

Catalyst Speciation During ansa-Zirconocene-Catalyzed Polymerization of 1-Hexene Studied by UV-vis Spectroscopy – Formation and Partial Re- Activation of Zr-Allyl Intermediates.

Valentina N. Panchenko ^{1,2}, Dmitrii E. Babushkin ¹, John E. Bercaw ^{3 *} and Hans H. Brintzinger ⁴

¹ Borekov Institute of Catalysis, Russian Academy of Sciences, Siberian Branch, RU-630090 Novosibirsk, Russian Federation; panchenko@catalysis.ru, dimi@catalysis.ru

² Novosibirsk State University, Pirogova Str. 2, 630090, Novosibirsk, Russian Federation

³ Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125, USA; bercaw@caltec.edu

⁴ Fachbereich Chemie, Universität Konstanz D-78464 Konstanz, Germany; hans.brintzinger@uni-konstanz.de

* Correspondence: hans.brintzinger@uni-konstanz.de

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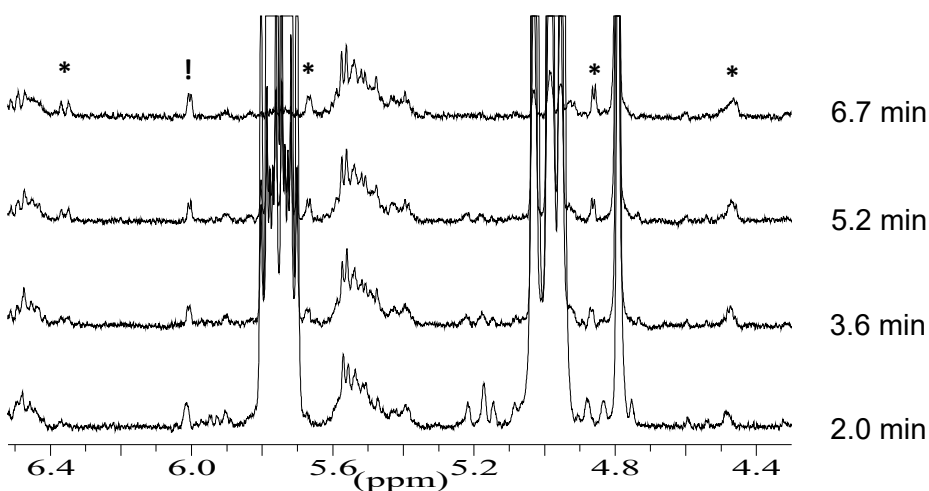
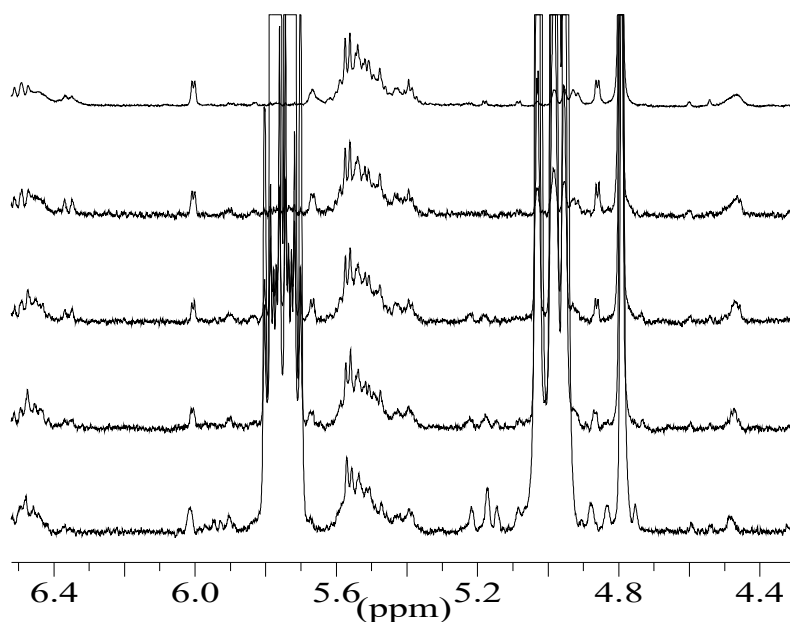


Figure S-1. ¹H NMR signals arising during polymerization of 1-hexene by the catalyst system described in Figure 1. First 4 traces (2.0 , 3.6, 5.2 and 6.7 min mean time). Signals at 6.36, 5.67, 4.87 and 4.48 ppm (marked by *), possibly due to polymer-carrying cations of type $\text{SBIZr-}\pi\text{-(1-R-2-pol-C}_3\text{H}_3\text{)}^+$ (**10**).



Additional traces after ca. 20 min.

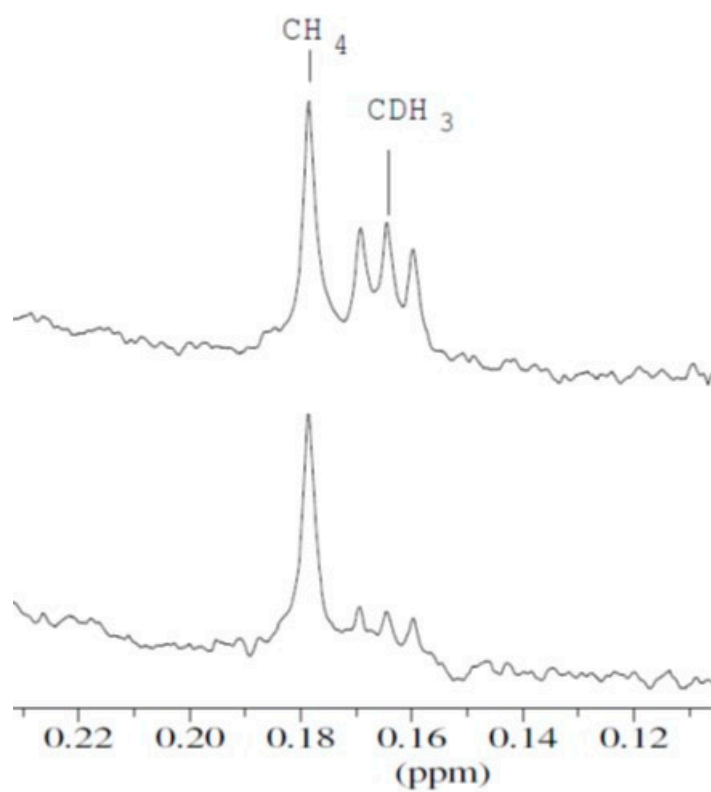


Figure S-2. ¹H NMR spectra of CH₄ and CH₃D in solutions obtained by addition of an equivalent amount of trityl perfluorotetraphenyl borate to a solution of SBIZrMe₂ in toluene-d₈, as described in Figure 3, after reaction times of ca. 4 h (bottom) and ca. 10 h (top).

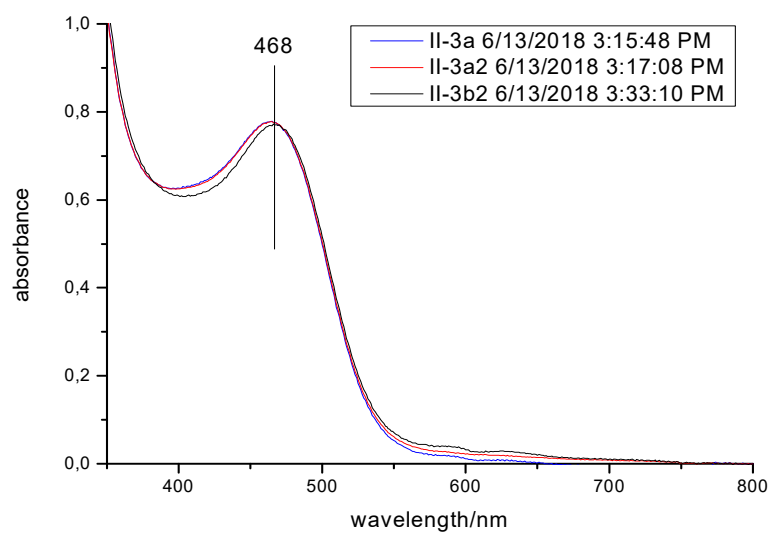


Figure S-3. UV-vis spectra of a 0.8 mM solution of SBIZr(Me)-CH₂SiMe₃ after addition of ca. 0.8 equiv. of trityl perfluorotetraphenyl borate.

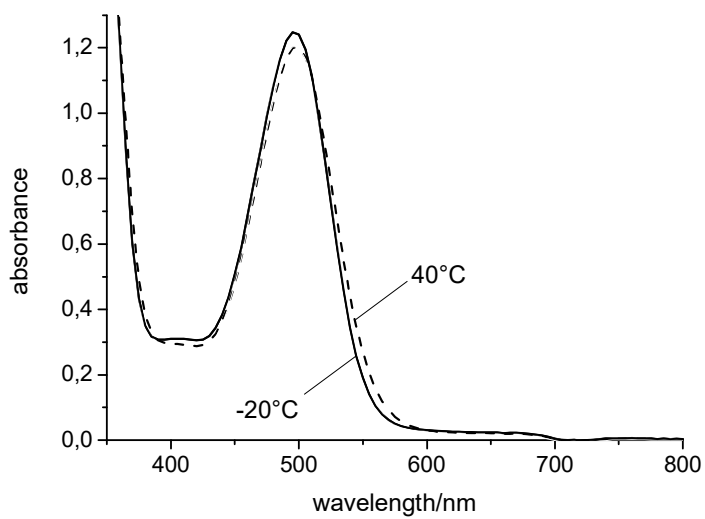


Figure S-4. UV-vis spectra of a ca. 0.5 mM toluene solution of (SBI)Zr(μ-Me)₂AlMe₂⁺ B(C₆F₅)₄⁻ at +40°C (broken line) and at -20°C (solid line).

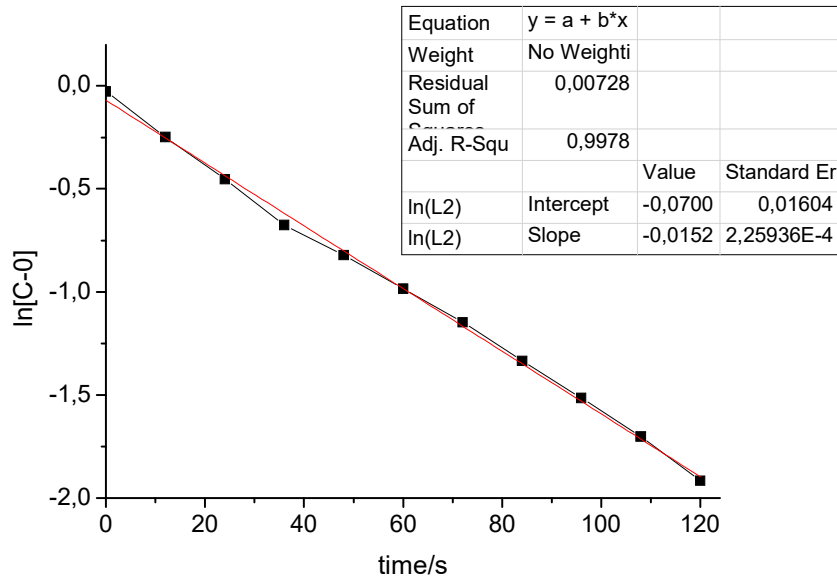


Figure S-5. Plot of $\ln[C-0]_t$ vs. t for reaction stage 1 ($t < 120$ s):

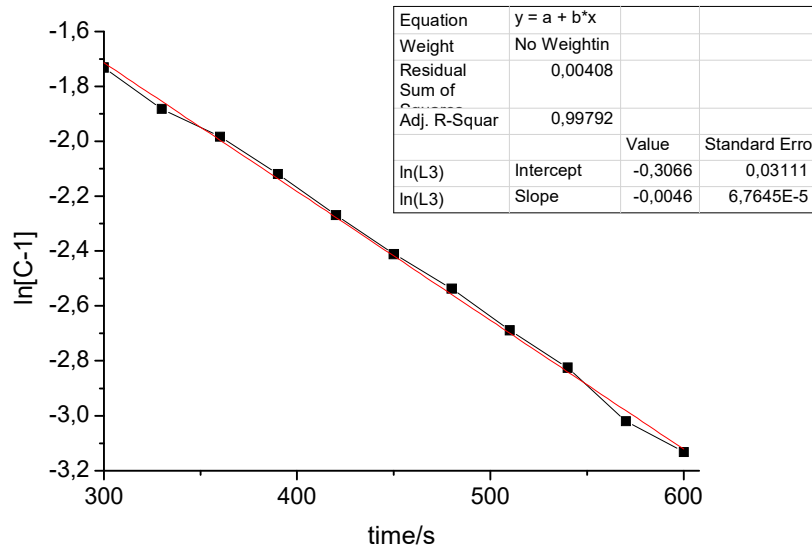


Figure S-6. Plot of $\ln[C-1]_t$ vs. t for $300 \text{ s} < t < 600 \text{ s}$

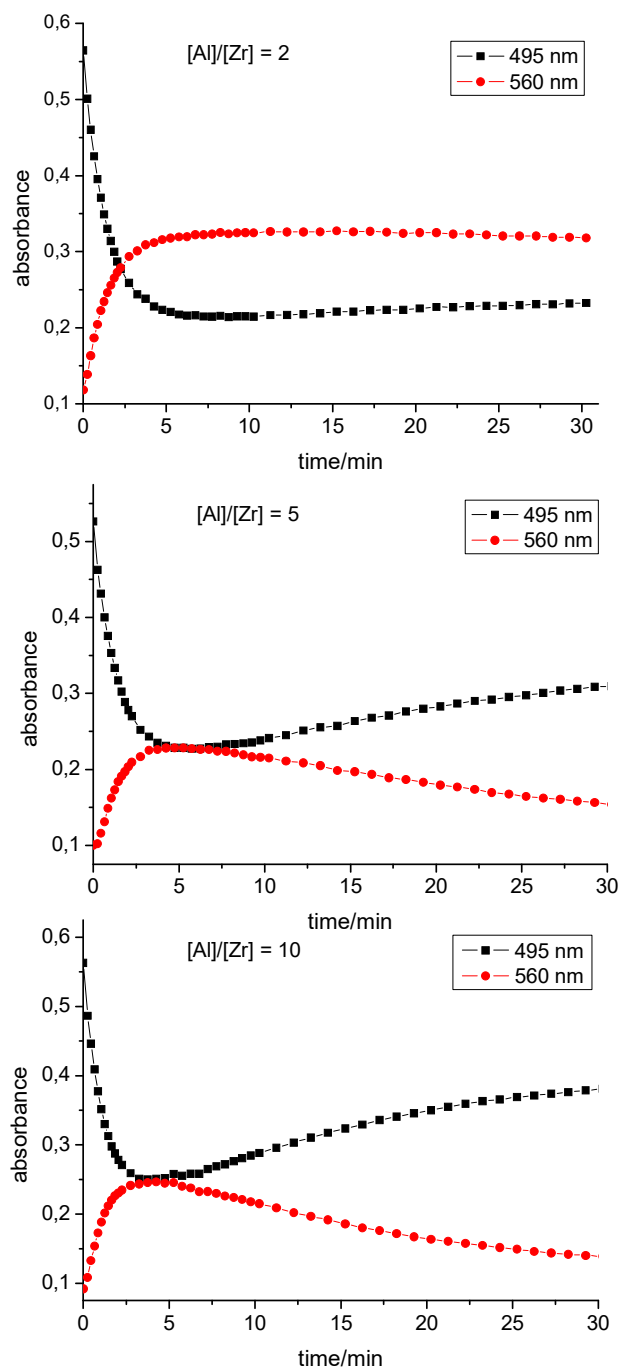


Figure S-7. Effects of initial [Al]/[Zr] ratio on the re-conversion of **C-2** ($\lambda_{\max} = 560$ nm) to **C-0** ($\lambda_{\max} = 495$ nm), conditions as described in Figure 1.