

Gas-Phase Formation of Grignard-type Organolanthanide(III) Ions 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 ; $\text{Ln} = \text{La}$, $\text{R} = \text{CH}_3\text{CH}_2$, CH_2CH , CHC , C_6H_5 and C_6H_{11}) ions were produced via ESI of LnCl_3 and $\text{RCO}_2\text{H}/\text{RCO}_2\text{Na}$ in methanol. Collision-induced dissociation (CID) was employed to examine whether 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 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 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 $\text{Ln(III)}/\text{Ln(II)}$ reduction potentials. When Ln was fixed as La and R groups were varied as CH_3CH_2 , CH_2CH , CHC , C_6H_5 and C_6H_{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 RLaCl_3^- . The relative intensities of 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 RLnCl_3^- ($\text{R} = \text{CH}_3$, $\text{Ln} = \text{La-Lu}$ except Pm ; $\text{Ln} = \text{La}$, $\text{R} = \text{CH}_3\text{CH}_2$, CH_2CH , CHC and C_6H_5) were generated from $(\text{RCO}_2)\text{LnCl}_3^-$ via 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 $\text{Ln(III)}/\text{Ln(II)}$ couples as well as the bulkiness and hybridization of hydrocarbyl groups play crucial roles in promoting or limiting the formation of RLnCl_3^- via decarboxylation.

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