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N-Heterocyclic Carbenes and Charge Separation in Heterometallic s-Block Silylamides

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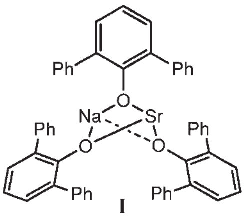
S Supporting Information

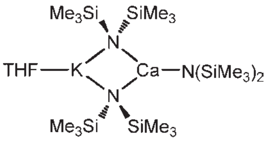
ABSTRACT: Addition of the N-heterocyclic carbene (NHC), 1,3-bis(2,6-di-isopropylphenyl)-imidazol-2-ylidene (IPr), to equimolar quantities of group 1 and group 2 bis(trimethylsilyl)-amides results in the isolation of charge separated species, $[M(IPr)_2]^+[M'\{N(SiMe_3)_2\}_3]^-$ (M = Li, Na, K; M′ = Mg, Ca, Sr, Ba). Although these systems were found to be prone to the separation of oily, most likely liquid clathrate, materials, either slow cooling or careful diffusion of the less polar solvent hexane into toluene solutions yielded nine crystalline heterobimetallic complexes in which the coordination sphere of the cationic group 1 center was found by X-ray diffraction analysis to be provided by two IPr ligands. These derivatives are the first examples of any compounds in which coordination at the central alkali metal cation is provided exclusively by NHC ligands and, for the cases where M = Na, are the first instances of any type in which an NHC ligand is bound to sodium. The anionic group 2-containing component of each compound was found to comprise three bis(trimethylsilyl)amido ligands coordinated in an approximately trigonal array about the divalent metal center. The bonding within the unusual cationic components of the compounds has been investigated by density functional theoretical (DFT) methods. Natural Bond Orbital (NBO) analyses have revealed that the coordination is provided by donation of the sp-hydridized IPr lone pair into the valence s-orbital of the alkali metal cation and are consistent with weaker binding, and consequently more labile solution behavior, as group 1 is descended.

INTRODUCTION

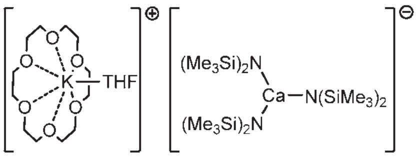
Although s-block heterobimetallics of the general form $MM'(E)_3$ (M = group 1 element Li, Na, K; M′ = group 2 element, Mg, Ca, Sr, Ba; E = anionic ligand, e.g., alkyl,[1] NR_2,[2] OR,[3] PR_2[4]) have a provenance that may be traced to the early 1950s,[1a] it is only in more recent times that such so-called ‘ate’ complexes have risen to prominence as reagents in their own right. Studies of structurally well-defined derivatives of amide bases in particular have given rise to an entire subset of potent and highly regiospecific bases capable of deprotonating even relatively nonacidic substrates in which the activation of a specific C−H bond is directed by a synergic relationship between the two differentiated metal centers.[5] Central to these efforts have been structural solid state studies which have given insight into the disposition of the group 1 and group 2 centers, both with respect to each other and/or to an activated or specifically oriented substrate molecule. Beautiful examples of this latter behavior are provided by Mulvey's isolation of a variety of transition metal derivatives in which the extent of mono-,[6] di-,[7] or tetra-magnesiation[8] of organometallic species such as bis(benzene)chromium and ferrocene was controlled by appropriate selection of the group 1 element and the basic organic residue. While the majority of structurally characterized heterometallic s-block ‘ate’ complexes display structures in which both metals are included in the same complex as a contact ion pair (e.g., the Na/Sr aryloxide, **I**,[3c] and the K/Ca silylamide, **II**[2j]) it has also been observed that charge separated species such as the potassium calciate species **III** may result through use of sterically demanding bis(trimethylsilyl)amide ligands in conjunction with multidentate or encapsulating neutral donors such as the 18-crown-6 ligand illustrated.[2k] Additionally, in the instances reported thus far, formation of the $[M\{N(SiMe_3)_2\}_3]^-$ anion is limited to cases where M = Mg[2d−g] or Ca.[2k,l] In this contribution we report that group 2 metalate formation may be extended across the entire series of heavier alkaline earth metals in conjunction with Li-, Na-, or K-based cations through the use of a sterically demanding N-heterocyclic carbene (NHC) ligand, 1,3-bis(2,6-di-isopropylphenyl)imidazol-2-ylidene (IPr).



I



II



III

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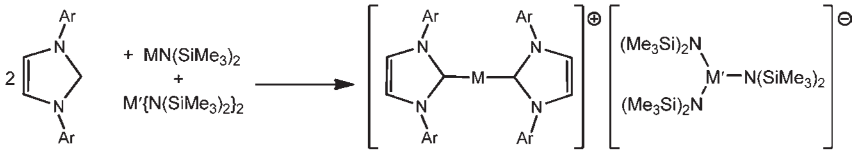
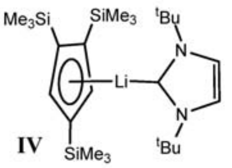
Scheme 1



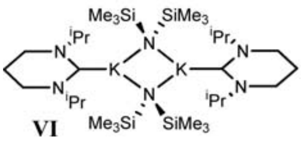
1: M = Li; M′ = Mg. **2**: M = Na; M′ = Mg.
3: M = K; M′ = Mg. **4**: M = Li; M′ = Ca.
5: M = Na; M′ = Ca. **6**: M = K; M′ = Ca.
7: M = Na; M′ = Sr. **8**: M = K; M′ = Sr.
9: M = K; M′ = Ba.

RESULTS AND DISCUSSION

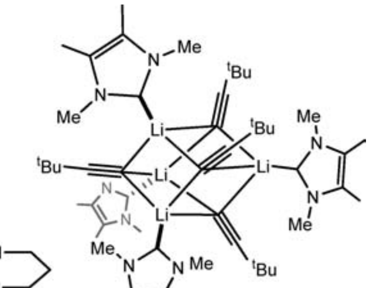
N-heterocyclic carbenes typically bind as potent two electron σ-donors, and their steric demands can be easily modulated by manipulation of the N-bound imidazolyl organic residues.[9] Although NHCs have a rich pedigree as ligands for the imposition of low coordination numbers or unusual bonding environments from across the entire periodic table,[10] their use in s-block systems is still relatively limited and crystallographically characterized examples of group 1 centers coordinated by neutral NHCs are limited to two lithium derivatives compounds **IV**[11a] and **V**[11b] and a single potassium complex, **VI**.[12,13]



IV



VI



V

The formation of such interactions down both groups 1 and 2 is likely to be dependent upon the cation size and to vary with the hardness of the metal centers involved. Furthermore, in a heterobimetallic system, the relative affinity of the NHC for either the group 1 or the group 2 center will be dictated by the relative hardness or (softness) of the individual M^+ and M'^{2+} ions involved as well as the identity of any other coligands. We speculated that the formation of group 1 NHC adducts, therefore, could be encouraged through the formation of charge separated ion pairs in competitive reactions with group 1 and group 2 silylamides. In this case the comproportionation reaction should be driven by the relative affinity of the harder amide donors for the harder group 2 cations leaving the group 1 metal to be encapsulated by the sterically demanding NHC ligand, IPr (Scheme 1).

This strategy was found to be broadly applicable, and a series of reactions employing the commercially available bis(trimethylsilyl)amides of Li, Na, and K have been undertaken to produce a series of nine new charge separated species of the general form $[M(IPr)_2]^+[M'\{N(SiMe_3)_2\}_3]^-$. In each case an equimolar mixture of the group 1 and group 2 reagents was combined with 2 equiv of IPr, weighed directly into a Schlenk tube, and dissolved in a minimal amount of toluene. Crystallization either by concentration or refrigeration of the reaction mixture in many cases resulted in the separation of an oily material, which we suggest was due to the formation of liquid clathrates of the type which has been most commonly observed for compounds of the general formulation $M[Al_2(CH_3)_6X]$ (where M = alkali metal and X = , e.g., alkyl, N_3^-, SCN^-, $SeCN^-$).[14] Bulk samples of the crystalline compounds **1**–**9** suitable for single crystal X-ray analysis were, however, formed either by slow cooling or slow diffusion into (layering of) the reaction mixture with the less polar hydrocarbon solvent hexane. In general, crystalline compounds containing the strontium and barium dications proved somewhat more difficult to isolate, a possible reflection of the more labile coordination chemistry associated with the largest alkaline earth centers (vide infra). Each compound was shown to comprise a well-defined separated ion structure in which the group 1 center is coordinated by two IPr ligands and the group 2 center is solely ligated by a trigonal array of bis(trimethylsilyl)amido ligands. The structures of two representative ion separated structures, the lithium magnesiate, compound **1**, and the sodium calciate compound, **5**, are illustrated in Figures 1 and 2, respectively, while details of the X-ray analyses, bond lengths, and bond angles for all 10 structures reported in this work are provided in Tables 1–3, respectively. The lithium compounds **1** and **4** and the potassium compounds **3**, **6**, **8**, and **9** are the first crystallographically characterized compounds containing these group 1 centers in which the coordination environment is entirely provided by an NHC donor. Furthermore, compounds **2**, **5**, and **7** provide the first examples of any type in which a neutral NHC is coordinated to sodium. Compounds **7** and **8** containing the $[Sr\{N(SiMe_3)\ _2\}_3]^-$ anion and the barium compound **9** also appear to be the first examples of bis(trimethylsilyl)amido strontiate and barate species, respectively. The lithium and sodium magnesiate structures, compounds **1** and **2**, and the sodium calciate compound, **5**, are isostructural (monoclinic $P2_1/_n$) as are the potassium magnesiate and calciate compounds **3** and **6** (monoclinic $C2/_c$) and the potassium strontiate and barate compounds **8** and **9** (monoclinic $P1\ 2_1/_n\ 1$). Each series/pair of isostructural derivatives reflects the bond lengths associated with the formation of the specific $[M(IPr)_2]^+[M'\{N(SiMe_3)_2\}_3]^-$ ions, and the unit cell volumes increase as expected for replacement of either the alkali or the alkaline earth center for a heavier congener within the ate complex structures. The lithium cations within compounds **1** and **4** each feature alkali metal centers in which the IPr ligands are bound entirely through the sp^2-hybridized imidazol-2-ylidene carbon centers. The C–Li–C bond angles

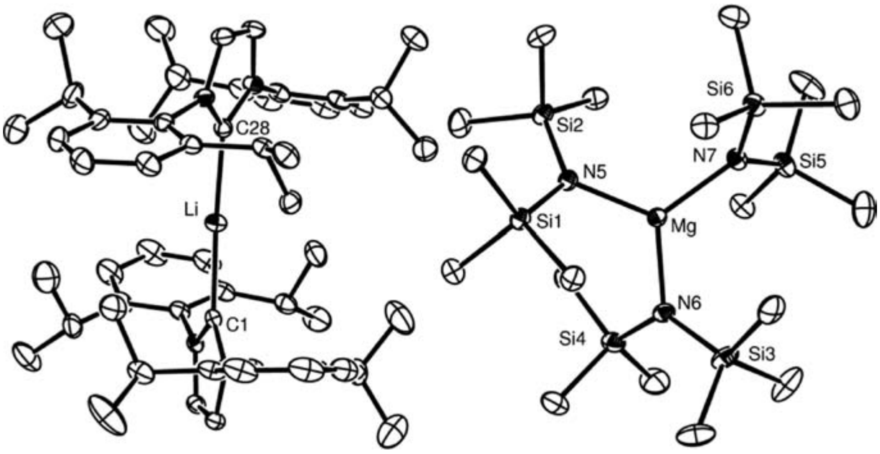


Figure 1. ORTEP representation (25% probability ellipsoids) of the separated ion compound **1**. Hydrogen atoms omitted for clarity.

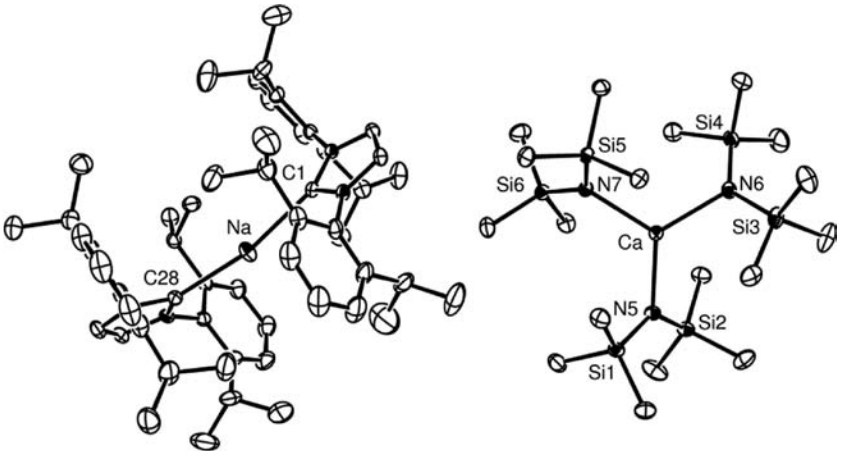


Figure 2. ORTEP representation (25% probability ellipsoids) of the separated ion compound **5**. Hydrogen atoms omitted for clarity.

(range 174.5(2)−177.7(4)°) deviate only slightly from linearity in both structures and, while comparable to values previously reported for Li to neutral NHC contacts (**IV** 2.155(4), **V** 2.207(3) Å), [11a,b] the individual Li−C bond lengths of all three cations (the structure of **4** comprises two unique Li centers) display a marked variability within the individual [(IPr)$_2$Li]$^+$ units (range of Li−C bond lengths 2.128(6)−2.179(6) Å). Although this latter observation is probably a reflection of the lability and deformability of the Li-NHC interactions with respect to even modest crystal packing forces, it is notable that the sodium cations within the structures of compounds **2**, **5**, and **7** display no such variability and allow us to suggest that the narrow range of Na−C distances observed (2.439(6)−2.452(2) Å) is typical of sodium to NHC interactions. In contrast to the unidentate coordination observed in the NHC binding to the lighter group 1 metals, the cationic components of the potassium compounds **3**, **6**, **8**, and **9** (the structure of the potassium barate compound, **9**, is illustrated in Figure 3) each consist of a centrosymmetric [(IPr)$_2$K]$^+$ structure in which coordination is augmented by an asymmetric but significant η^3-interaction with the π-system provided by the *ipso* and *ortho* carbon centers of one of the pendant di-*iso*-propylphenyl substituents (C_{ipso} distances, ca. 3.15 Å, C_{ortho} ca. 3.28−3.45 Å). Although these interactions are significant and are typical of potassium-π-aryl contacts,[15] the primary connection to each of the IPr ligands is still provided by the sp^2-hydridized imidazol-2-ylidene carbon center (**3**, 2.8614(17); **6** 2.8720(17); **8** 2.8210(2); **9** 2.825(2) Å). While several potassium-containing complexes have been reported in which the NHC fragment is supported by an anionic alkoxide,[13b] amide[13e] or fluorenyl substituent, [13h] the only previous neutral NHC derivative of this metal appears to be Alder's 1,3-di-isopropyl-3,4,5,6-tetrahydropyrimid-2-ylidene adduct of KN(SiMe$_3$)$_2$, **VI.**[12] In this latter case, K−C distances of 3.00 Å were observed upon coordination of the six-membered heterocycle, a distance which is somewhat longer than any of the analogous measurements observed in the ion separated structures reported herein (range 2.810(2) to 2.8720(17) Å).

Although the magnesiate and calciate tris(silylamido) anions comprising compounds **1**−**6** are unremarkable, [2d−g,l,k] the strontiate and barate centers of compounds **7**, **8**, and **9** appear to be the first crystallographically characterized examples of these particular moieties. The individual Sr−N (**7**, 2.461(3); **8**, 2.468(2) Å) and Ba−N (**9**, 2.639(2) Å) distances across the respective anions in the structures of compounds **7**−**9** are only marginally elongated in comparison with the terminal M′−N linkages observed in [M′{N(SiMe$_3$)$_2$}$_2$]$_2$ (M′ = Sr, 2.44; Ba 2.576(3) Å) in which similarly three-coordinate geometries are maintained through the formation of two μ-M′-N-M′ bridging interactions.[16]

Table 1. Crystallographic Data for Compounds 1−10

	1	2	3	4	5	6
molecular formula	$C_{72}H_{126}LiMgN_7Si_6$	$C_{72}H_{126}MgNaN_7Si_6$	$C_{72}H_{126}KMgN_7Si_6$	$C_{154.25}H_{265.25}Ca_2Li_2N_{14}Si_{12}$	$C_{72}H_{126}CaNaN_7Si_6$	$C_{72}H_{126}CaNaN_7Si_6$
formula weight (g mol^{-1})	1289.59	1305.64	1321.75	2747.17	1321.41	1337.52
crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$C2/c$	$P\bar{1}$	$P2_1/n$	$C2/c$
a (Å)	20.9711(2)	20.7615(4)	30.6548(3)	17.7709(2)	20.84100(10)	30.4315(5)
b (Å)	20.3806(2)	21.1624(5)	18.2165(3)	22.5526(3)	21.05920(10)	18.4286(3)
c (Å)	21.1365(2)	21.1223(3)	17.4146(2)	23.9297(3)	21.02590(10)	17.3923(2)
α (deg)	90	90	90	71.0000(10)	90	90
β (deg)	112.8540(10)	113.902(2)	120.3760(10)	81.6270(10)	112.9070(4)	119.3030(10)
γ (deg)	90	90	90	85.2310(10)	90	90
V (Å^3)	8324.64(14)	8484.5(3)	8389.76(19)	8964.84(19)	8500.40(7)	8505.7(2)
Z	4	4	4	2	4	4
μ (mm^{-1})	0.148	0.150	0.196	0.190	0.203	0.247
ρ (g cm^{-3})	1.029	1.022	1.046	1.018	1.033	1.044
θ range (deg)	4.62 to 27.49	4.89 to 25.06	3.48 to 27.46	4.81 to 25.35	4.89 to 27.53	4.82 to 27.47
R_1, wR_2 [$I > 2\sigma(I)$]	0.0551, 0.1249	0.0718, 0.1555	0.0495, 0.1136	0.0708, 0.1789	0.0485, 0.1160	0.0494, 0.1233
R_1, wR_2 (all data)	0.0892, 0.1447	0.1398, 0.1967	0.0801, 0.1301	0.1245, 0.2216	0.0686, 0.1325	0.0662, 0.1384
measured/independent reflections/ R_{int}	97063/18746/ 0.0577	116857/14751/ 0.1576	79431/9576/ 0.0698	134577/39285/ 0.0612	147116/19331/ 0.0646	69096/9660/ 0.0384

	7	8	9	10
molecular formula	$C_{295}H_{512}N_8$ $Na_4Si_{24}Sr_4$	$C_{79}H_{134}KN_7Si_6Sr$	$C_{79}H_{134}BaKN_7Si_6$	$C_{94}H_{140}K_2N_6Si_4$
formula weight (g mol^{-1})	5567.93	1477.19	1526.91	1544.68
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$Pcca$	$P\,1\,2_1/n\,1$	$P\,1\,2_1/n\,1$	$P\,1\,2_1/c\,1$
a (Å)	15.9859(2)	16.90140(10)	16.90150(10)	13.37860(10)
b (Å)	29.3812(5)	18.94360(10)	19.0122(2)	17.3987(2)
c (Å)	37.6290(6)	28.9610(2)	29.1601(3)	21.1682(2)
α (deg)	90	90	90	90
β (deg)	90	96.6690(10)	97.5770(10)	102.1640(10)
γ (deg)	90	90	90	90
V (Å^3)	17673.8(5)	9209.80(10)	9288.34(15)	4816
Z	2	4	4	2
μ (mm^{-1})	0.735	0.749	0.590	0.192
ρ (g cm^{-3})	1.046	1.065	1.092	1.065
θ range (deg)	3.85 to 25.02	3.52 to 27.38	2.92 to 30.10	4.57 to 27.49
R_1, wR_2 [$I > 2\sigma(I)$]	0.0647, 0.1304	0.0476, 0.1050	0.0499, 0.1035	0.0517, 0.1258
R_1, wR_2 (all data)	0.1664, 0.1664	0.0803, 0.1210	0.1178, 0.1258	0.0722, 0.1403
measured/independent reflections/ R_{int}	109357/15249/0.0974	131455/20750/0.0618	141691/26996/0.1013	77773/11005/0.0424

The empirical observation that these NHC-supported ion-separated complexes become less well-defined and increasingly labile in their coordination behavior was reinforced by an additional X-ray analysis of crystals formed from a further attempted synthesis of compound **9**. In this latter case the isolated product proved to be contaminated with the dimeric IPr adduct of $[K\{N(SiMe_3)_2\}]_2$, compound **10** shown in Figure 4, an analogue of the only previously reported potassium complex of a neutral NHC, compound **VI**, which presumably is formed in competition to compound **9** because of the decreased affinity of the larger and softer Ba^{2+} dication for the silylamide ligand. The structure of compound **10** resides on an inversion center and provides a $K-C_{IPr}$ bond length (3.0291(17) Å) commensurate with that reported for the similarly dimeric adduct **VI**.[12]

Although examples of coordinatively stable magnesium derivatives bearing the $N(SiMe_3)_2$ have been reported,[12b−d] the solution lability of all nine charge separated species was also apparent from inspection of their ^1H and $^{13}C\{^1H\}$ NMR spectra. The stability of each group 2 system is evidently perturbed by the presence of an equivalent of the group 1 center for all the magnesiate compounds **1**−**3**. For the lithium and sodium calciate species compounds **4** and **5**, the room temperature spectra were largely uninformative and evidenced multiple, broadened NHC and silylamido environments. A series of EXSY experiments indicated that the individual environments were subject to exchange on the NMR time scale. We propose, therefore, that these observations originate from the formation of several neutral and ion-paired species in solution as well as the

Table 2. Selected Bond Lengths (Å) for Compounds 1−10

	1[a]	2[b]	3[c]	4[d]	5[e]	6[f]	7[g]	8[h]	9[i]	10[j]
M−C(1)	2.150(4)	2.451(4)	2.8614(16)	2.132(6)	2.441(2)	2.8720(17)	2.452(4)	2.827(2)[t]	2.825(2)	3.0291(17)
M−C(28)	2.154(4)	2.446(5)		2.128(6)	2.442(2)		2.439(6)	2.810(2)[u]		
M′−N(5)	2.0257(19)	2.027(3)	2.0238(15)[k]	2.308(3)[m]	2.3096(16)	2.3066(15)[p]	2.461(3)[r]	2.4727(18)	2.629(2)[v]	2.8576(16)[y]
M′−N(6)	2.0222(19)	2.037(4)	2.033(2)[l]	2.326(3)[n]	2.3096(16)	2.328(2)[q]	2.461(5)[s]	2.4701(19)	2.629(2)[w]	2.7836(15)[z]
M′−N(7)	2.0262(19)	2.026(4)		2.312(3)[o]	2.3108(15)			2.468(2)	2.623(2)[x]	

[a] M = Li, M′ = Mg. [b] M = Na, M′ = Mg. [c] M = K, M′ = Mg. [d] M = Li, M′ = Ca. [e] M = Na, M′ = Ca. [f] M = K, M′ = Ca. [g] M = Na, M′ = Sr. [h] M = K, M′ = Sr. [i] M = K, M′ = Ba. [j] M = K. [k] Mg−N(3). [l] Mg−N(4). [m] Ca(1)−N(9). [n] Ca(1)−N(10); Ca(1)−N(11). [p] Ca−N(3). [q] Sr(1)−N(5). [s] Sr(1)−N(6). [t] K(2)−C(1). [u] K(1)−C(28). [v] Ba(1)−N(3). [w] Ba(1)−N(4). [x] Ba(1)−N(5). [y] K−N(3). [z] K−N(3)′.

Table 3. Selected Bond Angles (deg) for Compounds 1−10

	1[a]	2[b]	3[c]	4[d]	5[e]	6[f]	7[g]	8[h]	9[i]	10[j]
C(1)−M−C(28)	174.5(2)	168.94(18)	180.00(6)[k]	176.4(3)	165.78(8)	180.00(6)[r]	174.11(18)	180.00(8)[x]	180.0[r]	136.54(4)[dd]
N(1)−C(1)−M	123.22(19)	143.2(3)	153.73(12)	130.8(3)	117.24(12)	103.22(10)	137.5(3)	152.27(15)[y]	105.27(15)	133.08(11)
N(2)−C(1)−M	134.63(18)	114.4(3)	104.04(10)	126.7(3)	140.46(13)	154.76(12)	120.4(3)	105.34(13)[z]	152.52(17)	131.00(5)[ee]
N(5)−M′−N(6)	118.76(8)	119.86(15)	120.48(5)[l]	120.23(11)[o]	121.50(6)	122.03(4)[s]	120.04(9)	119.53(6)	125.01(7)[aa]	92.26(4)[ff]
N(6)−M′−N(7)	120.45(8)	120.72(15)	120.48(5)[m]	120.07(12)[p]	116.55(6)	122.03(4)[t]	120.04(9)[v]	117.59(7)	117.29(7)[bb]	
N(5)− M′−N(7)	120.78(8)	119.42(15)	119.04(10)[n]	119.67(11)[q,o]	121.57(6)	115.94(8)[u]	119.91(17)[w]	122.88(7)	117.69(6)[cc]	

[a] M = Li, M′ = Mg. [b] M = Na, M′ = Mg. [c] M = K, M′ = Mg. [d] M = Li, M′ = Ca. [e] M = Na, M′ = Ca. [f] M = K, M′ = Ca. [g] M = Na, M′ = Sr. [h] M = K, M′ = Sr. [i] M = K, M′ = Ba. [j] M = K. [k] C(1)−K−C(1)′. [l] N(3)−Mg−N(4). [m] N(4)−Mg−N(3)′. [n] N(3)−Mg−N(3)′. [o] N(9)−Ca(1)−N(10). [p] N(10)−Ca(1)−N(11). [q,o] N(11)−Ca(1)−N(9). [r] C(1)−K−C(1)′. [s] N(3)−Ca−N(4). [t] N(4)−Ca−N(3). [u] N(3)−Ca−N(3)′. [v] N(5)′−Sr(1)−N(6). [w] N(5)′−Sr(1)−N(5). [x] C(1)−K(2)−C(1)′. [y] N(1)−C(1)−K(2). [z] N(2)−C(1)−K(2). [aa] N(3)−Ba−N(4). [bb] N(4)−Ba−N(5). [cc] N(3)−Ba−N(5). [dd] C(1)−K−N(3). [ee] C(1)−K−N(3)′; N(3)−K−N(3)′.

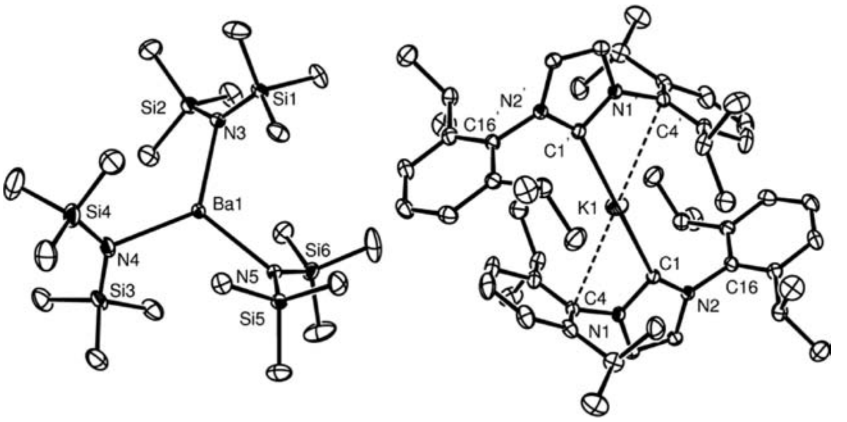


Figure 3. ORTEP representation (25% probability ellipsoids) of the separated ion compound **9**. Hydrogen atoms omitted for clarity. The dashed line indicates the close contact observed between the potassium center and the *ipso*-C of the C(4)-containing 2,6-di-*iso*-propylphenyl substituent.

ion separated structures deduced from the solid state X-ray determinations. Attempts to resolve this dynamic behavior through the acquisition of variable temperature NMR spectra were unsuccessful and generally resulted in further broadening as a result of the aforementioned liquid clathrate formation and the separation of ill-defined and oily materials. Although the ^{1}H NMR spectrum of the isolated sodium strotiate species, compound **7**, was similarly uninformative, it is notable that spectra collected for both the potassium calciate derivative, **6**, and the potassium strontiate, **8**, were observed to display single, sharp environments which, albeit shifted, were reminiscent of the spectra of the individual group 1 and group 2 silylamide and IPr components. Similar spectra were acquired from NMR scale reactions of both $LiN(SiMe_3)_2$ and $NaN(SiMe_3)_2$ with $[Ba\{N(SiMe_3)_2\}_2]_2$ and IPr and the isolated complex, **9**, and we ascribe these observations to sufficiently rapid exchange on the NMR time scale to allow the observation of completely time averaged environments. We propose that this apparently contrasting solution behavior is likely to be a consequence of the increasing lability of the reaction mixtures and decreasing affinity of the largest alkaline earth dications for the relatively hard amide ligands as group 2 is descended.

To provide an assessment of the binding of the IPr ligand to the alkali metals within the unusual cationic components of compounds **1**−**9** we have undertaken density functional theory (DFT) calculations upon model Li, Na, and K cations using the B3LYP DFT and LAN2DZ pseudopotentials (and basis set) implemented in Gaussian03.[17] The geometry optimizations were

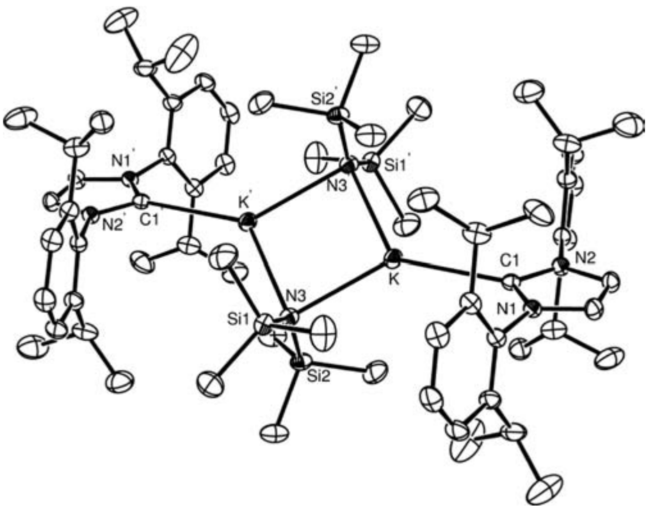


Figure 4. ORTEP representation (25% probability ellipsoids) of compound **10**. Hydrogen atoms omitted for clarity.

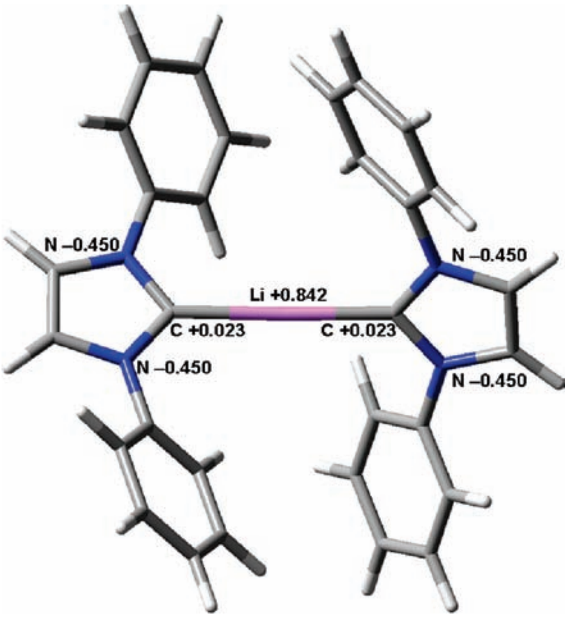


Figure 5. DFT-optimized structure (B3LYP/LAN2DZ) of the model lithium cation and calculated NBO charges.

performed by selecting initial geometries based upon those deduced for the structures of compounds **1**−**3** and, in each case, were confirmed as true minima by independent frequency calculations. To reduce computational expense the *iso*-propyl groups of the IPr di-*iso*-propylphenyl substituents were replaced by hydrogen atoms, and Figure 5 illustrates the results of these studies for the complex where M = Li. Although the M-C_{NHC} contact (Li−C 2.063 Å) was somewhat underestimated for the case where M = Li, possibly because of the reduced steric demands of the model cationic species, and the π-aryl interactions of the potassium-containing compounds were not replicated, all other bond measurements within the calculated structures were generally within 0.02 Å of the equivalent distances and angles deduced from the X-ray analyses performed upon compounds **1**−**9**. Natural bond orbital (NBO) analyses indicated that the majority of the positive charge was, in each case, borne primarily by the electropositive group 1 metal center (NBO charges, Li +0.842; Na +0.893; K +0.949) and only marginally dissipated onto the two NHC ligands. In the cases of the lithium and sodium model complexes, second order perturbation analyses of the donor−acceptor linkages in the NBOs indicated that the NHC ligands act as essentially pure σ-donors in which the principal C-M interactions are provided by donation of a carbon-based and sp-hybridized lone pair into the alkali metal 2s (Li) or 3s (Na) orbitals. These interactions are evidently very weak (Li−C 23 kcal mol^{-1}; Na−C 15 kcal mol^{-1}) and decrease with the increasing atomic number of the alkali metal to the extent that the calculated K−C bond could not be estimated above the threshold level of 0.5 kcal mol^{-1}). Although this observation serves to highlight the limitations of the applied basis set and level of theory, a trend toward progressively weaker M-C interactions is a qualitative reflection of the increasingly labile and ill-defined solution behavior of compounds **1**−**9** with increasing size and atomic weight of the metal cations.

In conclusion we have shown that homoleptic NHC-stabilized alkali metal cations may be isolated in the solid state in conjunction with tris(silylamido) alkaline earth anions. Although the solution lability of these species most likely mitigates against any NHC-dependent influence upon reactivity, we are currently seeking to assess the utility of these compounds as unusual basic reagents.

■ EXPERIMENTAL SECTION

General Procedures. Hexanes and toluene were dried using an Innovative Technology solvent purification system and stored over 4 Å molecular sieves prior to use. D_8-toluene was distilled from molten potassium and stored over 4 Å molecular sieves prior to use. All reactions were performed under an inert atmosphere (nitrogen or argon) using standard Schlenk or glovebox techniques. $MN(SiMe_3)_2$ (M = Li, Na, or K) were purchased from Sigma Aldrich Chemicals while $[M'\{N(SiMe_3)_2\}_2]_2$ (M′ = Mg, Ca, Sr, or Ba) and 1,3-bis(2,6-di-isopropylphenyl)imidazol-2-ylidene (IPr) were prepared according to literature methods.[18,19] NMR spectra were collected on either a Bruker AV-400 spectrometer ($^{13}C\{^1H\}$ NMR 100 MHz,), or a Bruker AV-300 spectrometer ($^{13}C\{^1H\}$ NMR 75 MHz). ^1H and $^{13}C\{^1H\}$ NMR spectra of those compounds which could not be unambiguously assigned at room temperature are provided in the Supporting Information to this paper. Microanalyses were performed by Mr. Stephen Boyer of London Metropolitan University.

Preparation of $[M(IPr)_2]^+[M'\{N(SiMe_3)_2\}_3]^-$: Representative Procedure. A 1:1:2 mixture of $MN(SiMe_3)_2$ (M = Li, Na, or K), $[M'\{N(SiMe_3)_2\}_2]_2$ (M′ = Mg, Ca, Sr, or Ba) and 1,3-bis(2,6-di-isopropylphenyl)imidazol-2-ylidene were weighed directly into a Schlenk flask and then dissolved in a minimal amount of toluene. The resulting solution was stirred for 30 min, filtered to remove small amounts of insoluble material, and then allowed to stand. An oily residue usually settled out from the mixture that crystallized on prolonged storage. In cases where an oil did not separate, the resulting solution was layered with hexane to give a crystalline product upon standing at room temperature.

$[Li(IPr)_2]^+[Mg\{N(SiMe_3)_2\}_3]^-$, (1). $LiN(SiMe_3)_2$ (0.5 mmol, 84 mg), $[Mg\{N(S_IMe_3)_2\}_2]$ (0.5 mmol, 172 mg), IPr (1 mmol, 388 mg) were dissolved in toluene (5 mL). The product crystallized from the resulting oil. Yield: 420 mg, 65%. Anal. Calcd: for $C_{72}H_{126}N_7Si_6LiMg$: C, 67.06; H, 9.85; N, 7.60. Found: C, 67.19; H, 9.71; N, 7.49. ^1H NMR ppm (298 K, D_8-toluene): −0.06 (s, ca. 2H, SiCH_3), 0.09 (s, ca. 5H, SiCH_3), 0.59, 0.61 (br. s, ca. 40H, SiCH_3), 0.67 (s, 18H, SiCH_3), 0.94, 1.16, 1.23 (d, ca. 12H, CHCH_3), 2.91 (m, 8H, CHCH$_3$), 6.27 (s, 2H), 6.90−7.10 (m, ca. 14H) all peaks broad.

$[Na(IPr)_2]^+[Mg\{N(SiMe_3)_2\}_3]^-$, (2). $NaN(SiMe_3)_2$ (0.5 mmol, 92 mg), $[MgN(SiMe_3)_2\}_2]$ (0.5 mmol, 172 mg), IPr (1 mmol, 388 mg) were dissolved in toluene (5 mL). The product precipitated from solution after mixing, dissolved on gentle heating and crystallized on slow cooling. Yield: 250 mg, 38%. Anal. Calcd. for $C_{72}H_{126}N_7Si_6MgNa$: C, 66.23; H, 9.73; N, 7.51. Found: C, 66.18; H, 9.80; N, 7.40. ^{1}H NMR ppm (298 K, D_8-toluene): −0.04, 0.08, 0.27, 0.35 (s, various intensities $\mathrm{SiC}\mathit{H}_3$), 1.12 (broad d, ca. 24H, $\mathrm{CHC}\mathit{H}_3$), 2.85 (m, 8H, $\mathrm{C}\mathit{H}\mathrm{CH}_3$), 6.59 (br. s, 2H), 6.97−7.23 (m, ca. 14H) all peaks broad.

$[K(IPr)_2]^+[Mg\{N(SiMe_3)_2\}_3]^-$, (3). $KN(SiMe_2)_2$ (0.5 mmol, 100 mg), $[Mg\{N(SiMe_3)_2\}_2]$ (0.5 mmol, 172 mg), IPr (1 mmol, 388 mg) were dissolved in toluene (5 mL). The product crystallized from the resulting oil. Yield: 430 mg, 65%. Anal. Calcd. for $C_{72}H_{126}N_7Si_6KMg$: C, 65.43; H, 9.61; N, 7.42. Found: C, 65.29; H, 9.44; N, 7.30. ^{1}H NMR ppm (298 K, D_8-toluene): 0.01, 0.08, 0.60, 0.35 (s, various intensities $\mathrm{SiC}\mathit{H}_3$), 1.13 (d, ca. 24H, $\mathrm{CHC}\mathit{H}_3$), 2.77 (m, 8H, $\mathrm{C}\mathit{H}\mathrm{CH}_3$), 6.46 (s, 2H), 6.97−7.10 (m, ca. 14H).

$[Li(IPr)_2]^+[Ca\{N(SiMe_3)_2\}_3]^-$, (4). $LiN(SiMe_3)_2$ (0.5 mmol, 84 mg), $[Ca\{N(SiMe_3)_2\}_2]$ (0.5 mmol, 180 mg), IPr (1 mmol, 388 mg) were dissolved in toluene (5 mL). The product crystallized after layering a concentrated toluene solution with hexane. Yield: 400 mg, 61%. Anal. Calcd. for $C_{72}H_{126}N_7Si_6CaLi$: C, 66.25; H, 9.73; N, 7.51. Found: C, 66.35; H, 9.61; N, 7.36. ^{1}H NMR ppm (298 K, D_8-toluene): −0.09, 0.54, 0.59 (s, various intensities $\mathrm{SiC}\mathit{H}_3$), 0.95 (d, 6H, $\mathrm{CHC}\mathit{H}_3$), 1.12 (unresolved d, 6H, $\mathrm{CHC}\mathit{H}_3$), 1.22 (d, 6H, $\mathrm{CHC}\mathit{H}_3$), 2.63−2.83 (m, 8H, $\mathrm{C}\mathit{H}\mathrm{CH}_3$), 6.28 (br. s, ca. 1H), 6.58 (br. s, ca. 1H) 6.91−7.01 (m, ca. 14H).

$[Na(IPr)_2]^+[Ca\{N(SiMe_3)_2\}_3]^-$, (5). $NaN(SiMe_3)_2$ (0.5 mmol, 92 mg), $[Ca\{N(SiMe_3)_2\}_2]$ (0.5 mmol, 180 mg), IPr (1 mmol, 388 mg) were dissolved in toluene (5 mL). The product crystallized after layering a concentrated toluene solution with hexane. Yield: 380 mg, 57%. Anal. Calcd. for $C_{72}H_{126}N_7Si_6CaNa$: C, 65.44; H, 9.61; N, 7.42. Found: C, 57.13; H, 7.09; N, 5.59. Despite repeated efforts, satisfactory elemental analysis could not be obtained for this sample. ^{1}H NMR ppm (298 K, D_8-toluene): 0.04, 0.08, 0.59 (s, various intensities $\mathrm{SiC}\mathit{H}_3$), 0.95 (d, 6H, $\mathrm{CHC}\mathit{H}_3$), 1.12 (unresolved d, 6H, $\mathrm{CHC}\mathit{H}_3$), 1.22 (d, 6H, $\mathrm{CHC}\mathit{H}_3$), 2.23−2.81 (m, 8H, $\mathrm{C}\mathit{H}\mathrm{CH}_3$), 6.44−6.56 (br. s, ca. 2H), 6.98−7.25 (m, ca. 14H).

$[K(IPr)_2]^+[Ca\{N(SiMe_3)_2\}_3]^-$, (6). $KN(SIMe_3)_2$ (0.25 mmol, 50 mg), $[Ca\{N(SiMe_3)_2)_2\}$ (0.25 mmol, 90 mg), IPr (0.5 mmol, 194 mg) were dissolved in toluene (5 mL). The product crystallized from the resulting oil. Yield: 220 mg, 66%. Anal. Calcd. for $C_{72}H_{126}N_7Si_6CaK$: C, 64.66; H, 9.50; N, 7.33. Found: C, 64.63; H, 9.42; N, 7.19. ^{1}H NMR ppm (298 K, D_8-toluene): 0.39 (s, 27H $\mathrm{SiC}\mathit{H}_3$), 1.06 1.11 (d, 12H, $\mathrm{CHC}\mathit{H}_3$), 2.67 (m, 8H, $\mathrm{C}\mathit{H}\mathrm{CH}_3$), 6.56 (s, 2H), 6.97−7.10 (m, ca. 14H).

$[Na(IPr)_2]^+[Sr\{N(SiMe_3)_2\}_3]^-$, (7). $NaN(SiMe_3)_2$ (0.25 mmol, 46 mg), $[Sr\{N(SiMe_3)_2\}_2]$ (0.25 mmol, 102 mg), IPr (0.5 mmol, 194 mg) were dissolved in toluene (5 mL). The product crystallized after layering a concentrated toluene solution with hexane. The X-ray structure contains uncoordinated toluene, which is lost on isolation/exposure to vacuum. Yield: 160 mg, 47%. Anal. Calcd. for $C_{72}H_{126}N_7Si_6NaSr$: C, 63.17; H, 9.28; N, 7.16. Found: C, 63.04; H, 9.20; N, 7.04. ^{1}H NMR ppm (298 K, D_8-toluene): 0.08 (s, 27H $\mathrm{SiC}\mathit{H}_3$), 1.16 1.25 (d, 12H, $\mathrm{CHC}\mathit{H}_3$), 2.90 (m, 8H, $\mathrm{C}\mathit{H}\mathrm{CH}_3$), 6.64 (s, 4H), 6.97−7.28 (m, ca. 14H).

$[K(IPr)_2]^+[Sr\{N(SiMe_3)_2\}_3]^-$, (8). $KN(SiMe_3)_2$ (0.25 mmol, 50 mg), $[Sr\{N(SiMe_3)_2\}_2]$ (0.25 mmol, 90 mg), IPr (0.5 mmol, 194 mg) were dissolved in toluene (5 mL). The product crystallized on storage of the resultant oil at −20 °C for several days. The X-ray structure contains uncoordinated toluene, which is lost on isolation/exposure to vacuum. Yield: 140 mg, 40%. Anal. Calcd. for $C_{72}H_{126}N_7Si_6KSr$: C, 62.44; H, 9.17; N, 7.08. Found: C, 62.44; H, 9.26; N, 7.00. ^{1}H NMR ppm (298 K, D_8-toluene): 0.00 (s, 27H $\mathrm{SiC}\mathit{H}_3$), 1.08 1.24 (d, 12H, $\mathrm{CHC}\mathit{H}_3$), 2.72 (m, 8H, $\mathrm{C}\mathit{H}\mathrm{CH}_3$), 6.54 (s, 2H), 7.09−7.23 (m, ca. 14H).

$[K(IPr)_2]^+[Ba\{N(SiMe_3)_2\}_3]^-$, (9). $KN(SiMe_3)_2$ (0.25 mmol, 50 mg), $[Ba\{N(SiMe_3)_2\}_2]$ (0.25 mmol, 90 mg), IPr (0.5 mmol, 194 mg) dissolved in toluene 5 g. The product crystallized on storage of the resultant oil at 4 °C for several days. The X-ray structure contains uncoordinated toluene, which is lost on isolation/exposure to vacuum. Yield: 140 mg, 40%. Anal. Calcd. for $C_{72}H_{126}N_7Si_6BaK$: C, 60.27; H, 8.85; N, 6.83. Found: C, 60.29; H, 8.74; N, 6.74. ^{1}H NMR ppm (298 K, D_8-toluene): 0.08 (s, 27H $\mathrm{SiC}\mathit{H}_3$), 1.14 1.24 (d, 12H, $\mathrm{CHC}\mathit{H}_3$), 2.87 (m, 8H, $\mathrm{C}\mathit{H}\mathrm{CH}_3$), 6.62 (s, 2H), 6.98−7.10 (m, ca. 14H).

Crystallographic Data. Data for compounds **1**−**9** were collected at 150 K on a Nonius KappaCCD diffractometer equipped with an Oxford Cryosystem, using graphite monochromated MoK_α radiation (λ = 0.71073 Å). Data were processed using the Nonius Software.[20] Crystal parameters and details on data collection, solution, and refinement for the complexes are provided in Table 1. Structure solution, followed by full-matrix least-squares refinement was performed using the WINGX-1.70 suite of programs throughout.[21] For compound **2** one isopropyl group in the Na complex showed disorder in a 1:1 ratio. There was also potential disorder in two more isopropyl groups. However, resolving those did not lead to a better result. For compound **4** the asymmetric unit consisted of two cations, two anions, and disordered toluene and hexane solvent. The toluene molecule was disordered over two sites in a 1:1 ratio and fitted to form a regular hexagon. Half a molecule of hexane which shared the same site was located around a center of inversion and was assigned idealized bond lengths. Two methyl groups in each of the $SiMe_3$ groups around Si3 and Si6 in the Ca1 molecule showed disorder in the ratio 40:60. The two highest residual electron density peaks were in proximity to Li1 and Li2. For compound **5** there was potential disorder in one of the ^{i}Pr-groups (C10 C11 C12). However, trying to resolve this did not lead to a better result. The crystal of compound **7** was not a good diffractor. There was a decay of intensity at higher angles above 50° in 2θ. The asymmetric unit contained one Na cation, two half Sr anions, and 0.25 toluene which lay on a mirror plane. One methyl group (C62) in one of the Sr complexes showed disorder in the ratio 65:35 and one ligand in the Na cation was completely disordered (C31−C42) in the ratio 60:40 and the other one partly (C13−C15) in the ratio 70:30. C13A and C36A had to be refined isotropically, and eight bond lengths in these disordered groups had to be restrained. For compound **8** the asymmetric unit consisted of one Sr anion, one toluene molecule, and two half dimers of the K cation. One disorder was modeled in an ^{i}Pr group of the K1-containing component in the ratio 80:20. There was also potential disorder in the molecule of toluene. However, trying to solve this disorder did not lead to a better result. The aromatic C atoms in the toluene were fitted to a regular hexagon, and the bond length toward the methyl group was fixed. For compound **9** the asymmetric unit consisted of one Ba anion and two half molecules of the K cation. Additionally there was a toluene molecule which showed some potential disorder which could not be solved. For compound **10** the asymmetric unit consisted of half a dimer of the K complex and two disordered toluene molecules. The two toluene molecules were disordered about a center of inversion in the ratio 55:45 (C34−C40) and 60:40 (C41−C47), and the phenyl ring atoms were fitted to a regular hexagon. The C41A C42A and C41A C43A bond distances were restrained.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic information files (CIF) for **1**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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