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Coordination Modes

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Organometallic Compounds of the Heavier s-Block Elements—What Next?

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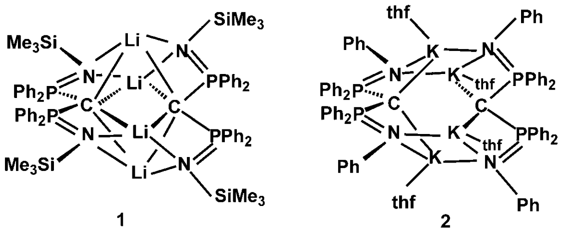
alkali metals · alkaline earth metals · coordination modes · methandiides · organometallic compounds

The organometallic chemistry of the s-block elements—from its origins 150 years ago to the present day—was recently reviewed in two fascinating essays.[1,2] Organolithium and Grignard reagents, now often bought in solution, have been used routinely in organic syntheses for many years. In contrast, much less is known about the potential, in synthesis or catalysis, of organometallic compounds of the heavier s-block elements. In part, this neglect is a natural consequence of the attention paid to compounds of the lighter elements, but development has also been held back by the simplistic view given in some textbooks that, whereas Li−C and Mg−C bonds are covalent, K−C and Ca−C bonds are ionic. The carbanions associated with the metal cations are, therefore, powerful nucleophiles that deprotonate ether solvents. This has made synthesis difficult and discouraged investigation.

The applications of organolithium and Grignard-type reagents have been greatly expanded by the development of so-called "superbases", that is, compounds containing two different metals,[2,3] but what of the organometallic compounds of individual heavier s-block elements in the absence of lighter atoms? A variety of alkali-metal compounds have been known for some time,[4] but it is only recently that researchers have made significant progress in exploring the chemistry of the organometallic compounds of the heavier alkaline earth metals.[5] As in organolithium compounds,[6] the bonding in all these compounds is highly ionic, but when the nucleophilicity of the carbanion is reduced by extensive delocalization of the negative charge on to bulky aryl, β-diketiminato or silicon-containing ligands, a range of compounds can be isolated. It is clear that these do not simply provide a minor variation on what is already known about the lighter elements. Unexpected reactions and unprecedented structures point to exciting new chemistry. This article highlights examples from two of the leading research groups in this area.[7,8] In each case, the compounds of the heavier elements differ from those of the lighter congeners, and show how changes in the size of the metals determine the structures of their organometallic compounds.

The synthetic potential of methandiides (R_2CM_2) has long been recognized,[9] but few have been isolated. The dimeric compounds $[\{[Ph_2P(NSiMe_3)]_2C\}_2M_4]$ (M = Li, **1**; Scheme 1),



1 **2**

Scheme 1. Methandiides of lithium (**1**) and potassium (**2**).

were obtained by the research groups of Cavell[10] and Stephan[11] 10 years ago. Further dimers in which $M_4 = Na_4$, Li_2Na_2, $LiNa_3$, Li_2K_2, and Na_3K were made by Henderson and co-workers by successive deprotonation of the bis(phosphinimine) $\{Ph_2P(NSiMe_3)\}_2CH_2$.[12]

An alternative route to such compounds is by displacement of lithium from the Li_4 derivative by reaction with a heavier metal alkoxide, but almost invariably only partial replacement is achieved. Calculations confirm that in many cases the mixed "superbase" species are the more stable. More recently, Harder and co-workers[7] tried to obtain the K_4 and Rb_4 compounds by reaction of $\{Ph_2P(NSiMe_3)\}_2CH_2$ with the benzylmetal compounds, but found that it was necessary to replace the $SiMe_3$ group with Ph, as in **2**, to get isolable products. The structures of methandiides with M = Li, Na, K, and Rb may now, for the first time, be compared.

For M = Li or Na, the four metal centers are essentially coplanar so that the distances from the carbanionic centers to the four metal atoms are almost equal. For M = K or Rb, however, there are only two short M−C distances and the dimer is held together mainly by M−N interactions. The M_4 unit is distorted towards a tetrahedron along an S_4 axis.

But can $[\{[Ph_2P(NSiMe_3)]_2C\}_2Cs_4]$ be made? Treatment of methandiide **1** with the cesium alkoxide $CsOCMe_2Et$ gave a red oil that slowly crystallized. An X-ray structure determination[7] showed that this was not the expected tetracesium compound, but a decomposition product comprising a new dicesium methandiide **3** (Scheme 2) that cocrystallized with

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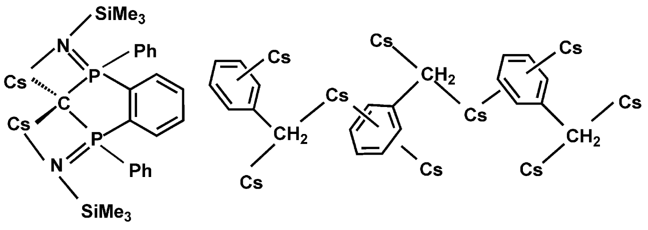


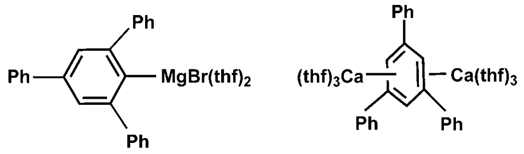
3 **4**

Scheme 2. Coordination of cesium to a cyclic methandiide (**3**) and a benzyl anion (**4**).

the hitherto unknown benzylcesium. The isolation of this compound was clearly a stroke of luck, given the extreme difficulty of the experimental work. The structure shows that, as in other organopotassium, -rubidium, and -cesium compounds,[4] it is difficult to describe the bonding in the manner established for conventional coordination chemistry. Large cations interact with large anions in which charge is delocalized, and there are strong interactions between the cations and the aryl groups as well as a complex series of Cs–C and Cs–N interactions. The benzyl anions are coordinated by four Cs cations, as in **4**.

The second example of the contrasting behavior of lighter and heavier s-block elements comes from the work of Westerhausen and co-workers.[8] A few years ago, his research group began an ongoing study of the calcium analogues of Grignard reagents. The first compounds to be made were phenyl (or monosubstituted phenyl) derivatives that were referred to in 1905, but inadequately characterized. They proved to be thermally unstable, as well as extremely air and moisture sensitive, and rapidly attacked the ether solvents in which they were prepared. Considerable skill was required to isolate the compounds at low temperatures and to obtain crystals for X-ray studies.[13] The greater stability of 2,4,6-triphenylphenyl derivatives, however, suggested that the nucleophilicity of the carbanion could be sufficiently reduced by delocalization to prevent attack on the solvent. The reaction of 1-bromo-2,4,6-triphenylbenzene with activated magnesium in the traditional way yielded the Grignard reagent **5** (Scheme 3) as colorless needles. The structure, with two molecules of thf coordinated to the magnesium center, was unexceptional.

The reaction of 1-bromo-2,4,6-triphenylbenzene with activated calcium in THF at −60 °C gave a quite different product, **6**, as black, pyrophoric crystals. Experiments in sealed NMR tubes showed that the mother liquor contained dissolved ethene and stoichiometric amounts of the vinylate anion $[H_2C{=}CHO]^-$ from cleavage of the solvent. Compound **6** could also be obtained in good yield by the direct reaction between 1,3,5-triphenylbenzene and activated calcium metal, also in THF, provided that a catalytic amount of 2,4,6-$Ph_3C_6H_2Br$ was present. The crystal structure shows that the product is an “inverse sandwich”, that is, a planar $[C_6H_3Ph_3]^{2-}$ dianion with $[Ca^I(thf)_3]^+$ cations on either side. The weak Lewis basicity of the dianion is shown by the presence of coordinated thf. The compound is pyrophoric and extremely sensitive towards moisture; its color depends on the solvent and the temperature.



5 **6**

Scheme 3. Grignard reagent (**5**) and inverse sandwich (**6**).

Magnetic and EPR measurements show the presence of two unpaired electrons, each interacting with the arene, which has acceptor orbitals with energies between the first and second ionization potentials of calcium. Calculations show that approximately one electron is transferred from each calcium center to the anion.

The isolation of compounds containing Ca–Ca and Mg–Mg bonds has been an undoubted highlight of recent coordination chemistry.[13,14] The Ca^I derivative **6**, which contains no Ca–Ca bonds, represents a further important step in the study of this unusual oxidation state.

So what next? Westerhausen and co-workers have recently shown that diarylcalcium compounds can be made from arylcalcium iodides and potassium *tert*-butoxide.[15] Diphenylcalcium, obtained thf-free as a tmeda (*N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethanediamine) complex, can be manipulated in benzene. We can expect more studies on the synthetic applications of organometallic compounds of the heavier s-block elements. We can also expect more unprecedented structures containing bulky anions with large metal cations attached as in **4** and **6**. Whereas in traditional coordination chemistry nucleophilic ligands are arranged around a relatively small cationic center, in the novel species described herein electrophilic ligands are arranged around bulky anions. Some of the species characterized by X-ray diffraction will not survive in solution, but others will, leaving the way open to new applications. Who knows what these will be?

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