Molecular structure of the lithium salt of the ligand $L_{Me2Ph}H$

The solid state structure of the lithium salt $[Li_2(L_{Me2Ph})_2(L_{Me2Ph}H)_2]$ was determined by X-ray diffraction analysis. It is displayed in Figure 1 including selected bond lengths and bond angles. Crystal data and refinement details are given in Table 3.

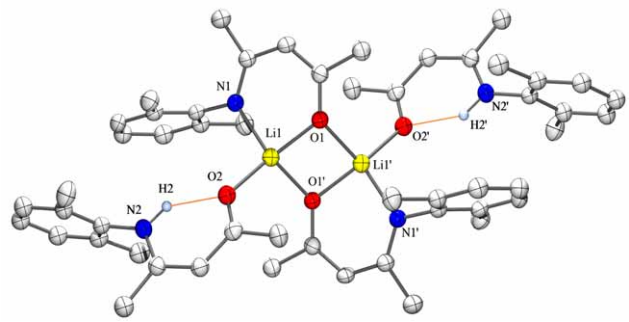

Figure 1. Molecular structure of $[Li_2(L_{Me2Ph})_2(L_{Me2Ph}H)_2]$. Hydrogen atoms have been omitted clarity. Selected bond lengths [Å] and angles [°]: Li1–O1 1.907(3); Li1–O1' 1.950(3); Li1–N1 2.026(3); Li1–O2 1.979(3); N1-Li1-O1 95.5(1); N1-Li1-O1' 131.9(2); N1-Li1-O2 105.1(1); O1-Li1-O1' 89.9(1); O1-Li1-O2 129.7(2); O1'-Li1-O2 107.6(1).

The crystal structure revealed a centrosymmetric dimeric lithium compound in which each lithium atom is coordinated by a bidentate deprotonated *β*-ketiminate ligand and by the nitrogen atom of a protonated ligand. A dimer is formed via the bridging anionic oxygen atoms forming a Li2O2 ring located on a center of symmetry. The geometry at Li can best be described as distorted tetrahedral (largest angle N1-Li1-O1' = 131.9(2)°; second largest angle O1-Li1-O2 = 129.7(2)°). Crystal structures of lithium *β*-ketiminates previously reported showed them to be tetranuclear aggregates[i]. However, in the presence of an additional donor similar dimeric arrangements have been found such as in $[\{i\text{PrNCMeCHCMeOLi}\cdot\text{OP}(\text{NMe}_2)_3\}_2]$[i] and with an internal donor in $[\{Et_2NCH_2CH_2NC(CF_3)CHC(CF_3)OLi\}_2]$[ii].

	[{Li(L_{Me2Ph})(L_{Me2Ph}H)}$_2$]
Empirical formula	$C_{52}H_{66}Li_2N_4O_4$
Mw	824.97
Temperature [K]	100(2)
Size [mm]	0.18 x 0.08 x 0.06
Crystal system	Monoclinic
Space group	$P2_1/n$
a [Å]	7.915(3)
b [Å]	15.694(3)
c [Å]	19.468(4)
β [°]	94.22(2)
V [Å^3]	2411.7(11)
Z	2
ρ_{calc} [gcm^{-3}]	1.136
Absorption coefficient [mm^{-1}]	0.550
F(000)	888
θ range	3.62<θ<59.00
Reflections collected/unique	10466/3446
Completeness to θ [%]	99.3
Data/restraints/parameters	3446/724/354
Goodness of fit on F^2	1.035
Final R indices [I>2σ(I)][a]	R1=0.0404, *w*R2=0.1011
R indices (all data)[a]	R1=0.0564, *w*R2=0.1086
Largest diff. Peak/hole [e$^-$/Å^3]	0.232/–0.156

Suitable crystal of **[{Li(L_{Me2Ph})(L_{Me2Ph}H)}$_2$]** was mounted on a nylon loop and placed immediately in a stream of a cold nitrogen. BRUKER-AXS SMART6000 CCD diffractometer with a mirror-monochromated Cu Kα radiation (1.54178 Å) was used for the data collection at 100 K. The geometry of this diffractometer allows collecting the data only to the θ 59 º, which led to one level B (the value of sin(θ_{max}) / wavelength is less than 0.575, calculated sin sin(θ_{max}) / wavelength = 0.556) and two level C (ratio of reflections to parameters is < 10 for a centrosymmetric structure and poor reflections to parameters 9.7345) alerts. The SHELXL[iii] restraints SAME, SIMU, DELU were used to refine the disordered 2,6-dimethylphenyl moiety.

Crystallographic data (excluding structure factors) for the structures of **[{Li(L_{Me2Ph})(L_{Me2Ph}H)}$_2$],** have been deposited with the Cambridge Crystallographic Data Center as no. CCDC-708730 . Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

The dependence of k_{obs} was investigated at different PMe_3 concentrations at 20°C.

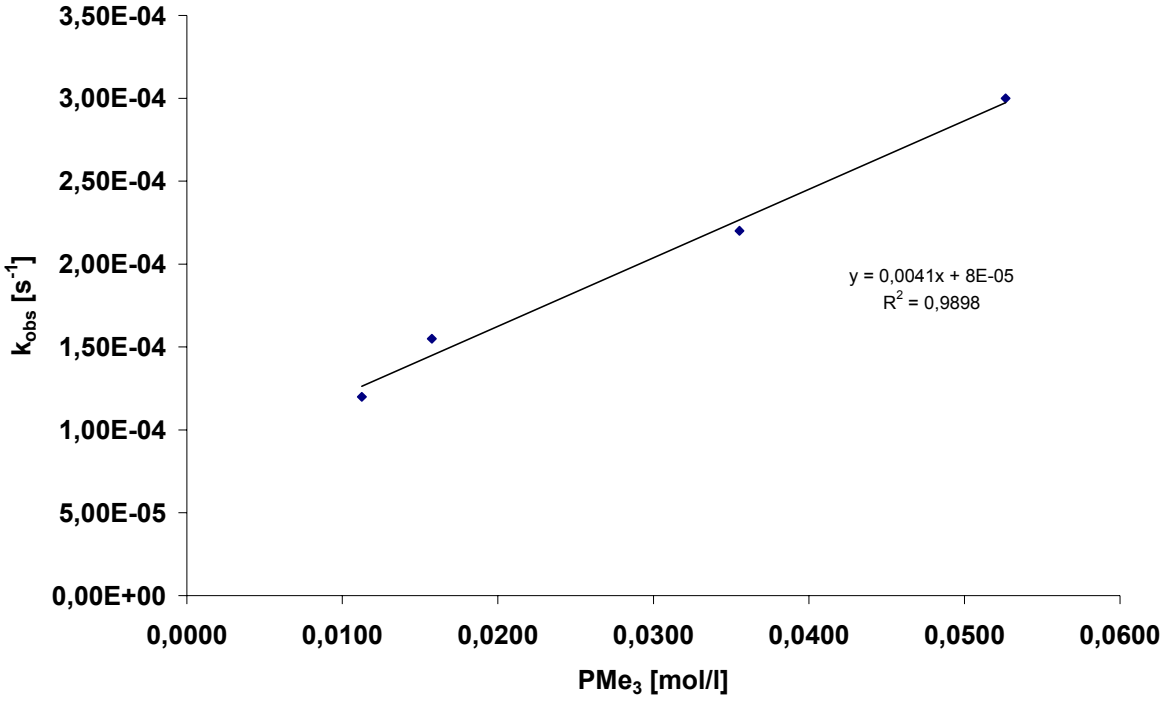

Figure 2: Dependence of k_{obs} and [PMe_3] at 20°C.

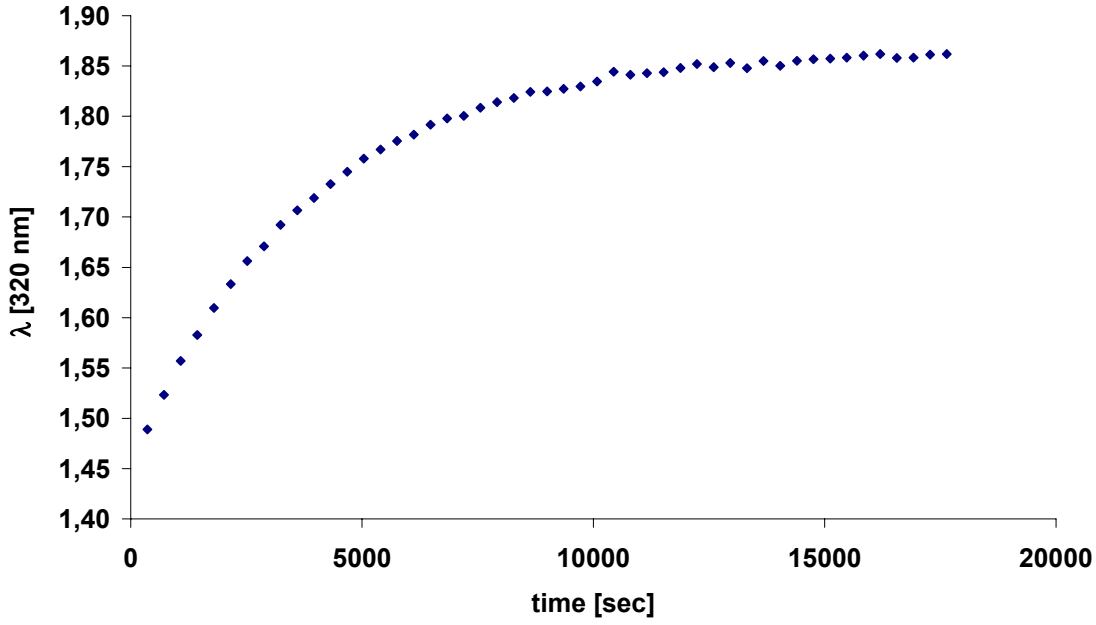

Figure 3: Reaction monitored over more than ten half – lives.

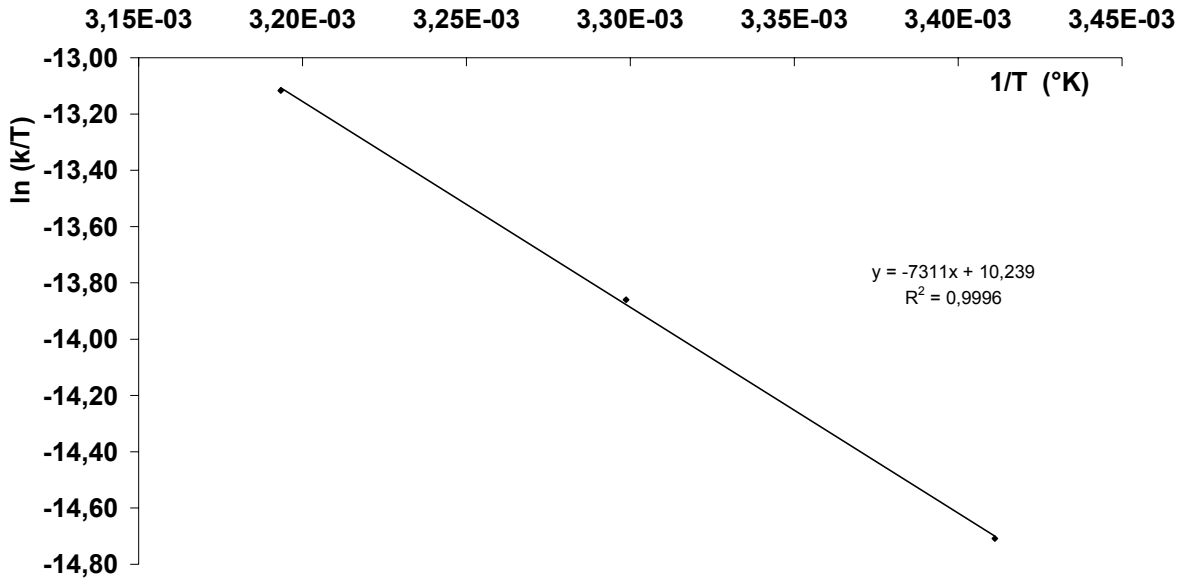

Figure 4: Eyring Plot for the kinetic experiment

[i] M. Brehon, E. K. Cope, F. S. Mair, P. Nolan, J. E. O'Brien, R. G. Pritchard, D. J. Wilcock, *J. Chem. Soc., Dalton Trans.*, 1997
[ii] D. Neculai, A. M. Neculai, H. W. Roesky, J. Magull, G. Bunkoczi, *J. Fluorine Chem.*, 2002, **118,** 131-134.
[iii] G. M. Sheldrick, *Program for the Refinement of Crystal Structures. University of Göttingen, Germany, 1997.*