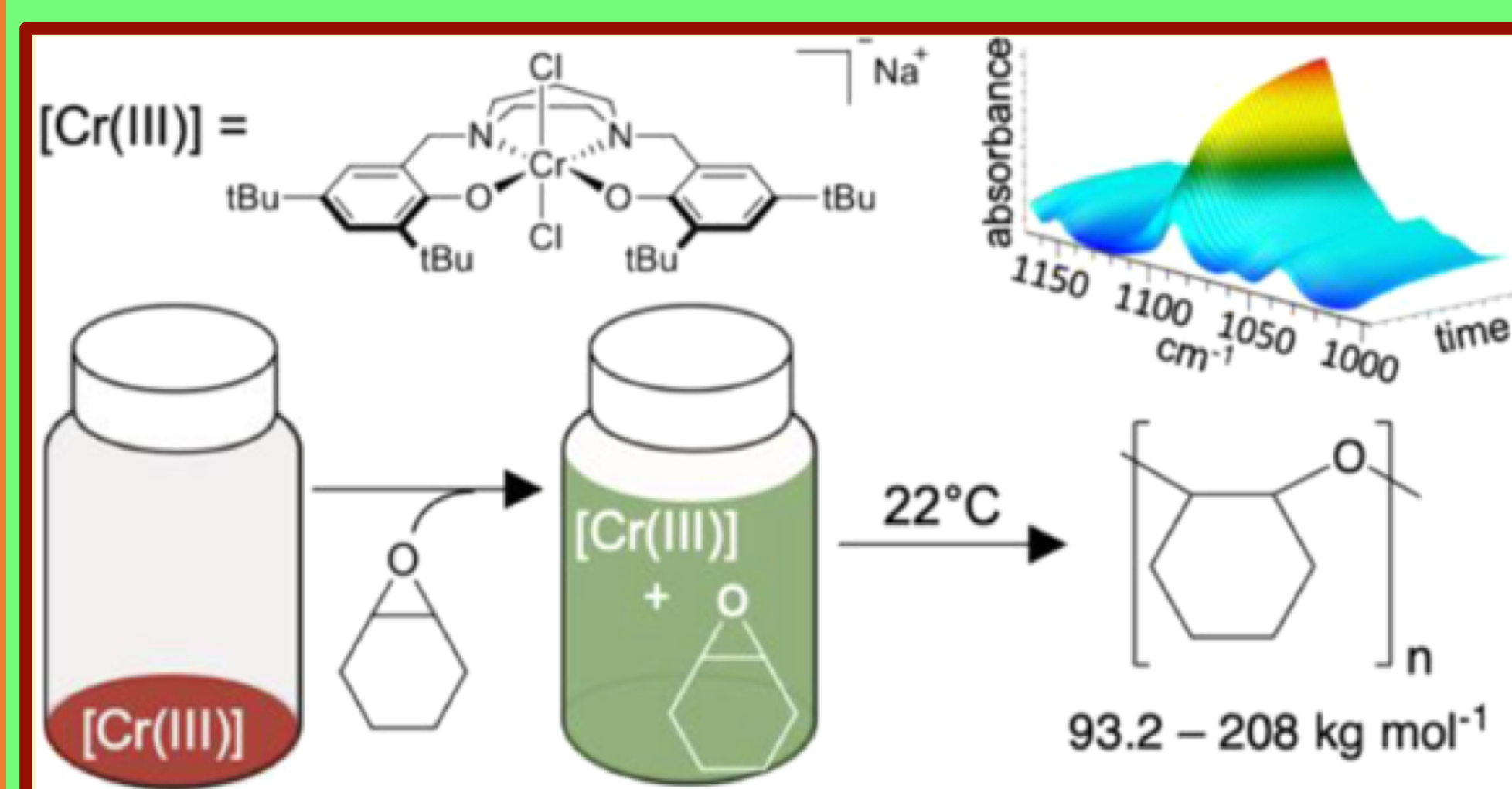


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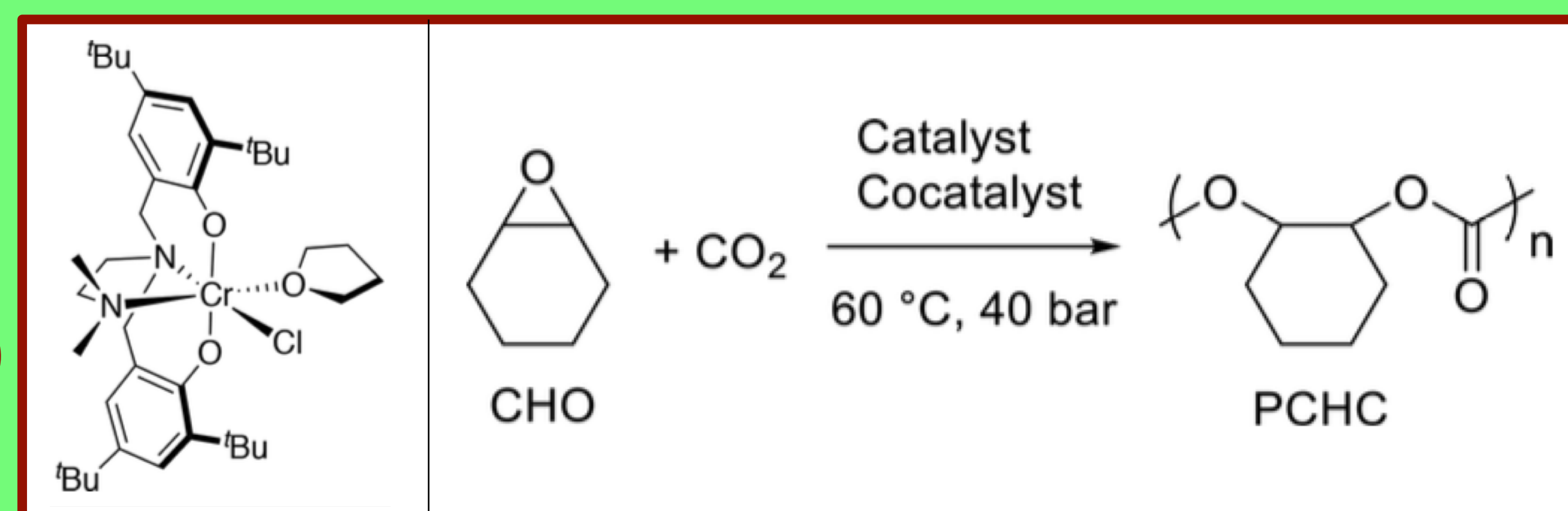
Previous related work by our group

The chromium(III) amino-bis(phenolate) “ate” complexes have been studied for catalyzing ring opening polymerization (ROP) and ring opening co-polymerization (ROCOP) in our previous work done by K. Ambrose (**1** and **2**) and K. Ni (**3**). The complex in **1** had shown good activity for the room temperature ROP of epoxides such as cyclohexene oxide (CHO). Activity towards ROCOP of CHO with carbon dioxide (CO₂) was shown in the previous work of both **2** and **3**. In **1** the ROP of CHO was able to be performed at room temperature with no significant benefit seen from the use of a co-catalyst, while in the ROCOP reactions of **2** and **3** co-catalysts of PPNCl and PPNN₃ were necessary for the reactions to occur as an extra nucleophilic source was required for the ROCOP reactions to proceed.



Schemes 1 and 2. Previous research done by Ambrose for the catalyzed ROP of CHO and ROCOP of CHO and CO₂ using similar chromium amino-bis(phenolate) catalysts.^{1,2}

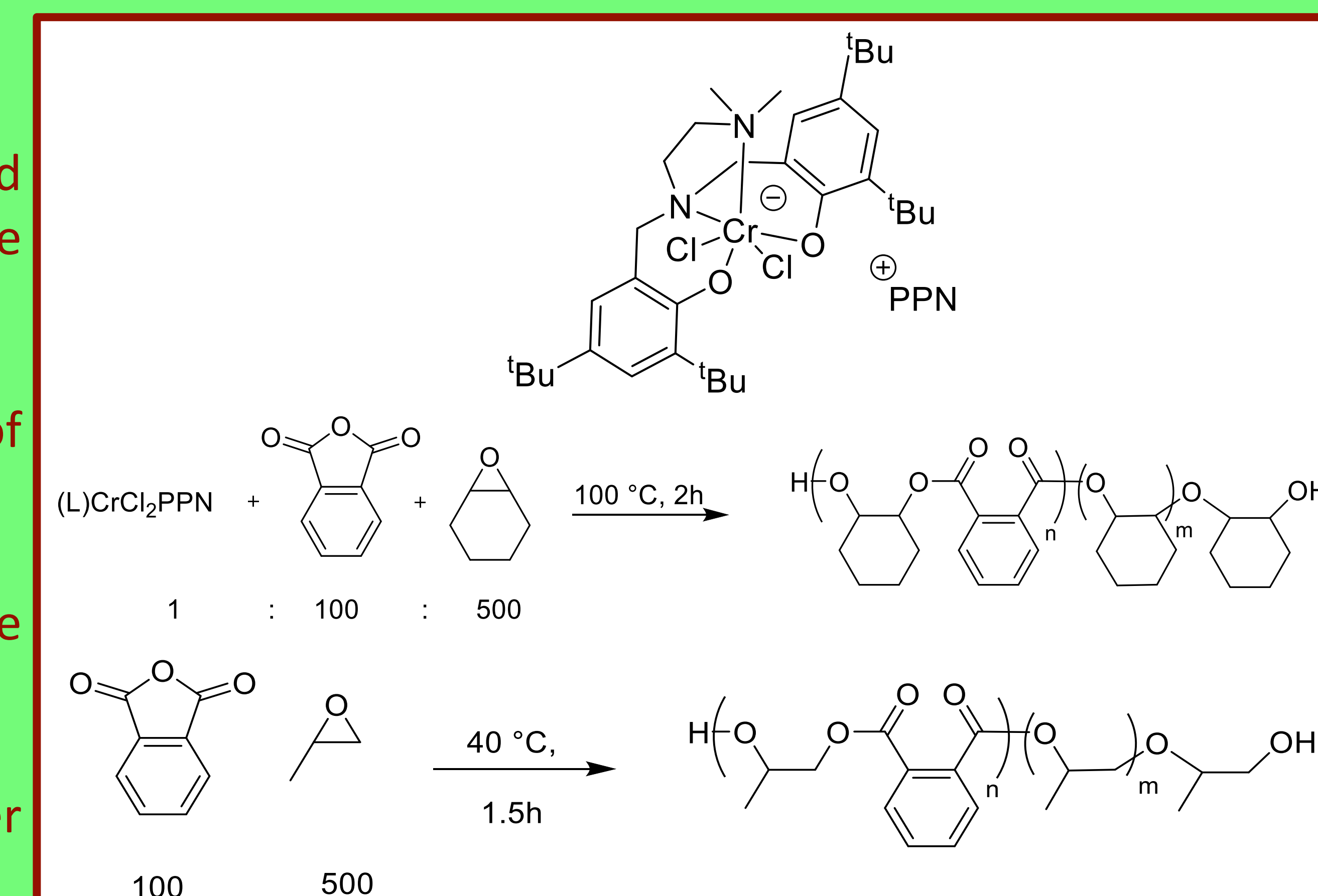
Scheme 3. Previous research done by Ni for the ROCOP of CHO and CO₂ catalyzed by a related diamino-bis(phenolate) chromium(III) complex.³



James Beament's work and Current Research

James Beament's work

- The catalyzed ROCOP of phthalic anhydride (PA) and CHO. The reaction showed complete conversion of PA to P(PA-*alt*-CHO) after approximately 15 mins with the resulting polymer having a dispersity value (Đ) of 1.13 and a M_n^{SEC} of 13.8 kg mol⁻¹.
- The ROP of maleic anhydride (MA) with the same reaction conditions, and the ROP of ε-Cl at 80°C for 2 hours. Both reactions used CHO as the solvent.
- Catalyzed ROCOP of limonene oxide and PA with a small amount of propylene oxide (PO) as an initiator. 100% conversion after 1 hour at 130°C.
- The catalyzed ROCOP of PO and PA, had 74% conversion after 1.5 hours, the polymer had the following properties: M_n^{SEC} = 13.6 kg mol⁻¹, Đ = 1.03, M_n^{theo} = 14.5 kg mol⁻¹.



Scheme 4. Catalyst system and reactions done by Beament.

Current Research

- Exploring the ROP of PO using the catalyst system from **1** at a higher temperature (in **1** the reaction was only attempted at room temperature).
- The catalyzed ROCOP of CHO and PA is being looked into both with and without the use of a co-catalyst (PPNCl).
- The ROCOP of PO with PA or MA is being explored both with and without PPNCl, as well as with and without an initiator (CHO at 10% of the PO).

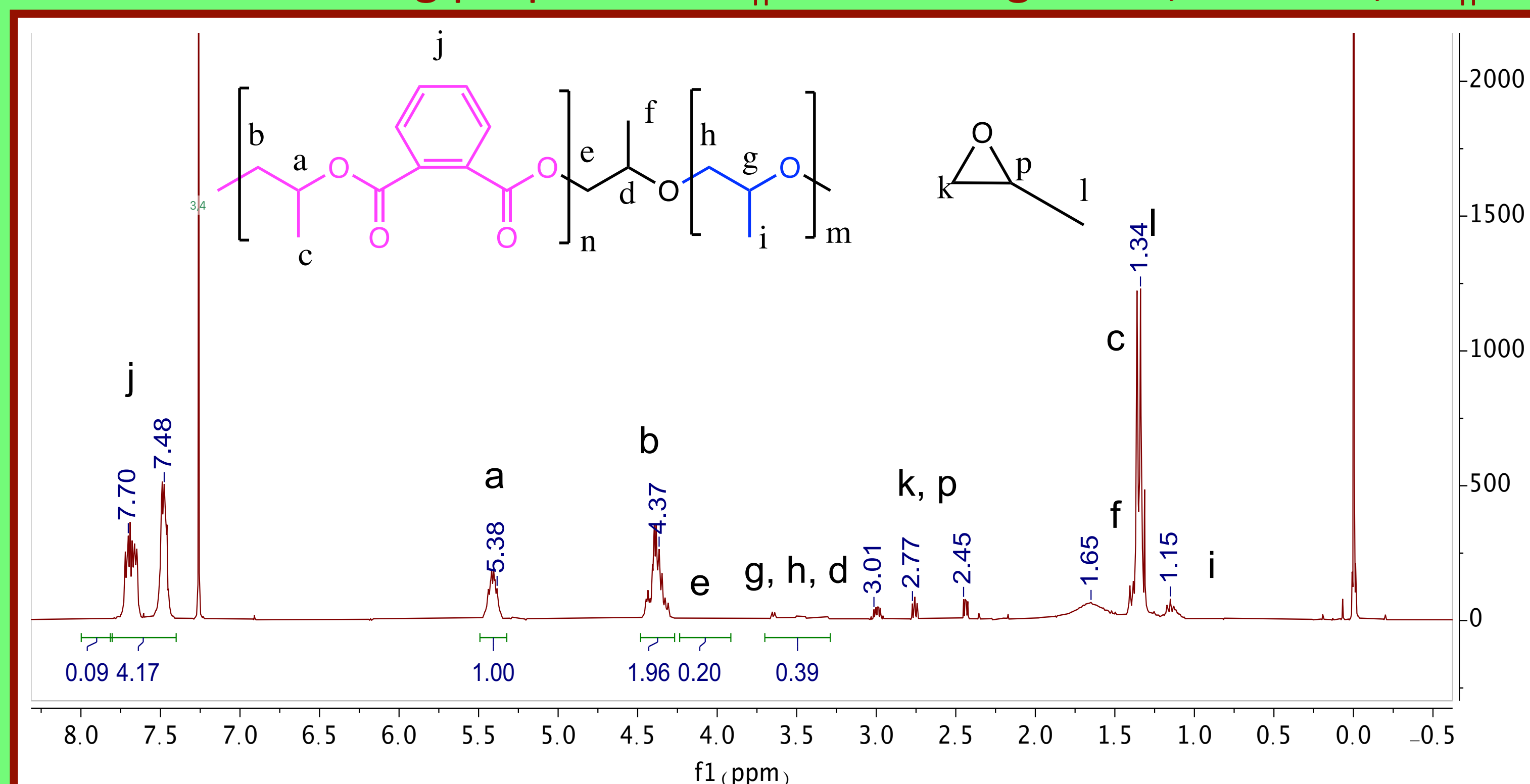


Figure 1. ¹H-NMR (CDCl₃) of the polymer produced by ROCOP using the Cr(III) complex from **1** with PO, PA, and a co-catalyst of PPNCl at 100°C for 2 hours. The ratio of Cr(III) complex:PPNCl:PO:PA was 1:0.5:500:100. M_n^{theo} was 20.7 kg mol⁻¹ while MALDI-TOF MS gave M_n^{actual} ≈ 8.3 kg mol⁻¹.

References

1. Ambrose, K., Murphy, J.N., and Kozak, C.M. Chromium Amino-bis(phenolate) Complexes as Catalysts for Ring-Opening Polymerization of Cyclohexene Oxide. *Macromolecules* **2019**, 52, 7403–7412.
2. Ambrose, K., Murphy, J.N., and Kozak, C.M. Chromium Diamino-bis(phenolate) Complexes as Catalysts for the Ring-Opening Copolymerization of Cyclohexene Oxide and Carbon Dioxide. *Inorg. Chem.* **2020**, 59, 15375–15383.
3. Ni, K. and Kozak, C.M. Kinetic Studies of Copolymerization of Cyclohexene Oxide with CO₂ by a Diamino-bis(phenolate) Chromium(III) Complex. *Inorg. Chem.* **2018**, 57, 3097–3106.