

Electronic Supplementary Information for:

**Trapping an Unusual Pentacoordinate Carbon Atom in a Neutral
Trialuminum Complex**

Nery Villegas-Escobar^{1,}, Javier Martínez², Ricardo A. Matute^{1,3}, Sebastián Saltarini⁴,
Constantin G. Daniliuc⁵, Lutz Gade⁶, and René S. Rojas^{4*}*

¹Centro Integrativo de Biología y Química Aplicada (CIBQA)
Universidad Bernardo O'Higgins, General Gana 1702,
Santiago 8370854, Chile

²Instituto de Ciencias Químicas, Facultad de Ciencias, Isla Teja, Universidad Austral de Chile, 5090000 Valdivia, Chile.

³Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA.

⁴Laboratorio de Química Inorgánica, Facultad de Química y Farmacia, Pontificia Universidad Católica de Chile, Santiago 6094411, Chile.

⁵Organisch-Chemisches Institut der Universität Münster, 48149 Münster, Germany

⁶Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

nery.villegas@ubo.cl, rrojasg@uc.cl

TABLE OF CONTENTS

Experimental Section	S1
Figure S1. ^1H -NMR spectrum of complex 1 in CDCl_3	S2
Figure S2. ^1H -NMR spectrum of complex 1 in CDCl_3 (region 8.0-4.4 ppm)	S2
Figure S3. ^1H -NMR spectrum of complex 1 in CDCl_3 (region 3.0-(-1.5) ppm)	S3
Figure S4. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of complex 1 in CDCl_3 .	S3
Figure S5. ^1H - ^{13}C g-HSQC spectrum of complex 1	S4
Figure S6. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ for complex 1 .	S4
X-Ray diffraction studies	S5
Figure S7. X-ray structure. Ellipsoids are drawn using 30% probability.	S5
Table S1. Crystallographic data and structure refinement of complex 1 .	S6
Table S2. Principal bond distances (\AA) for complex 1	S7
Table S3. Principal bond angles ($^\circ$) for complex 1	S8
Computational Section	S9
Computational Results	S9
Table S4. Comparison between crystal and optimized structures	S9
Table S5. Comparison of other Al-C bond distances in similar Al_3 -(μ^3 - CH_2) moieties.	S10
QTAIM	S10
Figure S8. Laplacian of the electron density map and bond critical points (BCPs) in blue balls around the pentacoordinate carbon atom. Value of the density at BCPs (a.u.) and Mayer bond orders MBOs (in parenthesis)	S11
Figure S9. Key bond critical points (BCPs) on the molecular structure. Density and Laplacian of the electron density at each BCP. Values in atomic units (a.u.)	S11
Figure S10. Bond and ring critical points together with bond paths are shown for complex 1	S12
Figure S11. Superposition of molecular structures obtained at the wB97XD/6-31G and wB97XD/def2-TZVPP (quadrants). RMSD = 0.0372	S12
Figure S12. Results from trajectory. (a) total energy, (b) HOMO-LUMO gap, (c) HOMO energy (d) LUMO energy	S13
XYZ coordinates	S14
References:	S16