Synthesis of Mixed Alkali-Metal−Zinc Enolate Complexes Derived from 2,4,6-Trimethylacetophenone: New Inverse Crown Structures

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The solution and solid-state characterization of two new mixed alkali-metal−zinc enolate compounds is reported. These compounds are prepared by reaction of the relevant mixed-metal base [MZn(HMDS)$_3$] (M = Na, K; HMDS = 1,1,1,3,3,3-hexamethyldisilazide) with a stoichiometric amount of the sterically demanding ketone 2,4,6-trimethylacetophenone. Thus, the new mixed-metal enolate compounds [Na$_2$-Zn$_2${OC(=CH$_2$)Mes}$_6${OC(CH$_3$)Mes}$_2$] (**2**) and [K$_2$Zn$_2${OC(=CH$_2$)Mes}$_6$(CH$_3$Ph)$_2$] (**3**) are obtained for M = Na, K, respectively. X-ray crystallographic studies reveal that both compounds adopt the same structural motif, which define them as inverse crown complexes, a cationic eight-membered [(MOZnO)$_2$]$^{2+}$ ring which hosts in its core two additional enolate ligands. Each Zn center is bonded to four anionic enolate ligands framing the structure, whereas the alkali metals form much weaker interactions with the oxygen atoms and complete their coodination sphere by bonding to a neutral molecule, an unenolised ketone for M = Na or toluene for M = K.

Introduction

Selective deprotonation of ketones to generate enolate anions is a key reaction in synthesis. Enolates participate in a wide variety of fundamental organic processes which involve C−C bond formation such as alkylations, aldol additions, Michael reactions, and acylations.[1] To shed some light on the factors that control the stereochemistries and selectivities of these reactions, the characterization and isolation of these intermediate metal enolates has become an important issue for synthetic chemists.[2] Most of the metal enolates employed in synthesis are (homometallic) alkali-metal enolates, particularly lithium enolates,[3] which are generally easily accessible by reaction of the relevant ketone with sterically hindered lithium amides. The latter are strong bases and poor nucleophiles, minimizing the possibility of competitive addition reactions to the carbonyl group. Recently new s-group metal reagents, such as magnesium bis(amides), have started to be used as alternative bases, showing in certain cases selectivities greater than those of related lithium amides.[4] In our research group we have developed a new kind of mixed-metal amide of empirical formula MM′(NR$_2$)$_3$ (M = Li, Na, K; M′ = Mg, Zn) which at least notionally combine the reactivity of a group 1 metal base with the selectivity of a Mg or Zn bis(amide).[5] These bases often display a unique synergic reactivity. Thus, some of the most remarkable examples that illustrate this cooperative effect between the two metals

are the unprecedented 1,1′,3,3′-fourfold deprotonation of ferrocene, ruthenocene, and osmocene by the tris(diisopropylamide) [NaMg(N^{i}Pr$_2$)$_3$][6] or the regioselective metalation of toluene at the meta ring position, leaving the more acidic Me site intact, effected by the mixed-metal alkyl−amido base [(TMEDA)-NaMg(Bu)(TMP)$_2$] (TMP = 2,2,6,6-tetramethylpiperidide).[7]

Previously we reported the synthesis and characterization of mixed-metal sodium−magnesium enolates derived from the ketone 2,4,6-trimethylacetophenone (**1**).[8] In the present paper we extend this study to zinc by investigating the reactivity of the alkali-metal amidozincates [MZn(HMDS)$_3$] (M = Na, K; HMDS = 1,1,1,3,3,3-hexamethyldisilazide)[9] toward **1**. This ketone is highly sterically demanding; thus, the possibility of competitive addition reactions is reduced, favoring deprotonation reactions to form enolates. A further incentive for employing this particular ketone is the excellent crystallization properties that enolate derivatives can have, which makes them amenable to X-ray crystallographic study.[10]

Zinc enolates are useful intermediates in organic synthesis,[11] as they can participate in a rich variety of important reactions such as addition to carbonyl compounds,[12] transition-metal-catalyzed reactions with carbon electrophiles,[13] and reactions with imines to generate β-lactams,[14] to name but a few. One of

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(2) For an authoritative review on lithium enolate structures and their influence on reactivity see: Seebach, D. *Angew. Chem. Int. Ed.* **1988**, *27*, 1624.

(3) See for example: (a) Hall, L. P.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 9575. (b) Zhao, P.; Condo, A.; Keresztes, I.; Collum, D. B. *J. Am. Chem. Soc.* **2004**, *126*, 3113.

(4) (a) Zhang, M.; Eaton, P. E.; *Angew. Chem. Int. Ed.* **2002**, *114*, 2169. (b) Bassindale, M. J.; Crawford, J. J.; Henderson, K. W.; Kerr, W. J. *Tetrahedron Lett.* **2004**, *45*, 4175. (c) He, X.; Allan, J. F.; Noll, B. C.; Kennedy, A. R.; Henderson, K. W. *J. Am. Chem. Soc.* **2005**, *127*, 6920.

(5) For a recent review on the reactivity and structures of these mixed-metal reagents, see: Mulvey, R. E. *Organometallics* **2006**, *25*, 1060.

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(7) Andrikopoulos, P. C.; Armstrong, D. R.; Graham, D. V.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T.; Talmard, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 3459.

(8) Hevia, E.; Henderson, K. W.; Kennedy, A. R.; Mulvey, R. E. *Organometallics* **2006**, *25*, 1778.

(9) The synergic metalation of toluene at the methyl position by the mixed potassium−zinc amide base KZn(HMDS)$_3$ has been the subject of a previous communication: Clegg, W.; Forbes, G. C.; Kennedy, A. R.; Mulvey, R. E.; Liddle, S. T. *Chem. Commun.* **2003**, 406.

(10) He, X.; Noll, B. C.; Beatty, A.; Mulvey, R. E.; Henderson, K. W. *J. Am. Chem. Soc.* **2004**, *126*, 7444.

(11) Nakamura, E. In *Organometallics in Synthesis. A Manual*, 2nd ed.; Schlosser, M., Ed.; Wiley: Chichester, U.K., 2002; Chapter 5.

(12) Hansen, M. H.; Bartlett, P. A.; Heathcock, C. H. *Organometallics* **1987**, *6*, 2069.

the main advantages of using zinc enolates in synthesis is that they possess a much higher functional group tolerance than is the case for analogous alkali-metal enolates. However, only a select few zinc enolate structures have been elucidated, as illustrated by the fact that the first structure of a Reformatsky reagent,[15] one of the oldest and most versatile types of organozinc reagent, an α-metalated ester ($BrZnCH_2COOR$), was elucidated as recently as 1984, nearly a century after the first publication of this type of compound.[16]

Enolate ligands can adopt several coordination modes (O-terminal, C-terminal, O-bridging or C,O-bridging) depending on the metal they are coordinated to, the reaction solvent, or the steric bulk of their organic substituents. For zinc there are a few examples of ester enolates[15] and amide enolates[17] with C,O-bridging structures, where the anionic charge of the enolate is delocalized with the C−C double bond. On the other hand, there are also some examples of O-bound compounds,[18] including a series of enolates derived from simple ketones reported in 2006 by Hagadorn.[19]

Herein we report the synthesis and characterization of the mixed alkali-metal−zinc enolates $[Na_2Zn_2\{OC(=CH_2)Mes\}_6$-$\{OC(CH_3)Mes\}_2]$ (**2**) and $[K_2Zn_2\{OC(=CH_2)Mes\}_6(CH_3Ph)_2]$ (**3**), which are, to the best of our knowledge, the first reported homoanionic mixed alkali-metal−zinc enolate compounds as well as the first bimetallic enolates of this kind to contain zinc.[20]

Results and Discussion

New metal enolates **2** and **3** were synthesized according to the reactions shown in Scheme 1. In the first part of the synthesis, the mixed-metal amides were prepared in situ by combining the alkali-metal amide MHMDS with the zinc bis-(amide) $Zn(HMDS)_2$ in hydrocarbon media. The addition of 3 equiv of **1** afforded the new mixed-metal enolates **2** and **3** as colorless crystalline solids in reasonably good isolated yields (55−65%). For **2**, the yield of the reaction is increased dramatically (from 23% to 55%) when 4 molar equiv of **1** is employed, as one unenolized neutral ketone molecule remains coordinated to each sodium. The fact that compound **2** is obtained even when a deficiency of **1** is employed implies that the rate of the formation of **2** is faster than the rate of deprotonation of **1** by the mixed-metal base $NaZn(HMDS)_3$ to form the unsolvated mixed-metal enolate "$NaZn(OR)_3$" (R = $C(=CH_2)Mes$). It suggests also that once **2** is formed the unenolized neutral molecules of **1** coordinated to sodium do not react over the time window studied (2 h) with the excess of base still remaining in the solution. For M = K, even when the reaction is carried out using an excess of the ketone, compound **3** is obtained as a single metal product (the byproduct of these

Scheme 1
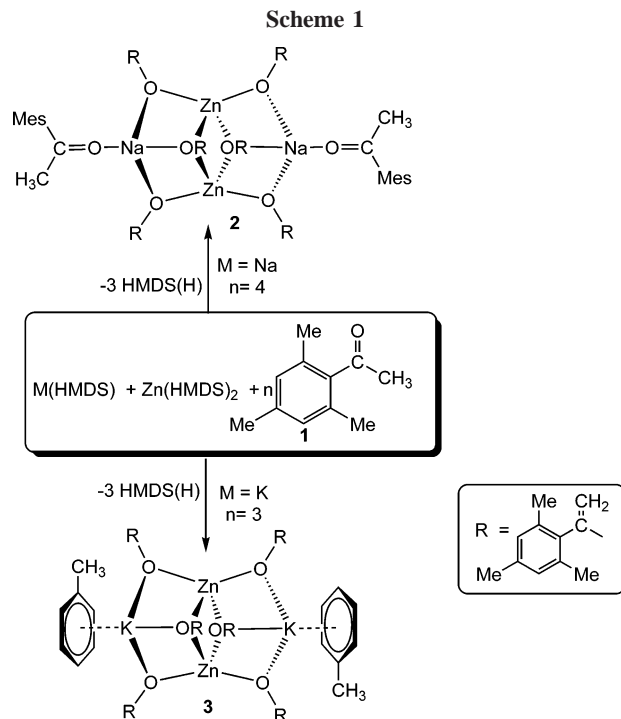
reactions is the amine HMDS(H)), where each potassium is bonded to a molecule of toluene, reflecting the higher affinity of this heavier alkali metal to form metal−carbon bonds (and metal−π-arene interactions in particular; vide infra) than metal−oxygen bonds.[21] In other words, in this system toluene is a better donor for potassium than the unenolized neutral ketone molecule.

As alluded to earlier, we have reported the synthesis and characterization of a series of mixed sodium−magnesium enolates, prepared by reaction of the stoichiometric variant trialkyl ($NaMgBu_3$) and tetraalkyl complexes (Na_2MgBu_4) toward the ketone **1**.[8] Following the same procedure, we have now prepared the corresponding trialkyl zincate $NaZnBu_3$, by mixing together equimolar amounts of BuNa and Bu_2Zn. However, compound **2** could not be obtained when this all-alkyl zincate was treated with 3 or 4 equiv of the ketone **1**. The ^1H NMR spectrum of the crude reaction solution revealed a mixture of two distinct enolate ligands and significant amounts of unreacted ketone, together with a butyl ligand. This experiment illustrates the higher covalent and carbophilic character of Zn versus Mg. Thus, while $NaMgBu_3$ is able to react cleanly at room temperature with 3 equiv of **1** to form the desired mixed-metal tris(enolate) complex, $NaZnBu_3$ fails to react in the same manner (or at least to completion), instead giving a mixture of products resulting from the incomplete conversion of the butyl groups to enolate ligands.

The structures of compounds **2** and **3** were successfully determined by X-ray crystallographic studies. Figure 1 shows the complete molecular structure of **2**, while Figure 2 highlights its inorganic core. Table 1 gives key bond lengths and angles for **2**. The structure of **2** can be viewed as a cationic eight-membered $[(NaOZnO)_2]^{2+}$ ring hosting in its interior two additional enolate ligands. This ring adopts a chair conformation, with the sodium atoms displaced on either side of the plane defined by $O1Zn1O3\cdots O1^*Zn1^*O3$ (Figure 2). The distortion of the sodium atoms from planarity can be quantified by the

(13) (a) Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1986**, *27*, 83. (b) Nakamura, E.; Sekiya, K. Kuwajima, I. *Tetrahedron Lett.* **1987**, *28*, 337. (c) Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z. *Angew. Chem., Int. Ed.* **1987**, *26*, 1157. (d) Sekiya, K.; Nakamura, E. *Tetrahedron Lett.* **1988**, *29*, 5155. (e) Kinoshita, N.; Kawabata, T.; Tsubaki, K.; Bando, M.; Fuji, K. *Tetrahedron* **2006**, *62*, 1756.

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(17) Hlavinka, M. L.; Hagadorn, J. R. *Organometallics* **2005**, *24*, 4116.

(18) van Vliet, M. R. P.; van Koten, G.; Buysingh, P.; Jastrzebski, T. B. H.; Spek, A. L. *Organometallics* **1987**, *6*, 537.

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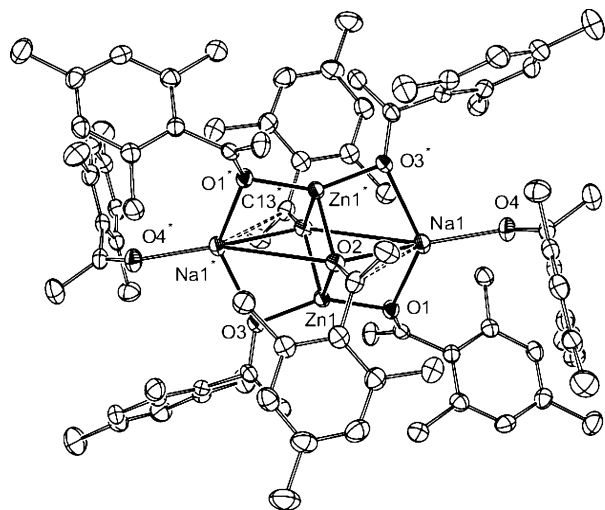
Figure 1. Molecular structure of **2** showing selected atom labeling, with hydrogen atoms omitted for clarity.
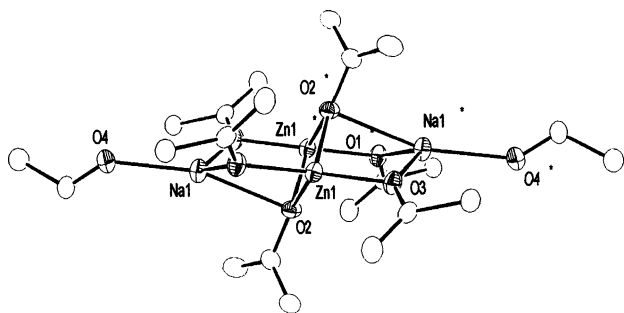

Figure 2. Inorganic core of **2** highlighting the chair conformation of the [(NaOZnO)$_2$] ring.

angle between the O1Na1O3* unit and the aforementioned plane, 145.03(6)°. The sodium atoms achieve tetracoordination by bonding to three enolate ligands, two of them being part of the eight-membered ring, and the remaining enolate is one of the guests of the ring (that is disposed syn to Na) and one molecule of unenolized ketone, acting as a σ donor through the oxygen atom. The Na–O(enolate) bond distances are modestly shorter for the ligands that are part of the ring (average length 2.348 Å) than for the enolates hosted in the core of the ring (2.4574(15) Å). These distances, although lying in a range similar to those found for other Na–alkoxide compounds,[22] are moderately longer than those found for other sodium enolates derived from ketone **1**, such as in homometallic [Na$_2${OC(= CH$_2$)Mes}$_2$(TMEDA)$_2$] (2.225(3) Å)[8] and heterometallic [Na$_2$- Mg$_2${OC(=CH$_2$)Mes}$_6$(TMEDA)$_2$] (from 2.2901(18) to 2.3295- (18) Å),[8] which indicates that the Na–O(enolate) bonds in **2** are fairly weak, presumably as a result of the large steric demands of the enolato R ligands.

A notable feature of **2** is the presence of a molecule of unenolized ketone solvating each sodium atom. Although the important role that solvated alkali-metal enolates may play in aldol additions and related enolate reactions has been a matter of much discussion,[23] little definite structural information is available on this type of solvated compound. The Na–O(ketone) bond length in **2** is of the same order as or even slightly shorter (2.2543(16) Å) than the lengths found for the enolate ligands,

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(23) (a) Seebach, D.; Amstutz, R.; Dunitz, J. D. *Helv. Chim. Acta* **1981**, *64*, 2622. (b) Williard, P. G.; Liu, Q.-Y. *J. Am. Chem. Soc.* **1993**, *115*, 3380.

Table 1. Key Bond Lengths (Å) and Bond Angles (deg) within the Structures of 2 and 3

Compound 2[a]			
Zn1–O3	1.9032(13)	Na1–O1	2.3468(15)
Zn1–O1	1.9149(13)	Na1–O3*	2.3501(15)
Zn1–O2	2.0130(13)	Na1–O2	2.4574(15)
Zn1–O2*	2.0430(13)	Na1–C13	2.840(2)
Na1–O4	2.2543(16)	Na1C12	2.941(3)
O3–Zn1–O1	145.22(6)	O1–Na1–O3*	128.51(6)
O3–Zn1–O2	114.26(5)	O4–Na1–O2	161.35(6)
O1–Zn1–O2	94.98(5)	O1–Na1–O2	74.11(5)
O3–Zn1–O2*	94.80(5)	O3*–Na1–O2	74.36(5)
O1–Zn1–O2*	108.89(6)	Zn1–O2–Zn1*	99.57(5)
O2–Zn1–O2*	80.43(5)	Zn1–O3–Na1*	93.55(5)
O4–Na1–O1	116.74(6)	Zn1–O1–Na1	94.68(5)
O4–Na1–O3*	105.75(6)		
Compound 3[b]			
Zn1–O2	1.9049(12)	K1–O1	2.7082(13)
Zn1–O1	1.9085(12)	K1–O3	2.9431(13)
Zn1–O3	2.0179(12)	K1–C24	3.1414(19)
Zn1–O3*	2.0398(12)	K1–C23	3.167(2)
K1–O2*	2.6534(13)		
O2–Zn1–O1	139.27(5)	O2*–K1–O3	64.86(4)
O2–Zn1–O3	115.24(5)	O1–K1–O3	62.16(4)
O1–Zn1–O3	96.23(5)	Zn1–O1–K1	102.50(5)
O2–Zn1–O3*	99.48(5)	Zn1–O3–K1	92.31(4)
O1–Zn1–O3*	110.01(5)	Zn1–O2–K1*	99.94(5)
O3–Zn1–O3*	82.80(5)	Zn1–O3–Zn1*	97.20(5)
O2*–K1–O1	109.13(4)		

[a] The asterisk denotes the symmetry operation 2 − x, 1 − y, 1 − z.
[b] The asterisk denotes the symmetry operation −x, −y, 2 − z.

which indicates that in this compound the interactions between the sodium atoms and the oxygens are approximately the same for the anionic enolate ligands as for the neutral ketone. Williard has reported the structure of a pinacolone-solvated sodium pinacolate, finding a similar trend for the distinct Na–O bond types.[24] More recently, Henderson has described the synthesis and characterization of a magnesium enolate derived from **1**, [Mg$_4${μ-OC(=CH$_2$)Mes}$_6${OC(=CH$_2$)Mes}$_2${OC(CH$_3$)Mes}- (CH$_3$Ph)$_2$], which exhibits a tetrameric OMg(μ-O)$_2$Mg(μ- O)$_2$Mg(μ-O)$_2$Mg(O) chain arrangement terminated at each end by a neutral ketone molecule.[25] This homometallic compound also shows similar Mg–O distances for the enolate ligands and the unenolized ketones, and it has been proposed by the authors as a model for aldol addition reactions.

On the other hand, each sodium atom in **2** also π-engages with the olefinic (C=CH$_2$) carbons of one of the enolate ligands encapsulated in the ring, as indicated by the short Na–C distances (Na1–C12 = 2.941(3) Å and Na1–C13 = 2.840(3) Å), in order to compensate for the comparative weakness of the Na–O bonds in **2**, as previously mentioned.

The Zn center in **2** is tetracoordinated in a distorted-tetrahedral geometry, bonded to four oxygen atoms from the enolate ligands. The Zn–O bond distances are significantly shorter for the enolates that are part of the eight-membered ring (1.9032- (13) and 1.9032(13) Å) than for the guest enolates (2.0130(13) and 2.0430(13) Å), which can be can be attributed to the different coordination numbers of both types of ligands; thus, while the ring enolates connect one sodium and one zinc center, the guest enolates bind to two zincs and one sodium. These Zn–O(enolato) bond distances are shorter than those found in other previously characterized zinc enolates. Thus, for example in the enolate [Et$_4$Zn$_4${O(OMe)C=(H)N(^{t}Bu)Me}$_4$], resulting

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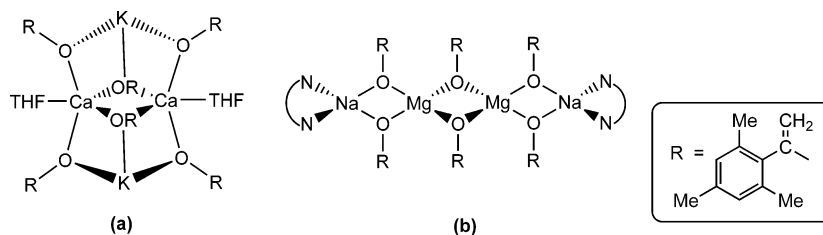
Figure 3. ChemDraw representations of (a) [K$_2$Ca$_2${OC(=CH$_2$)Mes}$_6$·2THF] and (b) [Na$_2$Mg$_2${OC(=CH$_2$)Mes}$_6$(TMEDA)$_2$].

from the reaction of EtZnN^{i}Pr$_2$ with an *N,N*-dialkylglycine ester,[26] where each enolate ligand links two zinc centers to give rise to a tetrameric Zn$_4$O$_4$ cyclic arrangement, the Zn−O bond lengths lie in the range 2.028(5)−2.076(6) Å. These facts show that the enolate ligands in **2** are bonded to the zinc centers through strong σ-covalent bonds while the sodium atoms interact much more weakly with the anionic oxygens, forming additional π-interactions with neighboring olefinic carbons.

The basic structural motif of **2** has been previously found for the series of "inverse crown" complexes [{M^{1}M^2(N^i-Pr$_2$)$_2$}$_2$X$_2$] (M^1 = Li, Na; M^2 = Mg; X = OR, H),[27] [{-(TMEDA)MMg(Bu)$_2$}$_2$(O^{t}Bu)$_2$] (M = Na, K),[21] and [K$_2$Ca$_2$-{OC(=CH$_2$)Mes}$_6$·2THF][10] but also extends to several other homometallic and heterometallic systems.[5] The aforementioned potassium−calcium complex [K$_2$Ca$_2${OC(=CH$_2$)Mes}$_6$·2THF] (Figure 3a) was the first example of a homoleptic inverse crown, as enolate ligands occupy both host ring and guest sites, and it is the closest precedent to **2**, as it contains the same anionic ligands. However, the main structural distinction is the reversal in the solvation of the metals. To explain, in this potassium/calcium enolate, a molecule of THF is bonded to each divalent calcium center, whereas the potassium atoms are unsolvated and form a series of π-stabilizing interactions with the neighboring phenyl rings and olefinic carbons from the enolate ligands. This reversal in metal solvation can be rationalized by the larger size and softer character of calcium in comparison to zinc.

As previously mentioned, the number of metal enolates that have been structurally characterized is relatively scarce.[2] To our knowledge, the only examples of bimetallic homoanionic enolates that combine one alkali metal and one divalent metal are the K/Ca compound mentioned above[10] and a series of Na/Mg enolates obtained by reaction of either NaMgBu$_3$ or Na$_2$-MgBu$_4$ with variable amounts of **1**, as for example [Na$_2$Mg$_2${μ-OC(=CH$_2$)Mes}$_6$(TMEDA)$_2$] (Figure 3b).[8] The latter compound has a structural arrangement significantly different from that of **2**. Thus, the sodium/magnesium enolate presents a linear tetranuclear Na···Mg···Mg···Na chain arrangement connected by six enolate ligands. Thus, while both compounds possess a {(OR)$_2$M(μ-OR)$_2$M(OR)$_2$}$^{2-}$ ate core, in the sodium/magnesium enolate, each sodium is coordinated to two terminal enolates, positioned in the same plane as the Mg centers of the Mg(μ-O)$_2$Mg inner ring, giving rise to a linear structure; however, in contrast in **2**, each sodium is bonded to three enolate ligands and is situated above and below the plane defined by OZnO···O*Zn*O* adopting the cyclic inverse crown structure. Given the similar sizes of magnesium and zinc, this fundamental difference in the structures of these mixed-metal enolates must be at least in part attributed to electronic factors and the greater
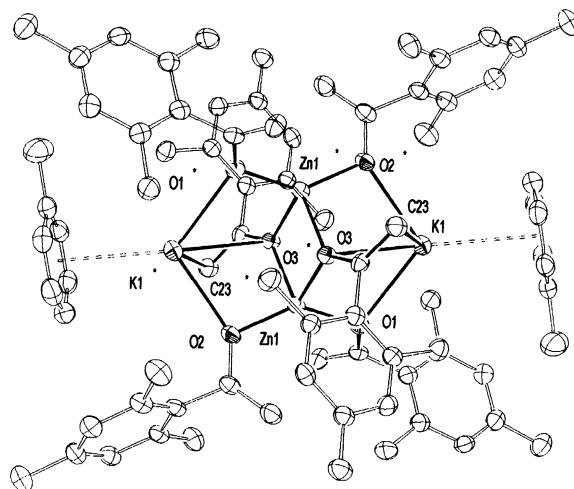

Figure 4. Molecular structure of **3** showing selected atom labeling, with hydrogen atoms omitted for clarity.

covalent character exhibited by zinc in its bonding in comparison to that of magnesium.

The potassium−zinc enolate **3** adopts a centrosymmetric structure analogous to that of **2** (Figure 4) with a cationic [(KOZnO)$_2$]$^{2+}$ eight-membered ring hosting an additional two enolate ligands. However, in this case, the alkali metal is solvated by a different donor molecule. Thus, in **3** a molecule of toluene binds to each potassium center through its π-system.[28] The six K−C(toluene) distances are within a short range (from 3.307(2) to 3.449(2) Å), which shows that although individually these interactions are weak, collectively they must be significant, as revealed by the relative shortness of the K−C(centroid) distance (3.081 Å).[29] The potassium center also interacts with three enolate ligands, two of them being part of the host ring, whereas the third occupies a "guest" position. However, these interactions are relatively weak, as indicated by a comparison of the K−O bond distances found for **3** (2.6534(13), 2.7082-(13), and 2.9431(13) Å) with those in the homometallic enolate [K$_4${OC(=CH$_2$)Mes}$_4$(CH$_3$Ph)$_4$][10] (range 2.528(6)−2.706(6) Å; mean 2.631 Å). The potassium centers in **3** complete their coordination sphere by forming a series of π-contacts with the olefinic carbons of the guest enolate ligands (K1−C24 = 3.1414(193) Å and K1−C23 = 3.167(2) Å). As previously discussed for compound **2**, the structure of **3** is similar to that of the potassium−calcium inverse crown [K$_2$Ca$_2${OC(=CH$_2$)-Mes}$_6$·2THF].[10] The K−O distances in the latter (2.633(2), 2.702(2), and 2.842(2) Å) are in the same range as those in **3**;

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Table 2. Selected ^{13}C NMR Chemical Shifts (δ in ppm) for Enolate Ligands

compd	δ(=CO)	δ(=CH$_2$)	$\Delta\delta^a$	solvent
2	166.59	83.98	82.61	d_5-pyridine
3	168.64	84.94	83.70	d_5-pyridine
[Na$_2$\{μ-OC(=CH$_2$)Mes\}$_4$-(TMEDA)$_2$]	169.94	79.60	90.34	d_6-benzene
[K$_2$\{OC(=CH$_2$)Mes\}$_4$·4(toluene)]	171.23	74.58	96.65	d_6-benzene

^{a} $\Delta\delta$ corresponds to the difference in chemical shift between the two ^{13}C resonances arising from the carbon–carbon double bond, =CO and =CH$_2$.

however, the potassium centers in this potassium–calcium enolate form more stabilizing π-interactions involving not only the olefinic carbons of the enolates but also the aromatic rings.

On the other hand, the Zn–O bond distances are nearly identical with those found within compound **2**, showing again the strong σ-coordination of the enolates to the zinc centers, which frame the inverse crown ate motif while the softer potassium cations form much weaker interactions with the oxygen atoms and adhere to the framework through additional π-contacts. At this point it should be noted that this σ- and π-bonding distinction for the alkali metal and its Zn (or Mg) copartner has become a signature feature of inverse crown complexes and other related mixed-metal compounds and clearly plays a major part in the often special reactivity that such "synergic" mixtures can display.[5]

Compounds **2** and **3** have also been characterized in solution using NMR spectroscopy (see hte Experimental Section); however, given the low solubility of these mixed-metal enolates in arene solvents such as toluene or benzene, their ^{1}H and ^{13}C NMR spectra have had to be recorded in the more polar solvent deuterated pyridine. As evidenced by these spectra, the solution structures of **2** and **3** in this solvent are different from those in the solid state. Thus, for both compounds, the solvating ligands within the solid state (**1** and toluene for **2** and **3**, respectively) appear free in solution, whereas only one single set of enolate signals is observed. Furthermore, the chemical shifts of the resonances attributed to the mesityl and the =CH$_2$ moieties in the ^{1}H and ^{13}C NMR spectra are nearly identical for **2** and **3**. This suggests that, in the presence of a strong coordinative solvent such as pyridine, these mixed-metal compounds undergo cleavage, probably to generate the solvent-separated ion pair [M(pyridine)$_x$]$^+$[Zn(enolate)$_3$]$^-$, which would explain the observations mentioned above.

As recently described by Hagadorn, the difference between the chemical shifts in the ^{13}C NMR spectrum of the C–O and =CH$_2$ resonances can be considered as a good indication of the degree of polarization of the C=C bond and the nucleophilicity of the enolate ligand.[19] The $\Delta\delta$ values of **2** and **3** (see Table 2) are significantly lower than those obtained for the analogous monometallic sodium and potassium enolates, consistent with the reduced polarization of the M–enolate bonds in the mixed-metal compounds and the greater covalent character of zinc. On the other hand, the chemical shift differences between **2** and **3** are very similar, showing that the alkali metal in these compounds has little influence in solution, which supports the idea that in pyridine solution **2** and **3** are present as the solvent-separated ion pair compounds [M(pyridine)$_x$]$^+$-[Zn(enolate)$_3$]$^-$.

To conclude, two mixed alkali-metal–zinc enolate inverse crowns derived from 2,4,6-trimethylacetophenone have been synthesized using the mixed-metal tris(amides) [MZn(HMDS)$_3$] as the base. These first compounds of their type have been fully

Table 3. Key Crystallographic and Refinement Parameters for Compounds 2 and 3

	2	**3**
empirical formula	C$_{88}$H$_{106}$Na$_2$O$_8$Zn$_2$	C$_{80}$H$_{946}$K$_2$O$_6$Zn$_2$
M_r	1468.45	1360.50
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a/Å	11.0238(3)	11.0836(2)
b/Å	12.6380(3)	20.0998(3)
c/Å	15.7638(4)	16.3947(3)
α/deg	80.211(1)	90
β/deg	76.930(2)	101.590(1)
γ/deg	68.384(1)	90
V/Å^3	1979.71(9)	3577.91(11)
Z	1	2
T/K	123(2)	123(2)
no. of indep rflns	9056	8168
goodness of fit	1.020	1.017
R1 ($I > 2\sigma(I)$)	0.0395	0.0344
wR2	0.0917	0.0801

characterized in solution and in the solid state. Their crystal structures show a common motif, a cationic eight-membered ring (MOZnO)$_2$ hosting two enolate ligands, which defines them as inverse crowns. These compounds have strong, anchoring Zn–O bonds that frame an anionic ate structure, onto which the alkali metals cling through weaker bonds to the anionic oxygens and through ancillary π-bonds to olefinic carbon atoms.

Experimental Section

General Considerations. All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane and toluene were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. ZnCl$_2$ was purchased from Aldrich Chemicals as a 1 M solution in diethyl ether. Butylsodium[30] and Zn(HMDS)$_2$[31] were prepared according to literature methods. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C. Elemental analyses of compounds **2** and **3** could not be obtained, due to their instability.

X-ray Crystallography. Single-crystal diffraction data were recorded by a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures were refined by full-matrix least squares and against F^2 to convergence using the SHELXL-97 program.[32] Specific crystallographic data and refinement parameters are given in Table 3.

Synthesis of [Na$_2$Zn$_2$\{OC(=CH$_2$)Mes\}$_6$\{OC(CH$_3$)Mes\}$_2$] (2). Zn(HMDS)$_2$ (1.8 mL, 5 mmol) was added to a suspension of NaHMDS (prepared in situ by reaction of BuNa (0.8 g, 5 mmol) and HMDS(H) (1.05 mL, 5 mmol)) in hexane (15 mL), affording a white suspension. 2,4,6-Trimethylacetophenone (3.34 mL, 20 mmol) was then added. The mixture was heated under reflux for 30 min. Toluene (5 mL) was introduced at this stage, and the mixture was gently heated until all the white solid had dissolved, affording a pale orange solution. Allowing this solution to cool slowly to room temperature produced a crop of colorless crystals (yield 2.27 g, 63%). ^{1}H NMR (400 MHz, 25 °C, C$_5$D$_5$N): 6.84 (s, 12H, m-H Mes, enolate), 6.79 (s, 4H, m-H Mes, ketone), 4.90 (s, broad, 6H, C=CHH'), 3.97 (s, broad, 6H, C=C$H$$H'$), 2.65 (s, 36H, o-CH_3, Mes, enolate), 2.44 (s, 6H, C(O)CH_3, ketone), 2.26 (s, 18H, p-CH_3, Mes, enolate), 2.21 (s, 18H, o-CH_3 and p-CH_3, Mes, ketone). ^{13}C\{^{1}H\} NMR (100.63 MHz, 25 °C, C$_5$D$_5$N): 208.31 (C=O), 166.59 (OC=CHH′), 143.61 (C_{ipso}, Mes, enolate), 141.14 (C_{ipso}, Mes, ketone), 138.77 (C_{para}, Mes, ketone), 135.99 (C_{ortho}, Mes,

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enolate), 135.40 (C_{para}, Mes, enolate), 132.98 (C_{ortho}, Mes, ketone), 129.31 (C_{meta}, Mes, ketone), 128.57 (C_{meta}, Mes, enolate), 83.98 (OC=CHH′), 32.58 (C(O)CH_3), 21.51 (p-CH_3, enolate), 21.39 (p-CH_3, ketone), 20.98 (o-CH_3, enolate), 19.54 (o-CH_3, ketone).

Synthesis of [K$_2$Zn$_2${OC(=CH$_2$)Mes}$_6$(CH$_3$Ph)$_2$] (3). K(H-MDS) (1.0 g, 5 mmol) was suspended in hexane (15 mL). Zn-(HMDS)$_2$ (1.8 mL, 5 mmol) was added, and the mixture was stirred for 30 min, affording a white suspension. 2,4,6-Trimethylacetophenone (2.5 mL, 15 mmol) was then introduced, and the mixture was heated under reflux for 30 min. The solution changed from colorless to pale orange, and most of the white solid remained suspended. At this stage toluene (5 mL) was added and the mixture was gently heated until all the solid had dissolved, affording an orange solution. Cooling this solution slowly to room temperature produced a crop of colorless crystals (yield 1.85 g, 54%). ¹H NMR (400 MHz, 25 °C, C$_5$D$_5$N): 7.32 (m, 2H, H_{para}, CH$_3$Ph), 7.21 (m, 8H, H_{ortho} and H_{meta}, CH$_3$Ph), 6.81 (s, 12H, m-H Mes), 4.91 (s, broad, 6H, C=CHH′), 3.94 (s, broad, 6H, C=CHH′), 2.69 (s, 36H, o-CH$_3$, Mes), 2.44 (s, 6H, CH$_3$, CH$_3$Ph), 2.23 (s, 18H, p-CH$_3$, Mes). ¹³C{¹H}

NMR (100.63 MHz, 25 °C, C$_6$D$_6$): 168.64 (OC=CHH′), 145.50 (C_{ipso}, Mes),140.12 (C_{ipso}, CH$_3$Ph), 137.35 (C_{ortho}, Mes), 136.63 (C_{para}, Mes), 131.42, 130.67 (C_{ortho} and C_{meta}, CH$_3$Ph), 130.09 (C_{meta}, Mes), 121.77 (C_{para}, CH$_3$Ph), 84.94 (OC=CHH′), 23.34 (CH$_3$, CH$_3$-Ph), 23.03 (p-CH$_3$, Mes), 22.61 (o-CH$_3$, Mes).

Supporting Information Available: CIF files giving crystal data and figures giving NMR spectra for compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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