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FULL PAPER

Synthesis and characterization of a new class of chelating bis(amidinate) ligands

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A series of diamidines based on *trans*-1,2-diaminocyclohexane have been prepared. Reactions of *trans*-1,2-diaminocyclohexane with a variety of aryl acid chlorides yields the corresponding diamides in very high (91–95%) yield. Conversion of the diamides to the diimine chloride is carried out by treatment with PCl_5 in CH_2Cl_2. Reaction of the diimine chloride with aniline in CH_2Cl_2 finally yields the diamidine in good yields on multi-gram scales. Alternatively, a one-pot reaction between the diamide, PCl_5 and aniline gives the products, although yields are generally lower. The solid-state structure of the unsubstituted diamidine shows localized C–N single and double bonds in the amidine moiety; intra- and inter-molecular hydrogen bonding is also observed between amidine groups. Alkali metal derivatives (M = Li, Na, K) were prepared by reaction of the diamidines with either ^nBuLi or $MN(SiMe_3)_2$. Isolated yields of these alkali metal derivatives, which crystallize as thf adducts, are moderate (34–64%). X-Ray crystallography shows that in all cases the alkali metal atoms bridge the two amidinate groups within the same molecule, forming a C_2 symmetric eight-membered ring. Nonetheless, there are marked differences in coordination geometries of the series.

Introduction

Benzamidinate ligands $[PhC(NSiMe_3)_2^-]$ are useful ancillary ligands that form complexes with a variety of metals from across the periodic table.[1–9] In particular, group 4 amidinates are known to support a variety of substitution and insertion reactions,[1,2,10–12] comparable to those of related metallocene complexes (Cp_2M, M = Sc, Ti, Zr).[13–15] Activity in this area has been intense recently, as interest grows in finding useful and robust ligands to support olefin polymerization reactions.[2,3,6,7,13,14,16–22]

We are interested in extending bisamidinate chemistry to systems where the two amidines are tethered by short linkers in a constrained manner similar to *ansa* metallocenes.[23–31] These systems differ considerably from their non-constrained relatives, most notably in the influence on polymer microstructure when C_2 symmetric catalysts are used in propylene polymerization.[26,32]

Our entry point to linked amidinate systems is based largely on work carried out in the 1950s,[33] where linked amidines were being investigated for their use as local anesthetics, with the hope that the linked functionality would offer lesser toxicity than that of related compounds available at the time. A highly attractive feature of ligands derived from this synthetic methodology is the extremely facile resolution that is available for chiral diamines.[34–36] Thus, the synthesis of C_2 symmetric ligands can proceed on frameworks that are already resolved and enantiomerically pure. Also appealing about this methodology is the ready commercial availability of starting diamines.

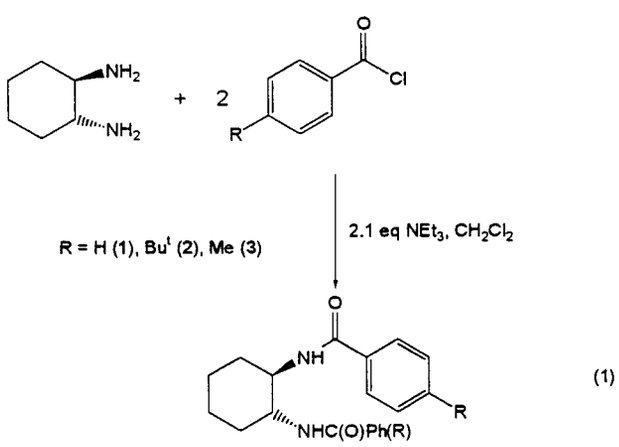
Here we describe the synthesis and characterization of the first examples of chiral C_2-symmetric bisamidines on a multigram scale and their conversion to alkali metal derivatives. The latter complexes are, in turn, useful reagents for the preparation of transition metal complexes.[37]

Results and discussion

Synthesis of diamidines

Resolution of *trans*-1,2-diaminocyclohexane can be performed at the outset of derivatization by preferential salt formation with either D- or L-tartaric acid, depending on whether the *R*,*R*- or *S*,*S*- form, respectively, is desired.[34,35] It should be noted that while all compounds reported herein were prepared from the unresolved diamine backbone, further reactivity studies will employ the resolved compound.

Synthesis of diamides **1**–**3** proceeded easily by reaction of *trans*-1,2-diaminocyclohexane with an appropriate aryl acid chloride in the presence of triethylamine as shown in eqn. (1).

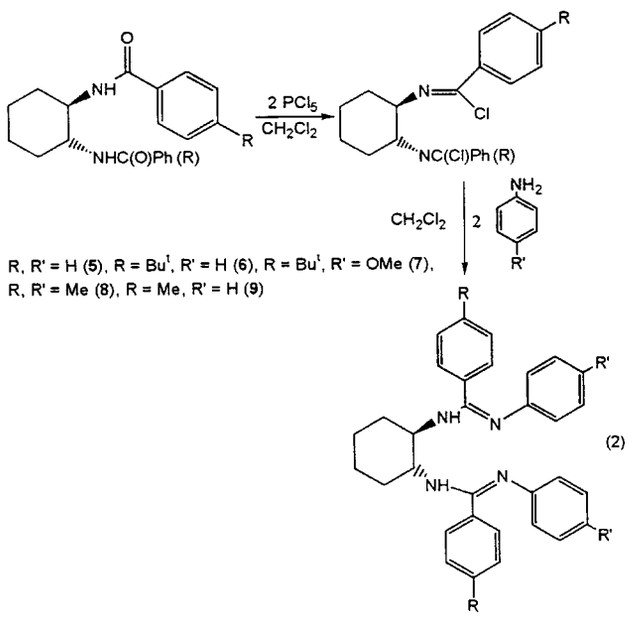


(1)

The reaction was nearly quantitative in all cases, regardless of the aryl acid chloride employed, and mechanical loss accounted for nearly all loss of final product. *p*-Toluoyl chloride is useful in this regard as the methyl group provided a good ^1H NMR handle for characterization of the diamide **3**, and the eventual diamidine.

Solubility of the diamides was greatly dependent on the substitution of the aryl acid chloride. As might be expected, the di-*tert*-butyl diamide **2** was the most soluble, dissolving readily in CH_2Cl_2 and $CHCl_3$ and sparingly in benzene, ether (Et_2O), and acetone. For comparison, the unsubstituted diamide **1** was soluble only in hot dimethyl sulfoxide (DMSO).

Preparation of diamidines from diamides is best accomplished in two steps. First, reaction of the diamide with two equiv. of PCl_5 in methylene chloride yields the corresponding diimine chloride (eqn. (2)).



The diimine chlorides are crystalline compounds soluble in Et_2O, benzene, tetrahydrofuran (thf) and methylene chloride, and can be prepared on large scales (~40 g).

In the second step, reaction of the diimine chloride with two equiv. of the desired aniline derivative gave the diamidine in high yield (89%). Alternatively, the whole reaction sequence can also be carried out as a one-pot reaction by formation of the diimine chloride *in situ*, followed by addition of aniline, although the scale of the reaction, and product purification appears to suffer somewhat in the process.

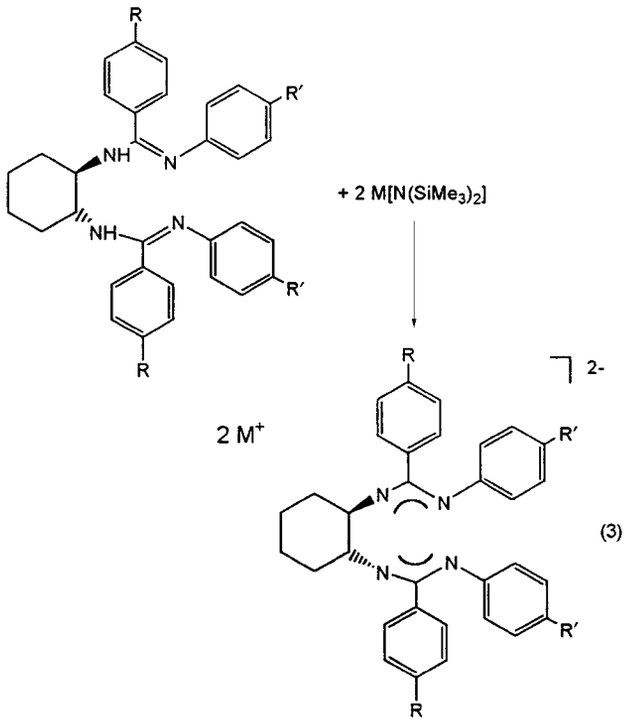
We abbreviate the completely unsubstituted diamidine as CDA-H_2. Substituted diamidines are abbreviated according to their substitution pattern. Thus, a diamidine with a *tert*-butyl group on the phenyl ring attached to the *ipso* carbon is abbreviated (Bu^t)CDA-H_2 (**6**), and one with a methyl group on the *ipso* carbon phenyl ring and a methoxy group on the phenyl ring attached to the terminal amidine nitrogen is abbreviated (Me, OMe)CDA-H_2.

A variety of diamidine compounds have been prepared using the above procedures. As mentioned above, substitution of the aryl rings in the *para* positions greatly affects solubility and characterization of the family of diamidines.

Proton NMR spectra of the series of diamidines are informative due to the number of different functionalities in the molecule. Resonances from the aryl ring attached to the C atom of the amidine functionality are consistently upfield of signals from the aryl ring attached to the N atom of the amidine. Protons on the amidine moieties appear at *ca.* 6 ppm, considerably farther upfield than common amines, but within the range of common amides.[38] Most resonances from the cyclohexyl ring are found between 2.5 ppm and 1.4 ppm, with that of the protons on the carbon atoms to which the amidines are attached near 4 ppm. IR spectra of the diamidines all showed a characteristic ν_{N-H} at approximately 3200 cm^{-1} along with a number of strong absorbances in the region from 1650 to 1500 cm^{-1} due to $\nu_{C=N}$.

Synthesis of alkali metal diamidinates

The lithium, sodium, and potassium derivatives were synthesized by reaction of a diamidine with the appropriate metal (bistrimethylsilyl)amide, $MN(SiMe_3)_2$ (M = Li, Na, K; eqn. (3)).



All the alkali metal derivatives crystallize nicely from thf as bright yellow solids, with coordinated thf clearly apparent in the ^1H NMR spectrum. The lithium and sodium derivatives contain two thf's per alkali metal, while the potassium derivative shows the presence of 2.5 thf molecules per K atom. Relative to the starting diamidine, the protons on the cyclohexyl ring α to the amidinate functionalities in the lithium derivative shift upfield considerably (~0.3 ppm), although this is not observed in the sodium and potassium derivatives.

The strongest absorbance in the IR spectrum of the diamidine is the C=N stretch at 1505 cm^{-1}. All alkali metal derivatives show strong absorptions at lower energy to the diamidines from which they were synthesized, indicative of the change from a localized double bond to a delocalized functionality. The stretches also decrease in energy from the lithium to the potassium derivative, with the lithium salt showing a strong absorbance at 1487 cm^{-1}, the sodium salt at 1475 cm^{-1}, and the potassium salt at 1470 cm^{-1}. We have already shown that these derivatives function as useful synthons in salt metathesis reactions with group 4 metal halides[37] and related work is continuing.

Structural studies

CDA-H_2. A view of the molecular structure is shown in Fig. 1 with relevant crystallographic details in Table 1 and selected metrical parameters in Table 2. The compound crystallizes racemically in the centrosymmetric space group $P2_1/n$. The cyclohexyl backbone is in the thermodynamically preferred chair conformation. All hydrogen atoms were found and refined. There is an intramolecular hydrogen bond at 2.00 Å between H61 on N1 and N4 on the other amidinate group, with an angle of 153°. Additionally, intermolecular hydrogen bonding is also observed between H62 on N3 and N2 on a neighboring diamidine molecule in the unit cell. The C–N bond lengths in each amidine functionality differ by approximately 0.07 Å, in accord with the expected localized structure.[39] The double bond present α to the cyclohexyl ring in the imine chloride precursor has migrated to a position between the two neighboring aryl groups.

Table 1 Crystal data and collection parameters

	CDA-H_2	(Me,Me)CDA-Li_2(thf)$_4$	(MeO,^{t}Bu)CDA-Na_2(thf)$_5$	(Me,Me)CDA-K_2(thf)$_5$
Formula	$C_{32}H_{32}N_4$	$C_{52}H_{70}N_4O_4Li_2$	$C_{62}H_{90}N_4O_7Na_2$	$C_{56}H_{78}N_4O_5K_2$
Formula weight	472.62	829.00	1049.40	965.44
Space group	$P2_1/n$	$P2/n$	$P\bar{1}$	$C2/c$
Temperature/°C	−115	−119	−125	−136 to −133
a/Å	13.941(5)	29.797(6)	11.352(9)	20.753(1)
b/Å	10.115(0)	11.613	13.831(8)	13.637(7)
c/Å	18.986(9)	30.359(1)	20.648(1)	19.852(1)
V/Å^3	2673.5(3)	10482.1(5)	3003.0(1)	5516.0(3)
α/°			73.041(1)	
β/°	93.125(0)	93.862(1)	89.784(1)	97.965(1)
γ/°			76.114(1)	
Z	4	8	2	4
d_{calc}/g cm^{-3}	1.174	1.051	1.160	1.153
Scan type, deg	ω, 0.3	ω, 0.3	ω, 0.3	ω, 0.3
Frame collection time/s	15	30	30	20
Reflections measured	Hemisphere	Hemisphere	Hemisphere	Hemisphere
2θ range/°	3–51.3	3–52.2	3–46.5	3–52.2
μ/cm^{-1}	0.697	0.652	0.869	2.198
T_{min}, T_{max}	0.694, 0.774	0.723, 0.923	0.685, 0.977	0.826, 0.904
Crystal dimensions/mm	0.18 × 0.45 × 0.49	0.18 × 0.22 × 0.30	0.27 × 0.17 × 0.10	0.13 × 0.16 × 0.22
No. of reflections measured	12320	49068	12485	25320
No. of unique reflections	4781	19443	8360	10142
No. of observations [$I > 3\sigma(I)$]	4847	7544	5499	2596
No. of variables	325	1203	694	300
R_{int} (%)	2.1	3.6	2.67	2.6
R (%)	5.0	7.0	6.00	5.4
R_w (%)	6.4	8.8	7.63	6.8
GOF	2.175	2.513	2.229	2.191

Table 2 Selected distances (Å) and angles (°) for CDA-H_2 **5**

C7–N1	1.352(2)	N1–H61	0.97
C7–N2	1.298(2)	N3–H62	1.01
C20–N3	1.368(2)	H61–N4	2.00
C20–N4	1.298(2)	H62–N2′	2.40
N1–C7–N2	121.2(2)	C7–N2–C14	120.6(1)
N3–C20–N4	118.9(2)	C20–N4–C27	120.6(2)
C1–N1–C7	122.4(1)	C6–C1–N1	111.2(1)
C6–N3–C20	123.5(1)	C1–C6–N3	113.3(1)

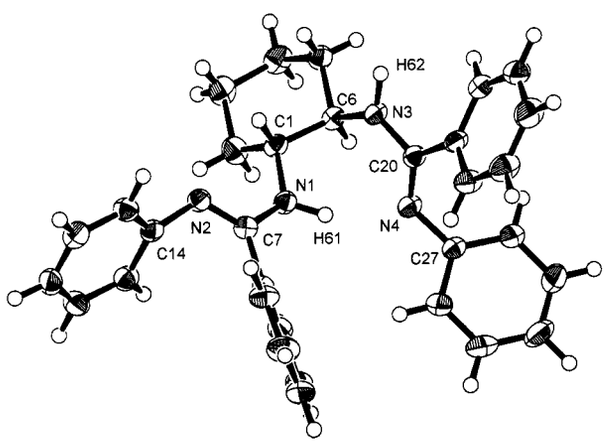


Fig. 1 ORTEP[49] plot of CDA-H_2 **5** with thermal ellipsoids at 50% probability level.

Table 3 Selected bond distances (Å) and angles (°) for (Me,Me)CDA-Li_2(thf)$_4$ **10**

C7–N1	1.303(8)	Li1–O2	2.01(1)
C7–N2	1.366(8)	Li2–N1	2.10(1)
C22–N3	1.314(8)	Li2–N4	2.10(1)
C22–N4	1.358(8)	Li2–O3	2.02(2)
C60–N5	1.317(8)	Li2–O4	1.97(1)
C60–N6	1.361(7)	Li3–N6	2.06(1)
C75–N7	1.334(7)	Li3–N7	2.13(1)
C75–N8	1.355(8)	Li3–O5	2.02(1)
Li1–N2	2.06(1)	Li3–O6	1.95(1)
Li1–N3	2.15(1)	Li4–N5	2.07(1)
Li1–O1	2.00(1)	Li4–N8	1.98(1)
		Li4–O7	1.98(1)
		Li4–O8	1.97(1)
N1–C7–N2	125.1(6)	O1–Li1–N3	112.2(6)
N3–C22–N4	124.7(6)	O2–Li1–N2	106.0(6)
N5–C60–N6	125.3(6)	O2–Li1–N3	120.0(6)
N7–C75–N8	123.9(6)	O3–Li2–N1	123.2(6)
N1–C1–C6	111.0(5)	O3–Li2–N4	106.0(6)
N3–C6–C1	110.9(6)	O4–Li2–N1	102.8(6)
N2–Li1–N3	108.2(5)	O4–Li2–N4	122.2(6)
N1–Li2–N4	108.1(6)	O5–Li3–N6	107.6(6)
N6–Li3–N7	110.0(5)	O5–Li3–N7	122.6(6)
N5–Li4–N8	110.6(5)	O6–Li3–N6	111.0(6)
O1–Li1–O2	100.1(5)	O6–Li3–N7	108.3(6)
O3–Li2–O4	95.5(5)	O7–Li4–N5	119.2(6)
O5–Li3–O6	96.4(5)	O7–Li4–N8	105.0(6)
O7–Li4–O8	101.3(5)	O8–Li4–N5	108.3(6)
O1–Li1–N2	109.8(6)	O8–Li4–N8	112.2(6)

Alkali metal derivatives. A few common features of all the alkali metal derivatives will be discussed first. Firstly, they all crystallize racemically in centrosymmetric space groups (Table 1). The C–N bonds in the amidinates are approximately equal at an average of 1.34 Å, in the range of other known main group and transition metal amidinate complexes (see Tables 3–5).[1–3,6–8] This value is intermediate to those observed in **5**, which showed bond lengths of 1.30 and 1.37 Å, and is indicative of the delocalized nature of the amidinate moiety. The alkali metal atoms bridge the separate amidinate groups of the same molecule, in a well-established bonding mode for these types of compounds.[40] Each alkali metal atom binds either two (Li,Na) or three (K) thf molecules to complete its coordination sphere.

The structure of (Me,Me)CDA-Li_2(thf)$_4$ **10**, shown in Fig. 2, confirms that the lithiums are bound in monodentate fashion to each of the nitrogen atoms, as evidenced by a typical C7–N2–Li1 angle of 113°, and that on average they lie only 1.38 Å from the planes defined by the amidinate groups. Each lithium is pseudo-tetrahedral, with two coordinated thf molecules and

Table 4 Selected bond distances (Å) and angles (°) for (^{t}Bu,OMe)-CDA-$Na_2(thf)_4$ **11**

C8–N1	1.339(5)	Na1–O3	2.336(4)
C8–N2	1.318(5)	Na1–O4	2.297(3)
C25–N3	1.315(6)	Na2–N2	2.367(4)
C25–N4	1.360(5)	Na2–N4	2.396(3)
Na1–N1	2.428(4)	Na2–O5	2.332(4)
Na1–N3	2.426(4)	Na2–O6	2.310(4)
N1–C8–N2	125.2(3)	N1–Na1–O4	114.4(1)
N3–C25–N4	124.8(4)	N3–Na1–O3	129.4(1)
N1–Na1–N3	107.4(1)	N3–Na1–O4	111.6(1)
N2–Na2–N4	104.8(1)	N2–Na2–O5	140.0(1)
O3–Na1–O4	94.3(1)	N2–Na2–O6	105.1(2)
O5–Na2–O6	88.9(1)	N4–Na2–O5	104.2(1)
N1–Na1–O3	99.2(1)	N4–Na2–O6	111.7(1)

Table 5 Selected bond distances (Å) and angles (°) for (Me,Me)CDA-$K_2(thf)_5$ **12**

C4–N1	1.319(5)	K1–O1	2.707(4)
C4–N2	1.346(5)	K1–O2	2.653(3)
K1–N1	2.737(3)	K1–O3	3.052(9)
K1–N2	2.781(4)		
N1–C4–N2	124.4(4)	O1–K1–N1	97.6(1)
N1–K1–N2	99.4(1)	O1–K1–N2	96.7(1)
N1–C3–C3*	108.5(3)	O2–K1–N1	158.5(1)
O1–K1–O2	88.4(1)	O2–K1–N2	100.4(1)
O1–K1–O3	156.8(2)	O3–K1–N1	90.6(2)
O2–K1–O3	76.7(2)	O3–K1–N2	103.4(2)

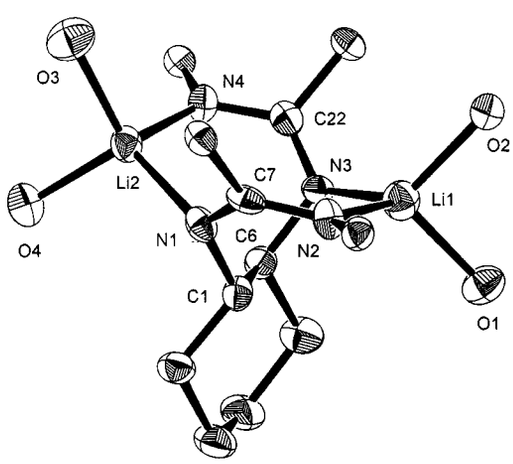


Fig. 2 ORTEP[49] plot of the core structure of (Me,Me)CDA-$Li_2(thf)_4$ **10** with thermal ellipsoids at 50% probability level. All hydrogens, thf ring carbons and aryl ring carbons (other than *ipso*) omitted for clarity.

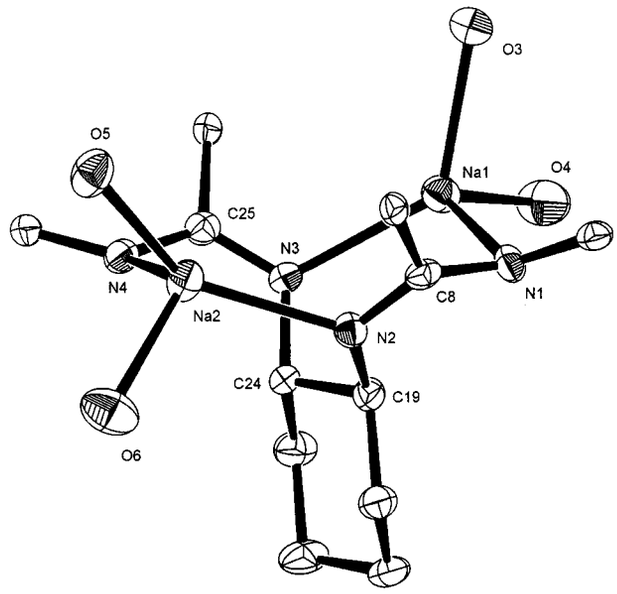


Fig. 3 ORTEP[49] plot of the core structure of (Bu^t,OMe)CDA-$Na_2(thf)_4$ **11** with thermal ellipsoids at 50% probability level. All hydrogens, thf ring carbons and aryl ring carbons (other than *ipso*) omitted for clarity.

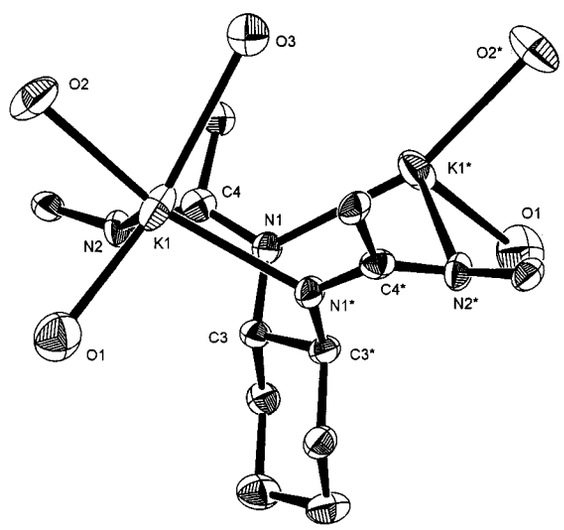


Fig. 4 ORTEP[49] plot of the core structure of (Me,Me)CDA-$K_2(thf)_5$ **12** with thermal ellipsoids at 50% probability level. All hydrogens, thf ring carbons and aryl ring carbons (other than *ipso*) omitted for clarity.

has average Li–N bond lengths of 2.09 Å, well in the range of similar alkali metal amidinate compounds.

The environment of the sodium atoms in the (Bu^t,OMe)-CDA-$Na_2(thf)_4$ (**11**, Fig. 3), parallels that of **10** with the main difference being that the alkali metal in the former compound sits slightly above the plane defined by the N–C–N of the amidinate, with a typical C8–N1–Na1 angle of 95°. This gives the complex a greater degree of η^3, allyl-like binding. As expected, the average Na–N bond length of 2.40 Å is longer than that observed in **10**, but is within the range of similar compounds.

In contrast to the lithium and sodium derivatives, the potassium atoms in (Me,Me)CDA-$K_2(thf)_5$ (**12**, Fig. 4), sit well above the plane defined by the amidinate N–C–N plane, with an angle of just less than 90°, and are bound primarily through the delocalized π system of the amidinates. Each potassium has a close contact with the central carbon of an amidinate; the bond length of 3.08 Å is very close to the bond length of the oxygen atom of a coordinated thf (3.05 Å). A close contact with one of the hydrogen atoms of one of a neighboring tolyl group at 2.73 Å suggests that some amount of electron density is donated to the potassium atom. All of the K–N bonds are approximately equal, with an average bond length of 2.76 Å. As might be expected, this value is much longer than the other alkali metal derivatives.

Conclusions

We have synthesized a new class of chelating bis(amidinate) ligands based on *trans*-1,2-diaminocyclohexane. The ready availability and resolution of this backbone make it ideal as a foundation upon which to build new C_2 symmetric ligands. Deprotonation by alkali metal amides provides an entry to synthetically useful derivatives for salt metathesis reactions with metal halides; preliminary studies along these lines have already appeared and further efforts are currently in progress with a wide range of transition metals.

Experimental

General considerations

All manipulation of air sensitive compounds was performed using standard inert atmosphere glove box and Schlenk techniques.[41] Tetrahydrofuran, diethyl ether and hexanes were either distilled from sodium/benzophenone under nitrogen or obtained as anhydrous materials from Aldrich that were passed through a column of activated alumina, then degassed with nitrogen or argon.[42] CH_2Cl_2 was distilled from CaH_2 under nitrogen prior to use. Toluene was distilled from sodium under nitrogen prior to use. Deuteriated solvents were pre-dried over 4 Å molecular sieves. C_6D_6 was vacuum transferred from sodium/benzophenone. $CDCl_3$ was vacuum transferred from CaH_2. Solutions of ^{n}BuLi in hexanes were purchased from commercial suppliers and were used without further purification. All ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded at ambient temperature in $CDCl_3$ unless otherwise specified. Chemical shifts (δ) are reported relative to tetramethylsilane at 0.00 ppm. IR samples were prepared as mineral oil mulls between KBr plates. Melting points were determined in sealed capillary tubes under nitrogen (where appropriate) and are uncorrected.

General conditions for synthesis of linked diamides

2 Equiv. of the acyl chloride (ArC(O)Cl) and 2.4 equiv. of NEt_3 were dissolved in methylene chloride or chloroform and stirred for about 10 min. To the resulting orange solution was added a solution of 1 equiv. of *trans*-1,2-diaminocyclohexane in the same solvent, forming a white precipitate. Addition was carried out slowly due to the exothermic nature of the reaction. A condenser was fitted to the flask and the reaction mixture was heated to reflux for 14 h. The solution was cooled to room temperature and filtered on a medium porosity glass frit. The resulting off-white solid was washed with water (2×), saturated sodium bicarbonate solution (1×), then water again (2×). The solid was dried with benzene using a Dean–Stark apparatus; benzene was then removed under reduced pressure to yield a colorless solid.

***Trans*-1,2-diphenylamidocyclohexane 1.** Yield: 37 g, 91%. Mp: >300 °C. ^{1}H NMR (d_6-DMSO): δ 8.23 (m, 2 H, aryl), 7.70 (d, 4 H, *J* 7.2 Hz, aryl), 7.44 (m, 2 H, aryl), 7.39 (m, 4 H, aryl), 3.93 (m, 2 H, amide), 1.92 (d, 2 H, *J* 12 Hz, cyclohexyl), 1.74 (m, 2 H, cyclohexyl), 1.50 (m, 2 H, cyclohexyl), 1.29 (m, 2H, cyclohexyl). $^{13}C\{^1H\}$ NMR (d_6-DMSO): δ 166, 134, 130, 128, 127, 115, 52, 31, 24. IR/cm^{-1}: 3311 (s), 1635 (s), 1551 (s), 1493 (w), 1455 (w), 1332 (w), 695 (w), 667 (w).

***Trans*-1,2-di(4-(*tert*-butyl)phenyl)amidocyclohexane·(benzene)$_{0.5}$ 2.** Yield: 18 g, 95%. The isolated product contains half an equivalent of benzene that remained even after extended drying under vacuum. Mp: 238–240 °C. ^{1}H NMR: δ 7.67 (d, 4 H, *J* 8.6 Hz, aryl), 7.30 (d, 4 H, *J* 8.5 Hz, aryl), 7.13 (s, 3 H, benzene), 4.03 (m, 2 H, amide), 2.22 (d, 2 H, *J* 10.9 Hz, cyclohexyl), 1.82 (m, 2 H, cyclohexyl), 1.25 (s, 18 H, *tert*-butyl). $^{13}C\{^1H\}$ NMR: δ 168, 154, 131, 128, 126, 125, 54, 34, 32, 31, 24. IR/cm^{-1}: 3325 (s), 1637 (s), 1634 (s), 1611 (s), 1559 (s), 1557 (s), 1553 (s), 1549 (s), 1544 (s), 1541 (s), 1509 (s), 1456 (w), 1331 (w), 1272 (w), 667 (s).

***Trans*-1,2-di(*p*-tolyl)amidocyclohexane 3.** Yield: 95 g, 95%. Mp: >300 °C. ^{1}H NMR: δ 7.64 (d, 4 H, *J* 8.2 Hz, aryl), 7.14 (d, 4 H, *J* 7.9 Hz, aryl), 7.01 (m, 2 H, amide), 3.92 (m, 2 H, cyclohexyl), 2.32 (s, 6 H, methyl), 2.15 (d, 2 H, *J* 10.4 Hz, cyclohexyl), 1.72 (d, 2 H, *J* 6.4 Hz, cyclohexyl), 1.31 (m, 4 H, cyclohexyl). $^{13}C\{^1H\}$ NMR: δ 168, 142, 131, 129, 127, 55, 32, 25, 21. IR/cm^{-1}: 3281 (m), 2924 (s), 2854 (s), 1640 (vs), 1614 (w, sh), 1571 (m), 1553 (m), 1508 (w), 1462 (m), 1452 (m), 1377 (w), 1333 (m), 834 (w), 757 (w), 712 (w), 685 (w).

General conditions for conversion of diamides to diimine chlorides

To a stirred suspension of PCl_5 in CH_2Cl_2 was added a suspension of the diamide in CH_2Cl_2. A condenser was fitted to the flask and the reaction mixture refluxed for 14 h. All volatile material was removed under reduced pressure and the resulting solid was extracted with Et_2O. Filtration through Celite followed by concentration resulted in the formation of crystalline material, which was isolated by filtration. Cooling the filtrate to −30 °C for 22 h gave the product as colorless crystals.

Conversion of 3 to diimine chloride 4. Yield: 17 g, 65%. Mp: 143–145 °C. ^{1}H NMR: δ 7.82 (d, 4 H, *J* 8.3 Hz, aryl), 7.12 (d, 4 H, *J* 8.0 Hz, aryl), 4.18 (m, 2 H, cyclohexyl), 2.32 (s, 6 H, tolyl), 1.93 (m. 4 H, cyclohexyl), 1.52 (m, 4 H, cyclohexyl). $^{13}C\{^1H\}$ NMR: δ 141.6, 141.5, 133.3, 129, 128.8, 67.1, 30.3, 24, 21.3. IR/cm^{-1}: 1676 (s), 1611 (w), 1508 (w), 1456 (m), 1377 (w), 1352 (w), 1311 (w), 1247 (w), 1223 (w), 1181 (w), 1134 (w), 1072 (w), 1024 (w), 932 (w), 886 (w), 861 (w), 837 (w), 821 (w), 780 (w), 714 (w), 628 (w), 616 (w), 535 (w).

General conditions for synthesis of linked diamidines

(a) PCl_5 was suspended in CH_2Cl_2. The chosen aniline was then added dropwise with immediate formation of a colorless solid in a very exothermic reaction. A condenser was fitted to the flask and the solution was refluxed for 16–23 h. Removal of all volatile material gave a solid that was washed successively with water and saturated sodium bicarbonate until the washes remained clear. The solid was then taken up in CH_2Cl_2 and the solution washed with 2 M KOH (2×) and brine (2×), followed by drying over $MgSO_4$. Removal of all volatile material under reduced pressure produced a yellow foam that was Soxhlet extracted with hexanes for 12 h. Removal of hexane from the filtrate under reduced pressure yielded a colorless solid as the final product. (b) It is found that separating the steps in (a), above, gives comparable yields while allowing the reaction to be carried out on a much larger scale. The diimine chloride was dissolved in CH_2Cl_2 and the solution cooled to 5 °C. Aniline was added dropwise, then the reaction warmed to room temperature. A condenser was fitted to the flask and the solution refluxed for 27 h. Removal of all volatile material under reduced pressure gave a white solid that was taken up in CH_2Cl_2. The solution was washed with 1 M KOH/H_2O (3×) and brine (1×), then dried over Na_2SO_4. Filtration from the Na_2SO_4 on a medium porosity glass frit followed by removal of all volatile material under reduced pressure produced a white solid which was washed with Et_2O (1×) to afford the desired diamidine.

CDA-H_2 5. (a) Yield: 9.9 g, 67%. Mp: 171–173 °C. ^{1}H NMR: δ 7.25 (m, 10 H, aryl), 6.94 (t, 4 H, *J* 7.10 Hz, aryl), 6.74 (t, 2 H, *J* 7.16 Hz, aryl), 6.31 (d, 4 H, *J* 6.97 Hz, aryl), 5.99 (s, br, 2 H, aryl), 4.15 (s, br, 2 H, amidine), 2.44 (m, 2 H, cyclohexyl), 1.81 (s, br, 2 H, cyclohexyl), 1.44 (s, br, 4 H, cyclohexyl). $^{13}C\{^1H\}$ NMR: δ 158.3, 150.7, 135.5, 129.0, 128.6, 128.2, 128.1, 123, 120.9, 56.1, 32.7, 24.9. IR/cm^{-1}: 3219 (w, broad), 1608 (w), 1590 (w), 1542 (w), 1526 (w), 1462 (m), 1377 (w), 695 (w). Anal. Calcd. for $C_{32}H_{32}N_4$: C, 81.32; H, 6.82; N, 11.85; Found: C, 81.13; H, 6.90; N, 11.95%.

(^{t}Bu)CDA-H_2 6. (a) Yield: 2.7 g, 67%. Mp: 212–215 °C. ^{1}H NMR: δ 7.22 (d, 4 H, *J* 9.1 Hz, aryl), 7.13 (d, 4 H, *J* 7.9 Hz, aryl), 6.93 (t, 4 H, *J* 7.1 Hz, aryl), 6.72 (t, 2 H, *J* 6.9 Hz, aryl), 6.34 (d, 4 H, *J* 7.1 Hz, aryl), 5.97 (s, 2 H, aryl), 5.27 (s, 2 H, amidine), 4.10 (m, 2 H, cyclohexyl), 2.43 (m, 2 H, cyclohexyl), 1.78 (m, 2 H, cyclohexyl), 1.42 (m, 6 H, cyclohexyl), 1.26 (s, 18 H, *tert*-butyl). $^{13}C\{^1H\}$ NMR: δ 158, 152, 151, 132, 128.4, 128.1, 125, 123, 120, 56, 53, 34, 32, 31, 24. IR/cm^{-1}: 3420 (w),

3306 (w, broad), 3227 (w, broad), 1605 (w), 1587 (w), 1525 (w), 1486 (w), 1462 (m), 1377 (w), 836 (w), 753 (w), 696 (w).

(^{t}Bu,OMe)CDA-H$_2$ 7. (a) Yield: 3.3 g, 44%. Mp: 206–211 °C. ^{1}H NMR: δ 7.23 (d, 4 H, *J* 8.9 Hz, aryl), 7.11 (d, 4 H, *J* 8.2 Hz, aryl), 6.51 (d, 4 H, *J* 8.6 Hz, aryl), 6.26 (d, 4 H, *J* 8.2 Hz, aryl), 5.29 (s, 2 H, amidine), 4.10 (s, br, 2 H, cyclohexyl), 3.64 (s, 6 H, methoxy), 2.42 (m, 2 H, cyclohexyl), 1.78 (s, br, 2 H, cyclohexyl), 1.41 (m, 4 H, cyclohexyl), 1.27 (s, 18 H, *tert*-butyl). ^{13}C{^{1}H} NMR: δ 158.34, 154, 151.98, 132.82, 128.44, 125.07, 123.74, 114.65, 113.49, 56.06, 55.29, 34.67, 32.77, 31.24, 24.99. IR/cm^{-1}: 3225 (w, broad), 1599 (s), 1502 (s), 1462 (s, broad), 1237 (s), 1038 (w), 832 (m).

(Me,Me)CDA-H$_2$ 8. (a) Yield: 26 g, 76%. Mp: 112–115 °C. ^{1}H NMR: δ 7.11 (d, 4 H, *J* 7.8 Hz, aryl), 7.03 (d, 4 H, *J* 7.8 Hz, aryl), 6.75 (d, 4 H, *J* 7.7 Hz, aryl), 6.21 (d, 4 H, *J* 7.5 Hz, aryl), 5.90 (s, br, 2 H, amidine), 4.12 (s, br, 2 H, cyclohexyl), 2.42 (d, 2 H, *J* 10.8 Hz, cyclohexyl, 2.32 (s, 6 H, methyl), 2.17 (s, 6 H, methyl), 1.8 (s, br, 2 H, cyclohexyl), 1.02 (m, 4 H, cyclohexyl). ^{13}C{^{1}H} NMR: δ 158, 148, 139, 133, 129.8, 129.7, 129.1, 128.8, 128.7, 128.6, 115, 56, 33, 25, 21, 20. IR/cm^{-1}: 3210 (m), 2922 (vs), 2856 (vs), 1615 (vs), 1600 (vs), 1528 (vs), 1505 (vs), 1463 (s), 1377 (m), 1340 (m), 1325 (m), 1259 (m), 824 (s).

(Me)CDA-H$_2$ 9. (a) Yield: 25 g, 78%. (b) Yield: 59 g, 89%. Mp: 191–194 °C. ^{1}H NMR: δ 7.08 (d, 4 H, *J* 8.0 Hz, aryl), 6.99 (d, 4 H, *J* 11.8 Hz, aryl), 6.92 (t, 4 H, *J* 7.6 Hz, aryl), 6.71 (t, 4 H, *J* 7.3 Hz, aryl), 6.29 (d, 2 H, *J* 7.6 Hz, aryl), 5.92 (s, br, amidine), 4.10 (s, br, 2 H, cyclohexyl), 2.41 (m, 2 H, cyclohexyl), 2.28 (s, 6 H, methyl), 1.78 (s, br, 2 H, cyclohexyl), 1.41 (m, 4 H, cyclohexyl). ^{13}C{^{1}H} NMR: δ 158.4, 151, 139, 132.7, 128.9, 128.6, 128.1, 123, 120.8, 56.1, 32.8, 25, 21.3. IR/cm^{-1}: 3226 (w, br), 1606 (s), 1590 (s), 1543 (s), 1526 (s), 1487 (m), 1462 (vs), 1377 (m), 1350 (w), 1339 (w), 1327 (w), 1308 (w), 1260 (w), 1252 (w), 1230 (w), 1211 (w), 1183 (w), 1139 (w), 1071 (w), 1023 (w), 926 (w), 914 (w), 898 (w), 863 (w), 844 (w), 823 (w), 802 (w), 767 (w), 722 (w), 696 (w), 637 (w), 593 (w).

(Me,Me)CDA-Li$_2$(thf)$_4$ 10. (a) A solution of ^{n}BuLi in hexanes (2.56 M solution, 7.58 mmol) was added dropwise to a cold (−78 °C) solution of compound **8** (2.00 g, 3.79 mmol) in toluene (50 mL). The cold bath was removed and the solution allowed to warm to room temperature. After 16 h all volatile material was removed under reduced pressure to yield a pale yellow solid. The solid was extracted with thf (50 mL), filtered, and concentrated to 20 mL under reduced pressure. Cooling to −30 °C yielded bright yellow crystals (1.8 g, 56%) which were isolated by filtration and dried under vacuum. On removal of all volatile material under reduced pressure the crystals were observed to become significantly more opaque, indicating some degree of coordinated solvent loss. (b) Deprotonation can be performed by addition of toluene to a solid mixture of LiN(SiMe$_3$)$_2$ (3.17 g, 18.9 mmol) and **8** (5.00 g, 9.47 mmol) at room temperature. Similar isolation of the product yielded a yellow crystalline solid (5.02 g, 64%). Mp: >300 °C. ^{1}H NMR (CD$_3$CN): δ 7.15 (d, 4 H, *J* 6.9 Hz, aryl), 6.99 (d, 4 H, *J* 7.7 Hz, aryl), 6.47 (d, 4 H, *J* 8.1 Hz, aryl), 5.86 (d, 4 H, *J* 8.0 Hz, aryl), 3.81 (d, 2 H, *J* 8.5 Hz, cyclohexyl), 3.65 (m, 16 H, thf), 2.29 (s, 6 H, methyl), 2.00 (s, 6 H, methyl), 1.81 (m, 16 H, thf), 1.77 (m, 2 H, cyclohexyl), 1.70 (m, 4 H, cyclohexyl). ^{13}C{^{1}H} NMR: δ 157, 154, 152, 144, 128, 125, 123, 113, 57, 55, 34, 32, 31, 25. IR/cm^{-1}: 1573 (w), 1514 (vs), 1487 (vs), 1467 (s), 1410 (m), 1365 (vs), 1337 (s), 1256 (s), 1044 (s), 823 (s). Anal. Calcd. for $C_{26}H_{35}LiN_2O_2$: C, 75.34; H, 8.51; Found: C, 74.98; H, 8.32%.

(^{t}Bu,OMe)CDA-Na$_2$(thf)$_5$ 11. A stirred suspension of **7** (5.00 g, 7.75 mmol) in 50 mL of ether was cooled to −20 °C. To this was added a cold (−20 °C) solution of Na[N(SiMe$_3$)$_2$] (2.84 g, 15.5 mmol) in ether (30 mL). The resulting yellow suspension was gradually warmed to room temperature and stirred for 14 h. All volatile material was removed under reduced pressure to yield a yellow-orange solid which was extracted with 60 mL of thf. The solution was filtered and concentrated to 12 mL. Crystallization at 5 °C for 2 days afforded 5.2 g (64%) of yellow, crystalline product. Mp: 122–127 °C. ^{1}H NMR (C_6D_6): δ 7.54 (m, 4 H, aryl), 7.20 (d, 4 H, *J* 8.0 Hz, aryl), 6.62 (d, 4 H, *J* 8.5 Hz, aryl), 6.31 (m, 4 H, aryl), 4.38 (m, 2 H, cyclohexyl), 3.49 (m, 18 H, thf), 3.30 (s, 6 H, methyl), 2.43 (m, 2 H, cyclohexyl), 2.13 (m, 2 H, cyclohexyl), 1.84 (m, 4 H, cyclohexyl), 1.36 (m, 18 H, thf), 1.17 (s, 16 H, *tert*-butyl). ^{13}C{^{1}H} NMR: δ 168, 151, 149, 142, 129.3, 129, 128, 125, 123, 114, 67, 62, 55, 36, 34, 31, 26, 25. IR/cm^{-1}: 1606 (w, br), 1564 (w, br), 1414 (w, br), 1376 (w, br), 1361 (w, br), 1268 (w, br), 1252 (w, br), 1228 (m, sh), 1046 (w, sh), 904 (w, br), 840 (w, br), 824 (w, sh). Anal. Calcd. for $C_{62}H_{90}N_4Na_2O_7$: C, 70.96; H, 8.64; N, 5.34; Found: C, 70.61; H, 8.56; N, 5.41%.

(Me,Me)CDA-K$_2$(thf)$_5$ 12. A solution of KN(TMS)$_2$ (3.78 g, 18.9 mmol) in ether was added to a cold (−78 °C) suspension of **8** (5.00 g, 9.47 mmol) in ether. The suspension was allowed to warm to room temperature and stirred for 16 h. Removal of all volatile material yielded a slightly yellow solid, which was extracted with 220 mL of thf to yield a bright yellow solution. The solution was filtered through Celite and concentrated to 125 mL. Cooling to −30 °C yielded 2.8 g (34%) of crystalline material in two crops. Mp: 218–221 °C. ^{1}H NMR (CD$_3$CN): δ 7.16 (d, 4 H, *J* 7.9 Hz, aryl), 6.96 (d, 4 H, *J* 7.7 Hz, aryl), 6.55 (d, 4 H, *J* 7.4 Hz, aryl), 5.97 (s, 4 H, broad, aryl), 3.84 (s, 2 H, broad, cyclohexyl), 3.64 (m, 16 H, thf), 2.26 (s, 6 H, methyl), 2.05 (s, 6 H, methyl), 1.80 (m, 16 H, thf), 1.70 (s, 2 H, broad, cyclohexyl), 1.36 (s, 4 H, broad, cyclohexyl). ^{13}C{^{1}H} NMR: δ 163, 153, 146, 139, 138, 134, 130.5, 130.3, 129, 128, 123, 116, 68, 61, 35, 27, 26, 21, 20.6, 20.5. IR/cm^{-1}: 1606 (m), 1572 (m), 1482 (vs), 1470 (vs), 1410 (s), 1366 (vs), 1341(s), 1301 (m), 1282(m), 1253 (m), 1172 (m), 1054 (s), 910 (m), 820 (s). Anal. Calcd. for $C_{56}H_{78}K_2N_4O_5$: C, 69.67; H, 8.14; N, 5.80; Found: C, 69.39; H, 8.18; N, 5.82%.

General procedures for X-ray crystallography of 5, 8, 9, and 10

Pertinent details for the individual compounds can be found in Table 1, and below. A crystal of appropriate size was mounted on a glass capillary using Paratone-N hydrocarbon oil. The crystal was transferred to a Siemens SMART diffractometer/CCD area detector,[43] centered in the beam (Mo-Kα), and cooled by a nitrogen flow low-temperature apparatus which had been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrix and cell constants were determined by collection of 60 ten second frames, followed by spot integration and least squares refinement. A hemisphere of data was collected then the raw data were integrated (XY spot spread = 1.60°; Z spot spread = 0.60°) using SAINT.[44] Cell dimensions reported in Table 1 were calculated from all reflections with $I > 10\sigma$. Data analysis and absorption correction were performed using Siemens XPREP[45] and SADABS. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. The reflections measured were averaged. The structure was solved and refined with the teXsan software package[46] using direct methods[47] and expanded using Fourier techniques.[48] All non-hydrogen atoms were refined anisotropically, unless stated otherwise. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations, but were not refined, unless stated otherwise. The final residuals were refined against the data for which $F^2 > 3\sigma(F^2)$. The quantity minimized by the least squares program was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p factor, used to reduce the weight of intense reflections, was set to 0.03 throughout the refinement. The analytical forms of the scattering factor tables

for the neutral atoms were used and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

CCDC reference number 186/1347.

CDA-H_2, 5. All hydrogen atoms were found in the difference Fourier map, and were not assigned idealized positions.

(Me,Me)CDA-$Li_2(thf)_4$, 8. O10, C116, and C117 were modelled isotropically at 1/2 occupancy as part of a disordered thf molecule on an inversion center. C110, C111, C112, C113, and C114 were modelled isotropically at 1/2 occupancy as a completely disordered thf molecule located in the crystal lattice. C51, and C52 were modelled anisotropically at 1/2 occupancy as a carbon atom disordered over two positions.

(^{t}Bu,OMe)CDA-$Na_2(thf)_4$, 9. C59, C60, C61, C62, C63, C64, and C65 were modelled anisotropically as part of a completely disordered thf molecule; C62, C63, C64, and C65 were modelled at 1/2 occupancy; C59, C60, and C61 were modelled at full occupancy.

(Me,Me)CDA-$K_2(thf)_5$, 10. C28, C29, C30, C31, and O3 were modelled isotropically at 1/2 occupancy as a thf molecule disordered between coordination to K1 and K1*.

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