Supporting Information for:

Ligand Influences on Homoleptic Group 12 *m*-Terphenyl Complexes

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Contents

Molecular Structures of 2,6-$Ar_2C_6H_3I$ [Ar = 2,6-$Me_2C_6H_3$ (2,6-Xyl); 3,5-$Me_2C_6H_3$ (3,5-Xyl); 2,3,4,5,6-Me_5C_6 (Pmp)]

The *m*-terphenyl iodides 2,6-$Ar_2C_6H_3I$ (Ar = 2,6-Xyl, 3,5-Xyl, Pmp)[S1-S3] were synthesised *via* modification of the 'one-pot' methodology reported by Hart *et al*.[S1] Pure crystalline samples of these compounds were obtained from saturated ethanol solutions at room temperature.

The crystal structures of 2,6-$Ar_2C_6H_3I$, along with relevant bond lengths and angles can be found in Fig. S1.

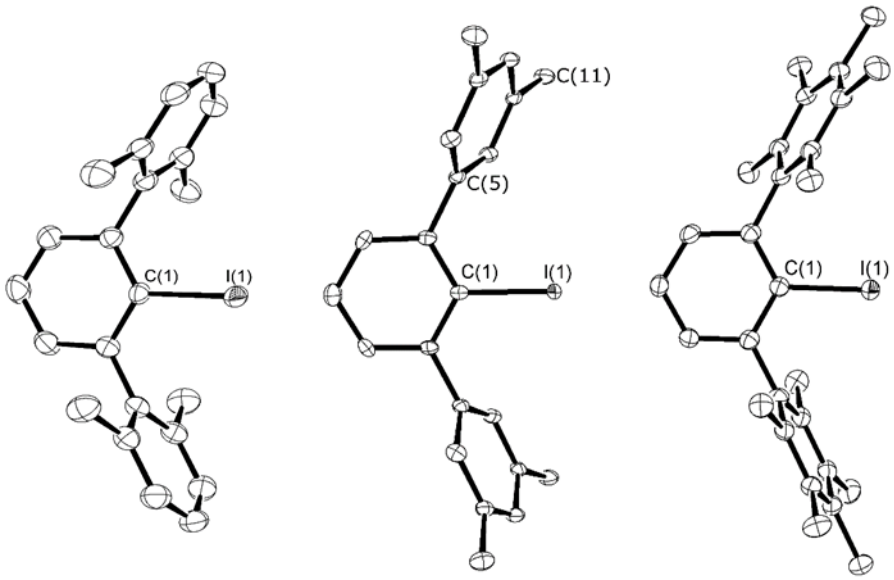

Fig. S1 Molecular structures of 2,6-$Ar_2C_6H_3I$ (Ar = 2,6-Xyl, 3,5-Xyl, Pmp), with displacement ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Relevant bond lengths (Å) and angles (°) for 2,6-(2,6-Xyl)$_2C_6H_3I$: C(1)−I(1) 2.106(4), ∠*ortho*-aryl-C_6H_3 rings 89.62(9), for 2,6-(3,5-Xyl)$_2C_6H_3I$: C(1)−I(1) 2.097(7), H(11A)···C(5) centroid = 2.752(2), C(11)···C(5) centroid = 3.699(6), I(1)···C(1) centroid = 3.776(3), ∠*ortho*-aryl-C_6H_3 rings 65.7(2), ∠C(11)−H(11A)···C(5) centroid = 162.48(3), ∠C(1)−I(1)···C(1) centroid = 121.94(18), and for 2,6-(Pmp)$_2C_6H_3I$: C(1)−I(1) 2.102(2), C(18) ring centroid···C(18) ring centroid = 4.3, ∠*ortho*-aryl-C_6H_3 rings 72.48(6), 78.98(8).

Molecular Structure of [2,6-(3,5-Xyl)$_2$C$_6$H$_3$Li]$_2$

The lithium complex [2,6-(3,5-Xyl)$_2$C$_6$H$_3$Li]$_2$ was prepared by reaction of the iodide with ^{n}BuLi, according to literature methods.[S4] Single crystals of [2,6-(3,5-Xyl)$_2$C$_6$H$_3$Li]$_2$ suitable for X-ray diffraction were obtained from storage of a saturated hexane solution of the complex at room temperature.

The crystal structure of [2,6-(3,5-Xyl)$_2$C$_6$H$_3$Li]$_2$, consists of two crystallographically independent molecules, and is shown in Fig. S2, along with relevant bond lengths and angles. The structures of both of these molecules consist of dimeric [2,6-(3,5-Xyl)$_2$C$_6$H$_3$Li]$_2$ units with no crystallographically-imposed symmetry, which is unlike that found for the solid state structures of the pentamethylphenyl-subtituted *m*-terphenyl lithiate [2,6-Pmp$_2$C$_6$H$_3$Li]$_2$[S2] and the phenoxy ether complex [2,6-(PhO)$_2$C$_6$H$_3$Li(OEt$_2$)]$_2$.[S5]

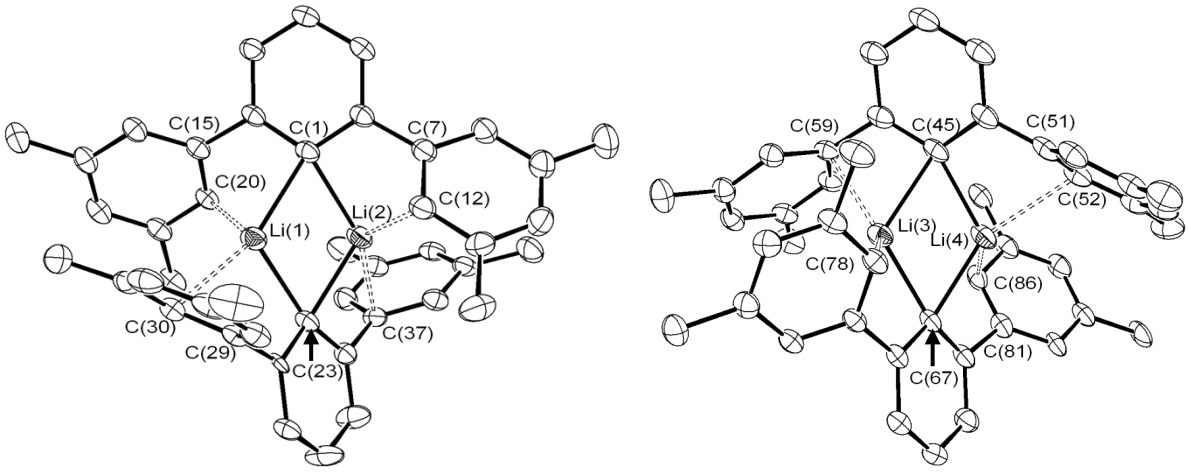

Fig. S2 Molecular structure of both crystallographically independent molecules of [2,6-(3,5-Xyl)$_2$C$_6$H$_3$Li]$_2$, with displacement ellipsoids set at the 40% probability level. Dashed lines indicate short C···Li distances. Hydrogen atoms and minor disorder components of the C(23)-C(28) and C(81)-C(86) rings are omitted for clarity. Relevant bond lengths (Å) and angles (°): Li(1)−C(1) = 2.170(6), Li(2)−C(1) = 2.177(6), Li(1)−C(23) = 2.12(2), Li(2)−C(23) = 2.14(2), Li(3)−C(45) = 2.190(6),

Li(4)−C(45) = 2.166(7), Li(3)−C(67) = 2.152(6), Li(4)−C(67) = 2.190(6), Li(1)···Li(2) = 2.322(8), Li(3)···Li(4) = 2.316(8), Li(1)−C(1)−Li(2) = 64.6(2), Li(1)−C(23)−Li(2) = 66.1(6), Li(1)−C(23A)−Li(2) = 62.8(6), Li(3)−C(45)−Li(4) = 64.4(2), Li(3)−C(67)−Li(4) = 64.5(2).

Table S1 Crystallographic data.

	2,6-(2,6-Xyl)$_2$C$_6$H$_3$I	2,6-(3,5-Xyl)$_2$C$_6$H$_3$I	2,6-(Pmp)$_2$C$_6$H$_3$I	[2,6-(3,5-Xyl)$_2$C$_6$H$_3$Li]$_2$
Formula	$C_{22}H_{21}I$	$C_{22}H_{21}I$	$C_{28}H_{33}I$	$C_{44}H_{42}Li_2$
M_w	412.29	412.29	496.44	584.65
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space Group	*C*2/*c*	*Pnma*	*P*-1	$P2_1/n$
Crystal size/mm	0.35 × 0.17 × 0.08	0.61 × 0.35 × 0.15	0.65 × 0.45 × 0.23	0.34 × 0.23 × 0.12
a (Å)	14.2219(8)	7.759(2)	8.708(2)	10.6871(3)
b (Å)	8.8418(8)	27.311(8)	9.292(3)	42.4827(9)
c (Å)	16.0675(13)	8.450(2)	15.373(4)	15.9595(4)
α (°)	90	90	73.294(4)	90
β (°)	112.897(7)	90	77.896(4)	106.596(3)
γ (°)	90	90	77.855(4)	90
V (Å^3)	1861.2(3)	1790.6(9)	1149.9(5)	6944.0(3)
Z	4	4	2	8
T (K)	90(2)	90(2)	90(2)	120(2)
D_{calc} (g cm^{-3})	1.471	1.529	1.434	1.118
F_{000}	824	824	508	2496
μ (mm^{-1})	1.718	1.786	1.404	0.460
θ range for data collection (°)	2.75-27.26	2.98-25.03	2.32-27.38	3.07-66.60
Max. and min. transmission	0.430 and 0.356	0.397 and 0.309	0.746 and 0.540	1.212 and 0.987
reflns measd	8903	7411	9719	30836
independent reflns	2084	1610	5041	12192
R_{int}	0.0363	0.0281	0.0256	0.0342
Final *GooF*	1.10	1.50	1.07	1.12
R_1, wR_2 [$I > 2\sigma(I)$]	0.0318, 0.0739	0.0412, 0.102	0.0329, 0.0891	0.0745, 0.182
R_1, wR_2 (all data)	0.0371, 0.0758	0.0417, 0.102	0.0336, 0.0900	0.0862, 0.186
min. and max. electron densities (e Å^{-3})	–0.70, 0.71	–2.63, 1.61	–1.46, 1.61	-0.28, 0.28

References

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