

SUPPLEMENTARY INFORMATION

New lanthanoid biphenolate complexes, their further reactivity with trimethylaluminium and catalytic activity for the polymerisation of *rac*-lactide

Angus C. G. Shephard,^a Safaa H. Ali,^a Jun Wang,^a Zhifang Guo,^a Murray S. Davies,^a Glen
B. Deacon,^{b*} Peter C. Junk^{a*}

^a College of Science & Engineering, James Cook University, Townsville, QLD. 4811, Australia

^b School of Chemistry, Monash University, Clayton, Vic, 3800, Australia

*Corresponding authors: glen.deacon@monash.edu; peter.junk@jcu.edu.au

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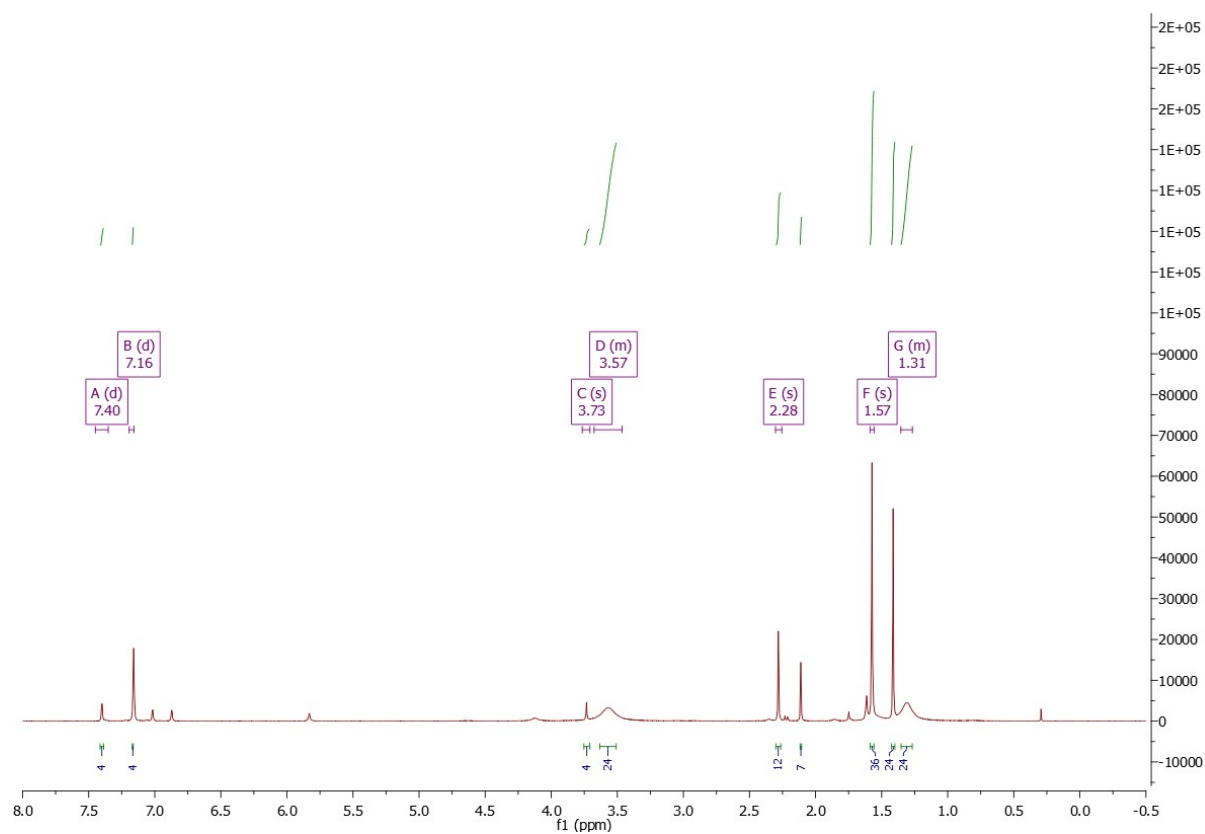


Figure S1. ¹H NMR spectrum of [Y(mbmpH)(mbmp)(thf)₃]·3thf (1)

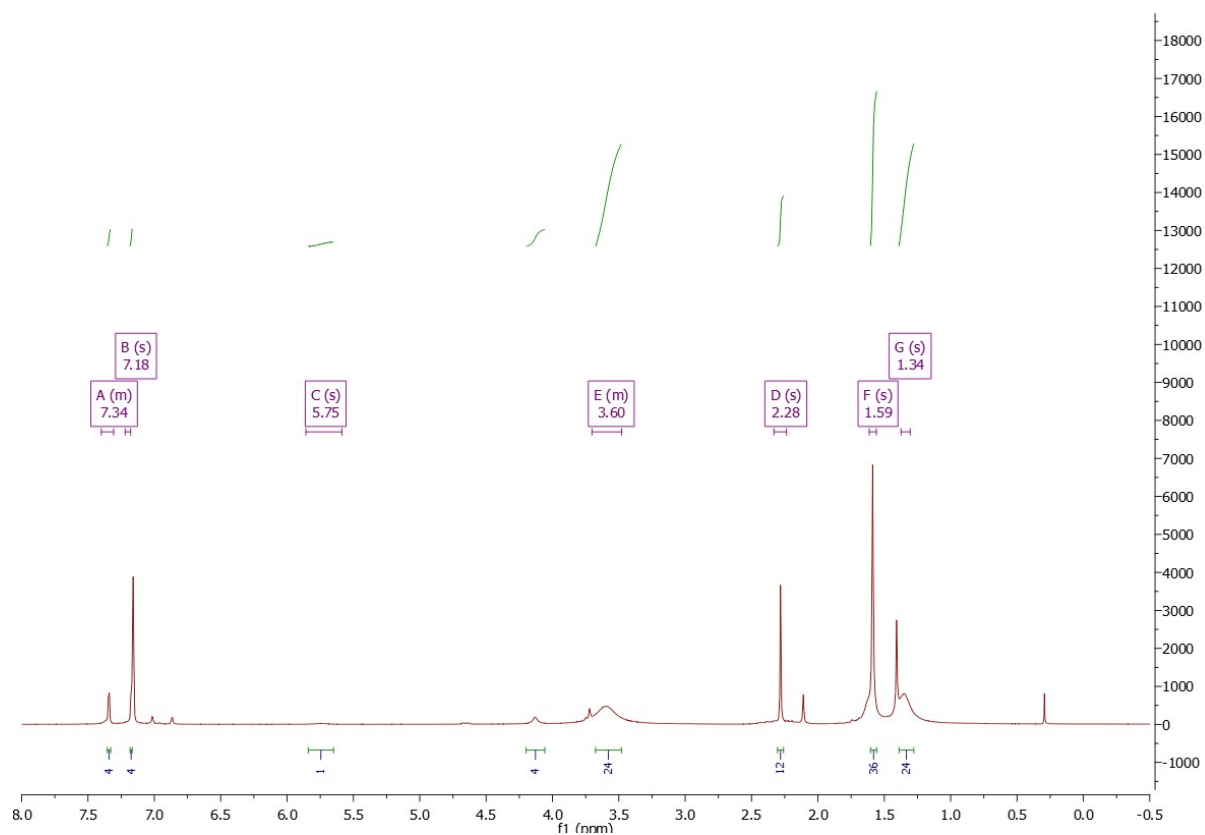


Figure S2. ¹H NMR spectrum of [Lu(mbmpH)(mbmp)(thf)₃]·3thf (7)

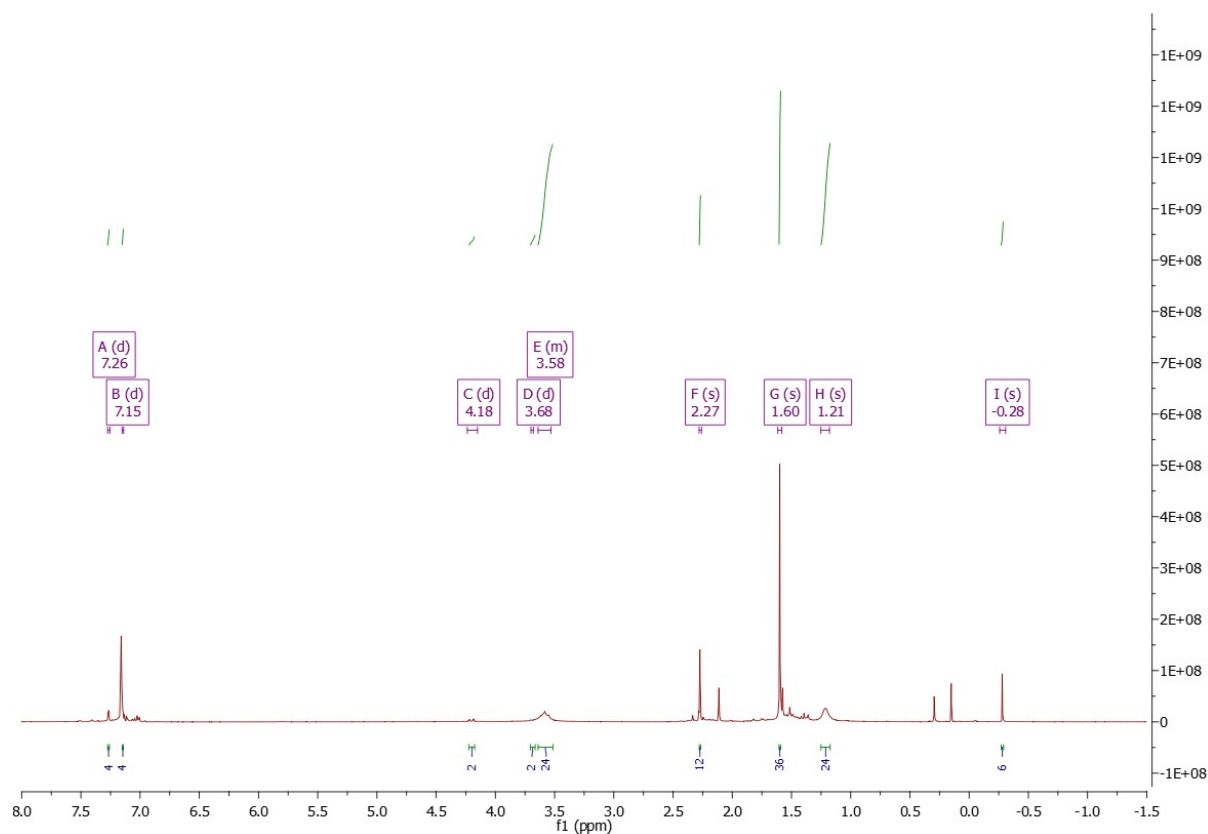


Figure S3. ¹H NMR spectrum of [AlMe₂Y(mbmp)₂(thf)₂] (9)

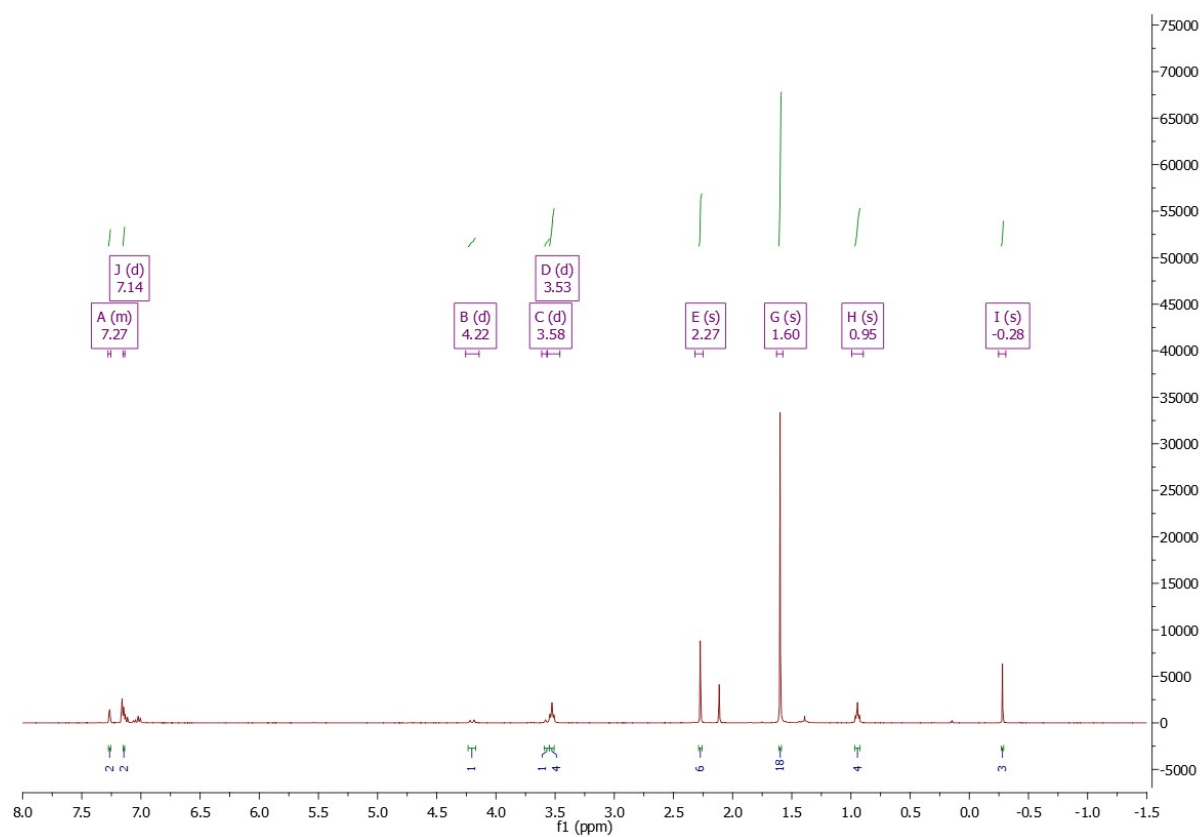


Figure S4. ¹H NMR spectrum of [AlMe(mbmp)(thf)]·PhMe (11)

X-ray crystallography:

Single crystals coated with viscous hydrocarbon oil were mounted on glass fibres or loops. Complexes were measured at the Australian Synchrotron on the MX1 beamline, data integration was completed using Blue-ice ¹ and XDS ² software programs. Structural solutions were obtained by either direct methods ³ or charge flipping ⁴ methods and refined using full-matrix least-squares methods against F^2 using SHELX2018,⁵ in conjunction with the X-Seed ⁶ or Olex2 ⁶ graphical user interface. All hydrogen atoms were placed in calculated positions using the riding model. Crystal data and refinement details are given in Table S1 and Table S2.

References

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Table S1. Crystal data and structural refinement for lanthanoid complexes **1-7**, **8a**, **8b** and **9-11**

	1	2	3
	[Y(mbmp)(mbmpH)(thf) ₃]·3thf	[Nd(mbmp)(mbmpH)(thf) ₃]·3thf	[Gd(mbmp)(mbmpH)(thf) ₃]·3thf
Formula	C ₇₀ H ₁₀₉ O ₁₀ Y	C ₇₀ H ₁₀₉ NdO ₁₀	C ₇₀ H ₁₀₉ GdO ₁₀
Formula weight	1199.48	1254.81	1267.82
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a/Å	13.254(3)	13.176(3)	13.228(3)
b/Å	17.600(4)	17.631(4)	17.675(4)
c/Å	28.387(6)	28.491(6)	28.481(6)
α/°	90	90	90
β/°	93.72(3)	93.50(3)	94.11(3)
γ/°	90	90	90
Volume/Å ³	6608(2)	6606(2)	6642(2)
Z	4	4	4
ρ _{calc} /cm ³	1.206	1.262	1.268
μ/mm ⁻¹	0.938	0.841	1.054
Reflections collected	83342	76138	88343
Independent reflections	15405 [R _{int} = 0.0632, R _{sigma} = 0.0363]	11605 [R _{int} = 0.0748, R _{sigma} = 0.0455]	15703 [R _{int} = 0.0341, R _{sigma} = 0.0215]
Goodness-of-fit on F ²	1.034	1.274	1.039
Final R indexes [I>=2σ (I)]	R ₁ = 0.0539, wR ₂ = 0.1255	R ₁ = 0.1274, wR ₂ = 0.2981	R ₁ = 0.0352, wR ₂ = 0.0858
Final R indexes [all data]	R ₁ = 0.0719, wR ₂ = 0.1365	R ₁ = 0.1965, wR ₂ = 0.3659	R ₁ = 0.0400, wR ₂ = 0.0888

	4	5	6
	[Dy(mbmp)(mbmpH)(thf) ₃]·3thf	[Er(mbmp)(mbmpH)(thf) ₃]·3thf	[Tm(mbmp)(mbmpH)(thf) ₃]·3thf
Formula	C ₇₀ H ₁₀₉ DyO ₁₀	C ₇₀ H ₁₀₉ ErO ₁₀	C ₇₀ H ₁₀₉ O ₁₀ Tm
Formula weight	1273.07	1277.83	1279.5
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a/Å	13.212(3)	13.282(3)	13.200(3)
b/Å	17.539(4)	17.590(4)	17.530(4)
c/Å	28.459(6)	28.362(6)	28.420(6)
α/°	90	90	90
β/°	93.44(3)	93.80(3)	93.32(3)
γ/°	90	90	90
Volume/Å ³	6583(2)	6612(2)	6565(2)
Z	4	4	4
ρ _{calc} /g/cm ³	1.285	1.284	1.294
μ/mm ⁻¹	1.191	1.325	1.407
Reflections collected	113072	54558	157911
Independent reflections	18449 [R _{int} = 0.0435, R _{sigma} = 0.0256]	15644 [R _{int} = 0.0546, R _{sigma} = 0.0438]	11559 [R _{int} = 0.0450, R _{sigma} = 0.0165]
Goodness-of-fit on F ²	1.056	1.042	1.050
Final R indexes [I>=2σ (I)]	R ₁ = 0.0511, wR ₂ = 0.1408	R ₁ = 0.0391, wR ₂ = 0.0911	R ₁ = 0.0463, wR ₂ = 0.1228
Final R indexes [all data]	R ₁ = 0.0581, wR ₂ = 0.1473	R ₁ = 0.0501, wR ₂ = 0.0967	R ₁ = 0.0512, wR ₂ = 0.1271

	7	8a	8b
	[Lu(mbmp)(mbmpH)(thf) ₃].3thf	[Y(mbmp)(mbmpH)(thf) ₂].PhMe	[Y(mbmp)(mbmpH)(thf) ₂].2C ₆ D ₆
Formula	C ₇₀ H ₁₀₉ LuO ₁₀	C ₆₁ H ₈₅ O ₆ Y	C ₆₆ H ₈₉ O ₆ Y
Formula weight	1285.54	1003.19	1067.28
Space group	P2 ₁ /c	P-1	C2/c
a/Å	13.210(3)	12.386(3)	23.753(5)
b/Å	17.490(4)	14.465(3)	12.686(3)
c/Å	28.400(6)	17.062(3)	19.936(4)
α/°	90	106.74(3)	90
β/°	93.23(3)	106.42(3)	103.50(3)
γ/°	90	93.08(3)	90
Volume/Å ³	6551(2)	2777.3(11)	5841(2)
Z	4	2	4
ρ _{calc} /g/cm ³	1.303	1.200	1.214
μ/mm ⁻¹	1.563	1.098	1.048
Reflections collected	70227	34526	17573
Independent reflections	11194 [R _{int} = 0.0685, R _{sigma} = 0.0408]	9003 [R _{int} = 0.0404, R _{sigma} = 0.0325]	4738 [R _{int} = 0.0964, R _{sigma} = 0.0967]
Goodness-of-fit on F ²	1.083	1.042	1.063
Final R indexes [I>=2σ (I)]	R ₁ = 0.0602, wR ₂ = 0.1598	R ₁ = 0.0413, wR ₂ = 0.1025	R ₁ = 0.0451, wR ₂ = 0.1229
Final R indexes [all data]	R ₁ = 0.0803, wR ₂ = 0.1776	R ₁ = 0.0492, wR ₂ = 0.1104	R ₁ = 0.0466, wR ₂ = 0.1251

	9	10	11
	[AlMe ₂ Y(mbmp) ₂ (thf) ₂]·2C ₆ D ₆	[Dy ₂ (mbmp) ₃ (thf) ₃]·2PhMe	[AlMe(mbmp)(thf)]·PhMe
Formula	C ₆₈ H ₉₄ AlO ₆ Y	C ₉₅ H ₁₃₀ Dy ₂ O ₉	C ₃₅ H ₄₉ AlO ₃
Formula weight	1123.32	1740.98	544.72
Space group	P2 ₁ /n	P-1	C2/c
a/Å	9.845(2)	13.158(3)	16.725(3)
b/Å	19.536(4)	16.671(3)	16.410(3)
c/Å	32.429(7)	22.238(4)	24.286(5)
α/°	90	70.76(3)	90
β/°	94.32(3)	76.21(3)	108.39(3)
γ/°	90	68.48(3)	90
Volume/Å ³	6219(2)	4246.1(19)	6325(2)
Z	4	2	8
ρ _{calc} /g/cm ³	1.2	1.362	1.144
μ/mm ⁻¹	1.001	1.802	0.096
Reflections collected	76823	51459	38583
Independent reflections	10557 [R _{int} = 0.0746, R _{sigma} = 0.0388]	14588 [R _{int} = 0.0301, R _{sigma} = 0.0263]	5741 [R _{int} = 0.0412, R _{sigma} = 0.0209]
Goodness-of-fit on F ²	1.04	1.049	1.028
Final R indexes [I>=2σ (I)]	R ₁ = 0.0998, wR ₂ = 0.2581	R ₁ = 0.0379, wR ₂ = 0.0972	R ₁ = 0.0486, wR ₂ = 0.1304
Final R indexes [all data]	R ₁ = 0.1122, wR ₂ = 0.2733	R ₁ = 0.0464, wR ₂ = 0.1026	R ₁ = 0.0584, wR ₂ = 0.1391