Organometallics **1998,** *17,* 3375−3382

Adducts of Carbenes with Group II and XII Metallocenes[†]

Anthony J. Arduengo, III,* Fredric Davidson, Roland Krafczyk,[1]
William J. Marshall, and Matthias Tamm[2]

DuPont Science and Engineering Laboratory, Experimental Station,
Wilmington, Delaware 19880-0328

Received May 26, 1998

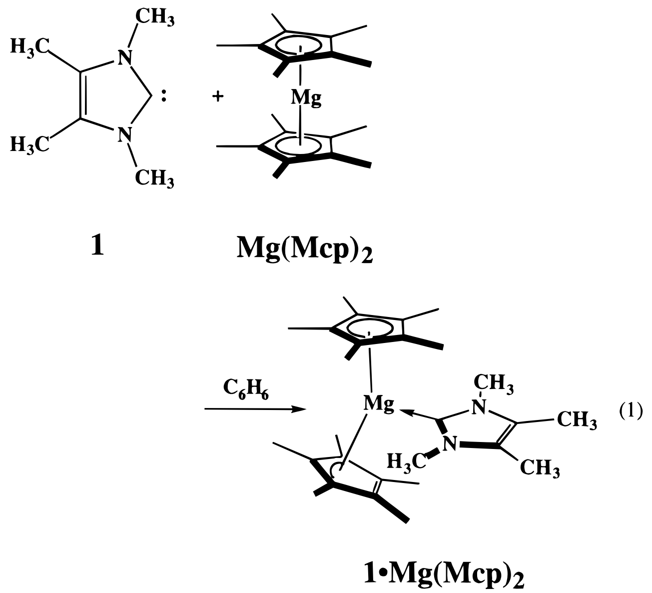
The reactions and adducts of 1,3,4,5-tetramethylimidazol-2-ylidene with bis(pentamethylcyclopentadienyl)magnesium, -calcium, -strontium, -barium, or -zinc are described. A consistent tend in the spectroscopic properties and structures of the alkaline earth metallocenes is observed. The adduct between 1,3,4,5-tetramethylimidazol-2-ylidene and bis(pentamethylcyclopentadienyl)zinc shows a structure in which the zinc is only σ-bonded to the three ligating groups. Among the alkaline earth adducts, the σ-bonded interaction to the former carbene center of the 1,3,4,5-tetramethylimidazol-2-ylidene shows the shortest metal−carbon distances in each of the structures but the difference between the carbene−metal and pentamethylcyclopentadienyl−metal distances decreases as the atomic number of the metal increases.

Introduction

Carbene or carbenoid complexes of magnesium or zinc (e.g., the Simmons−Smith reagent)[3−6] are of particular interest because of their extremely widespread use in syntheses.[7,8] The availability of very stable carbenes that can be easily handled using standard laboratory techniques makes it possible to extend main group II carbene complexes to structural types that were not previously accessible.[9] We have previously reported the formation of carbene metal adducts with the alkaline earth (main group II) metal magnesium and the transition group XII metals zinc, cadmium, and mercury.[10,11] This chemistry was subsequently extended to the lightest alkaline earth metal beryllium.[12] A few years ago, we further expanded this chemistry to include the heavier alkaline earth metals calcium, strontium, and barium. The structural and spectroscopic trends in this family of compounds show smooth trends that have been very helpful in extending the scope of the chemistry of these stable carbenes. We now report our results on this series of compounds.

Results

In benzene solution at room temperature, bis(pentamethylcyclopentadienyl)magnesium (**Mg(Mcp)$_2$**) reacts smoothly with tetramethylimidazol-2-ylidene (**1**) to produce the all-carbon-ligated magnesium adduct **1·Mg(Mcp)$_2$** (eq 1). This adduct is a colorless solid with a melting range of 197−199 °C.



1

Mg(Mcp)$_2$

1•Mg(Mcp)$_2$

The ^{1}H NMR of **1·Mg(Mcp)$_2$** in C_6D_6 solution at room temperature shows only a single resonance at δ 2.06 for the cyclopentadienyl methyls. The ^{13}C resonance for the imidazole 2-carbon appears at δ 185.7 (28 ppm upfield of the carbene resonance in **1**).

Crystals of **1·Mg(Mcp)$_2$** suitable for X-ray structure determination were grown from a toluene solution by cooling to −25 °C. This magnesium complex crystallizes

---

[1] Visiting scientist, 1997, from the Technische Universität Braunschweig.

[2] DuPont visiting Research Scientist 1993−1994.

[3] Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 5323.

[4] Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256.

[5] Blanchard, E. P.; Simmons, H. E. *J. Am. Chem. Soc.* **1964**, *86*, 1337.

[6] Blanchard, E. P.; Simmons, H. E. *J. Am. Chem. Soc.* **1964**, *86*, 1347.

[7] Motherwell, W. B.; Nutley, C. J. *Contemp. Org. Synth.* **1994**, *1*, 219.

[8] Satoh, T.; Takano, K.; Someya, H.; Matsuda, K. *Tetrahedron Lett.* **1995**, *36*, 7097.

[9] Arduengo, A. J., III; Krafczyk, R. *Chem. Unserer Zeit* **1998**, *32*, 6.

[10] Arduengo, A. J., III; Dias, H. V. R.; Davidson, F.; Harlow, R. L. *J. Organomet. Chem.* **1993**, *462*, 13.

[11] Arduengo, A. J., III; Marshall, W. J.; Harlow, R. L.; Prakasha, T. K. *Heteroatom Chem.* **1996**, *7*, 421.

[12] Herrmann, W. A.; Runte, O.; Artus, G. *J. Organomet. Chem.* **1995**, *501*, C1.

S0276-7333(98)00438-5 CCC: $15.00

Table 1. Selected Bond Lengths (pm) and Angles (deg) in 1 and Group II Metallocene Adducts

property	**1**	**1·Mg(Mcp)$_2$**	**1·Ca(Mcp)$_2$**	**1·Ba(Mcp)$_2$**	**1·Zn(Mcp)$_2$**	**(1) $_2$·Sr(Mcp)$_2$**
$r(C_2-N_{1(3)})$	136.1(1)	135.8(3), 135.5(3)	135.7(4), 135.9(4)	135.6(4), 135.5(4)	134.4(4), 135.3(4)	135.2(5), 136.1(5), 135.4(5), 136.3(5)
$r(C_4-C_5)$	135.2(2)	134.1(3)	133.6(4)	132.6(5)	133.5(5)	132.8(6), 135.1(6)
$r(N_{1(3)}-C_{5(4)})$	139.4(1)	139.9(3), 139.9(3)	139.2(4), 138.5(4)	139.2(4), 138.2(4)	139.7(4), 139.0(4)	139.4(5), 139.5(5), 138.5(5), 138.9(5)
$r(C_2-M)$		219.4(2)	256.2(2)	295.1(3)	202.2(3)	286.8(5), 285.4(5)
$r(Mcp_{(cent)}-M)$		224.1,[a] 216.5[b]	238.4, 238.1	274.1, 273.5	213.8(3),[c] 217.4(3)[c]	265.5, 266.9
$\bar{r}(C_{(Mcp)}-M)$		246.0(85),[a] 247.7(20)[b]	266.7(3), 266.5(5)	298.9(9), 298.5(19)		
$\theta(N_1-C_2-N_3)$	101.5(1)	102.8(2)	101.5(3)	101.8(3)	103.9(2)	102.2(4), 101.1(4)
$\theta(C_{5(4)}-N_{1(3)}-C_2)$	113.47(8)	112.5(2), 112.5(2)	113.1(3), 113.3(3)	112.5(3), 113.1(3)	111.6(3), 111.6(3)	112.8(4), 112.3(4) 113.9(4), 113.7(4)
$\theta(N_{1(3)}-C_{5(4)}-C_{4(5)})$	105.78(5)	106.0(2), 106.3(2)	106.0(3), 106.1(3)	106.3(3), 106.3(3)	106.4(3), 106.5(3)	106.2(4), 106.4(4) 105.8(4), 105.5(4)
$\theta(Mcp_{(cent)}-M-Mcp_{(cent)})$		139.2	143.9	137.0	117.1	131.0[d]
$\theta(C_2-M-Mcp_{(cent)})$		109.3,[a] 111.4[b]	107.5, 108.6	112.3, 101.1	118.1, 124.0	115.2, 99.4, 99.0, 117.6

[a] Calculated for the three allyl-like atoms. [b] Calculated for η^5-Mcp. [c] Calculated for the σ-bonded Mcp carbon. [d] $\theta(C_2-Sr-C_2') = 86.4°$.

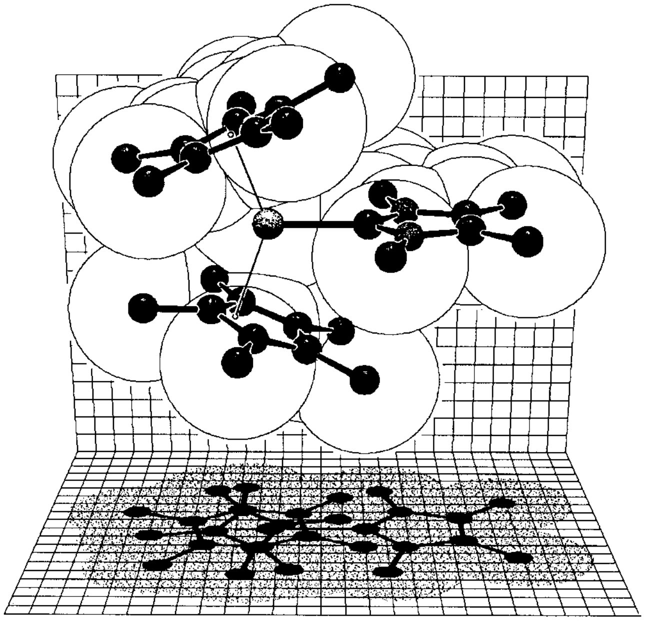


Figure 1. KANVAS representation of **1·Mg(Mcp)$_2$** (hydrogens have been omitted for clarity).

in the triclinic space group $P\bar{1}$. Selected bond geometric parameters are presented in Table 1, and the structure is depicted by the KANVAS[13] drawing in Figure 1. The solid-state structure of **1·Mg(Mcp)$_2$** reveals two different bonding modes for the pentamethylcyclopentadienyl (Mcp) ligands. One of the Mcp rings is coordinated in a η^5-fashion with an average Mg−C distance of 247.7(20) pm. The second Mcp ring exhibits a "slipped" geometry in which the three carbon atoms closest to magnesium (260.6, 230.9, and 246.6 pm) have an average C−Mg distance of 246.0(85) pm. The C−C bond distances within this second Mcp ligand (142.7, 140.4, 140.3, 140.5, and 143.4 pm) suggest a bond alternation pattern that is intermediate between an η^3 and κC^1(σ-bonded) arrangement for this group. However, the κC^1 arrangement is not as completely developed as it is in the analogous zinc compound (vide infra). This slipped Mcp arrangement places the two carbons of the Mcp ring that are most distant from the magnesium close to the π-orbital at C-2 of the carbene moiety. The resulting nonbonded carbon distances are 310.8(3) and 318.4(3) pm and lie within the sum of the van der Waals radii (340 pm). On the other side of the carbene there is also one carbon from the first η^5-Mcp ligand that approaches the carbene center from the π-direction at a distance of 317.6(3) pm. Although it is tempting to attribute these close nonbonded interactions to weak electron donation from the electron-rich Mcp ligands and the electron-deficient carbene p-orbital, this is probably not the primary driving force because such interactions are absent in the calcium and barium analogues and resurface only with the zinc derivative (vide infra). Thus, the size of the metal center is more likely the driving force that results in a steric crowding at the smaller metals and thus the nonbonded carbon−carbon interactions.

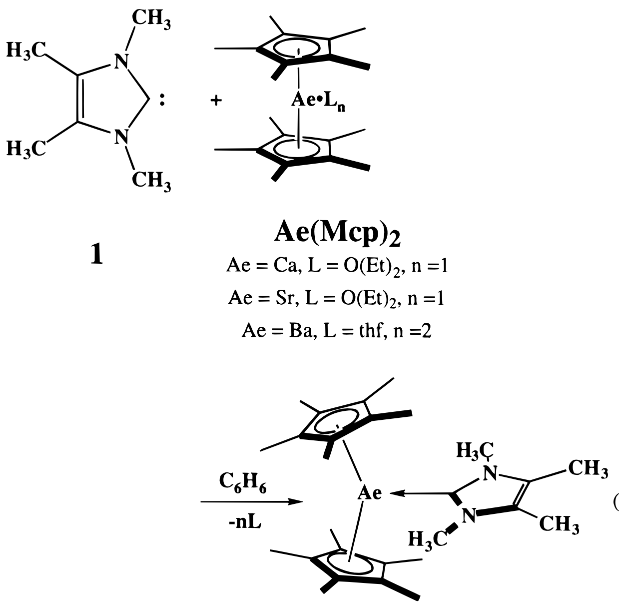
The closest C−Mg interaction in **1·Mg(Mcp)$_2$** is actually with the carbene center (219.4(2) pm). If in addition to the carbene one considers the centroids of η^3-Mcp and η^5-Mcp to each occupy a coordination site, then the magnesium can be regarded as essentially trigonal planar. The magnesium rises only 2.9 pm above the plane of the two centroids and the carbene center. The sum of the angles between coordination sites is 359.9°. Despite the interaction with the magnesium center, the geometry of the carbene fragement changes very little. The small N−C−N angle of the uncoordinated carbene opens only 1.3° in **1·Mg(Mcp)$_2$**, and other parameters remain largely unchanged (Table 1).

From the heavier alkaline earth (Ae = Ca, Sr, and Ba) metallocenes it is also possible to synthesize 1:1 adducts (**1·Ae(Mcp)$_2$**) with carbene **1** (eq 2). The calcium adduct is a colorless solid like the magnesium analogue but has a melting range that is 100 °C higher (298−301 °C). The carbene center coordinated to calcium in **1·Ca(Mcp)$_2$** resonates at δ 196.2. The shift in this carbene resonance relative to the free carbene is 17.5 ppm upfield (an 11 ppm smaller shift than that observed for **1·Mg(Mcp)$_2$**). The Mcp methyl groups exhibit a single resonance at δ 2.13 that is at slightly lower field than observed in the magnesium adduct (δ 2.06).

The solid-state structure of the calcium adduct was determined by single-crystal X-ray diffraction. The calcium structure is isomorphic with the magnesium

---

(13) These drawings were made with the *KANVAS* computer graphics program. This program is based on the program *SCHAKAL* of E. Keller (Kristallographisches Institut der Universität Freiburg, Germany), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes. The planes bear a 50-pm grid, and the lighting source is at infinity so that shadow size is meaningful.



1

Ae(Mcp)$_2$

Ae = Ca, L = O(Et)$_2$, n =1

Ae = Sr, L = O(Et)$_2$, n =1

Ae = Ba, L = thf, n =2

$\xrightarrow[\text{-nL}]{C_6H_6}$ (2)

1•Ae(Mcp)$_2$

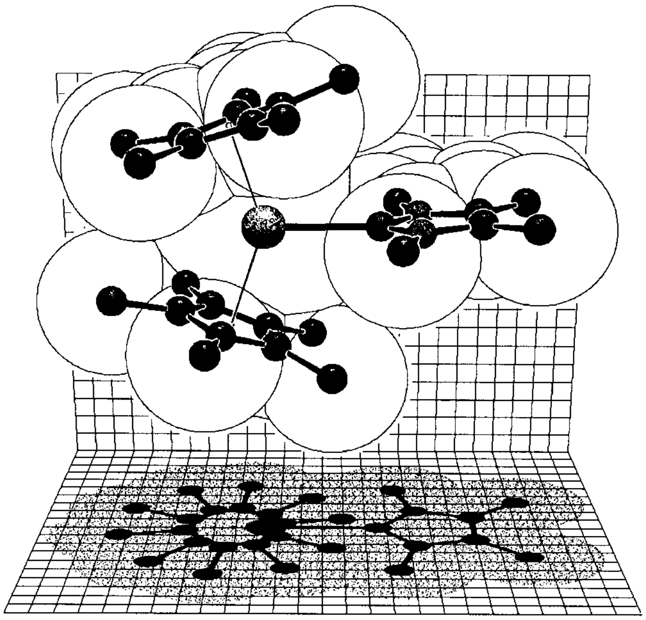


Figure 2. KANVAS representation of **1·Ca(Mcp)$_2$** (hydrogens have been omitted for clarity).

adduct, although the details of the two structures are slightly varied. The structure of the calcium adduct is illustrated by the KANVAS[13] drawing in Figure 2. Unlike the situation with the magnesium adduct, **1·Ca(Mcp)$_2$** exhibits η^5-coordination for both of the Mcp ligands. The centroids of the Mcp ligands lie 238.4 and 238.1 pm distant from the calcium center. This correspondes to average Ca−C distances of 266.7(3) and 266.6(5) pm to each of the rings. As with the magnesium analogue, the calcium center can be regarded as trigonal planar. The calcium center lies only 0.6 pm out of the plane of its substituents, and the sum of the three trigonal angles is 360°. The σ-bonded carbene center again is the shortest C−metal distance (256.1(3) pm), although the difference in Ca−C$_{(\mathrm{Mcp})}$ and Ca−C$_{(\mathrm{carbene})}$ distances (10.4 pm) is smaller than the analogous distances observed for the magnesium adduct (27.5 pm). The imidazole geometry in **1·Ca(Mcp)$_2$** is almost identical with that of the uncomplexed carbene.

The strontium adduct is also a colorless solid with a high melting point (291−294 °C) like the calcium analogue. The carbene center coordinated to strontium in **1·Sr(Mcp)$_2$** resonates at δ 198.2. This shift for the carbene resonance lies closer to that of the uncomplexed carbene ($\Delta\delta$ 15.5 ppm) than the magnesium or calcium analogues. The Mcp methyl groups exhibit a single proton resonance at δ 2.15 that is very simlar to that observed for the calcium adduct.

Unfortunately because of the small size of the crystals, we were unable to collect sufficient data to solve the X-ray structure of **1·Sr(Mcp)$_2$**. Interestingly, the unit cell found was orthorhombic (a = 1177.5 pm, b = 1615.6 pm, c = 1471.9 pm) whereas all the other adducts (Mg, Ca, Ba, and Zn) crystallized in the triclinic in space group $P\bar{1}$. The reason for this difference is unknown, but we note that we previously reported an analogous complex of samarium (**1·Sm(Mcp)$_2$**) whose unit cell was orthorhombic and had very similar dimensions (a = 1176.4 pm, b = 1608.3 pm, c = 1470.7 pm) as the strontium analogue reported here.[14]

The carbene−barium adduct was prepared from Ba(Mcp)$_2$·(thf)$_2$ and isolated as a high-melting (257−259 °C) colorless solid. In **1·Ba(Mcp)$_2$**, the carbene center coordinated to barium resonates at δ 203.5. Among the 1:1 carbene−alkaline earth metallocenes, the shift of the coordinated carbene center in the barium adduct is found at lowest field and thus closest to the uncomplexed carbene ($\Delta\delta$ 10.2). The Mcp methyl groups resonate at δ 2.13 in the ^{1}H NMR spectrum.

The solid-state structure of the barium adduct **1·Ba(Mcp)$_2$** is depicted in Figure 3. The barium structure is isomorphic with the magnesium and calcium adducts. As with the calcium adduct, **1·Ba(Mcp)$_2$** again exhibits η^5-coordination for both of the Mcp ligands. The barium Mcp−centroid distances are 274.1 and 273.5 pm, so that the average Ba−C distances are 298.9(9) and 298.5(19) pm to each of the Mcp ligands. Contrary to the observations at the magnesium and calcium centers, the barium center is not trigonal planar but rather noticeably pyramidal. The barium center resides 48.5 pm out of the plane of its substituents, and the sum of the three trigonal angles is 359.2°. The σ-bonded carbene center again is the shortest C−metal distance (295.1(3) pm), although the difference in Ba−C$_{(\mathrm{Mcp})}$ and Ba−C$_{(\mathrm{carbene})}$ distances (3.6 pm) is quite small. Finally, it can be noted from Figure 3 that the carbene−barium vector does not lie in the plane of the imidazole ring so that the carbene fragment appears “tipped”. This latter feature cannot be clearly attributed to crystal packing forces but is not unusual for such carbene complexes and will be discussed in more general terms in relation to other such “distorted” structures in future publications.

The reaction of bis(pentamethylcyclopentadienyl)zinc (**Zn(Mcp)$_2$**) with carbene **1** also affords an adduct that is similar in composition to the alkaline earth adducts

---

[14] Arduengo, A. J., III; Tamm, M.; McLain, S. J.; Calabrese, J. C.; Davidson, F.; Marshall, W. J. *J. Am. Chem. Soc.* **1994**, *116*, 7927.

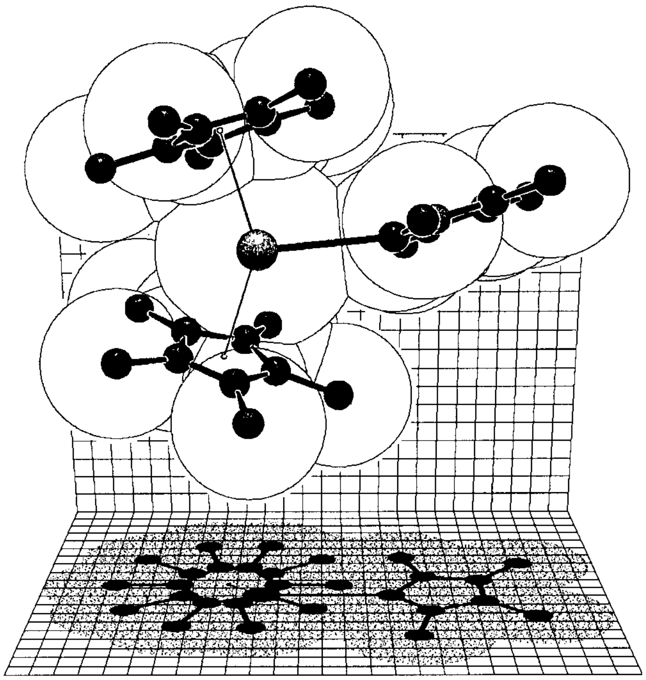
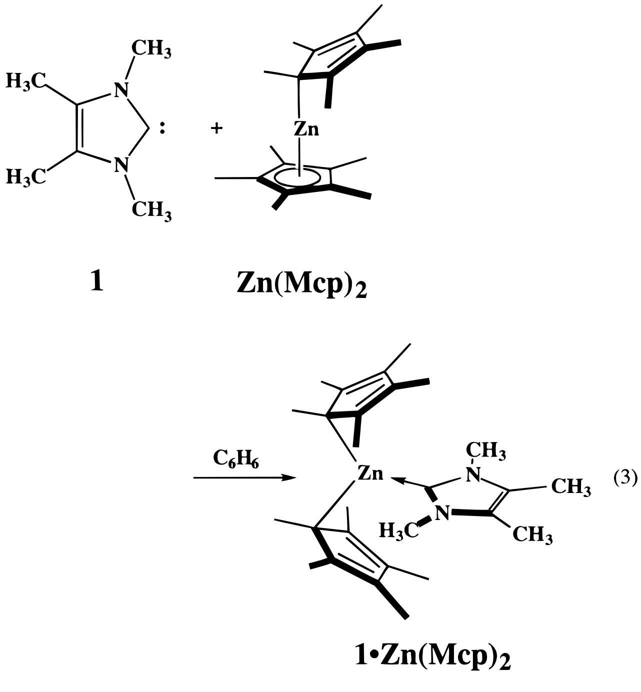


Figure 3. KANVAS representation of **1·Ba(Mcp)**$_2$ (hydrogens have been omitted for clarity).

described above (eq 3). The zinc adduct **1·Zn(Mcp)**$_2$ has a melting range of 210−221 °C that is similar to that of **1·Mg(Mcp)**$_2$ and lower than that observed for the heavier alkaline earth adducts. The ^{1}H NMR resonance for the Mcp group in this zinc adduct is observed at δ 2.07. This chemical shift is slightly upfield of the calcium, strontium, and barium compounds (δ 2.13−2.15) and is similar to the magnesium adduct (δ 2.06). The ^{13}C resonance of the carbene center in **1·Zn(Mcp)**$_2$ occurs at δ 175.4 and is the highest field of these metallocene−carbene complexes (38.3 ppm upfield of the free carbene).



(3)

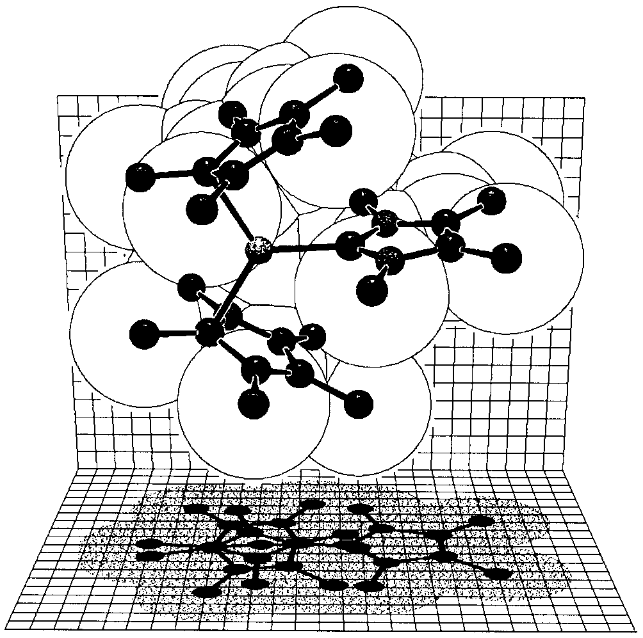
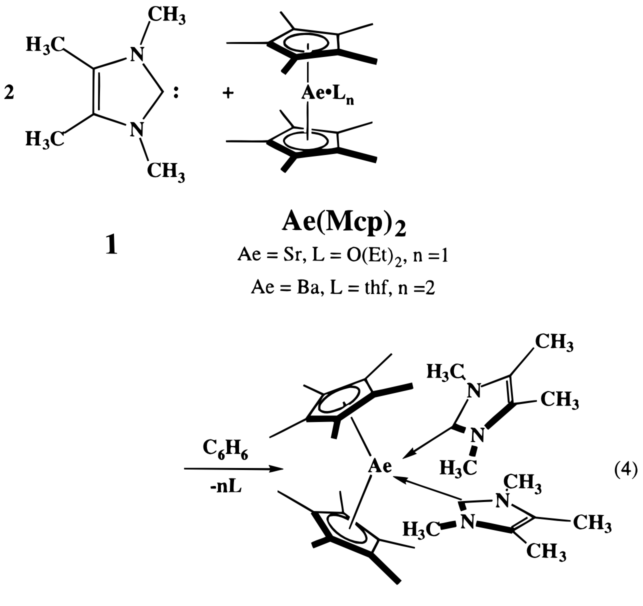


Figure 4. KANVAS representation of **1·Zn(Mcp)**$_2$ (hydrogens have been omitted for clarity).

In a manner similar to the previous adducts, crystals of **1·Zn(Mcp)**$_2$ suitable for X-ray structure determination were grown from a toluene solution by cooling to −25 °C. This zinc complex also crystallizes in the triclinic space group $P\bar{1}$ and is isomorphic with its magnesium, calcium, and barium analogues. The solid-state structure of **1·Zn(Mcp)**$_2$ (Figure 4) shows Mcp ligands that are clearly σ-bonded (κC^1) to the metal center. The σ-bonded Mcp carbons are 213.8 and 217.4 pm distant from the zinc center. The C−C bond distances in the Mcp ligands (143.6, 138.4, 140.7, 138.2, and 145.2 pm in one ring and 144.5, 140.8, 140.4, 139.0, and 144.5 pm in the other) present a bond alternation pattern that is consistent with the κC^1 (σ-bonded) arrangement. The σ-bonded arrangement is more clearly developed at zinc than for the Mcp−Mg bonding (vide supra). Reminiscent of the situation at magnesium, the σ-bonded Mcp arrangement at zinc places the internal "diene" carbons of the Mcp rings close to the π-orbital at C-2 of the carbene moiety. The resulting nonbonded carbon distances are 319.4(4) and 320.8(4) pm from one Mcp ligand and 323.2(4) and 333.8(4) pm from the second. These distances lie within the sum of the van der Waals radii (340 pm) but are longer than the interactions seen in **1·Mg(Mcp)**$_2$.

As observed for all the previous carbene adducts, the closest metal−carbon interaction in **1·Zn(Mcp)**$_2$ is to the carbene center (202.2(3) pm, 13.4 pm shorter than the average Zn−C distance to the σ-bonded Mcp carbons). The zinc center also exhibits trigonal-planar coordination, and in this case, the geometry is more regular (trigonal angles of 117.1°, 118.1°, and 124.0°) than that in the magnesium case. The zinc center rises 10.9 pm above the plane of its three attached substituents. This out-of-plane displacement renders the zinc adduct much less pyramidal than the larger barium analogue. The geometry of the carbene fragment in **1·Zn(Mcp)**$_2$ is more significantly changed relative to the free carbene than is observed for the alkaline earth adducts. In **1·Zn(Mcp)**$_2$, the N−C−N angle opens to 103.9°. The larger change in the imidazole structure is consistent with the Zn−C$_{\text{(carbene)}}$ distance that is shorter than all the other metallocene−carbene adducts described earlier. The overall geometry observed for **1·Zn(Mcp)$_2$** is reminiscent of the geometry observed for a diethylzinc adduct of 1,3-di(i-adamantyl)imidazol-2-ylidene.[10] The Zn−C(carbene) distance reported for this diethylzinc adduct was 209.6 pm with distances of 199.4 and 200.9 pm to the σ-bonded carbons of the ethyl groups.

In addition to the 1:1 metallocene−carbene adducts, we discovered that the heavier alkaline earth elements strontium and barium would also form bis(carbene) adducts (**(1)$_2$·Ae(Mcp)$_2$**) (eq 4).



1

Ae(Mcp)$_2$

Ae = Sr, L = O(Et)$_2$, n =1

Ae = Ba, L = thf, n =2

(1)$_2$•Ae(Mcp)$_2$

The reaction of 2 equiv of carbene **1** with either **Sr(Mcp)$_2$** or **Ba(Mcp)$_2$** proceeds smoothly at 23 °C to produce the corresponding 2:1 carbene−metallocene adduct. The strontium adduct **(1)$_2$·Sr(Mcp)$_2$** is closely related to an analogous samarium adduct.[14] This 2:1 carbene−strontium adduct is isolated as a colorless crystalline substance with a melting range of 301−303 °C. The Mcp methyls in **(1)$_2$·Sr(Mcp)$_2$** resonate at δ 2.22, which is slightly lower field than the corresponding 1:1 adduct (δ 2.15). The *N*-methyl resonances in **(1)$_2$·Sr(Mcp)$_2$** appear as a singlet at δ 3.21 (0.34 ppm downfield of the corresponding resonance in **1·Sr(Mcp)$_2$**). The carbene centers coordinated to strontium appear as a singlet in the ^{13}C NMR at δ 203.7 (5.5 ppm downfield of the 1:1 adduct).

The 2:1 carbene−barium adduct (**(1)$_2$·Ba(Mcp)$_2$**) is a colorless crystalline substance with a lower melting range (239−41 °C) than the strontium analogue. The Mcp methyls in **(1)$_2$·Ba(Mcp)$_2$** resonate at δ 2.29 (lower field than the coresponding 1:1 adduct, δ 2.13). A single resonance in the ^{1}H NMR is observed at δ 3.28 for the *N*-methyl resonances in **(1)$_2$·Ba(Mcp)$_2$**. This corresponds to the same $\Delta\delta$ of 0.34 ppm that is observed for the carbene−strontium 1:1 vs 2:1 adduct comparison. The carbene centers coordinated to barium appear as a singlet in the ^{13}C NMR at δ 208.8. Again, the shift in the resonances for the carbene centers between the 1:1 and 2:1 carbene−barium adducts (5.3 ppm) is almost identical to the relationship seen between the strontium compounds.

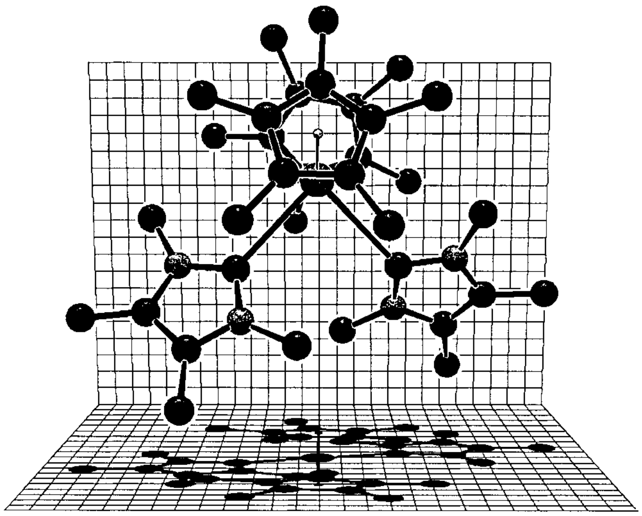


Figure 5. KANVAS representation of **(1)$_2$·Sr(Mcp)$_2$** (hydrogens have been omitted for clarity).

The solid-state structure of **(1)$_2$·Sr(Mcp)$_2$** was investigated by single-crystal X-ray diffraction. Crystals of **(1)$_2$·Sr(Mcp)$_2$** were readily obtained from a toluene solution. The solid-state structure of **(1)$_2$·Sr(Mcp)$_2$** is illustrated in Figure 5.[13] This bis(carbene)−strontium complex shows a pseudotetrahedral geometry at strontium with two carbenes and two pentamethylcyclopentadienyl ligands. The angle between the two carbene−strontium bonds is 86.4(1)°, and that between the two pentamethylcyclopentadienyl centroids is 131.0°. There is an approximate molecular 2-fold axis that bisects these angles between like substituents at the strontium. The twist between opposite edges of the tetrahedron is 76.8° along the pseudo 2-fold axis, so that there is a slight distortion toward a square-planar structure. The C−Sr distances to the two carbene ligands are 285.4(5) and 286.8(5) pm, while the mean C−Sr distance to the pentamethylcyclopentadienyl carbons is 291.7(12) pm (range 285.0(4)−297.0(5) pm; Sr−Mcp$_{\text{cent}}$ = 265.5, 266.9 pm). The ligated carbenes show a geometry that is very similar to the uncomplexed carbene[15,16] with ring internal valence angles at carbon of 102.2(4)° and 101.1(4)°. The overall geometry of **(1)$_2$·Sr(Mcp)$_2$** is very similar to that of **(1)$_2$·Sm(Mcp)$_2$** with which it is isomorphic.[14]

Discussion

The complexation chemistry of imidazol-2-ylidenes can be extended to include the heavier member of the main group II (alkaline earth) family. The various bis(pentamethylcyclopentadienyl)alkaline earth compounds react smoothly with 1,3,4,5-tetramethylimidazol-2-ylidene to afford carbene complexes in which the alkaline earth centers are ligated by only carbon centers. The carbene ligands show a preference for well-developed σ-bonding to the alkaline earth metal centers. For the mono(carbene) adducts derived from Mg, Ca,

---

(15) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.

(16) Arduengo, A. J., III; Dias, H. V. R.; Dixon, D. A.; Harlow, R. L.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 6812.

Ba, and Zn, the σ-bonded carbene−metal distance is always smaller than the metal−carbon$_{(Mcp)}$ distance regardless of whether the Mcp group is π- or σ-bonded to the metal center. The differential in these ligand−metal bond lengths is greatest for magnesium and smallest for barium.

In the solid state, the magnesium center of **1·Mg(Mcp)$_2$** shows different environments for the two pentamethylcyclopentadienyl groups. While one pentamethylcyclopentadienyl group remains η^5-bonded to the magnesium center, the second Mcp ligand adopts an arrangement that is intermediate between a σ-bonded and an η^3-bonded structure. For magnesium, this arrangement for the carbene adduct represents a change from the starting material (Mg(Mcp)$_2$) in which both Mcp ligands are bonded to magnesium in an η^5-coordination mode (with a linear arrangement between the ligand centroids).[17] The analogous transition group XII center, zinc, also forms a related carbene coordination compound. In the case of zinc, all the carbons attached to zinc (carbene and cyclopentadienyls) are σ-bonded so that the zinc center is quasi-trigonal planar. This structure represents a change from the bonding found in the gas phase for (Mcp)$_2$Zn in which both an η^5- and a σ-bonded methylcyclopentadienyl ring are observed.[18]

The base-free decamethylmetallocenes derived from calcium, strontium, and barium are known to possess bent geometries for both gas-phase and solid-state structures.[19] Thus, it is not surprising that the carbene·Ae(Mcp)$_2$ adducts for calcium and barium are also observed to have bent arrangements for the Mcp ligands. It is noteworthy that the degree of bending in the Mcp−Ae−Mcp fragment is similar for the base-free metallocenes (Ca, 147°; Ba, 131°)[20,21] and the mono(carbene) adducts (**1·Ca(Mcp)$_2$**, 143.9°; **1·Ba(Mcp)$_2$**, 137.0°).

The structural parameters discussed above demonstrate that the imidazol-2-ylidene ligand prefers to bind to the alkaline earth centers by means of a σ-interaction. Nonetheless, it is obvious from examination of the relative Ae−C bond distances in and among these structures (Table 1) that the strongest metal−carbene covalent interactions are observed with the lighter alkaline earth metals and with zinc. This trend is also reflected in the ^{13}C chemical shifts of the carbene centers coordinated to the various metals. For the mono(carbene) adducts, as one moves down the family from magnesium to barium, the resonance for the imidazole C$_2$ center shifts downfield from δ 185.7 (**1·Mg(Mcp)$_2$**) to δ 196.2 (**1·Ca(Mcp)$_2$**) to δ 198.2 (**1·Sr(Mcp)$_2$**) and finally to δ 203.5 (**1·Ba(Mcp)$_2$**). The corresponding zinc adduct (**1·Zn(Mcp)$_2$**) exhibits the highest resonance for this carbon center at δ 175.3. The lower field resonances actually approach those of the free carbene (δ 213.7). This chemical shift trend could also be attributed to magnetic shielding and/or magnetic isotropy from the metal centers, but we note that the changes in the cyclopentadienyl carbon resonances among the adducts are much smaller and rather irregular (**1·Mg(Mcp)$_2$**, δ 123.3; **1·Ca(Mcp)$_2$**, δ 124.0; **1·Sr(Mcp)$_2$**, δ 124.1; **1·Ba(Mcp)$_2$**, δ 123.9; **1·Zn(Mcp)$_2$**, δ 123.6). As the metal centers become larger and more electropostive, it is reasonable to expect that bonding to carbon should lose covalent character and become weaker. The structural and NMR spectroscopic trends among **1·Ae(Mcp)$_2$** fit with this expectation. The heaviest stable alkaline earth element, barium, thus shows near-equal bond distances to both the π-bonded and σ-bonded carbon centers, and the chemical shift of the coordinated carbene center is the most carbene-like.

In addition to the 1:1 carbene−alkaline earth adducts, it is also possible to add a second carbene ligand at the heavier (Sr and Ba) alkaline earth centers. The addition of a second σ-coordinating carbene center to these metal centers appears to weaken the carbene−metal interactions as judged by the chemical shift of the coordinated carbenes. Both **(1)$_2$·Sr(Mcp)$_2$** and **(1)$_2$·Ba(Mcp)$_2$** exhibit resonances for the imidazole C$_2$ centers at lower field than any of the mono(carbene) adducts (δ 203.7 and 208.8, respectively). Further supporting weaker carbene−metal interactions in the bis(carbene) adducts, the solid-state structure of **(1)$_2$·Sr(Mcp)$_2$** reveals carbene−strontium distances that are near those of the π-bonded cyclopentadienyl ligands.

Conclusion

The alkaline earth family of decamethylmetallocenes forms an interesting series of carbene adducts in which imidazol-2-ylidenes can be added to the alkaline earth metal center by means of a σ-bonding metal−carbon interaction. These adducts show smooth family trends in the nature of the carbene−metal bonding that ranges from somewhat covalent for magnesium to rather ionic for barium. These trends are reflected in both the structures and NMR spectra of the adducts. The analogous “zincocene” also gives a carbene adduct, but in contrast to the alkaline earth elements, it shows a much stronger preference for σ-covalent bonding. The heavier alkaline earth elements (Sr, Ba) are also capable of forming stable bis(carbene) adducts.

Experimental Section

Reactions and manipulations were carried out under an atmosphere of dry nitrogen, either in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Solvents were dried (using standard procedures),[22] distilled, and deoxygenated prior to use, unless otherwise indicated. Glassware was oven-dried at 160 °C overnight. The carbene **1** was prepared as previously described.[15] The bis(pentamethylcyclopentadienyl)metal complexes that were used as starting materials were prepared by established procedures.[18,23,24] The ^{1}H (300.75 MHz) and ^{13}C (75.629 MHz) NMR spectra were recorded on a GE Omega 300WB spectrometer. All NMR spectra are referenced to (CH$_3$)$_4$Si (^{1}H, ^{13}C). Mass spectra were recorded on a VG-ZAB-E instrument using FAB method and xenon gas.

---

(17) Andersen, R. A.; Blom, R.; Boncella, J. M.; Burns, C. J.; Volden, H. V. *Acta Chem. Scand., Ser. A* **1987**, *A41*, 24.

(18) Blom, R.; Boersma, J.; Budzelaar, P. H. M.; Fischer, B.; Haaland, A.; Volden, H. V.; Weidlein, J. *Acta Chem. Scand., Ser. A* **1986**, *A40*, 113.

(19) Hanusa, T. P. *Polyhedron* **1990**, *9*, 1345.

(20) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1045.

(21) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *Organometallics* **1990**, *9*, 1128.

(22) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: New York, 1985.

(23) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882.

Melting points were obtained on a Thomas−Hoover capillary apparatus and were not corrected. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Preparation of 1·Mg(Mcp)$_2$. A solution of $(C_5Me_5)_2Mg$[23] (800 mg, 2.7 mmol) in 20 mL of benzene was treated with a solution of 1,3,4,5-tetramethylimidazol-2-ylidene (337 mg, 2.7 mmol) in 10 mL of benzene. After the mixture was stirred for 1 h, the solvent was removed in vacuo. The ^{1}H NMR showed the presence of some impurities in the crude mixture. Purification was accomplished by recrystallization from a toluene solution at −26 °C: yield 640 mg (56%); mp 197−199 °C; ^{1}H NMR (C_6D_6) δ 1.34 (s, CCH_3, 6 H), 2.06 (s, Mcp−CH_3, 30 H), 2.88 (s, NCH_3, 6 H); ^{13}C NMR (C_6D_6) δ 8.19 (s, $NCCH_3$), 11.77 (Mcp−CCH_3), 35.78 (s, NCH_3), 110.57 (s, Mcp−CCH_3), 123.25 (s, NC*C*N), 185.72 (s, N*C*N). Anal. Calcd for $C_{27}H_{42}MgN_2$: C, 77.41; H, 10.11; N, 6.69. Found: C, 77.73; H, 10.31; N, 6.68.

Preparation of 1·Ca(Mcp)$_2$. A solution of $(C_5Me_5)_2Ca(OEt_2)$[24] (1.0 g, 2.6 mmol) in 30 mL of benzene was treated with a solution of 1,3,4,5-tetramethylimidazol-2-ylidene (32 mg, 2.6 mmol) in 30 mL of benzene. After the mixture was stirred overnight, the solvent was removed in vacuo to obtain a white crystalline solid (1.1 g, 100%). The crude product appeared pure by NMR. X-ray quality crystals were grown from a toluene solution at −26 °C: mp 298−301 °C; ^{1}H NMR (C_6D_6) δ 1.36 (s, CCH_3, 6 H), 2.13 (s, Mcp−CH_3, 30 H), 2.90 (s, NCH_3, 6 H); ^{13}C NMR (C_6D_6) δ 8.17 (s, CCH_3), 11.30 (Mcp−CCH_3), 35.11 (s, NCH_3), 112.01 (s, Mcp−CCH_3), 123.98 (s, NC*C*), 196.19 (s, N*C*N). Anal. Calcd for $C_{27}H_{42}CaN_2$: C, 74.60; H, 9.74; N, 6.44. Found: C, 74.73; H, 9.86; N, 6.35.

Preparation of 1·Sr(Mcp)$_2$. A solution of $(C_5Me_5)_2Sr(OEt_2)$[24] (416 mg, 1 mmol) in 20 mL of toluene was treated with a solution of 1,3,4,5-tetramethylimidazol-2-ylidene (124 mg, 1 mmol) in 20 mL of toluene. After the mixture was stirred for 2 h, the solution was filtered through Celite and the solvent was removed in vacuo to yield the crude product (480 mg, 100%). The crude product appeared pure by ^{1}H NMR, but samples were recrystallized from a toluene solution at −26 °C: mp 291−294 °C; ^{1}H NMR (C_6D_6) δ 1.33 (s, CCH_3, 6 H), 2.15 (s, Mcp−CH_3, 30 H), 2.87 (s, NCH_3, 6 H); ^{13}C NMR (C_6D_6) δ 8.14 (s, $NCCH_3$), 11.11 (Mcp−CCH_3), 34.71 (s, NCH_3), 111.78 (s, Mcp−CCH_3), 124.06 (s, NC*C*N), 198.22 (s, N*C*N). Anal. Calcd for $C_{27}H_{42}SrN_2$: C, 67.24; H, 8.78; N, 5.81. Found: C, 65.85; H, 8.86; N, 5.76.

Preparation of 1·Ba(Mcp)$_2$. A solution of $(C_5Me_5)_2Ba(thf)_2$[24] (552 mg, 1 mmol) in 20 mL of toluene was treated with a solution of 1,3,4,5-tetramethylimidazol-2-ylidene (124 mg, 1 mmol) in 20 mL of toluene. After the mixture was stirred for 2 h, the cloudy solution was filtered through Celite and the solvent was removed in vacuo. The crude product was recrystallized from a toluene solution at −26 °C: yield 430 mg (81%); mp 257−259 °C; ^{1}H NMR (C_6D_6) δ 1.36 (s, CCH_3, 6 H), 2.13 (s, Mcp−CH_3, 30 H), 2.94 (s, NCH_3, 6 H); ^{13}C NMR (C_6D_6) δ 8.14 (s, $NCCH_3$), 11.10 (Mcp−CCH_3), 34.48 (s, NCH_3), 112.91 (s, Mcp−CCH_3), 123.88 (s, NC*C*N), 203.47 (s, N*C*N).

Preparation of 1·Zn(Mcp)$_2$. A solution of $(C_5Me_5)_2Zn$[18] (880 mg, 2.6 mmol) in 20 mL of benzene was treated with a solution of 1,3,4,5-tetramethylimidazol-2-ylidene (325 mg, 2.6 mmol) in 20 mL of benzene. After the mixture was stirred for 1 h, the solvent was removed in vacuo to obtain a yellowish solid. The crude product was recrystallized from a toluene solution at −26 °C to give 817 mg (68%) of **1·Zn(Mcp)$_2$** as a sligltly off-white crystalline solid: mp 210−212 °C; ^{1}H NMR (C_6D_6) δ 1.27 (s, CCH_3, 6 H), 2.07 (s, Mcp−CH_3, 30 H), 2.89 (s, NCH_3, 6 H); ^{13}C NMR (C_6D_6) δ 7.81 (s, $NCCH_3$), 12.30 (Mcp−CCH_3), 35.37 (s, NCH_3), 113.45 (s, Mcp−CCH_3), 123.62 (s, NC*C*N), 175.38 (s, N*C*N). Anal. Calcd for $C_{27}H_{42}N_2Zn$: C, 70.50; H, 9.20; N, 6.09. Found: C, 70.57; H, 9.35; N, 6.04.

Preparation of (1)$_2$·Sr(Mcp)$_2$. A solution of $(C_5Me_5)_2Sr(OEt_2)$[24] (500 mg, 1.2 mmol) in 10 mL of toluene was treated with a solution of 1,3,4,5-tetramethylimidazol-2-ylidene (300 mg, 2.4 mmol) in 15 mL of toluene. After 10 min the solution became gradually cloudy, and stirring was continued overnight. After removal of the solvent, the white residue was suspended in hexane. The crude product was isolated by filtration of the hexane suspension (720 mg, 99%): mp 301−303 °C; ^{1}H NMR (C_6D_6) δ 1.47 (s, CCH_3, 12 H), 2.22 (s, Mcp−CH_3, 30 H), 3.21 (s, NCH_3, 12 H); ^{13}C NMR (C_6D_6) δ 8.48 (s, $NCCH_3$), 11.88 (Mcp−CCH_3), 35.28 (s, NCH_3), 111.39 (s, Mcp−CCH_3), 123.46 (s, NC*C*N), 203.74 (s, N*C*N).

Preparation of (1)$_2$·Ba(Mcp)$_2$. A solution of $(C_5Me_5)_2Ba(thf)_2$[24] (552 mg, 1 mmol) in 20 mL of toluene was treated with a solution of 1,3,4,5-tetramethylimidazol-2-ylidene (248 mg, 2 mmol) in 20 mL of toluene. After the mixture was stirred overnight, the cloudy reaction mixture was evaporated to yield the product. Proton NMR analysis of the crude product showed only the desired product and no impurities were detected: mp 239−241 °C; ^{1}H NMR (C_6D_6) δ 1.49 (s, CCH_3, 12 H), 2.29 (s, Mcp−CH_3, 30 H), 3.28 (s, NCH_3, 12 H); ^{13}C NMR (C_6D_6) δ 8.56 (s, $NCCH_3$), 11.80 (Mcp−CCH_3), 35.16 (s, NCH_3), 111.82 (s, Mcp−CCH_3), 123.17 (s, NC*C*N), 208.76 (s, N*C*N).

X-ray Crystal Structure of 1·Mg(Mcp)$_2$. Formula: $C_{27}H_{42}N_2Mg$, triclinic, space group $P\bar{1}$ (No. 2), $a = 913.0(3)$ pm, $b = 984.6(2)$ pm, $c = 1480.3(3)$ pm; $\alpha = 100.98(2)°$, $\beta = 91.96(2)°$, $\gamma = 106.96(2)°$; $T = -70$ °C, $Z = 2$, $V = 1243.8$ Å^3, fw = 418.96, $D_c = 1.119$ g·cm^{-3}, μ(Mo Kα) = 0.83 cm^{-1}. Crystal description: colorless parallelopiped (0.37 × 0.20 × 0.52 mm) grown from a saturated toluene solution at −25 °C. A total of 4819 reflections were collected, $2.8° \leq 2\theta \leq 50.0°$, maximum h,k,l = 10, 11, 17; data octants +++, +−+, −++, −−+; ω scan method, scan width = 1.20−2.20° ω, scan speed = 1.70−4.00 deg·min^{-1}, on a Enraf-Nonius CAD4 diffractometer with graphite monochromator using Mo Kα radiation ($\lambda = 71.073$ pm). Typical half-height peak width = 0.15° ω, 2 standards collected 32 times, no adjustment for a 2% fluctuation in intensity, 3.5% variation in azimuthal scan, no absorption correction; 447 duplicates, 1.4% R-merge, 2678 unique reflections of intensity greater than $3.0\sigma(I)$, the structure was solved by direct methods (SHELXS) and refined by full-matrix least squares on F. Anomalous terms for Mg were included, weights $\propto [\sigma^2(I) + 0.0009I^2]^{-1/2}$ (excluded 3). Refined isotropic: all non-hydrogen atoms. Hydrogen atoms on the carbene refined isotropic. Hydrogens on Mcps were placed in fixed positions. There were 439 parameters (data/parameter ratio = 6.09). The final R factors were $R = 0.040$, $R_w = 0.038$. The error of fit was 1.38, max $\Delta/\sigma = 0.02$. The final difference Fourier showed the largest residual density to be 0.19 10^{-6} e·pm^{-3} near C14. Further details of the crystal structure are available in the Supporting Information.

X-ray Crystal Structure of 1·Ca(Mcp)$_2$. Formula: $C_{27}H_{42}N_2Ca$, triclinic, space group $P\bar{1}$ (No. 2), $a = 960.7(1)$ pm, $b = 984.3(1)$ pm, $c = 1485.3(2)$ pm; $\alpha = 95.82(1)°$, $\beta = 98.50(2)°$, $\gamma = 106.25(2)°$; $T = -70$ °C, $Z = 2$, $V = 1318.4$ Å^3, fw = 434.73, $D_c = 1.095$ g·cm^{-3}, μ(Mo Kα) = 2.45 cm^{-1}. Crystal description: colorless wedge (0.35 × 0.31 × 0.51 mm) grown from a saturated toluene solution at −25 °C. A total of 6266 reflections were collected, $2.8° \leq 2\theta \leq 55.0°$, maximum h,k,l = 12, 12, 19; data octants +++, +−+, −++, −−+; ω scan method, scan width = 1.20−2.20° ω, scan speed = 1.70−5.00 deg·min^{-1}, on a Enraf-Nonius CAD4 diffractometer with graphite monochromator using Mo Kα radiation ($\lambda = 71.073$ pm). Typical half-height peak width = 0.17° ω, 1 standard collected 31 times, no adjustment for a 1% fluctuation in intensity, 5.8% variation in azimuthal scan, no absorption correction; 237 duplicates, 1.4% R-merge, 2855 unique reflections of intensity greater than $3.0\sigma(I)$, the structure was solved by direct methods (MULTAN) and refined by full-matrix least squares on F. Anomalous terms for Ca were included, weights $\propto [\sigma^2(I) + 0.0009I^2]^{-1/2}$ (excluded 1). Refined isotropic: all non-

---

(24) Burns, C. J.; Andersen, R. A. *J. Organomet. Chem.* **1987**, *325*, 31.

hydrogen atoms. Hydrogen atoms on the carbene refined isotropic. Hydrogens on Mcps placed in fixed positions. There were 319 parameters (data/parameter ratio = 8.95). The final *R* factors were $R = 0.051$, $R_w = 0.044$. The error of fit was 1.37, max $\Delta/\sigma = 0.02$. The final difference Fourier showed the largest residual density to be 0.22 10^{-6} e·pm^{-3} near C25. Further details of the crystal structure are available in the Supporting Information.

X-ray Crystal Structure of 1·Ba(Mcp)$_2$. Formula: $C_{27}H_{42}N_2Ba$, triclinic, space group $P\bar{1}$ (No. 2), $a = 883.6(2)$ pm, $b = 1084.8(2)$ pm, $c = 1526.4(2)$ pm, $\alpha = 76.59(1)°$, $\beta = 88.37(2)°$, $\gamma = 72.10(2)°$; $T = -70$ °C, $Z = 2$, $V = 1352.9$ Å^3, fw = 531.99, $D_c = 1.306$ g·cm^{-3}, μ(Mo Kα) = 14.81 cm^{-1}. Crystal Description: colorless parallelpiped (0.37 × 0.20 × 0.52 mm) grown from a saturated toluene solution at −25 °C. A total of 4819 reflections were collected, $2.8° \leq 2\theta \leq 55.0°$, maximum h,k,l = 10, 11, 17; data octants +++, +−+, −++, −−+; ω scan method, scan width = 1.20−2.70° ω, scan speed = 1.70−5.00 deg·min^{-1}, on a Enraf-Nonius CAD4 diffractometer with graphite monochromator using Mo Kα radiation ($\lambda = 71.073$ pm). Typical half-height peak width = 0.34° ω, 2 standard collected 39 times, no adjusted for a 3% decrease in intensity, 8.8% variation in azimuthal scan, no absorption correction; 254 duplicates, 1.4% *R*-merge, 5574 unique reflections of intensity greater than $3.0\sigma(I)$, the structure was solved by direct methods (SHELXS) and refined by full-matrix least squares on *F*. Anomalous terms for Ba were included, weights $\propto [\sigma^2(I) + 0.0009I^2]^{-1/2}$ (excluded 1). Refined isotropic: all non-hydrogen atoms. Hydrogen atoms placed in fixed positions. There were 271 parameters (data/parameter ratio = 20.56). The final *R* factors were $R = 0.032$, $R_w = 0.031$. The error of fit was 1.05, max $\Delta/\sigma = 0.01$. The final difference Fourier showed the largest residual density to be 0.90 10^{-6} e·pm^{-3} near the barium. Further details of the crystal structure are available in the Supporting Information.

X-ray Crystal Structure of 1·Zn(Mcp)$_2$. Formula: $C_{27}H_{42}N_2Zn$, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.87(2)$ pm, $b = 969.8(1)$ pm, $c = 1488.0(2)$ pm, $\alpha = 101.22(1)°$, $\beta = 94.27(1)°$, $\gamma = 103.54(1)°$; $T = -70$ °C, $Z = 2$, $V = 1244.8$ Å^3, fw = 460.02, $D_c = 1.227$ g·cm^{-3}, μ(Mo Kα) = 10.24 cm^{-1}. Crystal Description: colorless parallelpiped (0.26 × 0.26 × 0.43 mm) grown from a saturated toluene solution at −25 °C. A total of 4052 reflections were collected, $2.8° \leq 2\theta \leq 48.0°$, maximum h,k,l = 10, 11, 17; data octants +++, +−+, −++, −−+; ω scan method, scan width = 1.20−1.50° ω, scan speed = 1.70−6.70 deg·min^{-1}, on a Enraf-Nonius CAD4 diffractometer with graphite monochromator using Mo Kα radiation ($\lambda = 71.073$ pm). Typical half-height peak width = 0.16° ω, 2 standards collected 14 times, none adjusted for a 6% decrease in intensity, no absorption correction; 167 duplicates, 1.2% *R*-merge, 2899 unique reflections of intensity greater than $3.0\sigma(I)$, the structure was solved by direct methods (SHELXS) and refined by full-matrix least squares on *F*. Anomalous terms for Zn were included, weights $\propto [\sigma^2(I) + 0.0009I^2]^{-1/2}$ (excluded 1). Refined isotropic: all non-hydrogen atoms. Hydrogen atoms on the carbene were refined isotropic. Hydrogens on Mcps placed in fixed positions. There were 319 parameters (data/parameter ratio = 8.95). The final *R* factors were $R = 0.051$, $R_w = 0.044$. The error of fit was 1.37, max $\Delta/\sigma = 0.02$. The final difference Fourier showed the largest residual density to be 0.22 10^{-6} e·pm^{-3} near C25. Further details of the crystal structure are available in the Supporting Information.

X-ray Crystal Structure of (1)$_2$·Sr(Mcp)$_2$. Formula: $C_{34}H_{54}N_4Sr$, triclinic, space group $P\bar{1}$ (No. 2), $a = 1031.1(2)$ pm, $b = 1059.3(2)$ pm, $c = 1728.7(5)$ pm, $\alpha = 75.93(2)°$, $\beta = 74.94(2)°$, $\gamma = 69.29(2)°$; $T = -70$ °C, $Z = 2$, $V = 1636.7$ Å^3, fw = 606.45, $D_c = 1.230$ g·cm^{-3}, μ(Mo Kα) = 16.23 cm^{-1}. Crystal Description: colorless irregular block (0.36 × 0.28 × 0.35 mm) grown from a saturated toluene solution at −25 °C. A total of 7749 reflections were collected, $2.5° \leq 2\theta \leq 55.0°$, maximum h,k,l = 13, 13, 22; data octants: +++, +−+, −++, −−+; ω scan method, scan width = 1.20−2.00° ω, scan speed = 1.70−5.00 deg·min^{-1}, on a Enraf-Nonius CAD4 diffractometer with graphite monochromator using Mo Kα radiation ($\lambda = 71.073$ pm). Typical half-height peak width = 0.16° ω, 2 standard collected 36 times, no adjustment for a 2% fluctuation in intensity, 13.1% variation in azimuthal scan, no absorption correction; 141 duplicates, 1.8% *R*-merge, 4155 unique reflections of intensity greater than $3.0\sigma(I)$, the structure was solved by direct methods (MULTAN) and refined by full-matrix least squares on *F*. Anomalous terms for Sr were included, weights $\propto [\sigma^2(I) + 0.0009I^2]^{-1/2}$ (excluded 2). Refined isotropic: all non-hydrogen atoms. Hydrogen atoms placed in fixed positions. There were 352 parameters (data/parameter ratio = 11.80). The final *R* factors were $R = 0.054$, $R_w = 0.043$. The error of fit was 1.19, max $\Delta/\sigma = 0.00$. The final difference Fourier showed the largest residual density to be 0.54 10^{-6} e·pm^{-3}. Further details of the crystal structure are available in the Supporting Information.

Acknowledgment is made for the excellent technical assistance of H. A. Craig.

Supporting Information Available: A complete description of the X-ray crystallographic determinations on **1·Mg(Mcp)$_2$**, **1·Ca(Mcp)$_2$**, **1·Ba(Mcp)$_2$**, **1·Zn(Mcp)$_2$**, and **(1)$_2$·Sr(Mcp)$_2$**, including tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, bond angles, and ORTEP drawings (47 pages). Ordering information is given on any current masthead page.

OM980438W