

# Gas-Phase Formation of Grignard-type Organolanthanide(III) Ions $\text{RLnCl}_3^-$ : the Influences of Lanthanide Center and Hydrocarbyl Group

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## Abstract

**Rationale:** The fundamental understanding of Grignard-type organolanthanides(III) is still in its infancy. Decarboxylation of metal carboxylate ions is a powerful method to obtain organometallic ions which are well suited for gas-phase investigation by using ESI-MS in combination with DFT calculations. **Methods:**  $(\text{RCO}_2)\text{LnCl}_3^-$  ( $\text{R} = \text{CH}_3$ ,  $\text{Ln} = \text{La-Lu}$  except Pm;  $\text{Ln} = \text{La}$ ,  $\text{R} = \text{CH}_3\text{CH}_2$ ,  $\text{CH}_2\text{CH}$ ,  $\text{CHC}$ ,  $\text{C}_6\text{H}_5$  and  $\text{C}_6\text{H}_{11}$ ) ions were produced via ESI of  $\text{LnCl}_3$  and  $\text{RCO}_2\text{H}/\text{RCO}_2\text{Na}$  in methanol. Collision-induced dissociation (CID) was employed to examine whether  $\text{RLnCl}_3^-$  can be obtained via decarboxylation of  $(\text{RCO}_2)\text{LnCl}_3^-$ . With the aid of DFT calculations, the influences of Ln and R on the formation of  $\text{RLnCl}_3^-$  can be uncovered. **Results:** When R was fixed as methyl, CID of  $(\text{CH}_3\text{CO}_2)\text{LnCl}_3^-$  ( $\text{Ln} = \text{La-Lu}$  except Pm) all gave  $(\text{CH}_3)\text{LnCl}_3^-$  and  $\text{LnCl}_3^-$  with a variation in the relative intensity ratio of  $(\text{CH}_3)\text{LnCl}_3^-/\text{LnCl}_3^-$ . The trend is following as  $(\text{CH}_3)\text{EuCl}_3^-/\text{EuCl}_3^- < (\text{CH}_3)\text{YbCl}_3^-/\text{YbCl}_3^-$  [?]  $(\text{CH}_3)\text{SmCl}_3^-/\text{SmCl}_3^- < \text{other } (\text{CH}_3)\text{LnCl}_3^-/\text{LnCl}_3^-$ , which generally complies with the trend of Ln(III)/Ln(II) reduction potentials. When Ln was fixed as La and R groups were varied as  $\text{CH}_3\text{CH}_2$ ,  $\text{CH}_2\text{CH}$ ,  $\text{CHC}$ ,  $\text{C}_6\text{H}_5$  and  $\text{C}_6\text{H}_{11}$ , the fragmentation behaviors of these  $(\text{RCO}_2)\text{LaCl}_3^-$  are diverse. Except for  $(\text{C}_6\text{H}_{11}\text{CO}_2)\text{LaCl}_3^-$ , the rest four  $(\text{RCO}_2)\text{LaCl}_3^-$  ions all underwent decarboxylation to give  $\text{RLaCl}_3^-$ . The relative intensities of  $\text{RLaCl}_3^-$  compared to  $(\text{RCO}_2)\text{LaCl}_3^-$  decrease as follow:  $\text{CHC} > \text{CH}_2\text{CH} > \text{C}_6\text{H}_5 > \text{CH}_3 > \text{CH}_3\text{CH}_2 \gg \text{C}_6\text{H}_{11}$  (not visible). **Conclusion:** A series of Grignard-type organolanthanide(III) ions  $\text{RLnCl}_3^-$  ( $\text{R} = \text{CH}_3$ ,  $\text{Ln} = \text{La-Lu}$  except Pm;  $\text{Ln} = \text{La}$ ,  $\text{R} = \text{CH}_3\text{CH}_2$ ,  $\text{CH}_2\text{CH}$ ,  $\text{CHC}$  and  $\text{C}_6\text{H}_5$ ) were generated from  $(\text{RCO}_2)\text{LnCl}_3^-$  via  $\text{CO}_2$  loss while  $(\text{C}_6\text{H}_5)\text{LaCl}_3^-$  not. The experimental and theoretical results suggest that the reduction potentials of Ln(III)/Ln(II) couples as well as the bulkiness and hybridization of hydrocarbyl groups play crucial roles in promoting or limiting the formation of  $\text{RLnCl}_3^-$  via decarboxylation.

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