

## How Can f-Block Monocations Behave as Monocations of d-Block Transition Metals?

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The electronic structures of LnNH<sup>+</sup> species are studied by DFT (B3LYP) quantum calculations for the Ln = La, Eu and Gd 4f-block elements (lanthanides). Ln≡N triple bonds of essentially d character are formed for La and Gd, which explains why La<sup>+</sup> and Gd<sup>+</sup> behave like ions of d-block transition metals, as experimentally evidenced by mass spectrometry, and why the Ln<sup>+</sup> reactivity is correlated with its electron-promotion energy: the present theoretical study is a support to such a correlation and qualitative knowledge. The Ln<sup>+</sup> + NH<sub>3</sub> → LnNH<sub>3</sub><sup>+</sup> → transition state → HLn=NH<sub>2</sub><sup>+</sup> → transition state → Ln≡NH<sup>+</sup> + H<sub>2</sub> reaction pathway is calculated. The formation of H-Ln=NH<sub>2</sub><sup>+</sup> corresponds to the formation of new co-

valent bonds associated with more electron pairing and corresponding lowering of the spin multiplicity–spin crossing reaction. It is in this step that low electron-promotion energy is required to promote a 4f electron into a 5d orbital as is typical for La<sup>+</sup> and Gd<sup>+</sup>. A similar geometry, bonding and electronic configuration are calculated for NpNH<sup>+</sup> – an actinide complex observed by mass spectrometry – with higher participation of 5f orbitals (20% and 25% for the σ and π bonds, respectively) as compared to the 4f orbitals (3% and 8%) of GdNH<sup>+</sup>: Gd<sup>+</sup> and Np<sup>+</sup> are the only lanthanide and actinide monocations with one s- and one d-valence electrons in their ground states.

### Introduction

Very different chemical behaviours have been evidenced in mass spectrometry analysis across the lanthanide (Ln) series of f-block elements<sup>[1]</sup> – they can even behave as the Sc and Y d-block transition elements.<sup>[2]</sup> It has been proposed that the reactivity of Ln<sup>+</sup> with gas in collision-reaction cells of mass spectrometers is correlated with its electron-promotion energy, the energy to obtain two non-f valence electrons. This is in contrast with the well-established

picture for the chemistry of the f-block elements in condensed phases.

Most of the rare earths are lanthanides. La, the first lanthanide in the periodic table is usually stable in the form of the La<sup>3+</sup> hard cation, where La<sup>III</sup> is in its group oxidation state. The heavier Ln elements are f-block elements corresponding to the progressive filling of the 4f shell, with a few exceptions. The 4f orbitals of Ln<sup>3+</sup> do not easily participate in covalent bonding, which is consistent with the hard character of Ln<sup>3+</sup>.<sup>[3]</sup> This accounts for the chemical analogy among the Ln<sup>3+</sup> ions – despite their having different electronic configurations – and with other hard trications of similar sizes as typically the trications (An<sup>3+</sup>) of the actinides (the series of the 5f-block elements).

This behaviour is in contrast with those of the d-block transition series, whose ions often are rather soft and form covalent bonds: their chemical behaviour is driven by their electronic configurations, which vary across the d-transition-metal series. Nevertheless, another rare earth Y (the d transition metal above La in the third column of the periodic table) is a chemical analogue of La. Y<sup>3+</sup> has a similar size to that of heavy Ln<sup>3+</sup> as a result of the Ln contraction – it behaves as heavy Ln<sup>3+</sup>, while Sc<sup>3+</sup> (Sc is the d transition metal above Y) is clearly smaller.<sup>[4]</sup>

Sc<sup>+</sup>, Y<sup>+</sup> or Ln<sup>+</sup> can be viewed as reduced Sc<sup>3+</sup>, Y<sup>3+</sup> or Ln<sup>3+</sup> stable hard ions, on which two electrons have been added: M<sup>3+</sup> + 2e<sup>-</sup> → M<sup>+</sup>. These two added electrons are not expected to be firmly retained in the monocations, since rare earths are usually more stable in the trication chemical

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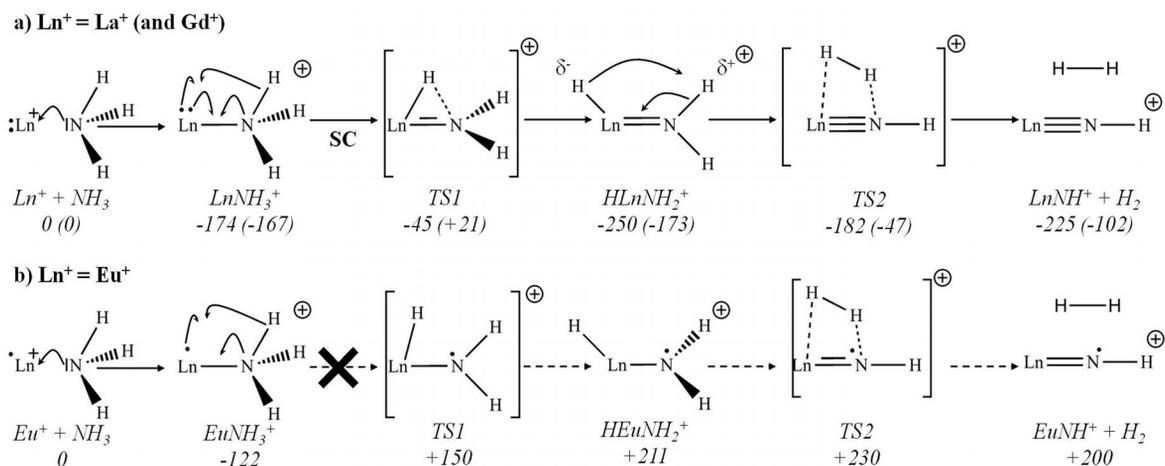
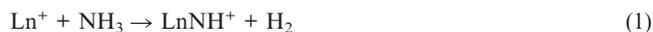


Figure 1. Scheme for reaction  $\text{Ln}^+ + \text{NH}_3 \rightarrow \text{LnNH}^+ + \text{H}_2$  for (a)  $\text{La}^+/\text{Gd}^+$  and (b)  $\text{Eu}^+$ . The MP2 energies<sup>[5]</sup> written below the species are in  $\text{kJ mol}^{-1}$ . Transition states are in square brackets. The dots ( $\bullet$ ) represent valence electrons. The electrons (f unpaired) that do not participate in the bonding are not represented. The limiting step for the reaction of Eu is represented by the bold cross; the spin crossing (SC) reaction is the key step that requires a low electron-promotion energy. Dotted arrows are for reactions that are not observed.

forms, i.e. these monocations are not especially expected to have a hard character, in contrast with stable trications. Namely,  $\text{Ln}^+$  chemistry is not especially expected to be similar to that of the  $\text{Sc}^+$  or  $\text{Y}^+$  d cation, when there are two extra  $\text{Ln}^+$  electrons in the f orbitals. Conversely, some analogy is not unexpected for those  $\text{Ln}^+$  ions of similar electronic configurations to that of  $\text{Sc}^+$  and  $\text{Y}^+$ , namely when the promotion energy to the  $4f^0 5d^1 6s^1$  electronic configuration is small. Note that the d valence orbitals can be more easily stabilized than the f orbitals involved in covalent bonding, since the d orbitals usually have greater spatial expansions, which facilitate covalency; the electronic configuration can change on covalent bonding.

Experimental mass spectrometry shows the formation of  $\text{MNH}^+$ , the key product for the reactivities of the d elements ( $\text{M}^+ = \text{Sc}^+$  and  $\text{Y}^+$ ), for  $\text{Ln}^+$  ions of small ( $\text{La}^+$ ) or zero ( $\text{Gd}^+$ ) electron-promotion energies (see Supporting Information).<sup>[1a,5]</sup>



where  $\text{Ln}^+$  acts as a strong reducer and inserts into the N–H bond to produce  $\text{H}_2$ . The  $\text{LnNH}^+$  product can be described with usual formal oxidation states for its atoms –  $\text{Ln}(\text{III})$ ,  $\text{N}(-\text{III})$ ,  $\text{H}(\text{I})$  –; however, this is not enough to explain the stability of the  $\text{LnNH}^+$ , since Reaction 1 is experimentally observed only when  $\text{Ln}^+$  has a low electron-promotion energy.

Herein, we discuss the chemical stabilities of the  $\text{LnNH}^+$  species for  $\text{Ln} = \text{La}$ ,  $\text{Eu}$  and  $\text{Gd}$ , on the basis of their electronic structures.  $\text{Eu}^+$  and  $\text{Gd}^+$  have different reactivities<sup>[1a,5]</sup> – the electronic structure of  $\text{LnNH}^+$  is similar to that of a d element only for those lanthanides ( $\text{La}$  and  $\text{Gd}$ ) for which Reaction 1 is experimentally observed, while such an electronic structure is not possible for  $\text{Eu}^+$ , a monocation of low reactivity.<sup>[1a,5]</sup> Actinide monocations are also compared. More details on the mass spectrometry results, reaction mechanisms (Figure 1) and potential energy sur-

faces will be given elsewhere together with higher levels of calculation; MP2, CCSD(T), and CASPT2 confirm that DFT/B3LYP is enough for the calculations presented here.<sup>[5]</sup>

## Results and Discussion

$\text{LnNH}^+$  is linear with  $\text{Ln}-\text{N}$  bond lengths of 1.88 Å ( $\text{La}$ ) and 1.83 Å ( $\text{Gd}$ ) (Table 1). These bond lengths are not unexpected [compare with the published  $\text{Sc}-\text{NH}^+$  (1.71 Å) and  $\text{Y}-\text{NH}^+$  (1.85 Å) distances].<sup>[6]</sup> Ma et al.<sup>[7]</sup> observed a  $\text{Ce}-\text{NH}^+$  bond (1.92 Å) that is longer than the  $\text{La}-\text{NH}^+$  bond by 0.04 Å – virtually the same distances are indeed expected, since Ce is just after La in the Ln series. The  $\text{Ln}-\text{N}$  bond length is the shortest in  $\text{LnNH}^+$  relative to those in all the intermediate species.<sup>[5]</sup> We calculated that the  $\text{LaNH}^+$  geometry is more stable by 400  $\text{kJ mol}^{-1}$  than the  $\text{HLaN}^+$  geometry.

Table 1. Electronic configuration and published electron-promotion energy ( $PE$ )<sup>[11]</sup> in  $\text{kJ mol}^{-1}$  of  $\text{M}^+$ . M–N bond length (in Å), M NBO5.9 charge and  $\nu_\sigma$  M–N  $\sigma$  harmonic vibrational frequency (in  $\text{cm}^{-1}$ ) in  $\text{MNH}^+$ .

$\text{M}^+$	Electron configuration	$PE$	$d(\text{M}-\text{N})$	M charge	$\nu_\sigma$ M–N
$\text{La}^+$	$4f^0 5d^2$	19	1.88	1.98	838
$\text{Eu}^+$	$4f^7 6s^1$	388	2.16	1.83	575
$\text{Gd}^+$	$4f^7 5d^1 6s^1$	0	1.83	1.92	850
$\text{Np}^+$	$5f^4 6d^1 7s^1$	0	1.88	1.93	862
$\text{Am}^+$	$5f^7 7s^1$	245	2.16	1.70	574

The linear geometry of  $\text{LnNH}^+$  suggests an sp hybridization for N, thus associated with a  $\text{Ln}\equiv\text{NH}^+$  triple bond. Indeed, NBO5.9 population analysis shows a ( $\text{La}\equiv\text{N}-\text{H}$ )<sup>+</sup> Lewis structure; namely four covalent bonds (Table 2).

Table 2. Molecular orbitals of  $\text{LaNH}^+$ , energy ( $E$ ) is in eV.  $\text{LaNH}^+$  is linear along the  $z$  axis.

$E$	Main character	Sym.	La	N	H
-23.0	$\sigma$ N-H	A1	$6s5d_{z^2}$	$2s$ $2p_z$	$1s$
-20.4	$\sigma$ La-N	A1	$5d_{z^2}4f_z(5z^2-3r^2)$	$2s$ $2p_z$	$1s$
-11.5	$\pi$ La-N	E1	$5d_{xy}4f_x(5z^2-3r^2)$	$2p_x$	
-11.5	$\pi$ La-N	E1	$5d_{yz}4f_y(5z^2-r^2)$	$2p_y$	

The participation of the Ln 4f orbitals is small: 16% (La) or 8% (Gd). As expected, the  $\sigma$ -valence orbitals are lower in energy than the  $\pi$  orbitals, which are the HOMOs, and the less nodal planes, the lower the energy among the  $\sigma$ -valence orbitals is (Figure 2 and Table 2). Hui-Zhen et al.<sup>[6b]</sup> also reported a linear structure for  $\text{Y}\equiv\text{NH}^+$  with a triple bond formed by the  $s$  and  $d$  orbitals of Y and the sp-hybridized N orbitals. According to the octet rule, the maximum possible number of covalent bonds is formed: in the Lewis interpretation, the NH fragment cannot form more than 3 covalent bonds corresponding to the sp hybridization.

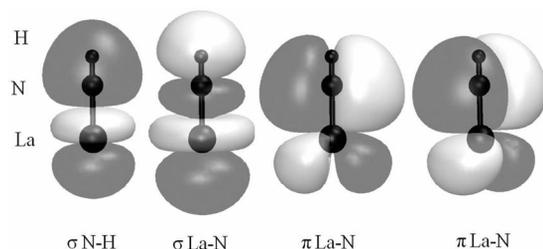


Figure 2. Molecular valence orbitals of  $\text{LaNH}^+$ .

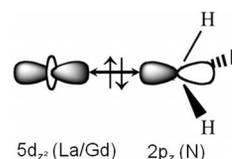
To check the influence of the  $f$  orbitals, we also suppressed the  $f$  functions from the basis set, and we re-optimized the geometry of  $\text{LaNH}^+$ . NBO5.9 still indicates the  $(\text{La}\equiv\text{N}-\text{H})^+$  Lewis structure, despite the fact that the La-N distance is longer by 0.10 Å and the complex is destabilized by 115  $\text{kJ mol}^{-1}$ . This compares well with similar calculations across the  $\text{ThO}_2$ ,  $\text{PaO}_2^+$ ,  $\text{UO}_2^{2+}$  seemingly isoelectronic series.<sup>[8]</sup> The addition of  $f$  functions decreases the  $\text{Th}\equiv\text{O}$  bond length by 0.12 Å and stabilizes the complex by 376  $\text{kJ mol}^{-1}$  (188  $\text{kJ mol}^{-1}$  per  $\text{Th}\equiv\text{O}$  bond); this influence is more important for Pa and U. This was an argument to indicate that  $\text{Th}^{\text{IV}}$  behaves as a  $d$  element in  $\text{ThO}_2$ , while the isoelectronic transthorium actinides behave as true  $f$ -block elements in  $\text{AnO}_2^{(z-4)+}$ . The effects of the  $f$  orbitals appear to be of the same order of magnitude: slightly (20%) smaller with respect to both energy and geometry for the  $\text{La}\equiv\text{N}$  triple bond than for the  $\text{Th}\equiv\text{O}$  bond, which confirms that the importance of  $f$  type functions is moderate for  $\text{LaNH}^+$ . The  $\text{La}\equiv\text{NH}^+$  and  $\text{Gd}\equiv\text{NH}^+$  triple bonds essentially comprise the N  $2sp$  hybridized orbitals and the Ln  $5d$  orbitals. These ( $\text{La}^+$  and  $\text{Gd}^+$ ) so called 4f-block monocations actually have a similar chemical behaviour to that of the  $d$ -block ions – they form covalent bonds with dominating  $d$  character. Furthermore, the atomic charges of M ( $M = \text{Y}, \text{La}$  and  $\text{Gd}$ ) are similar in  $\text{MNH}^+$  for La (1.98),

Gd (1.92) (Table 1) and for Y (reported as 1.94)<sup>[6b]</sup> with similar participation of the M electrons in the M-N bond. Note that Y is a  $d$ -block transition metal.

$\text{Np}^+$  is the only  $\text{An}^+$  with zero electron-promotion energy, the same as for  $\text{Gd}^+$  (Table 1) – they both have one  $s$  and one  $d$  valence electrons. They both form  $\text{MNH}^+$  ( $M = \text{Gd}$  and  $\text{Np}$ , see Supporting Information). The  $\text{Np}-\text{NH}^+$  distance (1.88 Å) is a little longer than that of  $\text{Gd}-\text{NH}^+$  (1.83 Å), in line with the small expansion usually observed from Ln to An ions.<sup>[9]</sup> The participation of the Np  $5f$  orbitals (40% in the  $\sigma$  Np-N bond and 20% in the two  $\pi$  bonds) is greater than those of the Gd  $4f$  orbitals (3% in the  $\sigma$  bond and 8% in the  $\pi$  bonds), in line with the less compact geometry of the An  $5f$  orbitals relative to the Ln  $4f$  orbitals.<sup>[10]</sup>

Several intermediate species are involved in the reaction between  $\text{La}^+$  and  $\text{NH}_3$  to form the final product  $\text{LaNH}^+$ .<sup>[5]</sup> The first intermediate species is  $\text{LaNH}_3^+$ . The optimized geometry of this species is  $C_{3v}$  tetrahedral. The  $\text{La}-\text{NH}_3^+$  distance (2.61 Å) is larger than that of  $\text{La}-\text{NH}^+$  (1.88 Å). This corresponds to weaker  $\text{La}-\text{NH}_3^+$  interaction as also reflected by the  $\sigma$ -bond vibrational frequency (283  $\text{cm}^{-1}$  for  $\text{La}-\text{NH}_3^+$  relative to 838  $\text{cm}^{-1}$  for  $\text{La}-\text{NH}^+$ ). This suggests a purely electrostatic  $\text{La}-\text{NH}_3^+$  interaction or, at most, a single  $\text{La}-\text{NH}_3^+$  covalent bond. In both cases it corresponds to the  $sp^3$  hybridization of N in  $\text{LaNH}_3^+$ . NOB5.9 population analysis does not indicate any La-N covalent bond; however, the donation of the lone pair from N to the  $5d_{z^2}$  orbital of La results in a stabilization of 53  $\text{kJ mol}^{-1}$ .

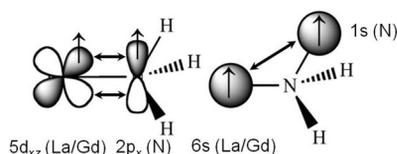
This is in line with the charge of La (0.92) in  $\text{LaNH}_3^+$  – virtually unchanged from that of initial  $\text{La}^+$ . The two electrons initially described as the N  $2p_z$  lone pair in  $\text{NH}_3$  are now (in  $\text{La}-\text{NH}_3^+$ ) shared with the La  $5d_{z^2}$  orbital, formally corresponding to donation of one of the  $2p_z$  N electrons to the La  $5d_{z^2}$  orbital (see the reaction scheme for  $\text{La}^+ + \text{NH}_3 \rightarrow \text{LaNH}_3^+$  in Figure 1 and Scheme 1).



Scheme 1.

The rearrangement of  $\text{LaNH}_3^+$  into the  $\text{HLaNH}_2^+$  intermediate species involves an H transfer from  $\text{NH}_3$  to La by breaking an N-H covalent bond of  $\text{LaNH}_3^+$  and by making new covalent bonds in  $\text{H}-\text{La}=\text{NH}_2^+$ . This results in more covalent bonds, and more electron pairing, which decreases the spin multiplicity. La must have the electronic configuration  $4f^05d^16s^1$  to make the new  $\text{HLa}=\text{NH}_2^+$  covalent bond (see the reaction scheme for  $\text{LaNH}_3^+ \rightarrow \text{HLaNH}_2^+$  in Figure 1 and Scheme 2). It is in this step that low electron-promotion energy is required.

$\text{HLaNH}_2^+$  has a planar structure, in line with the  $sp^2$  hybridization for N and  $\text{La}=\text{N}$  double bond, and five bonds: one  $\sigma$  Ln-H bond, two  $\sigma$  N-H bonds (one for each

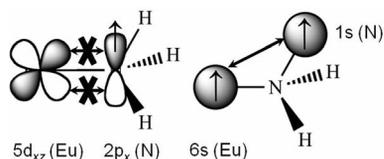


Scheme 2.

of the two H atoms bonded to N), one  $\sigma$  Ln–N bond (La 6s5p5d/N 2s2p) and one  $\pi$  Ln–N bond (La 5d/N 2p). The 4f orbitals slightly participate (16% for La and 4% for Gd) in the  $\sigma$  Ln–N bonds.

LaNH<sup>+</sup> can further be formed from HLaNH<sub>2</sub><sup>+</sup> via La(H<sub>2</sub>)NH<sup>+</sup>, a four-centered transition state (TS2) in which H<sub>2</sub> is weakly bonded to LaNH<sup>+</sup> by both its La and N atoms (Figure 1). Further, H<sub>N</sub> (+0.5) and H<sub>La</sub> (–0.5) are attracted to each other because of their opposite charges to finally form H<sub>2</sub>; LaNH<sup>+</sup> is formed with the loss of H<sub>2</sub>.

Eu is just before Gd in the periodic table. For this reason differences in their chemical behaviour cannot be because of the different sizes of their ions at the same oxidation state; rather, it can be accounted for by the differences in their electronic configuration. Eu<sup>+</sup> has the highest electron-promotion energy (388 kJ mol<sup>–1</sup>) among the Ln<sup>+</sup> cations from the 4f<sup>7</sup>6s<sup>1</sup> to the 4f<sup>6</sup>5d<sup>1</sup>6s<sup>1</sup> electronic configuration (Table 1). This high value is not unexpected; in the ground state of Eu<sup>+</sup>, the 4f sublayer is half occupied, which confers a great stability to this fundamental electronic configuration (4f<sup>7</sup>6s<sup>1</sup>). In the EuNH<sub>3</sub><sup>+</sup> initial complex, Eu has only one non-f electron, a 6s electron, which would pair with an H 1s electron to give the Eu–H covalent bond if HEuNH<sub>2</sub><sup>+</sup> would form, but one electron would remain unpaired on N, since the 4f to 5d promotion energy is too high to allow the formation of a second Eu–N bond (see the reaction scheme for EuNH<sub>3</sub><sup>+</sup> → HEuNH<sub>2</sub><sup>+</sup> in Figure 1 and Scheme 3). This is consistent with the NBO5.9 population analysis that indicates one  $\sigma$  HEu–NH<sub>2</sub><sup>+</sup> bond, as also found for Eu–NH<sub>3</sub><sup>+</sup>.



Scheme 3.

HEuNH<sub>2</sub><sup>+</sup> has a nonplanar structure, which indicates that N is not sp<sup>2</sup> hybridized – Ln–N cannot be a double bond. Finally, all this suggests that HEuNH<sub>2</sub><sup>+</sup> is not very stable, because the electronic configuration of Eu<sup>+</sup> does not sufficiently facilitate covalency for the HEu–NH<sub>2</sub><sup>+</sup> bond. It is further confirmed by Eu=NH<sup>+</sup>, where no triple bond is found. This confirms that the formation of HLnNH<sub>2</sub><sup>+</sup> is the step in which the electron-promotion energy plays a key role.

Am<sup>+</sup> is the equivalent An<sup>+</sup> ion with a similar electronic configuration as Eu<sup>+</sup>. They have a high electron-promotion energy (Table 1), and their valence f sublayers are half occupied, which confers a great stability to their fundamental electronic configuration. The Am–NH<sup>+</sup> distance (2.16 Å) is the same as that for Eu–NH<sup>+</sup> (2.16 Å). They have similar electronic structures with double M=N bonds, in line with their similar reactivities – MNH<sup>+</sup> is not formed for either M = Eu or M = Am (see Supporting Information).

## Conclusions

The original MOs used for the quantum calculations show covalent bonding with dominant d character for the contributions of La<sup>+</sup> and Gd<sup>+</sup> in compounds along their reaction pathways with NH<sub>3</sub>. This is confirmed by NBO5.9 population analysis. Any Ln<sup>3+</sup> hard trication can be viewed as La<sup>3+</sup> – which does not have any valence electron – where the extra electrons are usually added onto 4f orbitals that do not participate in the bonding. Double reduction of some Ln<sup>3+</sup> ions into Ln<sup>+</sup> ions – typically La<sup>+</sup> and Gd<sup>+</sup> – can easily bring about one electron in an s orbital and another in a d orbital that participate in covalent bonds, as for the Sc<sup>+</sup> and Y<sup>+</sup> d-block ions of the transition metals (Sc<sup>+</sup> and Y<sup>+</sup> are isoelectronic to La<sup>+</sup> in M≡NH<sup>+</sup>). The same is calculated here for Np<sup>+</sup>, the only An<sup>+</sup> 5f-block cation with one s and one d electron in its ground state (5f<sup>4</sup>6d<sup>1</sup>7s<sup>1</sup>).

**Supporting Information** (see footnote on the first page of this article): Computational and experimental details are presented.

- a) G. K. Koyanagi, P. Cheng, D. K. Bohme, *J. Phys. Chem. A* **2010**, *114*, 241–246; b) V. Blagojevic, E. Flaim, M. J. Y. Jarvis, G. K. Koyanagi, D. K. Bohme, *Int. J. Mass Spectrom.* **2006**, *249*, 385–391; c) P. Cheng, D. K. Bohme, *Inorg. Chem.* **2006**, *45*, 7856–7863; d) G. K. Koyanagi, D. K. Bohme, *J. Phys. Chem. A* **2001**, *105*, 8964–8968; e) P. Cheng, G. K. Koyanagi, D. K. Bohme, *J. Phys. Chem. A* **2006**, *110*, 12832–12838; f) J. B. Schilling, J. L. Beauchamp, *J. Am. Chem. Soc.* **1988**, *110*, 15–24; g) H. H. Cornehl, C. Heinemann, D. Schroder, H. Schwarz, *Organometallics* **1995**, *14*, 992–999; h) J. K. Gibson, *J. Phys. Chem.* **1996**, *100*, 15688–15694; i) J. A. Carretas, J. Marcalo, A. P. de Matos, *Int. J. Mass Spectrom.* **2004**, *234*, 51–61; j) A. Shayesteh, V. V. Lavrov, G. K. Koyanagi, D. K. Bohme, *J. Phys. Chem. A* **2009**, *113*, 5602–5611.
- a) M. A. Tolbert, J. L. Beauchamp, *J. Am. Chem. Soc.* **1984**, *106*, 8117–8122; b) Y. Huang, M. B. Wise, D. B. Jacobson, B. S. Freiser, *Organometallics* **1987**, *6*, 346–354; c) R. Kretschmer, M. Schlangen, H. Schwarz, *Chem. Eur. J.* **2012**, *18*, 40–49.
- O. Eisenstein, L. Maron, *J. Organomet. Chem.* **2002**, *647*, 190–197.
- a) R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751–767; b) P. D'Angelo, A. Zitolo, V. Migliorati, G. Chillemi, M. Duval, P. Vitorge, S. Abadie, R. Spezia, *Inorg. Chem.* **2011**, *50*, 4572–4579.
- A. Quemet, R. Brennetot, P. Vitorge, C. Marsden, J. Y. Salpin, R. Spezia, M. P. Gageot, J. Tortajada, A. Cimas, S. Liu, L. Gagliardi; to be submitted for publication.
- a) N. Russo, E. Sicilia, *J. Am. Chem. Soc.* **2001**, *123*, 2588–2596; b) L. Hui-Zhen, W. Yong-Cheng, G. Zhi-Yuan, Z. Qing-Li, W. Qing-Yun, S. Yu-Bing, *THEOCHEM* **2008**, *866*, 5–10.

- [7] W. P. Ma, Y. C. Wang, L. L. Lv, Y. Z. Jin, J. Y. Nian, D. F. Ji, C. L. Wang, M. J. La, X. B. Wang, Q. Wang, *Comput. Theor. Chem.* **2011**, 977, 69–77.
- [8] B. Siboulet, C. J. Marsden, P. Vitorge, *New J. Chem.* **2008**, 32, 2080–2094.
- [9] P. Pyykko, *Chem. Rev.* **1988**, 88, 563–594.
- [10] M. Dolg, *Encyclopedia of Computational Chemistry*, John Wiley & Sons, **1998**.
- [11] J. K. Gibson, *J. Phys. Chem. A* **2003**, 107, 7891–7899.

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