

Modulation of Zn–C Bond Lengths Induced by Ligand Architecture in Zinc Carbatrane Compounds

Serge Ruccolo, Wesley Sattler, Yi Rong, and Gerard Parkin*

Department of Chemistry, Columbia University, New York, New York 10027, United States

S Supporting Information

ABSTRACT: Bond lengths between pairs of atoms in covalent molecules are generally predicted well by the sum of their respective covalent radii, such that there are usually only small variations in related compounds. It is, therefore, significant that we have demonstrated that the incorporation of appropriately sized linkers between carbon and a metal center provides a means to modulate the length and nature of a metal–carbon interaction. Specifically, X-ray diffraction studies on a series of tris(1-methylimidazol-2-ylthio)methyl zinc complexes, $[\text{Titm}^{\text{Me}}]\text{ZnX}$, demonstrate how the Zn–C bond lengths are highly variable (2.17–2.68 Å) and are up to 0.67 Å longer than the average value listed in the Cambridge Structural Database (2.01 Å). Furthermore, density functional theory calculations on $[\text{Titm}^{\text{Me}}]\text{ZnCl}$ demonstrate that the interaction is very flexible, such that either increasing or decreasing the Zn–C length from that in the equilibrium structure is associated with little energy change in comparison to that for other compounds with Zn–C bonds.

Despite the fact that the concept of the chemical bond continues to evolve as new characterization techniques and calculations provide additional ways to probe its nature,¹ the ability to assign covalent radii to elements is a consequence of the fact that the bond lengths between a given pair of atoms in covalent molecules are reasonably constant. For example, analysis of the structurally characterized compounds in the Cambridge Structural Database (CSD)² indicates that the mean Zn–C single bond length is 2.01 Å, with a standard deviation of only 0.07 Å. Here we describe how the Zn–C bond length can be manipulated in a significant manner by modifying the ligand architecture.

Tridentate tripodal ligands that feature three nitrogen donors, as exemplified by the tris(pyrazolyl)hydroborato class of ligands,³ are a common feature in coordination chemistry. Closely related are C_3 -symmetric tetradentate tripodal variants in which the bridgehead donor also binds to the metal, thereby generating an atrane motif.^{4,5} The majority of such ligands, however, feature a bridgehead comprised of an L-type⁶ nitrogen atom donor, as illustrated by tris(amidoethyl)amine and related derivatives.^{4,5,7} By comparison, atranes that feature a transannular M–C interaction have received little attention. Recently, however, the tris(2-pyridylthio)methyl ligand, $[\text{Tptm}]$, has been shown to be able to form metallacarbatranes (Figure 1) with a variety of different metals.^{7–9} Furthermore, we have also demonstrated that $[\text{Tptm}]$ is a useful ligand for Zn that allows

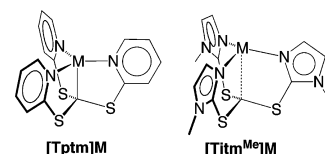
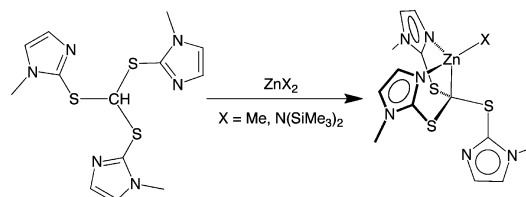


Figure 1. Tris(2-pyridylthio)methyl (left) and tris(1-methylimidazol-2-ylthio)methyl (right) ligands.

for the isolation of a monomeric alkyl zinc hydride compound, which is an effective catalyst for transformations such as hydrosilylation of aldehydes, ketones, and carbon dioxide.^{10,11} Prompted by these studies, we have extended our investigations to the application of a closely related multidentate alkyl ligand, namely tris(1-methylimidazol-2-ylthio)methyl, $[\text{Titm}^{\text{Me}}]$, which differs from $[\text{Tptm}]$ by virtue of the presence of a 5-membered imidazolyl moiety, rather than a 6-membered pyridyl group (Figure 1). Albeit a relatively small perturbation in the nature of the heterocyclic donor, the modification has a profound structural impact, as described herein.

Coordination of the tris(1-methylimidazol-2-ylthio)methyl ligand to Zn may be achieved by several approaches, two of which include the reactions of either Me_2Zn or $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ with tris(1-methylimidazol-2-ylthio)methane, $[\text{Titm}^{\text{Me}}]\text{H}$,¹² to afford $[\kappa^3\text{-Titm}^{\text{Me}}]\text{ZnMe}$ and $[\kappa^3\text{-Titm}^{\text{Me}}]\text{ZnN}(\text{SiMe}_3)_2$, respectively (Scheme 1). X-ray diffraction studies demonstrate that the

Scheme 1. Synthesis of $[\kappa^3\text{-Titm}^{\text{Me}}]\text{ZnMe}$



$[\text{Titm}^{\text{Me}}]$ ligands of $[\kappa^3\text{-Titm}^{\text{Me}}]\text{ZnMe}$ and $[\kappa^3\text{-Titm}^{\text{Me}}]\text{ZnN}(\text{SiMe}_3)_2$ coordinate in a hypodentate¹³ κ^3 -manner, as illustrated for $[\kappa^3\text{-Titm}^{\text{Me}}]\text{ZnMe}$ in Figure 2. The compounds are, nevertheless, fluxional in solution, analogous to the $[\kappa^3\text{-Tptm}]\text{ZnMe}$ and $[\kappa^3\text{-Tptm}]\text{ZnN}(\text{SiMe}_3)_2$ counterparts.

$[\kappa^3\text{-Titm}^{\text{Me}}]\text{ZnMe}$ and $[\kappa^3\text{-Titm}^{\text{Me}}]\text{ZnN}(\text{SiMe}_3)_2$ are useful precursors for a variety of other $[\text{Titm}^{\text{Me}}]\text{ZnX}$ derivatives, as illustrated in Scheme 2. For example, the Zn–Me bond of $[\kappa^3\text{-Titm}^{\text{Me}}]\text{ZnMe}$ is readily cleaved protolytically by H–X ($X =$

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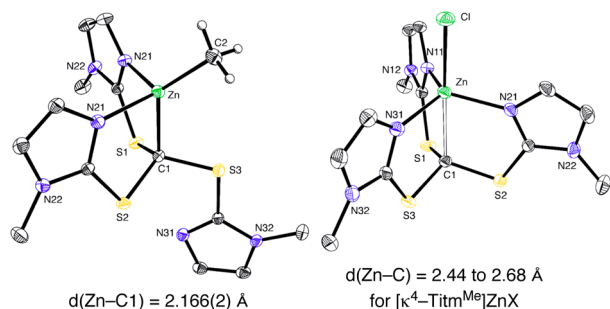
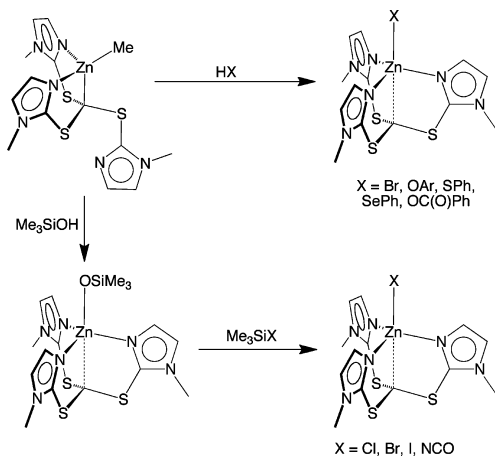


Figure 2. Molecular structures of $[\kappa^3\text{-Titm}^{\text{Me}}]\text{ZnMe}$ (left) and $[\text{Titm}^{\text{Me}}]\text{ZnCl}$ (right).

Scheme 2. Synthesis of $[\text{Titm}^{\text{Me}}]\text{ZnX}$ Complexes



Br, OSiMe_3 , OAr, SPh, SePh, OC(O)Ph) to afford $[\text{Titm}^{\text{Me}}]\text{ZnX}$. Likewise, the trimethylsilyloxy compound, $[\text{Titm}^{\text{Me}}]\text{ZnOSiMe}_3$, can be employed to form the halide and isocyanate complexes, $[\text{Titm}^{\text{Me}}]\text{ZnX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCO}$), by treatment with Me_3SiX . Furthermore, $[\kappa^3\text{-Titm}^{\text{Me}}]\text{ZnN}(\text{SiMe}_3)_2$ reacts with CO_2 to form the isocyanate complex, $[\text{Titm}^{\text{Me}}]\text{-ZnNCO}$, thereby resulting in the deoxygenation of CO_2 .

The molecular structures of a variety of $[\text{Titm}^{\text{Me}}]\text{ZnX}$ complexes have been determined by X-ray diffraction (Table 1), thereby demonstrating that the $[\text{Titm}^{\text{Me}}]$ ligand coordinates in a κ^4 -manner, such that the compounds have an approximately trigonal bipyramidal geometry, as illustrated for $[\text{Titm}^{\text{Me}}]\text{ZnCl}$ in Figure 2.¹⁴ These compounds, therefore, possess an atrane motif that is quite distinct from the aforementioned κ^3 -structures observed for $[\kappa^3\text{-Titm}^{\text{Me}}]\text{ZnMe}$ and $[\kappa^3\text{-Titm}^{\text{Me}}]\text{ZnN}(\text{SiMe}_3)_2$.

Although the hypodentate and atrane structural classes are also observed for the $[\text{Tptm}]\text{ZnX}$ system,⁸ a particularly important distinction pertains to the nature of the $\text{Zn}-\text{C}$ interactions in the atrane complexes. Specifically, whereas the $\text{Zn}-\text{C}$ bond lengths of the various $[\text{Tptm}]\text{ZnX}$ atrane complexes span a relatively narrow range of 2.11–2.22 Å, the corresponding interactions for $[\text{Titm}^{\text{Me}}]\text{ZnX}$ are considerably longer and range from 2.44 to 2.68 Å (Table 1).¹⁵ These distances are 0.43–0.67 Å longer than the mean $\text{Zn}-\text{C}$ bond length of 2.01 Å for compounds listed in the CSD.^{2,16} Albeit longer than the sum of covalent radii, the $\text{Zn}\cdots\text{C}$ distances are, nevertheless, distinctly shorter than the sum of the crystallographic van der Waals radii (3.8 Å)¹⁷ such that they correspond to a bonding interaction.

In contrast to the variable and long $\text{Zn}-\text{C}$ interactions for the $[\text{Titm}^{\text{Me}}]\text{ZnX}$ atrane derivatives, however, the corresponding $\text{Zn}-\text{C}$ bond distance for the κ^3 -complex, $[\kappa^3\text{-Titm}^{\text{Me}}]\text{ZnMe}$

Table 1. Comparison of $\text{Zn}-\text{C}$ and $\text{Zn}-\text{N}$ Bond Lengths (Å) for $[\text{Titm}^{\text{Me}}]\text{ZnX}$

X	$d(\text{Zn}-\text{C})$	$d(\text{Zn}-\text{N})_{\text{av}}$	$d(\text{Zn}-\text{X})$	τ_5 (ref 14)
CH_3 (κ^3)	2.166(2)	2.058	1.961(2)	-
Cl	2.479(3)	2.008	2.346(1)	0.97
	2.509(3)	2.008	2.348(1)	0.92
Br	2.580(2)	1.998	2.514(1)	0.93
I	2.476(6)	1.998	2.793(1)	0.91
NCO	2.477(5)	2.021	2.029(7)	0.87
	2.575(5)	2.013	2.065(5)	0.95
OSiMe_3	2.684(3)	2.012	1.911(1)	0.92
OPh	2.646(2)	2.009	1.967(2)	0.88
$p\text{-OC}_6\text{H}_4\text{Br}$	2.607(4)	2.002	1.967(3)	0.89
$p\text{-OC}_6\text{H}_4\text{Me}$	2.633(2)	2.005	1.972(2)	0.89
$p\text{-OC}_6\text{H}_4\text{NO}_2$	2.448(5)	2.012	2.014(3)	0.83
	2.478(5)	2.010	2.028(3)	0.81
$p\text{-OC}_6\text{H}_4\text{OMe}$	2.599(2)	2.010	1.990(2)	0.86
$p\text{-OC}_6\text{H}_4\text{Me}$	2.436(2)	2.027	2.042(2)	0.76
($p\text{-HOC}_6\text{H}_4\text{Me}$)				
OC(O)Ph	2.513(4)	2.017	2.034(3)	0.80
SPh	2.564(2)	2.020	2.389(1)	0.95
SePh	2.555(3)	2.019	2.514(1)	0.98

[2.166(2) Å],¹⁸ is in the range observed for the $[\text{Tptm}]\text{ZnX}$ atrane compounds. Also contrasting with the unusually long $\text{Zn}-\text{C}$ bond lengths of $[\text{Titm}^{\text{Me}}]\text{ZnX}$, the corresponding $\text{Zn}-\text{N}$ bond lengths [1.998(2)–2.027(2) Å] do not vary significantly (0.029 Å) and are similar to those for $[\text{Tptm}]\text{ZnX}$ (2.04–2.16 Å). As such, the similarity of the $\text{Zn}-\text{N}$ bond lengths further emphasizes the novelty associated with the unusually long and variable $\text{Zn}-\text{C}$ bond lengths within $[\text{Titm}^{\text{Me}}]\text{ZnX}$.

In this regard, an interesting illustration of the variability of the $\text{Zn}-\text{C}$ bond lengths is provided by the observation that hydrogen bonding of ArOH ($\text{Ar} = p\text{-Tol}$) to the aryloxy ligand of $[\text{Titm}^{\text{Me}}]\text{ZnOAr}$ results in a lengthening of the $\text{Zn}-\text{O}$ bond by 0.070 Å, but a much more significant contraction of the $\text{Zn}-\text{C}$ bond by 0.197 Å.

While bond distances longer than the sum of the covalent radii are sometimes observed between the bridgehead atoms in atrane complexes¹⁵ the interactions typically involve *dative* bonds that are well-known to be highly variable and sensitive to the coordination environment.^{19,20} Bond length changes have also been observed upon oxidation of molecules,^{9e,f,21} but it is very unusual to observe significant variations for normal covalent bonds in molecules with the same oxidation state, as exemplified by the fact that the standard deviation for the mean $\text{Zn}-\text{C}$ bond length of 2.01 Å for compounds listed in the CSD is only 0.07 Å.^{2,22} It is, therefore, evident that the unusually long $\text{Zn}-\text{C}$ interactions in $[\kappa^4\text{-Titm}^{\text{Me}}]\text{ZnX}$ cannot be described as conventional covalent bonds. The interactions are, therefore, proposed to possess a significant ionic component such that the compounds are best described as zwitterionic, with carbon and zinc centers that are formally anionic and cationic, respectively.

Zwitterionic metal compounds that feature anionic carbon centers are uncommon and are typically encountered in situations where geometric factors prevent the carbon lone pair from interacting with the metal.⁷ For example, the two-atom linkers between carbon and zinc in the zwitterionic tris(3,5-dimethylpyrazolyl)methyl zinc compounds, $[\text{C}(\text{pz}^{\text{Me}_2})_3]\text{ZnX}$ [$\text{X} = \text{Me}, \text{Cl}, \text{N}(\text{SiMe}_3)_2$],²³ prohibit direct $\text{Zn}-\text{C}$ interactions because the lone pairs point directly away from the metal center (Figure 3).^{24–26}

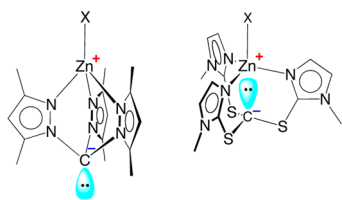


Figure 3. The two-atom linkers between carbon and zinc in $[\text{C}(\text{pz}^{\text{Me}})_3]\text{ZnX}$ (left) direct the lone pair away from the metal atom, whereas the more flexible three-atom linkers in $[\text{Titm}^{\text{Me}}]\text{ZnX}$ allow the lone pair to point towards the metal atom.

This is in marked contrast to the $[\text{Titm}^{\text{Me}}]\text{ZnX}$ complexes described here, in which the lone pair on the formally anionic bridgehead carbon atom is oriented directly towards the Zn center, yet does not participate in a conventional covalent bond.

One of the reasons for the differences between the $[\text{Titm}^{\text{Me}}]\text{ZnX}$ and $[\text{Tptm}]\text{ZnX}$ structures is undoubtedly associated with the different bond angles of the 5-membered imidazole and 6-membered pyridine rings. As a result, for a C_{3v} geometry, the donor orbitals of the nitrogen atoms of the $[\kappa^4\text{-Titm}^{\text{Me}}]$ ligand are directed further from the $[\text{N}_3]$ plane than are those for the $[\kappa^4\text{-Tptm}]$ ligand system (Figure 4).²⁷ Thus, the zinc atoms of $[\kappa^4\text{-Titm}^{\text{Me}}]\text{ZnX}$ are displaced by 0.27–0.41 Å from the respective $[\text{N}_3]$ plane, whereas the zinc atoms of $[\kappa^4\text{-Tptm}]\text{ZnX}$ are displaced by only 0.05–0.16 Å.

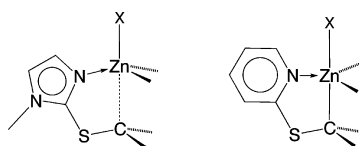


Figure 4. The different angles associated with the 5- and 6-membered rings result in the nitrogen lone pair orbitals being more displaced from the $[\text{N}_3]$ plane for the $[\text{Titm}^{\text{Me}}]$ system, thereby favoring a longer M–C bond.

A natural consequence of the out-of-plane directionality of the nitrogen atom donor orbitals of $[\text{Titm}^{\text{Me}}]$ is to lengthen the Zn–C distance. The most stable geometry of $[\kappa^4\text{-Titm}^{\text{Me}}]\text{ZnX}$ is, therefore, a compromise that maximizes the sum of the Zn–N and Zn–C bond energies. Specifically, displacement of the Zn center from the $[\text{N}_3]$ plane maximizes the Zn–N interactions at the expense of the Zn–C interaction. The observation that the Zn–C distances vary more significantly than the Zn–N distances indicates that the Zn←N bonds play a more dominant role in determining the structure than does the Zn–C bond. Since the Zn←N bonds represent dative interactions, which are often flexible,¹⁹ the preferential variability of the Zn–C bond lengths is most likely a consequence of the fact that the axial Zn–C bond of a pseudo-trigonal bipyramidal structure is a component of a 3-center-4-electron (3c-4e) “hypervalent” ω interaction,²⁸ rather than a conventional 2c-2e bond. Such axial bonds are often longer^{28–30} and, as a consequence, play a less significant role in determining the overall structure.

The two occupied molecular orbitals pertaining to the 3c-4e interactions for both $[\text{Titm}^{\text{Me}}]\text{ZnCl}$ and $[\text{Tptm}]\text{ZnCl}$ are illustrated in Figure 5. Of these, the lower energy orbital for each molecule possesses largely chlorine character, while the higher energy orbital possesses largely carbon character. With respect to the latter orbital, the principal difference between $[\text{Titm}^{\text{Me}}]\text{ZnCl}$ and $[\text{Tptm}]\text{ZnCl}$ is that the former possesses a

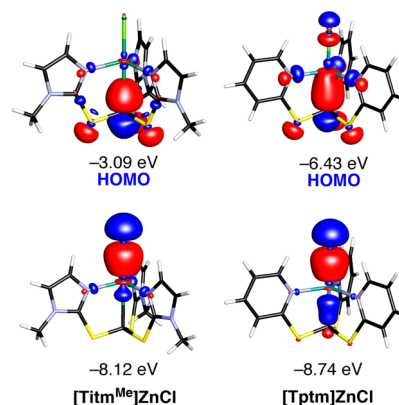


Figure 5. Occupied orbitals of the 3c-4e interactions of $[\text{Titm}^{\text{Me}}]\text{ZnCl}$ and $[\text{Tptm}]\text{ZnCl}$. The HOMO of $[\text{Titm}^{\text{Me}}]\text{ZnCl}$ is effectively a carbon-based sp^n hybrid lone pair orbital.

much greater degree of carbon character, such that the HOMO is effectively an sp^n hybrid lone pair orbital on carbon. Alternatively, rather than invoking a molecular orbital description, the axial hypervalent interaction can be described in terms of resonance involving the zwitterionic structures, $[\text{C}^- \text{Zn}^+ \text{Cl}]$ and $[\text{C}-\text{Zn}^+ \text{Cl}^-]$. Of these, the resonance structure with the formal negative charge on C, i.e., $[\text{C}^- \text{Zn}^+ \text{Cl}]$, is considered to be the dominant contributor for $[\text{Titm}^{\text{Me}}]\text{ZnCl}$.³¹

While the displacement of Zn from the $[\text{N}_3]$ plane maximizes the Zn–N interactions for a C_{3v} geometry of $[\text{Titm}^{\text{Me}}]\text{ZnX}$, the large variability in the Zn–C distances suggests that the out-of-plane preference is not strong. Supporting this statement, density functional theory (DFT) calculations demonstrate that the energy surface associated with varying the Zn–C bond length is rather shallow. Specifically, a series of geometry optimization calculations, in which the Zn–C distance of $[\text{Titm}^{\text{Me}}]\text{ZnCl}$ is varied, demonstrates that the energy of the molecule changes relatively little as the Zn–C distance is modified (Figure 6).³² For example, increasing the Zn–C bond by 0.2 Å from the value in the fully geometry optimized structure results in an increase in energy of only 0.38 kcal mol^{−1} (Figure 6). Likewise, shortening the Zn–C bond by 0.2 Å increases the energy of the molecule by only 0.41 kcal mol^{−1}.

Similar DFT calculations have been performed on $[\text{Tptm}]\text{ZnCl}$. Significantly, in addition to the equilibrium Zn–C bond being shorter than that for $[\text{Titm}^{\text{Me}}]\text{ZnCl}$, the energy surface is much steeper (Figure 6). Thus, lengthening the

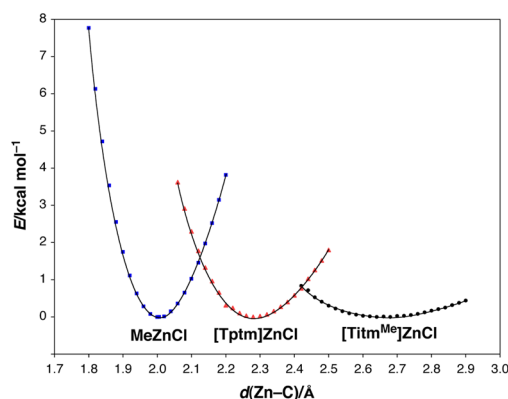


Figure 6. Relative energies of $[\text{Titm}^{\text{Me}}]\text{ZnCl}$, $[\text{Tptm}]\text{ZnCl}$, and MeZnCl as a function of Zn–C distance.

Zn–C bond by 0.2 Å increases the energy of the molecule by 1.51 kcal mol⁻¹, as compared to a value of 0.38 kcal mol⁻¹ for the corresponding change in [Titm^{Me}]ZnCl.

It is also pertinent to compare the flexibility of the Zn–C bonds of [Titm^{Me}]ZnCl and [Tptm]ZnCl with that of MeZnCl, which is devoid of additional donor groups. Thus, as would be expected, the Zn–C bond of MeZnCl (2.01 Å) is significantly shorter than those of [Titm^{Me}]ZnCl and [Tptm]ZnCl and the energy of the molecule is much more sensitive to perturbations in bond length (Figure 6). For example, lengthening of the Zn–C bond of MeZnCl by 0.2 Å increases the energy substantially by 3.82 kcal mol⁻¹, thereby reiterating the significance of the long and variable Zn–C bond lengths in [Titm^{Me}]ZnCl (Figure 6).

In summary, we have demonstrated that the incorporation of donor substituents, with appropriately sized spacers, can be used to modulate the length and nature of a metal–carbon bond. Specifically, a linker that comprises a 5-membered imidazolyl ring has the ability to create zwitterionic Zn⁺⋯C⁻ interactions in [Titm^{Me}]ZnX compounds that are up to 0.67 Å longer than the average value listed in the CSD. DFT calculations also demonstrate that, in comparison to other compounds with Zn–C bonds, the interactions in [Titm^{Me}]ZnX are highly flexible and that little energy is required to increase or decrease the length from that in the equilibrium structure.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b09250.

Experimental details and computational data (PDF)

Crystallographic data in CIF format (ZIP)

■ AUTHOR INFORMATION

Corresponding Author

*parkin@columbia.edu

Notes

The authors declare no competing financial interest.

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- (25) For other examples of zwitterionic Zn compounds with anionic carbon centers, see: (a) Mou, Z.; Liu, B.; Wang, M.; Xie, H.; Li, P.; Li, L.; Li, S.; Cui, D. *Chem. Commun.* **2014**, 50, 11411. (b) Mou, Z. H.; Xie, H. Y.; Wang, M. Y.; Liu, N.; Yao, C. G.; Li, L.; Liu, J. Y.; Li, S. H.; Cui, D. M. *Organometallics* **2015**, 34, 3944.
- (26) For other metal compounds with formally anionic carbon centers, see ref 7.
- (27) On geometric grounds alone, replacing a 6-membered ring with a 5-membered ring shifts the direction of the nitrogen lone pair by ~12°.
- (28) Weinhold, F.; Landis, C. R. *Valency and Bonding: a natural bond orbital donor-acceptor perspective*; Cambridge University Press: New York, 2005.
- (29) Akiba, K., Ed. *Chemistry of Hypervalent Compounds*; Wiley-VCH: New York, 1999.
- (30) In this regard, it is worth noting that the Zn–X bond lengths are longer than those in pseudo-tetrahedral [Tp^{f-Bu}]ZnX derivatives. See: Yoon, K.; Parkin, G. *J. Am. Chem. Soc.* **1991**, 113, 8414.
- (31) In the extreme that there is no Zn⋯C interaction, the bonding at the four-coordinate Zn center may be simply expressed in terms of four 2c-2e bonds.
- (32) Interestingly, geometry-optimized structures with Zn–C distances of less than 2.4 Å possess C_{3v} rather than C_{3h} symmetry due to the introduction of a propeller-like twist of the imidazole groups in order to maintain reasonable bond angles.