# **ORGANOMETALLICS**

# $\beta$ -Hydrogen Elimination of Ionic Butylzinc Complexes

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**Supporting Information** 

**ABSTRACT:** Gas-phase experiments on deuterium-labeled BuZn-(TMEDA)<sup>+</sup> (TMEDA = N,N,N',N'-tetramethylethylenediamine) prove that the loss of butene from this species corresponds to a  $\beta$ -H elimination. Quantum-chemical calculations corroborate this finding and furthermore predict that the fragmentations of related cationic butylzinc complexes as well as of Bu<sub>3</sub>Zn<sup>-</sup> follow similar mechanisms.



# 1. INTRODUCTION

 $\beta$ -H eliminations constitute a prototypical reaction mode of alkylmetal compounds.<sup>1–4</sup> Although these reactions occur particularly easily for coordinatively unsaturated transitionmetal species due to the participation of empty d orbitals,<sup>1,5-8</sup> they can also proceed for main-group and post-transition-metal complexes.<sup>3</sup> Some of these reactions merely correspond to unwanted decomposition processes,  $^{9-14}$  but others are made use of for the preparation of thin metal layers by metal-organic chemical vapor deposition<sup>15–19</sup> and thus have gained significant importance in the semiconductor industry.<sup>20,21</sup> For example, the formation of zinc-containing layers from deposited Et<sub>2</sub>Zn has been suggested to proceed at least partially according to this reaction type.  $2^{2-25}$  Unambiguous experimental evidence for this hypothesis is lacking, however, because the reaction conditions favor the occurrence of consecutive processes and thus complicate mechanistic studies. In fact, clear-cut examples of  $\beta$ -H eliminations from well-defined organozinc compounds are exceedingly rare,  $^{26,27}$  despite the wide applications of organozinc reagents.<sup>28</sup>

To fill this gap and complete our understanding of organozinc chemistry, we have investigated a series of ionic butylzinc model complexes. As we had shown previously,<sup>29</sup> butylzinc halides and chelating ligands L (L = N,N,N',N'-tetramethylethylenediamine (TMEDA), 2-N,N-dimethylamino-1-methoxyethane (DMAME), and 1,2-dimethoxyethane (DME)) form complexes BuZn(L)<sup>+</sup> (Scheme 1) in tetrahydrofuran (THF).<sup>30</sup> In the gas phase, the mass-selected

#### Scheme 1. Butylzinc Complexes under Investigation



complexes lose butene and yield the corresponding hydrido zinc species upon collision-induced dissociation (CID) (eq 1).

$$BuZn(L)^{+} \rightarrow HZnL^{+} + C_{4}H_{8}$$
<sup>(1)</sup>

Here, we probe these reactions by deuterium labeling experiments (for BuZn(TMEDA)<sup>+</sup>) and quantum-chemical calculations (for BuZn(L)<sup>+</sup>, L = TMEDA, DMAME, DME, and the related complex BuZn(THF)<sup>+</sup>; Scheme 1).<sup>31</sup> Moreover, we extend the theoretical calculations to anionic butylzinc species, such as Bu<sub>3</sub>Zn<sup>-</sup>, which have also been shown to release butene upon CID (eq 2).<sup>32</sup>

$$Bu_3Zn^- \to Bu_2ZnH^- + C_4H_8 \tag{2}$$

### 2. EXPERIMENTAL AND THEORETICAL METHODS

**2.1. Sample Preparation.** Standard Schlenk techniques were applied to exclude moisture and oxygen. THF was freshly distilled from sodium benzophenone ketyl under argon. 1-Bromobutane-2- $d_2$  was purchased (Ehrenstorfer, 99.3% D), and 1-bromobutane-2- $d^{33}$  was synthesized according to adapted standard procedures (reduction of propanal with LiAlD<sub>4</sub> followed by bromination with Br<sub>2</sub>/PPh<sub>3</sub>, conversion to the corresponding Grignard reagent, and carboxylation with CO<sub>2</sub>, reduction with LiAlH<sub>4</sub>, and bromination of the resulting 1-butanol-2-d with Br<sub>2</sub>/PPh<sub>3</sub>).<sup>33,34</sup> Deuterium-labeled BuZnBr was prepared by reaction of the labeled butyl bromides with Rieke zinc in THF.<sup>35</sup> The Rieke zinc was carefully washed with THF to remove lithium salts,<sup>35</sup> which otherwise can interfere with the detection of the butylzinc complexes. The sample solutions were prepared by adding TMEDA (10 equiv) to the labeled BuZnBr in THF ( $c \approx 2$  mM, 1 equiv).

**2.2. Mass Spectrometry.** The sample solutions were infused into the ESI source of an HCT quadrupole ion trap mass spectrometer (Bruker Daltonik) by a syringe pump at a flow rate of 0.30 mL h<sup>-1</sup>. The ESI source was operated with nitrogen as spraying gas (backing pressure p = 0.7 bar) and drying gas (5 L min<sup>-1</sup>, 60–100 °C) at an ESI voltage of 3 kV. The ion transfer and trapping parameters applied were similar to those reported previously (except for a voltage of 30 V for the first transfer octopole).<sup>29,36</sup> For the CID experiments, the mass-selected ions (isolation widths of 1.0 amu) were accelerated by

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excitation voltages of peak-to-peak amplitudes  $V_{\text{exc}} = 0.0-0.5$  V (applied to one of the end caps of the ion trap) and allowed to collide with He (estimated pressure  $p(\text{He}) \approx 2$  mTorr) for 40 ms. The collisions raise the internal energy of the 2-D-BuZn(TMEDA)<sup>+</sup> and 2,2-D<sub>2</sub>-BuZn(TMEDA)<sup>+</sup> ions, which then undergo unimolecular decomposition. Previous studies have shown that a correlation of the excitation voltages with the absolute amount of energy imparted to the trapped ions is not straightforward for the employed instrument.<sup>37</sup> For determining the kinetic isotope effect (KIE) associated with the butene elimination from 2-D-BuZn(TMEDA)<sup>+</sup> with high accuracy, the recorded peaks of the HZn(TMEDA)<sup>+</sup>/DZn(TMEDA)<sup>+</sup> fragments were fitted by Gaussian functions. To reduce statistical errors, several individual mass spectra were averaged for each experiment. The given uncertainties correspond to one standard deviation.

2.3. Computational Methods. Theoretical calculations were performed with the program package Gaussian 03.38 The calculations refer to the gas phase and thus make possible a direct comparison with the experiments. For the analysis of the fragmentation pathways of BuZn(TMEDA)<sup>+</sup>, both density functional theory (DFT) and Møller-Plesset perturbation theory (MP) calculations were employed with different basis sets and a multiconfiguration Dirac-Fock (MDF) effective core potential<sup>39</sup> (10 electrons) for the zinc atom (B3LYP/6-31G\*/MDF, B3LYP/6-311+G\*/MDF, B3LYP/cc-pVTZ/MDF, MP2/6-31G\*/MDF, and MP2/6-311+G\*/MDF). Similar approaches have recently been successfully applied to the theoretical character-ization of other zinc complexes.<sup>30b-f,40,41</sup> The different methods afforded comparable results (see Table S2 in the Supporting Information), and so all further calculations used the cost-efficient B3LYP/6-31G\*/MDF scheme. Vibrational analyses were performed to classify stationary points as local minima (zero imaginary frequencies) or transition states (one imaginary frequency). All energies given are zero-point corrected. Partial charges were calculated according to the Mulliken,<sup>42</sup> APT (atomic polar tensors),<sup>43</sup> and NPA (natural population analysis)<sup>44</sup> approaches, respectively.

# 3. RESULTS

**3.1. Gas-Phase Experiments.** ESI of a solution of 2,2-D<sub>2</sub>-BuZnBr/TMEDA in THF afforded, as expected, 2,2-D<sub>2</sub>-BuZn(TMEDA)<sup>+</sup> (m/z 239 for the <sup>64</sup>Zn isotopologue), which could be identified thanks to its characteristic isotope pattern (Figure S2, Supporting Information). Upon CID, the ions consistently lost a neutral fragment of  $\Delta m = 57$ , which corresponds to C<sub>4</sub>H<sub>7</sub>D and thereby proves the operation of a  $\beta$ -H elimination (Figure 1 and Figures S3–S7 (Supporting



**Figure 1.** Mass spectrum of mass-selected  $2,2-D_2$ -BuZn(TMEDA)<sup>+</sup> (m/z 239, <sup>64</sup>Zn isotopologue) and its fragment ions produced upon CID ( $V_{exc} = 0.30$  V). Inset: enlarged section from the spectrum showing the peak of the DZn(TMEDA)<sup>+</sup> fragment.

Information)) (eq 3). The virtual absence of neutral  $C_4H_6D_2$ (and  $C_4H_8$ ) fragments ( $\leq 1\%$ ) shows the high selectivity of this process. As additional primary fragments, an iminium ion derived from the TMEDA ligand, i.e., [TMEDA-H]<sup>+</sup>, and an ion originating from decomposition of the ligand, i.e., [ $C_4H_8N$ ]<sup>+</sup>, were formed (eqs 4 and 5, respectively).<sup>29</sup>

$$2,2-D_2-BuZn(TMEDA)^+ \rightarrow DZn(TMEDA)^+ + C_4H_7D$$
(3)

$$2,2-D_2-BuZn(TMEDA)^+$$
  
 $\rightarrow [TMEDA-H]^+ + 2,2-D_2-BuZnH$  (4)

$$2,2-D_2-BuZn(TMEDA)^+ \rightarrow [C_4H_8N]^+ + [ZnC_6H_{15}D_2N]$$
(5)

Employing monodeuterated 2-D-BuZnBr, we observed a shift of the isotope pattern by 1 mass unit  $(m/z \ 238$  for the <sup>64</sup>Zn isotopologue), in accordance with the formation of 2-D-BuZn(TMEDA)<sup>+</sup> (Figure S8, Supporting Information). Moreover, a strong peak at m/z 239 indicated the presence of  $Li(TMEDA)_{2}^{+}$ , as was confirmed by CID experiments, resulting in the loss of one TMEDA ligand. Apparently, the Rieke zinc employed for the sample solution still contained significant amounts of Li<sup>+</sup> salts (see section 2.1). The measured intensity distribution of the peaks at m/z 238–243 could be well reproduced if a  $(57 \pm 5)/(43 \pm 5)$  mixture of 2-D- $BuZn(TMEDA)^+$  and  $Li(TMEDA)_2^+$  was assumed (Figure S9, Supporting Information). This analysis also showed that the peaks at m/z 238 and 240 did not correspond to pure 2-D-BuZn(TMEDA)<sup>+</sup> but contained isobaric contaminations from  ${}^{6}\text{Li}(\text{TMEDA})_{2}^{+}$  and  ${}^{7}\text{Li}(\text{TMEDA})_{2}^{+}$ .

CID of the different isotopologues of 2-D-BuZn(TMEDA)<sup>+</sup> in all cases led to the loss of fragments of  $\Delta m = 56$  and 57, which are assigned to C<sub>4</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>7</sub>D, respectively (Figure 2 and Figures S10–S14 (Supporting Information)). The ratio of the signal intensities of the corresponding HZn(TMEDA)<sup>+</sup> and DZn(TMEDA)<sup>+</sup> fragment ions equals the KIE of the  $\beta$ -H elimination. The absolute fragmentation yield strongly



**Figure 2.** Mass spectrum of mass-selected 2-D-BuZn(TMEDA)<sup>+</sup> (m/z 238, <sup>64</sup>Zn isotopologue) and its fragment ions produced upon CID ( $V_{\text{exc}} = 0.30$  V). Inset: enlarged section from the spectrum showing the peaks of the HZn(TMEDA)<sup>+</sup>/DZn(TMEDA)<sup>+</sup> fragments. The peak marked with an asterisk corresponds to <sup>6</sup>Li(TMEDA)<sup>+</sup> (m/z 122), which results from the fragmentation of <sup>6</sup>Li(TMEDA)<sub>2</sub><sup>+</sup>, an isobaric contamination of the mass-selected precursor ion.



**Figure 3.** Calculated schematic potential energy surface for the elimination reactions of  $BuZn(TMEDA)^+$ ,  $BuZn(DMAME)^+$ ,  $BuZn(DME)^+$ , and  $BuZn(THF)^+$  (B3LYP/6-31G\*/MDF) and associated structures for the  $BuZn^+/TMEDA$  system as representative examples. Energies of minima and transition structures are given in parentheses (in kJ mol<sup>-1</sup>).

Table 1. Selected Interatomic Distances (in	pm) Calculated for BuZn	(TMEDA) <sup>+</sup> , TS-BuZn(TM	/IEDA) <sup>+</sup> , HZn(TMEDA)(	$(C_4H_8)^+$ ,
and HZn(TMEDA) <sup>+</sup> (B3LYP/6-31G*/MD	<b>F</b> )			

	BuZn(TMEDA) <sup>+</sup>	TS-BuZn(TMEDA) <sup>+</sup>	$HZn(TMEDA)(C_4H_8)^+$	$HZn(TMEDA)^+$
r(Zn-C1)	196	205	252	
r(Zn-C2)	297	226	277	
$r(Zn-H_{\beta})$	315	170	155	152
r(Zn-N1)	215	211	217	212
r(Zn-N2)	215	211	217	212

increased for higher excitation voltages and, thus, fragmentation energies, whereas the KIE did not show a statistically significant dependence (KIE =  $1.9 \pm 0.1$  for  $V_{\text{exc}} = 0.3-0.5$  V, Table S1 (Supporting Information)). As in the case of 2,2-D<sub>2</sub>-BuZn-(TMEDA)<sup>+</sup>, [TMEDA-H]<sup>+</sup> and  $[C_4H_8N]^+$  were observed as additional fragments. Furthermore, CID of the ions at m/z 238 and 240 also gave rise to fragments at m/z 122 and 123/124, respectively, which resulted from the loss of one TMEDA ligand from Li(TMEDA)<sub>2</sub><sup>+</sup>, thus once more pointing to the presence of the latter as an isobaric contaminant in the massselected precursor ions.

**3.2. Theoretical Calculations.** The theoretical calculations predict that the loss of butene from  $BuZn(TMEDA)^+$  indeed follows a  $\beta$ -H elimination mechanism. In the bent transition structure TS-BuZn(TMEDA)<sup>+</sup> (Zn-H $_{\beta}$ -C2 angle of 83°), one of the  $\beta$ -H atoms of the butyl substituent has approached the Zn center at a distance of 170 pm, indicating an attractive interaction (Figure 3 and Table 1). At the same time, the Zn-C2 distance has also shrunk considerably, whereas the Zn-C1 distance is slightly increased. In comparison to BuZn(TMEDA)<sup>+</sup>, TS-BuZn(TMEDA)<sup>+</sup> lies 169.0 kJ mol<sup>-1</sup> higher in energy (Figure 3). For 2-D-BuZn(TMEDA)<sup>+</sup>, both the  $\beta$ -H and D atoms can migrate. The resulting transition structures differ in their zero-point energies (ZPE) by approximately 5 kJ mol<sup>-1</sup>. This difference mainly results from the loss of the real stretching mode of the migrating H or D atom, respectively.

The higher ZPE of the lost C–H vibration implies that the migration of the H atom is energetically more favorable.

In the elimination product, the Zn–H distance is further reduced and the formation of the butene moiety is completed (Figure 3). At the same time, the Zn–C1 and Zn–C2 distances have increased significantly. Upon elimination of the butene molecule, the Zn–H as well as the Zn–N distances further decrease by a small extent. The butene elimination apparently occurs without a barrier in addition to the reaction energy of 23.2 kJ mol<sup>-1</sup>,<sup>45</sup> thus rendering the overall reaction endothermic by 85.8 kJ mol<sup>-1</sup>. As a possible alternative decomposition channel, we also consider loss of the TMEDA ligand. According to our calculations, this reaction proceeds directly with a loose transition structure that equals the separated products. In comparison to the elimination of butene, the release of the ligand is energetically much more demanding.

DFT calculations on BuZn(DMAME)<sup>+</sup>, BuZn(DME)<sup>+</sup>, and BuZn(THF)<sup>+</sup> suggest that these complexes undergo  $\beta$ -H eliminations that involve analogous transition structures, intermediates, and products. In comparison to the corresponding TMEDA complexes, the Zn-C1, Zn-H, and Znheteroatom distances of these species are gradually shortened (Tables S3–S5 and Figures S15–S17, Supporting Information). A parallel trend is also found for the calculated Mulliken and APT charges of the zinc centers, which show an increase in the given order, whereas the NPA approach predicts a deviating behavior (Table S6, Supporting Information). Poor consistency between different methods to calculate partial charges has been noted even for much simpler cases.<sup>46</sup> The computed energies of the transition structures **TS**-BuZn(L)<sup>+</sup> increase in the series L = TMEDA, DMAME, DME, THF (Figure 3). The relative energies of the resulting  $HZn(L)(C_4H_8)^+$  complexes are all quite similar, whereas those of the separated  $HZn(L)^+/C_4H_8$ products point to a somewhat lowered stability of  $HZn(THF)^+$ . The spread in energies becomes even more pronounced for the loss of the ligand, with the dissociation energies  $D(BuZn^+-L)$ strongly decreasing in the order TMEDA, DMAME, DME, THF.

DFT calculations show that the expulsion of butene from Bu<sub>3</sub>Zn<sup>-</sup> corresponds to a  $\beta$ -H elimination as well (Figure S18, Supporting Information). Both the reaction energy and the activation energy are lower than for the cationic systems (by 14.7 and 19.2 kJ mol<sup>-1</sup> in comparison to the BuZn(TMEDA)<sup>+</sup> system, respectively; Figure S20, Supporting Information). Unlike the case of the BuZnL<sup>+</sup> species, the reaction does not involve a zinc-butene complex as an intermediate but directly yields the separated products. In the transition structure, the migrating H atom has approached the zinc center at a distance of 179 pm (Figure S18 and Tables S7 and S8, Supporting Information). As an alternative fragmentation channel, we also consider the loss of a butyl anion, but this process is energetically more demanding by 116.2 kJ mol<sup>-1</sup> (Figure S20, Supporting Information). For Bu<sub>2</sub>ZnCl<sup>-</sup>, a  $\beta$ -H elimination mechanism with a transition structure similar to that of the Bu<sub>3</sub>Zn<sup>-</sup> system is found (Figure S19, Supporting Information). Here, however, the loss of Cl<sup>-</sup> can compete and is predicted to be energetically more favorable by 51.7 kJ mol<sup>-1</sup> (Figure S20, Supporting Information). A comparison of partial charges calculated with the Mulliken, APT, and NPA approaches again affords deviating trends (Table S9, Supporting Information) and thus does not permit a further analysis.

#### 4. DISCUSSION

Both the labeling experiments and theoretical calculations agree that the release of butene from BuZn(TMEDA)<sup>+</sup> corresponds to a  $\beta$ -H elimination. The experimentally observed high selectivity of this process and the absence of any H/D scrambling products in the case of 2,2-D<sub>2</sub>-BuZn(TMEDA)<sup>+</sup> are in line with the calculated energy profile, which shows that the loss of butene from the HZn(TMEDA)( $C_4H_8$ )<sup>+</sup> intermediate requires only a small amount of energy. As the expulsion of the olefin is also strongly favored entropically, this process is expected to occur rapidly. Therefore, it seems improbable that the butene molecule can undergo a  $180^\circ$  rotation and then reinsert into the Zn-D bond to give rise to scrambling of the deuterium label. The intramolecular KIE of  $1.9 \pm 0.1$  measured for the dissociation of 2-D-BuZn(TMEDA)<sup>+</sup> (at  $V_{\text{exc}} = 0.3-0.5$ V) provides further evidence for the H migration as the ratelimiting step. A comparison of the present value with KIEs reported for  $\beta$ -H eliminations of deuterated transition-metal complexes<sup>47</sup> is complicated by the fact that the latter almost completely refer to intermolecular assays. Intra- and intermolecular KIEs are not necessarily equivalent, however.<sup>48</sup>

The good agreement between experiment and theory also holds for the other systems studied. The previous experiments found exclusive butene elimination from  $BuZn(TMEDA)^+$  and  $BuZn(DMAME)^+$ , while loss of the ligand starts to compete for  $BuZn(DME)^+$  and completely dominates for  $BuZn(THF)^{+.29}$ In accordance with this observation, the calculated differences between the energy barriers of butene elimination on the one hand and ligand loss on the other continuously decrease in the series BuZn(TMEDA)<sup>+</sup>, BuZn(DMAME)<sup>+</sup>, BuZn(DME)<sup>+</sup>, and BuZn(THF)<sup>+</sup>. This trend largely results from a decrease of the binding energies  $D(BuZn^+-L)$ . As noted previously,<sup>29</sup> the interaction of the more basic dimethylamino group with the cationic zinc center is apparently more favorable than that of the less basic methoxy group. The relatively poorer Lewis basicity of THF and the resulting electron deficiency of its zinc complexes also explain why the increase of the coordination number in HZn(THF)( $C_4H_8$ )<sup>+</sup> stabilizes this species compared to the complexes of the bidentate ligands (Figure 3); for the latter, the presence of an additional ligand presumably leads to steric congestion. The effect of different steric requirements and electronic properties is also reflected in the calculated bond lengths. As a comparison of the Zn-O and Zn-N distances shows, the monodentate ligand THF can approach the metal center more closely than its bidentate counterparts (Table 1 and Tables S2-S4 (Supporting Information)). The relative electron deficiency of the THF-containing complexes enhances this effect because the higher partial charge at the zinc center amplifies the attraction of the ligand. With increasing Lewis basicity of the ligand and decreasing charge at the metal, the Zn-C1 and Zn-H distances also become larger.

In the case of the anionic complexes, the DFT calculations predict the elimination of butene to be the most favorable process for Bu<sub>3</sub>Zn<sup>-</sup>, whereas the loss of chloride should be more facile for Bu<sub>2</sub>ZnCl<sup>-</sup>. Again, these predictions are fully borne out by the previous experiments.<sup>32</sup> The computed transition structures for the  $\beta$ -H elimination from the anionic complexes qualitatively resemble those of their analogues predicted for the cationic complexes. The main difference refers to the larger bond distances of the anionic systems. As outlined above, this bond elongation probably results from a decrease of the partial charge at the zinc atom. The diminished positive charge at the metal center also explains why for the anionic systems the interaction with the nascent butene molecule is weakened to such an extent that its release proceeds without the involvement of  $Bu_2Zn(C_4H_8)^-$  or  $BuZnCl(C_4H_8)^$ intermediates.

The present results on ionic butylzinc complexes can be compared to those of previous theoretical studies on the  $\beta$ -H elimination of neutral Et<sub>2</sub>Zn.<sup>24c,25</sup> The activation energy calculated for this reaction,  $\Delta E^{\ddagger} \approx 190$  kJ mol<sup>-1,24c,25</sup> is similar to those derived for the BuZn(L)<sup>+</sup> complexes, although this comparison is somewhat complicated by the fact that the employed theoretical methods are slightly different. Likewise, the bond lengths in the neutral transition structure (r(Zn-C1) = 214,  $r(Zn-H_{\beta}) = 170$  pm according to DFT calculations)<sup>24c</sup> do not strongly deviate from those in its cationic analogues. This similarity suggests that the dissociation of the BuZn(L)<sup>+</sup> complexes can be considered as a model for the decomposition of neutral Et<sub>2</sub>Zn.

# 5. CONCLUSIONS

The present deuterium labeling experiments unequivocally demonstrate that the release of butene from BuZn(TMEDA)<sup>+</sup> corresponds to a  $\beta$ -H elimination as the rate-limiting step. Theoretical calculations agree with this finding and moreover predict that the fragmentations of the related cationic complexes BuZn(DMAME)<sup>+</sup>, BuZn(DME)<sup>+</sup>, and BuZn-(THF)<sup>+</sup> also follow this mechanism. The energetic and structural differences between the individual fragmentation reactions can be rationalized by simple electronic and steric

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arguments. As a key parameter, the Lewis basicity of the ligand determines how strongly the latter binds to the zinc center and whether simple expulsion of the ligand can compete with the  $\beta$ -H elimination. The predicted trends fully match recent experimental observations, thus adding to the reliability of the computational results. A comparison with previous theoretical calculations on the decomposition of neutral Et<sub>2</sub>Zn reveals close similarities to the reactions of the cationic butylzinc complexes. The present computations on anionic Bu<sub>3</sub>Zn<sup>-</sup> show that the loss of butene from this species also corresponds to a  $\beta$ -H elimination.

# ASSOCIATED CONTENT

#### **S** Supporting Information

Figures, tables, and text giving additional ESI mass spectra, CID mass spectra, results of theoretical calculations, and full ref 38. This material is available free of charge via the Internet at http://pubs.acs.org.

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# Notes

The authors declare no competing financial interest.

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