

Electronic supplementary information (ESI)

Syntheses, structures and flexible coordination of sterically demanding di- and “tri”- lithiated methandiides

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Figures S1-S3

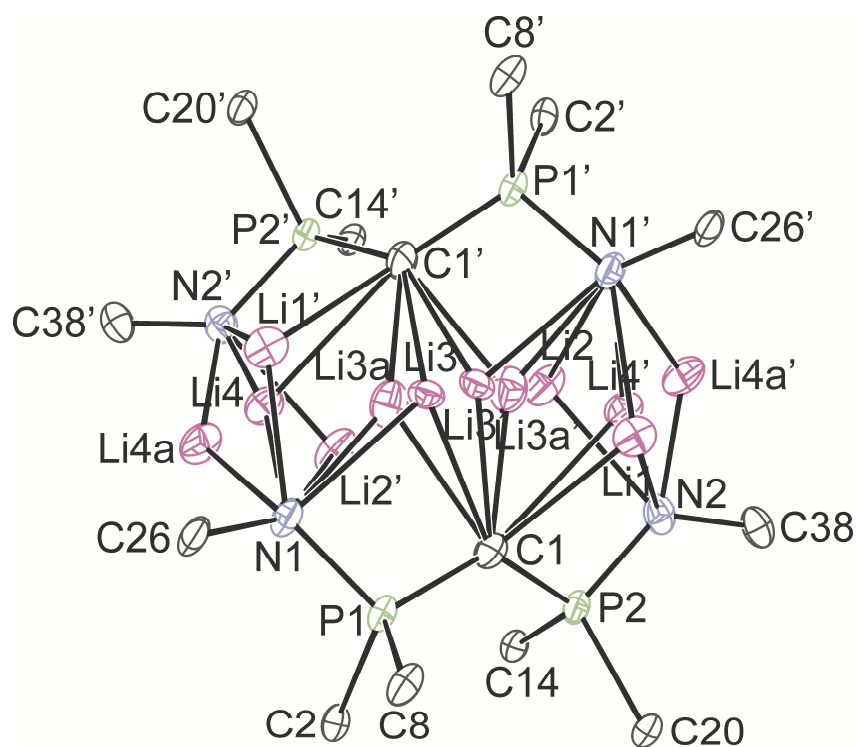
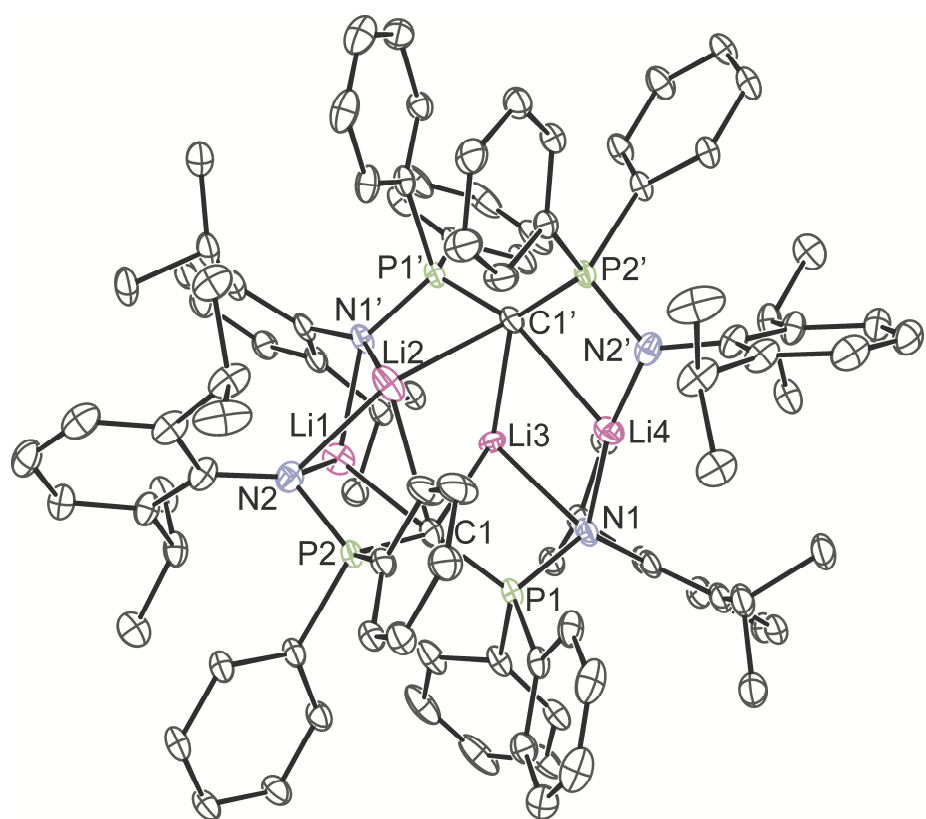


Fig. S1 Molecular structure of compound **2·4** C₆H₆ (30% probability thermal ellipsoids). Top: full molecule with main Li positions; Bottom: inorganic core showing only ipso-carbon atoms of substituents and all partial and symmetry-generated Li positions. See the cif-file for further details. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)-N(1) 1.6544(13), P(1)-C(1) 1.6877(18), P(2)-N(2) 1.6259(14), C(1)-P(2)

1.7112(17), N(1)-Li(4) 1.888(11), N(1)-Li(4A) 1.927(11), N(1)-Li(3A) 1.940(16), N(1)-Li(1)'1 2.099(6), N(1)-Li(2)'1 2.198(5), N(1)-Li(3) 2.259(11), C(1)-Li(3A)'1 2.017(16), C(1)-Li(3)'1 2.184(14), C(1)-Li(3) 2.232(13), C(1)-Li(3A) 2.237(16), C(1)-Li(1) 2.324(6), C(1)-Li(4)'1 2.528(14), C(1)-Li(2)'1 2.562(6), C(1)-Li(2) 2.598(7), Li(1)-N(1)'1 2.099(6), Li(1)-N(2) 2.179(5), Li(1)-C(26)'1 2.694(6), N(2)-Li(4)'1 1.603(11), N(2)-Li(4A)'1 1.849(14), N(2)-Li(2) 2.224(6), Li(2)-N(1)'1 2.198(5), Li(2)-C(1)'1 2.562(6), Li(3)-C(1)'1 2.184(14), Li(4)-N(2)'1 1.603(11), Li(4)-C(1)'1 2.528(14), Li(4)-C(38)'1 2.670(12); P(1)-C(1)-P(2) 126.33(11), N(1)-P(1)-C(1) 107.33(8), N(2)-P(2)-C(1) 103.14(8); Symmetry operations: '1 -x+1,y,-z+1/2.

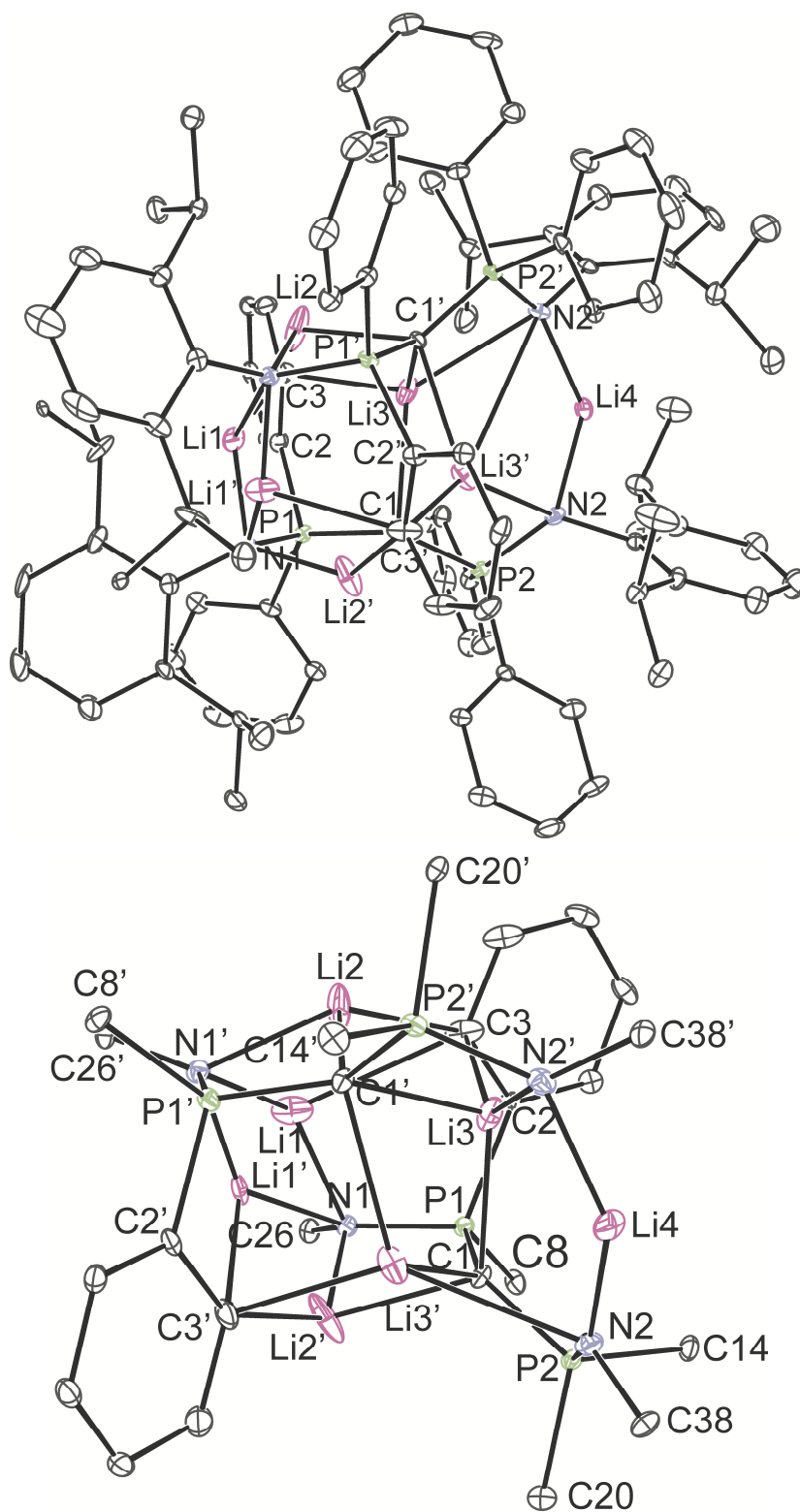


Fig. S2 Molecular structure of compound **8·2** C₇H₈ (30% probability thermal ellipsoids). Top: full molecule including all full and partial Li positions; Bottom: inorganic core showing only ipso-carbon atoms of organic substituents except full metallated phenyl group and all full and partial Li positions. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)-N(1) 1.655(5), P(2)-N(2) 1.636(5), P(1)-C(1) 1.698(6), C(1)-P(2) 1.697(5), P(1)-C(2) 1.840(6), P(1)-C(8) 1.843(6), P(2)-C(14) 1.839(6), P(2)-C(20) 1.847(6), N(1)-Li(1) 1.94(2), N(1)-Li(1)′ 1.97(2), N(1)-Li(2)′ 2.014(13), C(1)-Li(2)′ 2.136(13), C(1)-Li(3)′ 1

2.259(12), C(1)-Li(3) 2.396(13), Li(1)-N(1)'1 1.97(2), Li(1)-C(3) 2.58(3), Li(1)-C(3) 2.58(3), C(2)-C(3) 1.431(8), C(2)-C(7) 1.391(8), C(2)-Li(3) 2.759(13), N(2)-Li(4) 1.888(7), N(2)-Li(3)'1 2.614(12), C(2)-Li(3) 2.759(13), Li(2)-N(1)'1 2.014(13), Li(2)-C(3) 2.107(14), Li(2)-C(1)'1 2.136(13), Li(2)-C(4) 2.757(13), C(3)-C(4) 1.399(9), C(3)-Li(3) 2.236(12), Li(3)-C(1)'1 2.259(12), Li(3)-N(2)'1 2.614(12), C(4)-C(5) 1.412(10), Li(4)-N(2)'1 1.888(7), C(5)-C(6) 1.385(9), C(6)-C(7) 1.385(8); N(1)-P(1)-C(1) 105.4(3), P(2)-C(1)-P(1) 131.8(4), Li(2)-C(3)-Li(3) 69.5(4), Li(2)-C(3)-Li(1) 52.2(7), Li(3)-C(3)-Li(1) 88.5(6); symmetry operations: '1 -x+1,y,-z+1/2.

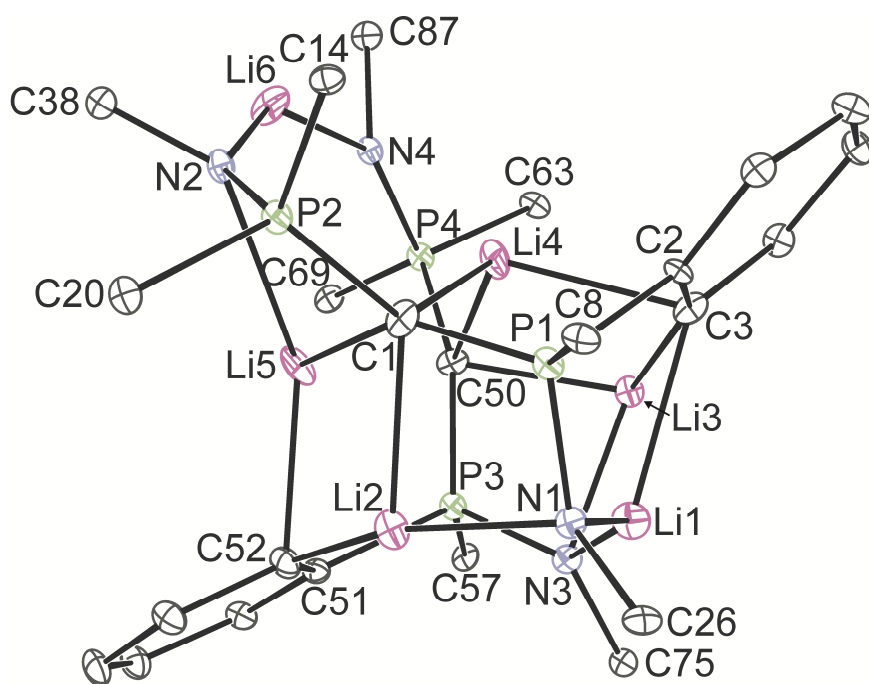


Fig. S3 Molecular structure of the inorganic core of compound **8**·3 C₆H₆ (30% probability thermal ellipsoids), showing only ipso-carbon atoms of organic substituents except the metallated phenyl groups. Hydrogen atoms and solvent molecules have been omitted for clarity. For selected bond lengths and angles see the main text.