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Electronic Supplementary Information for:

Group 13 Organoderivatives Supported on a Metallic Oxide Model.

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Experimental Details and Characterization Data:

General Considerations. All work was performed under anaerobic and anhydrous conditions by using Schlenk-line and glovebox techniques. Solvents were carefully dried from the appropriate drying agents and distilled prior to use. $[\text{AlMe}_3]$ and 9-Borabicyclo[3.3.1]nonane (9-BBN) were purchased from Aldrich and used without further purification. $[\{\text{TiCp}^*(\mu\text{-O})\}_3(\mu_3\text{-CH})]$ (**1**) was synthesized according to the published procedure.^[1] Elemental analysis (C, H, N) were performed with a Heraeus CHN-O-RAPID. NMR spectra were recorded on Varian NMR System spectrometers: Gemini-200, Unity-300 or Mercury-VX, and infrared spectra were acquired for samples in KBr pellets on a FT-IR Perkin-Elmer SPECTRUM 2000 spectrophotometer.

Synthesis of $[\{\text{Me}_3\text{Al}\}\{(\mu_3\text{-O})(\mu\text{-O})_2(\text{TiCp}^*)_3(\mu_3\text{-CH})\}]$ (2**):** 0.49 mmol of **1** (0.30 g) was dissolved in 30 mL of hexane in an amber-stained 100-mL Carious tube with Young-valve, and an excess (0.29 mL, 2.0 M in hexane, 0.58 mmol) of $[\text{AlMe}_3]$ was dissolved in 10 mL of the same solvent in a second flask. The trimethylaluminium solution was then slowly combined with the alkylidyne solution. The resulting mixture was stirred for one day at room temperature, followed by filtration, concentration and cooling at -20°C ; 0.24 g of a orange microcrystalline solid were obtained (70%). ^1H NMR (300 MHz, $[\text{D}_6]$ benzene, 25°C , TMS): $\delta = -0.17$ (s, 9H, AlMe_3), 1.82 (s, 15H, C_5Me_5), 1.94 (s, 30H, C_5Me_5), 13.14 (s, 1H, $\mu_3\text{-CH}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, $[\text{D}_6]$ benzene, 25°C , TMS): $\delta = -2.6$ (AlMe_3), 11.9, 12.5 (C_5Me_5), 121.8., 123.4 (C_5Me_5), 401.2 ($\mu_3\text{-CH}$); IR (KBr, cm^{-1}): $\bar{\nu} = 2913$ (vs), 1436 (s), 1377 (s), 1262 (w), 1175 (m), 1023 (m), 791 (m), 680 (vs), 627 (vs), 435 (w); EI-MS EI mass spectrum: m/z (%) 610 (28) $[\text{M}^+ - \text{AlMe}_3]$; elemental analysis calcd (%) for $\text{C}_{34}\text{H}_{55}\text{AlO}_3\text{Ti}_3$ (682.41): C 59.83, H 8.12; found C 60.37, H 7.57.

Synthesis of $[\{C_8H_{14}B\}(\mu-H)\{\mu_3-O\}(\mu-O)_2(TiCp^*)_3(\mu_3-CH)]$ (4): To a stirred hexane solution (30 mL) of **1** (0.4 g, 0.65 mmol) placed in a 100-mL Carious tube with Young-valve, was added 9-BBN (0.08 g, 0.65 mmol) dissolved in 10 mL of the same solvent. The reaction mixture was stirred at room temperature overnight. The solution was filtered, concentrated and cooled at -20°C , giving yellow crystals identified as **3** (0.38 g, 79%); ^1H NMR (300 MHz, $[D_6]$ benzene, 25°C , TMS): $\delta = 0.80\text{-}2.70$ (m, CH and CH_2 in 9-BBN), 1.86, 1.88, 1.98 (s, 15H, C_5Me_5), 13.35 (s, 1H, $\mu_3\text{-CH}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, $[D_6]$ benzene, 25°C , TMS): $\delta = 12.01, 12.17, 12.62$ (C_5Me_5),), 24.5-26.5 (vb, CH_2CHB), 25.9, 26.2, 31.6, 34.1, 35.2, 36.2 (CH_2CHB), 119.7, 120.3, 122.0 (C_5Me_5), 384.6 ($\mu_3\text{-CH}$); (IR (KBr, cm^{-1}): $\bar{\nu} = 2979$ (w), 2944 (m), 2910 (vs), 2859 (vs), 2819 (m), 1820 (w), 1786 (w), 1752 (w), 1485 (m), 1434 (s), 1375 (s), 1339 (m), 1312 (m), 1282 (m), 1262 (m), 1203 (s), 1024 (m), 935 (s), 865 (s), 795 (s), 747 (m), 679 (vs), 650 (s), 632 (m), 624 (m), 618 (m), 559 (s), 428 (s); EI mass spectrum: m/z (%) 610 (29) $[M^+ - 9\text{-BBN}]$; elemental analysis calcd (%) for $C_{39}H_{61}BO_3Ti_3$, (732.33): C 63.96, H 8.40; found C 63.79, H 8.77.

X-ray structure determination of $3 \cdot C_6H_{14}$ and 4. X-ray quality crystals of both compounds were grown from saturated hexane solutions at -20°C , removed from the Schlenks and covered with a layer of a viscous perfluoropolyether (Fomblin®Y). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data for all the complexes are presented in Table 1. The structures were solved, using the WINGX package,² by direct methods (SHELXS-97)³ and refined by least-squares against F^2 (SHELXL-97).³

Elemental analysis for the complex $3 \cdot C_6H_{14}$ revealed the existence of one molecule of hexane. The solvent presented severe disorder and it was not possible to get a chemical sensible model for it, so Squeeze⁴ procedure was used to remove its contribution to the structure factors. Finally, all non-hydrogen atoms were anisotropically refined and the hydrogen atoms were positioned geometrically and refined by using a riding model, except those of the methylidyne moiety and the bridging hydroxo fragment, which were located in the Fourier difference map and isotropically refined.

All non-hydrogen atoms of compound **4** were anisotropically refined and the hydrogen atoms were positioned geometrically and refined by using a riding model except the hydrogen atom bridging the boron and titanium atoms, which was located in the Fourier difference map and refined isotropically.

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- (2) L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837-838.
- (3) G. M. Sheldrick, *SHELX97, Program for Crystal Structure Analysis (Release 97-2)*, Universität Göttingen, Germany, 1998.
- (4) PLATON. A. L. Spek, *J. Appl. Cryst.* 2003, **36**, 7-13

Table 1.- Crystallographic data for complexes **3** and **4**.

| Compound | 3·C₆H₁₄ | 4 |
|--|--|---|
| Empirical formula | C ₆₃ H ₉₇ AlO ₈ Ti ₆ ·C ₆ H ₁₄ | C ₃₉ H ₆₁ BO ₃ Ti ₃ |
| Formula weight | 1382.96 | 732.33 |
| Temperature | 200(2) K | 200(2) K |
| Wavelength | 0.71073 Å | 0.71073 Å |
| Crystal system | Monoclinic | Monoclinic |
| Space group | C2/c | P2 ₁ /c |
| a(Å) | 24.039(7) | 11.313(3) |
| b(Å); β(°) | 26.797(7); 101.57(5) | 19.171(17); 105.61(3) |
| c(Å) | 13.441(8) | 19.088(12) |
| Volume | 8482(6) Å ³ | 3987(4) |
| Z | 4 | 4 |
| Density (calculated) | 1.083 Mg/m ³ | 1.220 Mg/m ³ |
| Absorption coefficient | 0.590 mm ⁻¹ | 0.619 mm ⁻¹ |
| F(000) | 2936 | 1560 |
| Crystal size | 0.30 x 0.25 x 0.23 mm ³ | 0.20 x 0.20 x 0.20 mm ³ |
| Theta range for data collection | 3 to 25° | 3 to 25° |
| Index ranges | -28 to 28, -31 to 31, -15 to 15 | -13 to 13, -22 to 22, -22 to 22 |
| Reflections collected | 84262 | 48845 |
| Independent reflections | 7496 [R(int) = 0.076] | 6984 [R(int) = 0.134] |
| Reflections [I > 2σ(I)] | 4750 | 4126 |
| Completeness to theta = 25° | 99.1 % | 99.3% |
| Goodness-of-fit on F ² | 1.031 | 1.047 |
| Final R indices [I > 2σ(I)] | R1 = 0.070, wR2 = 0.180 | R1 = 0.067, wR2 = 0.141 |
| R indices (all data) | R1 = 0.106, wR2 = 0.199 | R1 = 0.134, wR2 = 0.176 |
| Largest diff. peak and hole (e.Å ⁻³) | 0.456 and -0.451 | 0.451 and -0.373 |