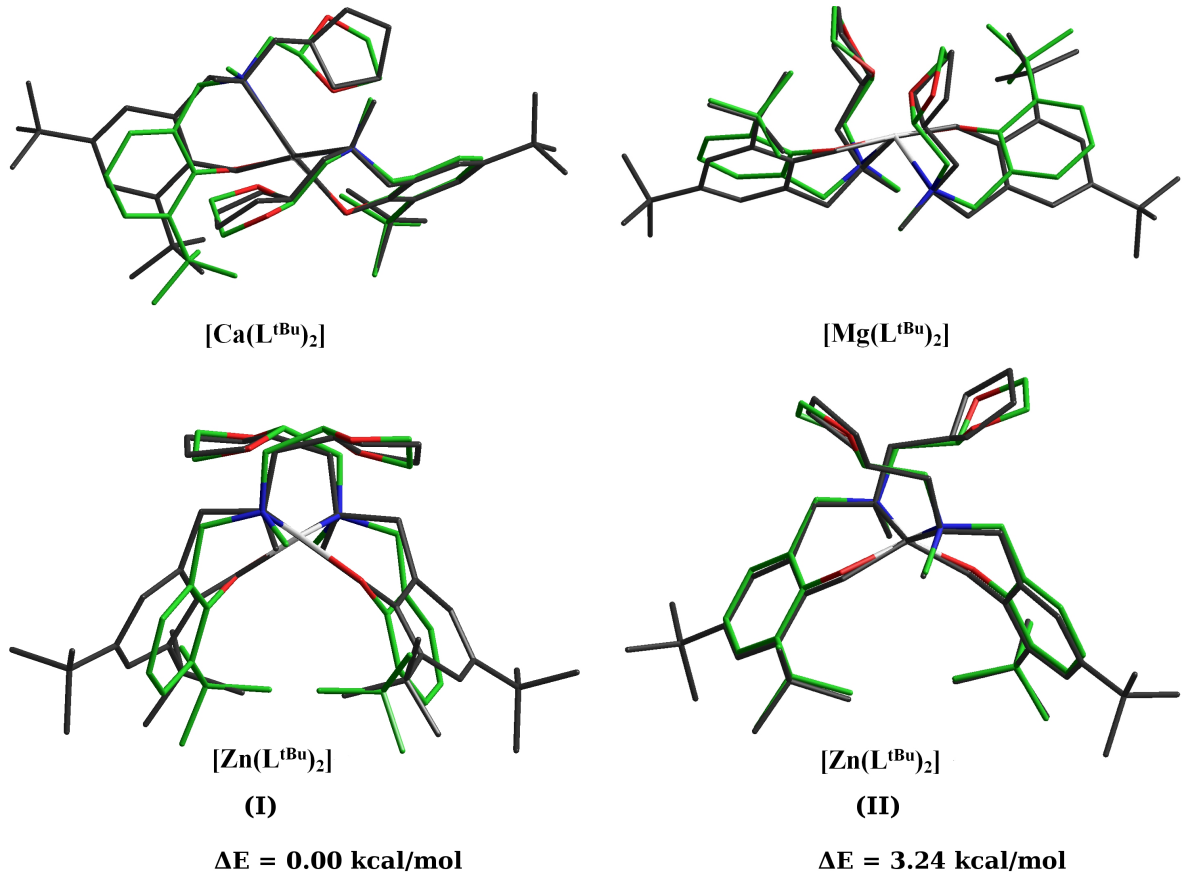


Figure 1S. Superposition of X-ray structures (in black color) with the TPSS-D3/def2-TZVPPD level energy-minimized conformations.

(*) The direct transition between **1** and **3** is also possible (Figure 3) through a second order saddle point SOSP (stationary point with two imaginary frequencies). The **1→3** reaction coordinate can be assigned to the smaller frequency (in absolute value) imaginary mode with preserved C_2 symmetry. SOSPs are very rarely objects of interest (see for example D. Heidrich, W. Quapp, *Theor. Chim. Acta*, 70, 1986, 89) because they do not appear in transition state theory. But even apart from the discussion about chemical significance of SOSP the barrier for **1→3** is much higher than for **1→2** or **2→3**, thus the stepwise path is more favorable.

(*)

Tabela 2S. Geometric parameters (in Å and degrees) for all Zn-complexes computed at TPSS-D3/TZVPPD level of theory. For the atom numbering see Figure 1.

	r(M-O2)	r(M-O46)	r(M-N28)	r(M-N72)	r(C5-C49)	R(C3-C47)	r(C20-C64)	d(M-N28-C33-C36)	d(N28-C33-C36-H45)	d(M-N72-C77-C80)	d(N72-C77-C80-H81)
1	1.952	1.952	2.153	2.153	5.379	4.387	8.156	-56.8	160.9	-56.8	160.9
1'	1.951	1.949	2.166	2.160	5.434	4.447	8.229	-58.7	160.6	-56.3	164.1
1"	1.949	1.949	2.172	2.172	5.468	4.491	8.249	-57.9	163.3	-57.9	163.3
2	1.921	1.937	2.129	2.133	5.531	4.524	8.439	-169.4	-166.7	-58.8	164.1
2'	1.918	1.934	2.124	2.132	6.102	4.925	9.41	-169.4	-167.0	-55.6	170.2
2"	1.923	1.940	2.138	2.143	5.488	4.494	8.353	162.6	164.5	-57.0	163.7
3	1.914	1.924	2.124	2.124	5.440	4.48	8.258	-168.3	-165.9	-168.3	-165.9
3'	1.901	1.901	2.125	2.125	6.667	5.353	10.306	-166.2	-166.6	-166.2	-166.6
4	1.922	1.941	2.132	2.133	5.495	4.504	8.389	174.2	40.8	-57.6	163.3
5	1.917	1.945	2.127	2.128	5.672	4.627	8.655	-57.3	23.1	-57.9	162.7
6	1.906	1.910	2.126	2.113	6.440	5.208	10.009	-55.0	17.7	-164.7	-166.5
7	1.906	1.910	2.129	2.113	6.423	5.188	9.945	-53.7	19.0	-177.2	51.4
8	1.932	1.923	2.139	2.134	6.305	5.059	9.607	-45.1	-43.5	-45.1	-32.4
8'	1.922	1.922	2.122	2.122	6.384	5.127	9.754	-49.8	-23.1	-49.8	-23.1
8"	1.912	1.912	2.116	2.116	6.439	5.207	10.006	-56.3	18.9	-56.3	18.9
9	1.923	1.937	2.126	2.128	5.507	4.513	8.415	-178.8	-40.1	-59.2	163.0
10	1.937	1.944	2.143	2.128	5.480	4.468	8.355	-66.1	-58.9	-56.1	162.2
11	1.900	16.980	2.126	2.121	6.608	5.319	10.223	-172.9	51.6	-166.0	-166.5
12	1.902	1.902	2.119	2.119	6.601	5.31	10.214	-170.7	53.7	-170.7	53.7

Tabela 2S. (continued)

	d(C41-C38-O37-C36)	d(C38-O37-C36-O44)	d(O37-C36-O44-C41)	d(C36-O44-C41-C38)	d(O44-C41-C38-O37)	d(C86-C83-O82-C80)	d(C83-O82-C80-O89)	d(O82-C80-O89-C86)	d(C80-O89-C86-C83)	d(O89-C86-C83-O82)
1	-38.4	32.9	-13.1	-10.4	29.6	-38.4	32.9	-13.1	-10.4	29.6
1'	-38.3	31.8	-11.5	-11.9	30.4	10.6	8.6	-25.7	31.3	-25.5
1"	9.5	9.3	-25.5	30.5	-24.2	9.5	9.3	-25.5	30.5	-24.2
2	-38.5	35.0	-16.5	-7.4	28.0	-37.8	33.0	-14.0	-9.3	28.6
2'	-38.4	35.1	-16.6	-7.2	27.9	13.3	7.2	-26.2	33.4	-28.3
2"	-37.6	36.7	-20.1	-3.4	25.2	-37.7	34.7	-17.0	-6.4	26.8
3	-38.4	35.4	-17.2	-6.7	27.5	-38.4	35.4	-17.2	-6.7	27.5
3'	-38.3	35.5	-17.4	-6.4	27.3	-38.3	35.5	-17.4	-6.4	27.3
4	-38.3	37.4	-20.6	-3.3	25.5	-37.8	34.3	-16.2	-7.1	27.3
5	-2.3	26.6	-41.1	38.3	-22.0	-38.3	34.3	-15.6	-8.0	28.1
6	-10.6	33.4	-43.3	35.1	-15.1	-38.4	35.8	-17.9	-6.0	27.1
7	-10.2	33.3	-43.6	35.7	-15.6	-22.9	0.4	23.9	-37.1	36.6
8	35.5	-19.9	-5.5	26.9	-38.0	-35.4	43.6	-33.5	10.5	15.5
8'	-35.0	43.1	-33.1	10.4	15.3	-35.0	43.1	-33.1	10.4	15.3
8"	-8.4	31.6	-42.8	36.0	-17.0	-8.4	31.6	-42.8	36.0	-17.0
9	-37.8	39.5	-24.4	0.6	22.8	-37.9	33.4	-14.7	-8.6	28.2
10	-35.7	42.8	-31.9	8.8	16.6	-38.4	34.1	-15.1	-8.5	28.5
11	-36.1	39.6	-26.4	3.4	20.1	-38.3	35.6	-17.6	-6.3	27.2
12	2.8	21.4	-38.2	38.6	-25.4	2.8	21.4	-38.2	38.6	-25.4

	Front view		Side view	
1	H45 →	← H81	H45 →	← H81
1'	H45 →	← H81	H45 →	← H81
1''	H45 →	← H81	H45 →	← H81
2	H45 →	← H81	H45 →	← H81
2'	H45 →	← H81	H45 →	← H81
2''	H45 →	← H81	H45 →	← H81

Figure 2S. Schematic structure of $[Zn(L^{tBu})_2]$ complexes (H atoms omitted except for the CH protons of oxolane rings). (Continued on the next page.)

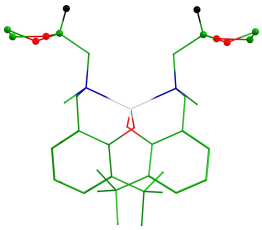
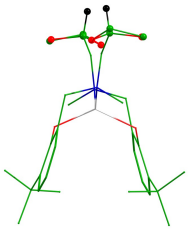
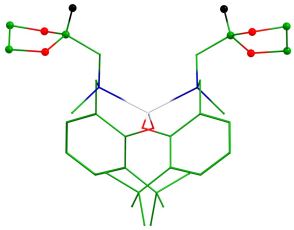
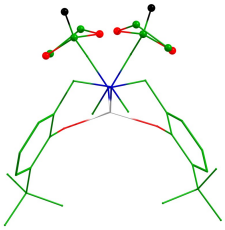
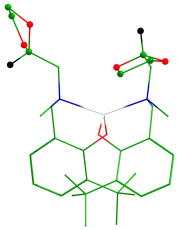
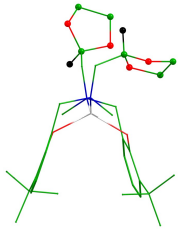
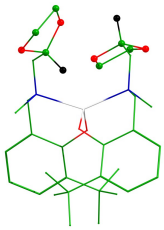
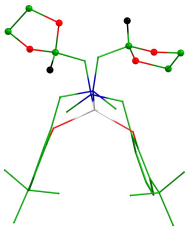
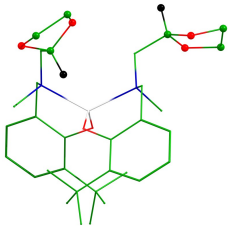
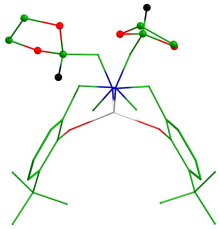
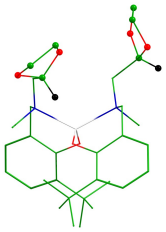
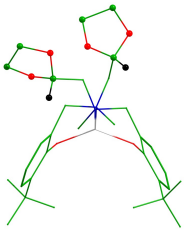
	Front view	Side view
3	H45 →  ← H81	H45 →  ← H81
3'	H45 →  ← H81	H45 →  ← H81
4	H45 →  ← H81	H45 →  ← H81
5	H45 →  ← H81	H45 →  ← H81
6	H45 →  ← H81	H45 →  ← H81
7	H45 →  ← H81	H45 →  ← H81

Figure 2S. (continued)

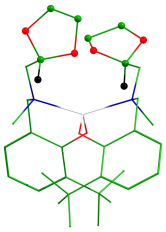
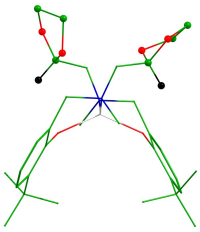
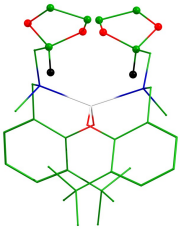
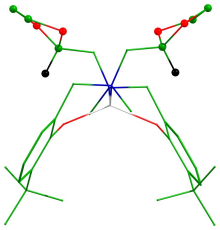
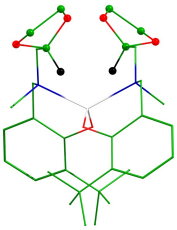
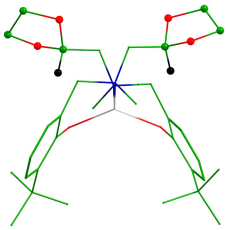
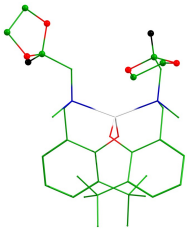
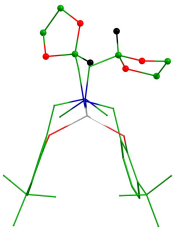
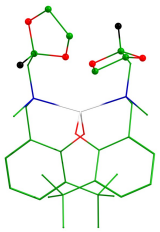
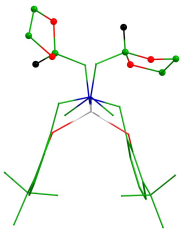
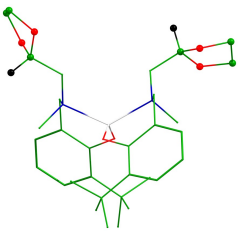
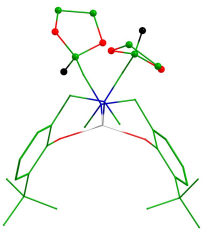
	Front view	Side view
8	H45 →  ← H81	H45 →  ← H81
8'	H45 →  ← H81	H45 →  ← H81
8''	H45 →  ← H81	H45 →  ← H81
9	H45 →  ← H81	H45 →  ← H81
10	H45 →  ← H81	H45 →  ← H81
11	H45 →  ← H81	H45 →  ← H81

Figure 2S. (continued)

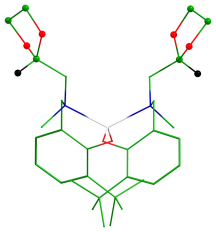
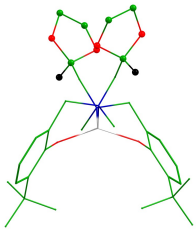
	Front view	Side view
12	H45 →  ← H81	H45 →  ← H81

Figure 2S. (continued)

(*) The contributions of individual fragments of the ligand (dioxolane ring, amine part, and phenyl ring) to the total interaction energy were estimated using the following formulas (see also Figure 3S):

$$\Delta E(\text{dioxolane ring}) = -\{[E(LML) - E(ML^{+}) - E(L^{-})] - [E(LML') - E(ML^{+}) - E(L'^{-})]\}$$

$$\Delta E(\text{amine part}) = -\{[E(LML') - E(ML^{+}) - E(L'^{-})] - [E(LML'') - E(ML^{+}) - E(L''^{-})]\}$$

$$\Delta E(\text{phenyl ring}) = -\{E(LML'') - E(ML^{+}) - E(L''^{-})\}$$

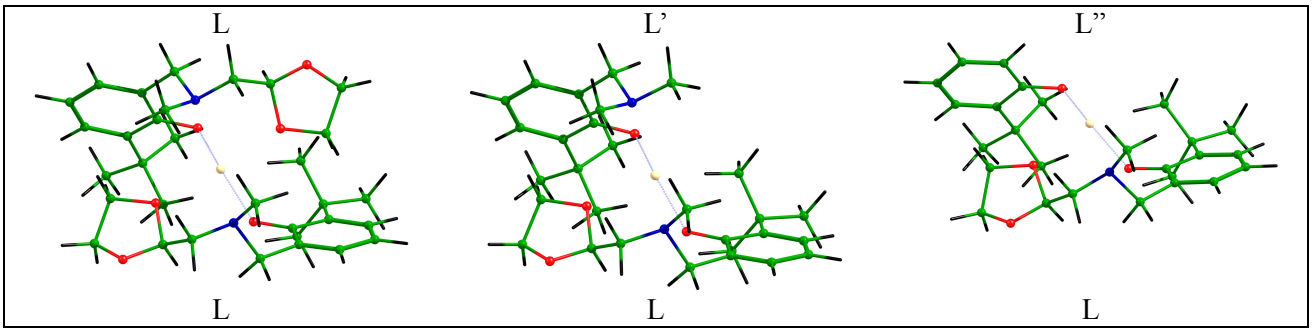


Figure 3S. Structures used as the models to calculate the contributions of individual fragments of the ligand (dioxolane ring, amine part, and phenyl ring) to the total interaction energy.