A Monomeric Cyclopentadienyl Aluminylene

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INTRODUCTION

The isolation of mono-substituted aluminum compounds with the aluminum atom in the oxidation state +1 – so called aluminylenes – is challenging and typically requires bulky substituents for kinetic stabilization and/or donor-type ligands to compensate the inherent electron deficiency. In 1991, Schnöckel reported the isolation and structural characterization of (pentamethycyclopentadienyl)aluminum(II) tetramer \([\text{Cp}_5\text{Al}]_4\), highlighting the ability of cyclopentadienyl ligands to stabilize negative charges. However, this compound does not exhibit the general formula \(\text{R}_2\text{Al}^\text{III}\), but exists in tetrameric form in the solid-state and in solution at room temperature, although Schnöckel demonstrated in a follow-up work that monomeric cyclopentadienyl aluminums can be isolated at low temperature, with more bulky substitution patterns on the Cp moiety.\(^\text{1}\) The first isolation of a monomeric cyclopentadienyl aluminylene was achieved by Braunischweig only recently, complementing some other aluminylenes reported by Rosny, Power, Li and Hinsz in recent years.\(^\text{2}\)

SYNTHESIS AND STRUCTURE

(Pentamethycyclopentadienyl)aluminylene (\(\text{Cp}^\text{Al}\)) 1 was synthesized by treatment of the pentamethycyclopentadienyl aluminum(II) tetramer \([\text{Cp}_5\text{Al}]_4\) \(\text{Cp}^\text{Al}\)/with (pentamethycyclopentadienyl)lithium diethyl etherate \([\text{Cp}_5\text{Li}(\text{OEt})_2]\). 1 was fully characterized by multinuclear NMR spectroscopy in solution and in the solid-state, and its structure was determined by single crystal X-ray diffraction.

The molecular structure of 1 shows well-separated monomeric (pentamethycyclopentadienyl)aluminylene moieties with an \(\eta^5\)-coordination of the \(\text{Cp}^\text{Al}\) ligand towards aluminum, resulting in a pentagonal pyramidal structure, or rather a nido cluster.

METAL COMPLEXES

Treatment of 1 with \(\text{AlBr}_3\) at room temperature in toluene gives adduct 2 with a \(\text{Al} – \text{Al}\) bond length of 255.5(1) pm, which is similar to that found in Braunischweig’s (triethylcyclopentadienyl) aluminylene aluminum tribromide complex (255.4(1)).\(^\text{3}\)

Reaction of 1 with \(\text{W(CO)}_5\) in toluene under UV irradiation (365nm) yields the corresponding tungsten pentacarbonyl complex 3.

In both complexes, 2 and 3, the \(\text{Al} – \text{Cp}^\text{Al}\) distance decreases in comparison to 1, due to the electron deficiency at the aluminum(II) center, the electron-withdrawal power of the coordinated metal fragment respectively, and the corresponding compensation by the \(\text{Cp}^\text{Al}\) ligand.

REFERENCES:


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