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# Cyclopentadienyl Chromium $\beta$ -Diketimate Complexes: Initiators, Ligand Steric Effects, and Deactivation Processes in the Controlled Radical Polymerization of Vinyl Acetate

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4 **Cyclopentadienyl Chromium  $\beta$ -Diketiminato Complexes:**  
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7 **Initiators, Ligand Steric Effects, and Deactivation Processes in the**  
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9 **Controlled Radical Polymerization of Vinyl Acetate**  
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**Abstract**

The new compounds  $\text{CpCr}(\text{nacnac}^{\text{Ar,Ar}'})$  with  $\text{nacnac}^{\text{Ar,Ar}'} = \text{Ar-N}=\text{C}(\text{Me})=\text{CH}=\text{C}(\text{Me})=\text{N-Ar}'$  ( $\text{Ar} = \text{Ar}' = \text{C}_6\text{H}_2\text{Me}_{3-2,4,6}$  or mes, **2**;  $\text{C}_6\text{H}_3\text{Et}_{2-2,6}$  or dep, **3**;  $\text{Ar} = \text{C}_6\text{H}_3\text{Me}_{2-2,6}$  or xyl and  $\text{Ar}' = \text{C}_6\text{H}_3i\text{Pr}_{2-2,6}$  or dipp, **4**) have been synthesized and used in polymerization experiments in addition to the previously known analogues with  $\text{Ar} = \text{Ar}' = \text{xyl}$ , **1**, or dipp, **5**. The compounds were used as moderators for the polymerization of vinyl acetate (VAc) initiated by V-70, according to an OMRP mechanism. The alkylchromium(III) thermal initiator  $\text{CpCr}(\text{nacnac}^{\text{xyl,xyl}})(\text{CH}_2\text{CMe}_3)$  (**8**) was synthesized from  $\text{CpCr}(\text{nacnac}^{\text{xyl,xyl}})(\text{OTs})$  (**7**) and  $\text{Mg}(\text{CH}_2\text{CMe}_3)_2(\text{dioxane})$ , while **7** was obtained from  $\text{CpCr}(\text{nacnac}^{\text{xyl,xyl}})\text{Cl}$  (**6**) and AgOTs. The polymerizations carried out with (**1-5**)/V-70/VAc at elevated temperatures yielded rapid deactivation, suggestive of irreversible radical trapping. On the other hand, room temperature polymerizations carried out with **6**/VAc proceeded, albeit slowly, to greater conversions. A labilizing effect of the Ar/Ar' steric bulk is suggested by QM/MM calculations of  $\text{Cr}^{\text{III}}\text{-C BDE}$  for models of the OMRP dormant species with **1**, **5**, and the parent system where  $\text{Ar} = \text{Ar}' = \text{Ph}$ . Thermal deactivation of the  $\text{nacnac}^{\text{xyl,xyl}}$  system has been evidenced, with formation of the acetate complex  $\text{CpCr}(\text{nacnac}^{\text{xyl,xyl}})(\text{OAc})$ , **9**, as confirmed by an UV-vis study and by independent synthesis. This product is proposed to form by  $\beta$ -acetate transfer from the growing radical chain, triggered by a head-head monomer insertion. Compounds **2**, **3**, **6**, **7**, **8** and **9** have been structurally characterized by X-ray diffraction methods.

## Introduction

The controlled polymerization of functionalized monomers like vinyl acetate continues to pose a formidable challenge to transition metal chemists. Early metal catalysts that effectively polymerize non-polar monomers by an insertion mechanism are incompatible with vinyl ester substrates.<sup>1</sup> More functional group tolerant late metal catalysts experience problems for copolymerization of vinyl acetate and ethylene due to low  $\pi$ -bonding affinity, chelate formation, and  $\beta$ -acetate elimination.<sup>2-4</sup> Vinyl acetate is also a difficult monomer for controlled radical polymerization methods due to the relatively high reactivity of the propagating radical species compared to more tractable substrates such as styrene or methyl acrylate.<sup>5</sup>

Organometallic radical polymerization (OMRP) provides a new route to poly(vinylacetate). In the OMRP mechanism, unwanted bimolecular radical coupling reactions are effectively prevented by reversible formation and homolytic cleavage of metal-alkyl bonds.<sup>6</sup> Cobalt-mediated radical polymerization is the most well explored system for OMRP of vinyl acetate. The mechanistic details of these polymerizations are rather complex, with a range of termination and chain transfer steps playing a role dictated by the degree of solvent coordination and the spin state of the Co(II) and Co(III) intermediate species.<sup>7</sup>

In principle, well-defined high spin Cr<sup>II</sup> and Cr<sup>III</sup> complexes could serve as a simpler system for preparing poly(vinylacetate) via OMRP. Chromium(II) species such as aqueous  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  or  $\text{CrCl}_2$  in coordinating aprotic solvents have long been known to effectively trap organic radicals at close to diffusion controlled rates to

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4 form Cr<sup>III</sup>-alkyl intermediates.<sup>8</sup> This fundamental reactivity mode is the key step in  
5  
6 the chromium-mediated coupling of organic halides and aldehydes.<sup>9, 10</sup> The homolytic  
7  
8 bond dissociation energy (BDE) of a Cr<sup>III</sup>-alkyl bond is typically greater than that of a  
9  
10 Co<sup>III</sup>-alkyl. Homolytic transfer of alkyl groups from Co<sup>III</sup>-R to Cr<sup>II</sup> is used in the  
11  
12 Takai-Utimoto reaction where catalytic amounts of B<sub>12</sub> or cobalt phthalocyanine are  
13  
14 used to activate alkyl halides and transfer the organic radical from Co to Cr prior to  
15  
16 coupling with aldehydes.<sup>11</sup> While the trapping of organic radicals with Cr<sup>II</sup> to form  
17  
18 octahedral Cr<sup>III</sup> organometallic species is usually considered to be rapid and  
19  
20 irreversible, the reaction can be reversible for secondary or tertiary radicals due to the  
21  
22 lowering of the Cr-R BDE through adverse steric interactions.<sup>12, 13</sup>  
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31 CpCr(nacnac) complexes are high spin, well characterized species that do not  
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33 bind coordinating solvents but have been shown to trap CH<sub>3</sub> radicals.<sup>14, 15</sup>  
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35 CpCr(nacnac)(CH<sub>3</sub>) complexes can be independently synthesized by the reaction of  
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37 Grignard reagents with the corresponding Cr<sup>III</sup> triflate or halide compounds.  
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39 Modifying the size of the *ortho* substituents of the nacnac N-aryl groups should exert  
40  
41 a dramatic influence on the Cr<sup>III</sup>-R BDE for CpCr(nacnac)R complexes, as indicated  
42  
43 by preliminary DFT calculation.<sup>16</sup> This desired tunability of the M-R BDE is critical  
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45 for both exploring structure-activity relationships for these reagents and for  
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47 developing a class of well-defined organometallic complexes capable of mediating  
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49 OMRP reactions for a range of activated olefin substrates.<sup>6</sup>  
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57 In 2008, we communicated our preliminary studies towards OMRP of vinyl  
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59 acetate using CpCr(nacnac) complexes and V-70.<sup>16</sup> In this paper, we further examine  
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4 the structure-activity relationships of vinyl acetate polymerization using isolated  
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7 CpCr(nacnac) compounds with V-70. Although the paramagnetic nature of the Cr<sup>II</sup>  
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9 and Cr<sup>III</sup> complexes makes interpretation of their NMR spectra difficult, the UV-vis  
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11 spectra of these intensely coloured species proved to be quite informative.  
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14 Employing elevated temperatures to accelerate initiation in the  
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16 CpCr(nacnac)/V-70/vinyl acetate system unexpectedly led to a decrease in the  
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18 observed rate of polymerization due to formation of an inactive Cr<sup>III</sup> acetate thermal  
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20 decomposition product. As an alternative to thermolysis of CpCr(nacnac) with V-70,  
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23 a well-defined Cr<sup>III</sup> neopentyl complex was developed as a single-component OMRP  
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26 reagent. The choice of the neopentyl group was based on the high steric demand of  
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28 this specific alkyl ligand, which has long been used to provoke unique organometallic  
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31 reactivity, both of non-radical<sup>17-20</sup> and of radical type.<sup>21-23</sup>  
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## Experimental Section

**Materials.** All reactions, unless otherwise stated, were carried out under dry, oxygen-free argon or nitrogen, using standard Schlenk and glove box techniques. Solvents were dried by using the method of Grubbs<sup>24</sup> or they were distilled under argon from appropriate drying agents and degassed by three freeze-vacuum-thaw cycles prior to use.<sup>25</sup> Celite (Aldrich) was dried overnight at 110 °C before being evacuated and then stored under argon or nitrogen. Vinyl acetate (VAc, 99 %, Alfa Aesar or 99+%, Aldrich) was passed through a neutral alumina column to remove the stabilizer, dried over calcium hydride, distilled at 90 °C, degassed by three freeze-vacuum-thaw cycles and stored under argon or nitrogen at -20 °C. 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, 96%, Wako) was used as received. *n*-BuLi (1.6 M in hexanes), *p*-toluenesulfonic acid monohydrate, acetylacetonate, 2,6-dimethylaniline, 2,6-diisopropylaniline, 2,6-diethylaniline, 2,4,6-trimethylaniline, CrCl<sub>3</sub> (anhydrous), 1,4-dioxane, silver *p*-toluenesulfonate and silver acetate were purchased from Aldrich and used as received. The symmetric  $\beta$ -diketiminato ligands, (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NHC(Me)CHC(Me)N(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>),<sup>26</sup> (2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NHC(Me)CHC(Me)N(2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub>),<sup>27</sup> (2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)NHC(Me)CHC(Me)N(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sup>27</sup> and the mixed N-aryl  $\beta$ -diketiminato ligand, (2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NHC(Me)CHC(Me)N(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sup>28</sup> were prepared according to the literature procedure. NaCp was prepared according to the literature procedure,<sup>29</sup> or was purchased from Aldrich as a 2.0 M solution in THF and

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4 used as received. Compounds  $\text{Mg}(\text{CH}_2\text{CMe}_3)_2 \cdot x(1,4\text{-dioxane})$ <sup>30</sup>  $\text{CrCl}_2(\text{tmeda})$ ,<sup>31</sup> **1**<sup>16</sup>  
5  
6  
7 and **5**<sup>16</sup> were prepared according to literature procedures.

8  
9 **Characterizations.** <sup>1</sup>H NMR spectra were recorded on a Bruker ARX 250 or a  
10 Bruker DPX 300 spectrometer. A Varian Cary 100 Bio UV–visible spectrophotometer  
11 was used to conduct measurements using a specially constructed cell for air-sensitive  
12 samples: a Kontes Hi-Vac Valve with PTFE plug was attached by a professional  
13 glassblower to a Hellma 10 mm path length quartz absorption cell with a  
14 quartz-to-glass graded seal. Size exclusion chromatography (SEC) of poly (vinyl  
15 acetate) was carried out in filtered THF (flow rate: 1 ml/min) at 35°C on a 300x7,5  
16 mm PL gel 5micrometer mixed-D column (polymer laboratories), equipped with  
17 multiangle light scattering (minidawn Tristar, Wyatt Technology Corporation) and  
18 refractive index (RI2000, Sopares) detectors, with a waters column pack (300x7,5 mm,  
19 ultrastyrigel 104,103,100 Å), equipped with multiangle light scattering (miniDawn  
20 Tristar, Wyatt Technology Corp.) and refractive index (waters 410) detectors or at  
21 30°C on a Polymer Labs PL-GPC 50 plus (two PLgel mixC columns in series) with a  
22 PL-AS RT autosampler and PL-RI detector. The isolated polymer samples were  
23 dissolved in THF and the polymer solutions were filtered (pore size = 0.45 μm) before  
24 chromatographic analysis. The columns were calibrated against linear polystyrene  
25 standards (Polymer Laboratories). Elemental analyses were performed by Guelph  
26 Chemical Laboratories, Guelph, ON, Canada. Solution magnetic susceptibilities were  
27 determined by the Evans method.<sup>32</sup>

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**Synthesis of  $\text{CpCr}(\text{nacnac}^{\text{mes,mes}})$  (2):** Following a procedure similar to that

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4 previously reported for compound **1**,<sup>16</sup> compound (2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)NHC(Me)-  
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7 CHC(Me)N(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) (744 mg, 2.23 mmol) was dissolved in THF (12 mL).  
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10 *n*-BuLi (1.60 mL, 2.56 mmol, 1.15 equiv) was added dropwise and the resulting  
11  
12 yellow solution was stirred for 30 min at room temperature. In a separate Schlenk  
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14 flask, CrCl<sub>2</sub>(tmeda) (531 mg, 2.22 mmol, 1 equiv) was suspended in THF (35 mL)  
15  
16 followed by the addition of NaCp (1.25 mL, 2.50 mmol, 1.13 equiv). The resulting  
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18 mixture was stirred for 30 min at room temperature. To this solution, the lithium salt  
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20 prepared above was added dropwise and the mixture was stirred at room temperature  
21  
22 overnight. The solvent was evaporated *in vacuo* and the residue was extracted with  
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24 hexanes, followed by filtration through Celite. The solvent was again removed *in*  
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26 *vacuo* and the complex was dissolved in hexanes (20 mL), filtered and cooled to  
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28 -35°C for several days. 730 mg of black crystals were isolated in two crops. Yield:  
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30 73%.  $\mu_{\text{eff}}$  (Evans, C<sub>6</sub>D<sub>6</sub>) 4.8(1)  $\mu_{\text{B}}$ . Anal. Calcd. for C<sub>28</sub>H<sub>34</sub>CrN<sub>2</sub>: C, 74.64; H, 7.61;  
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32 N, 6.22. Found: C, 74.83; H, 7.96; N, 6.42. UV/Vis (hexanes;  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  
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34 M<sup>-1</sup>cm<sup>-1</sup>)): 308 (11700), 427 (7210), 573 (376).  
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44 **Synthesis of CpCr(nacnac<sup>dep,dep</sup>) (3):** Following a procedure similar to that  
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46 previously reported for compounds **1**,<sup>16</sup> compound (2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NHC(Me)-  
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48 CHC(Me)N(2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (1.00 g, 2.76 mmol) was dissolved in THF (10 mL) and  
49  
50 cooled to -40 °C in an acetonitrile/liquid nitrogen bath. *n*-BuLi (1.75 mL, 2.80 mmol,  
51  
52 1.01 equiv) was added dropwise and the resulting yellow solution was stirred for one  
53  
54 hour at -40°C. In a separate Schlenk flask, CrCl<sub>2</sub>(tmeda) (660 mg, 2.76 mmol, 1 equiv)  
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56 and NaCp (243 mg, 2.76 mmol, 1 equiv) were suspended in THF (15 mL) and the  
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4 contents stirred for 20 min at room temperature. To this solution, the lithium salt  
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6 prepared above was added dropwise via a cannula and the mixture was stirred at room  
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8 temperature overnight. The solvent was evaporated *in vacuo* and the residue was  
9  
10 extracted with pentane, followed by filtration through Celite. The solvent was again  
11  
12 removed in vacuo and the complex was dissolved in the minimum amount of pentane,  
13  
14 filtered and cooled to -80°C overnight to yield 462 mg of black crystals. Yield: 35%.  
15  
16  $\mu_{\text{eff}}$  (Evans, C<sub>6</sub>D<sub>6</sub>) 4.6(1)  $\mu_{\text{B}}$ . Anal. Calcd. for C<sub>30</sub>H<sub>38</sub>CrN<sub>2</sub>: C, 75.28; H, 8.00; N, 5.85.  
17  
18 Found: C, 74.97; H, 8.30; N, 5.96. UV/Vis (hexanes;  $\lambda_{\text{max}}$ , nm ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>)): 308  
19  
20 (12200), 428 (7910), 576 (411).  
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28 **Synthesis of CpCr(nacnac<sup>xy1,dipp</sup>) (4).** Using a procedure identical to that  
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30 described above for compound **2**, compound CpCr(nacnac<sup>xy1,dipp</sup>) (**4**, 223 mg) was  
31  
32 obtained as black crystals from (2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NHC(Me)CHC(Me)N(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)  
33  
34 (316 mg, 0.872 mmol). Yield: 54%.  $\mu_{\text{eff}}$  (Evans, C<sub>6</sub>D<sub>6</sub>) 4.4(1)  $\mu_{\text{B}}$ . Anal. Calcd for  
35  
36 C<sub>30</sub>H<sub>38</sub>CrN<sub>2</sub>: C, 75.28; H, 8.00; N, 5.85. Found: C, 75.00; H, 8.38; N, 5.62.  
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41 **Synthesis of CpCr(nacnac<sup>xy1,xy1</sup>)Cl (6).** Compound (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NHC(Me)-  
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43 CHC(Me)N(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (1.43 g, 4.67 mmol) was added to a Schlenk flask and  
44  
45 dissolved in THF (30 mL) and cooled to 0°C in an ice-water bath. *n*-BuLi (3.20 mL,  
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47 5.12 mmol, 1.10 equiv) was added dropwise and the resulting yellow solution was  
48  
49 allowed to warm to room temperature while stirring for 1 hour. The lithium salt was  
50  
51 then cannulated into a suspension of CrCl<sub>3</sub> (744 mg, 4.70 mmol, 1.00 equiv) in THF (20  
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53 mL) and stirred at room temperature overnight. NaCp (2.60 mL, 5.20 mmol, 1.11  
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55 equiv) was added to the solution which was again stirred at room temperature  
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overnight. The solvent was evaporated *in vacuo* and the residue was extracted with 40 mL of a hexanes/dichloromethane mixture (3:1), filtered through Celite and rinsed with hexanes (3 × 5 mL). The green to incident and orange to transmitted light filtrate was concentrated and cooled to -20°C to yield 1.66 g of dark green crystals over several days in three crops. Yield: 78%. Anal. Calcd. for C<sub>26</sub>H<sub>30</sub>CrN<sub>2</sub>Cl: C, 68.19; H, 6.60; N, 6.12. Found: C, 67.88; H, 6.50; N, 5.73. UV/Vis (hexanes; λ<sub>max</sub>, nm (ε, M<sup>-1</sup>cm<sup>-1</sup>)): 418 (7220), 581 (504).

**Synthesis of CpCr(nacnac<sup>xy1,xy1</sup>)OTs (7).** Compound **6** (1.28 g, 2.79 mmol) and AgOTs (781 mg, 2.80 mmol, 1.00 equiv) were placed in a Schlenk flask followed by the addition of THF (60 mL). The mixture was stirred overnight at room temperature, filtered through Celite and the solvent was evaporated *in vacuo*. The residue was extracted with 32 mL of a hexanes/dichloromethane mixture (4:1), filtered through Celite and rinsed with hexanes (2 × 5 mL). The green to incident and orange to transmitted light filtrate was cooled to -20°C to yield 1.40 g of black crystals over several days in four crops. Yield: 84%. Anal. Calcd. for C<sub>33</sub>H<sub>37</sub>CrO<sub>3</sub>N<sub>2</sub>S: C, 66.76; H, 6.28; N, 4.72. Found: C, 66.50; H, 6.20; N, 4.34. UV/Vis (diethyl ether; λ<sub>max</sub>, nm (ε, M<sup>-1</sup>cm<sup>-1</sup>)): 411 (8140), 571 (548).

**Synthesis of CpCr(nacnac<sup>xy1,xy1</sup>)CH<sub>2</sub>CMe<sub>3</sub> (8).** Compound **7** (600 mg, 1.01 mmol) was added to a Schlenk flask followed by the addition of diethyl ether (30 mL). Mg(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>·1.05(1,4-dioxane) (143 mg, 0.554 mmol, 0.549 equiv) in diethyl ether (5 mL) was added dropwise to the Schlenk. The mixture was stirred for 1.5 h at room temperature, the solvent was evacuated *in vacuo* and the residue was extracted with

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4 hexanes (30 mL), filtered through Celite and rinsed with hexanes (3 × 5 mL). The  
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6 solvent was again evacuated *in vacuo* and the residue was extracted with hexanes (15  
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8 mL), filtered and cooled to -35°C to yield 335 mg of black crystals over several days in  
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10 four crops. Yield: 67%. Anal. Calcd. for C<sub>31</sub>H<sub>41</sub>CrN<sub>2</sub>: C, 75.42; H, 8.37; N, 5.67.  
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12 Found: C, 75.27; H, 8.69; N, 5.66. UV/Vis (hexanes; λ<sub>max</sub>, nm (ε, M<sup>-1</sup>cm<sup>-1</sup>)): 404  
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14 (5170), 567 (1050).  
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20 **Synthesis of CpCr(nacnac<sup>xy1,xy1</sup>)OC(O)Me (9).** Compound **7** (259 mg, 0.566  
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22 mmol) and AgOAc (95.2 mg, 0.570 mmol, 1.01 equiv) were placed in a Schlenk flask  
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24 followed by the addition of THF (20 mL). The mixture was stirred overnight at room  
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26 temperature in the absence of light, the solvent was evacuated *in vacuo* and the residue  
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28 was extracted with 12 mL of a hexanes/dichloromethane mixture (3:1), filtered through  
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30 Celite and rinsed with hexanes (3 × 3 mL). The green filtrate was concentrated  
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32 slightly and cooled to -20°C to yield 187 mg of black crystals over several days in three  
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34 crops. Yield: 69%. UV/Vis (hexanes; λ<sub>max</sub>, nm (ε, M<sup>-1</sup>cm<sup>-1</sup>)): 411 (9160), 508 (446),  
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36 588 (574).  
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44 **General procedures for the radical polymerization of vinyl acetate. (a)**

45 **OMRP procedure: Cr<sup>II</sup> + V-70.** All polymerisations were conducted following the  
46  
47 same experimental protocol. A typical experiment is described here as a representative  
48  
49 example with complex **4** (Cr:V-70:VAc = 1:0.8:500). All operations were carried out  
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51 under a protective argon atmosphere. Complex **4** (41 mg, 0.086 mmol, 1 equiv) and  
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53 V-70 (18.7 mg 0.061 mmol, 0.8 equiv) were introduced in a Schlenk tube, followed  
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55 by the addition of degassed vinyl acetate (4 mL, 43 mmol, 500 equiv). The Schlenk  
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4 tube was degassed by three freeze-vacuum-thaw cycles and then immersed in an oil  
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6 bath preheated at 50°C. At the desired time, the Schlenk flask was rapidly cooled to  
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8 room temperature by immersion into iced water before sample withdrawal. The  
9  
10 monomer conversion was determined gravimetrically after removal of the  
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12 unconverted monomer under reduced pressure and the resulting residue was used for  
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SEC characterization.

**(b) OMRP procedure: Cr<sup>III</sup>-Np.** The experimental protocol is similar to that described above for the OMRP procedure: Cr<sup>II</sup> + V-70. As an example, complex **8** (17.5 mg, 0.035 mmol, 1 equiv) and VAc (4 mL, 43 mmol, 1200 equiv) were introduced into a Schlenk flask and stirred at room temperature. At the desired time, a sample was removed from the Schlenk flask and analyzed as described above.

**X-ray crystallography.** A single crystal of each compound was mounted on a glass fiber and centered on the optical path of a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K $\alpha$  radiation. The data were collected at a temperature of  $-100.0 \pm 0.1^\circ\text{C}$  in a series of  $\phi$  and  $\omega$  scans in  $0.50^\circ$  oscillations. Data were collected and integrated using the Bruker SAINT software package<sup>33</sup> and were corrected for absorption effects using the multi-scan technique (SADABS),<sup>34</sup> and for Lorentz and polarization effects. All structures were solved by direct methods with SIR97.<sup>35</sup> For structures **2**, **3** and **6** the Cp ring was found disordered among different orientations (four for **2** and two for **3** and **6**). Two of the four orientations in **2** are symmetry-related to the other two since the molecule sits on a twofold axis with half molecule in the asymmetric unit. Refinement of the population of each of these

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4 fragments resulted in near equivalent values of 0.25. For compounds **3** and **6**, the two  
5  
6 Cp orientations had equal population. In addition, one disordered half-molecule of  
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8 hexane is present in the asymmetric unit of **6**. This disorder was modeled in two  
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10 orientations, with restraints employed to maintain similar geometries. Compound **8**  
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12 crystallizes with two independent molecules in the asymmetric unit. Compound **9**  
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14 crystallizes as a two-component split crystal with the two components related by a 51°  
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16 rotation about the (0 0 1) real axis. Data were integrated for both twin components,  
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18 including both overlapping and non-overlapping reflections. The structure was  
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20 solved using non-overlapped data from the major twin component. Subsequent  
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22 refinements of **9** were carried out using HKLF 5 format data set containing complete  
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24 from component 2 and all overlapped reflections from component 1. The batch scale  
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26 refinement showed a roughly 53:47 ratio between the major and minor twin  
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28 components. All non-hydrogen atoms (except those of the Cp ring for compound **2**  
29  
30 and the disorder solvent atoms for **6**) were refined anisotropically. All hydrogen atoms  
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32 were placed in calculated positions but were not refined. All refinements were  
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34 performed using the SHELXTL crystallographic software package of Bruker-AXS.<sup>36</sup>  
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36 The molecular drawings were generated by the use of ORTEP-3<sup>37</sup> and POV-Ray.  
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Crystal data and structure refinement parameters are collected in the Supporting  
Information.

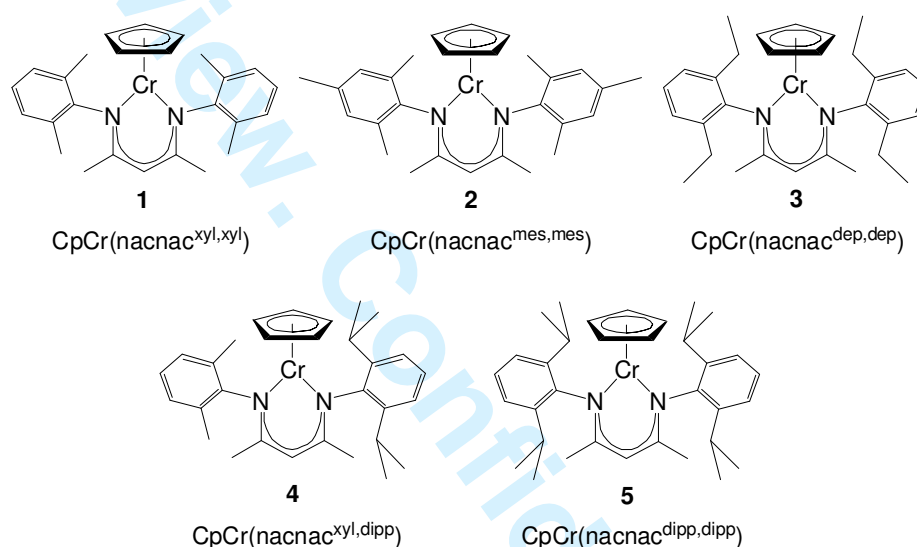
**Computational details.** QM/MM calculations were carried out by use of the  
Gaussian03 suite of programs<sup>38</sup> with use of the B3LYPfunctional<sup>39</sup> within the DFT  
methodology for the QM part and of the UFF<sup>40</sup> for the MM part. The basis set

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4 chosen for the QM calculations comprised the 6-31G\* set for the C, N and O atoms,  
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6 the 6-31G\*\* set for the H atoms, and the SDD set, which includes a pseudopotential,  
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8 augmented by an f polarization function with the optimized<sup>41</sup> 1.941 coefficient for the  
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10 Cr atom. The cutoff between the QM and MM parts was placed at the level of the  
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12 Ar-N bonds, with the N=C(Me)-CH-C(Me)=N diketiminato moiety being treated  
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14 quantomechanically together with the Cr atom, the Cp ring, and the CH(OAc)CH<sub>3</sub>  
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16 ligand, while the entire aryl substituents were handled at the MM level. The input  
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18 geometries were obtained or adapted from the crystallographically characterized  
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20 compounds. Spin contamination was negligible, all calculations converging with  $\langle S^2 \rangle$   
21  
22 close to the expected values (6 for the quintet state of Cr<sup>II</sup> - 6.022 for all three  
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24 compounds; 3.75 for the quartet state of Cr<sup>III</sup> - 3.824 for the Dipp derivative). The  
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26 values reported are the electronic energies without ZPVE correction.  
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## Results and Discussion

### (a) Syntheses and characterization of $\text{CpCr}^{\text{II}}(\text{nacnac})$

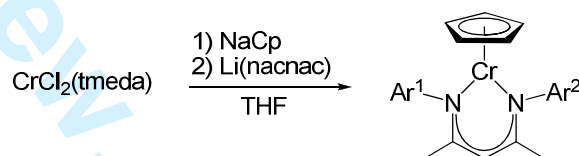
The  $\text{CpCr}^{\text{II}}(\text{nacnac})$  compounds used in this study are shown in Scheme 1 (xyl = 2,6-dimethylphenyl; mes = 2,4,6-trimethylphenyl; dep = 2,6-diethylphenyl; dipp = 2,6-diisopropylphenyl). Of these, only compounds **1**<sup>16</sup> and **5**<sup>14, 16</sup> have previously been described in the literature.



### Scheme 1

The new  $\text{CpCr}^{\text{II}}(\text{nacnac})$  complexes (**2-4**) were prepared following the literature procedure reported for **1**,<sup>14, 16</sup> which consists of the one-pot reaction of  $\text{CrCl}_2(\text{tmeda})$  with one equivalent of  $\text{NaCp}$ , followed by one equivalent of the appropriate  $\text{nacnacLi}$  salt (Scheme 2). Compounds **1-5** are highly air sensitive. The  $^1\text{H}$  NMR spectra of compounds **2-4** in  $\text{C}_6\text{D}_6$  all displayed multiple broad, overlapping, unassignable signals between 0 and 13 ppm. The magnetic susceptibilities of complexes **2-4** were determined using the Evans method,<sup>32</sup> and were consistent with the high spin  $\text{Cr}^{\text{II}}$

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4 configuration previously determined for **1**.<sup>14</sup> As previously reported for compound  
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7 **5**,<sup>14</sup> solutions of the Cr<sup>II</sup> complexes **1-4** are green to incident light with a distinctive  
8  
9 magenta color to transmitted light. They exhibit two very strong bands at 307–308  
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11 nm and 427–430 nm, comparable to those observed for three coordinate Cr<sup>II</sup> nacnac  
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13 alkyl complexes.<sup>42</sup> Compounds **1-5** also have a less intense single band at 558–576  
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18 nm.

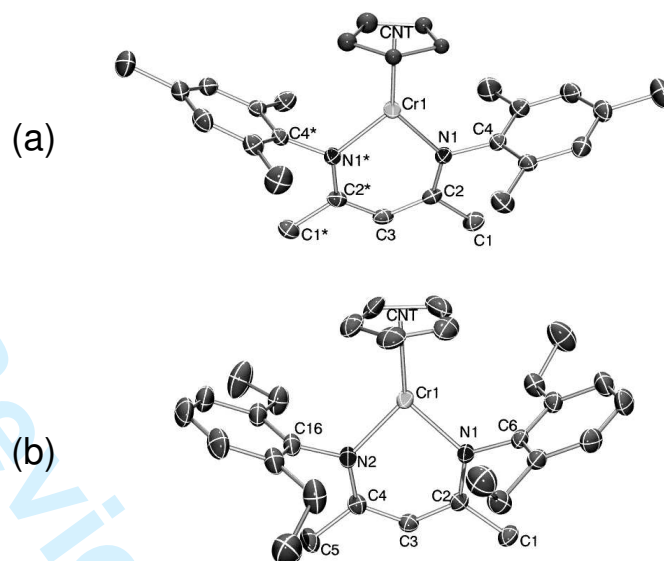


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## Scheme 2

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Compounds **2** and **3** have also been characterized by single crystal X-ray diffraction. The geometry of the two Cr<sup>II</sup> compounds (Figure 1) can be described as a “two-legged piano stool”, with the Cp ring centroid lying close to the plane defined by the Cr1, N1 and N2 or N1\* atoms. Relevant bond distances and angles are collected in Table 1. The bonding parameters for compounds **2** and **3** are very similar to those found in previously reported structures for CpCr(nacnac) Cr<sup>II</sup> complexes.<sup>14, 16</sup>



**Figure 1.** Views of compounds **2** (a) and **3** (b), with thermal ellipsoids drawn at the 50% probability level. All H atoms are omitted and only one Cp orientation is shown for clarity.

**Table 1.** Selected bond distances (Å) and angles (°) for compounds **2** and **3**.

	<b>2</b>	<b>3</b>
<i>Distances</i>		
CNT-Cr	2.00(1)	2.013(12)
Cr-N	2.007(2)	2.0276(12)
Cr-N		2.0260(12)
<i>Angles</i>		
CNT-Cr-N	134.0(3)	134.8(3)
CNT-Cr-N		134.5(3)
CNT-(CrN <sub>2</sub> ) <sup>a</sup>	177.7(3)	173.8(3)
N-Cr-N	91.2(1)	90.37(5)

<sup>a</sup>Angle between the CNT-Cr vector and the CrN<sub>2</sub> plane

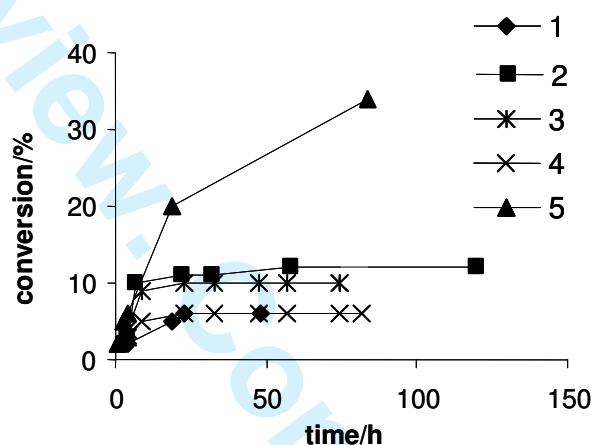
### (b) VAc polymerizations under OMRP: V-70 initiator

Before presenting the new results, it is necessary to review those already described in a recent communication.<sup>16</sup> Compound **1** was shown to trap radicals produced by V-70 in the presence of VAc, since a polymerization test with

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4 VAc/V-70/1 = 500:0.8:1 at 50°C for 4 h, and then at 90°C gave only an 11% monomer  
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6 conversion after 8 h ( $M_{n,SEC} = 11500$  vs. the expected value of 4730,  $M_w/M_n = 1.81$ ),  
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8 which no longer increased upon warming at 90°C for 66 h. Conversely, compound **5**  
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10 gave a much higher monomer conversion, since a polymerization with VAc/V-70/5 =  
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12 500:0.8:1 gave a linearly growing  $M_n$  up to a conversion of 70% ( $M_{n,SEC} = 67300$  vs.  
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14 the expected value of 30100,  $M_w/M_n = 1.80$ ) in 46 h under much milder conditions ( $T$   
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16 = 30°C). Although the controlling ability was poor (low initiator efficiency, high  
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18 polydispersity), the sustained polymerization and the  $M_n$  growth with conversion  
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20 demonstrated the reversibility of radical trapping. The hypothesis that both complexes  
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22 operate with formation of an organometallic dormant chain,  
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24  $Cp(nacnac^{Ar,Ar})Cr^{III}-PVAc$ , with a much weaker  $Cr^{III}-PVAc$  bond when Ar = dipp  
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26 (compound **5**) relative to Ar = xyl (compound **1**) seemed fully consistent with DFT  
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28 calculations of the bond strengths. The larger system with Ar = dipp was not  
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30 calculated, but a comparison of the bond dissociation energy for the two related  
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32 systems with Ar = xyl and Ph (19.7 and 28.4 kcal mol<sup>-1</sup> at the B3LYP/6-31G\* level,  
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34 respectively) indicated a strong effect of the steric congestion created by the aryl  
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36 substituents on the ability of the organometallic dormant chain to release free radicals  
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38 in solution.  
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52 We now report subsequent studies with compounds **1** and **5**, as well as with  
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54 compounds **2-4**, which revealed a more complex and interesting state of affairs.  
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56 Compounds **2-4** were synthesized with the idea of fine controlling the  $Cr^{III}-PVAc$   
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58 BDE, thus allowing the development of a system capable of yielding a suitable  
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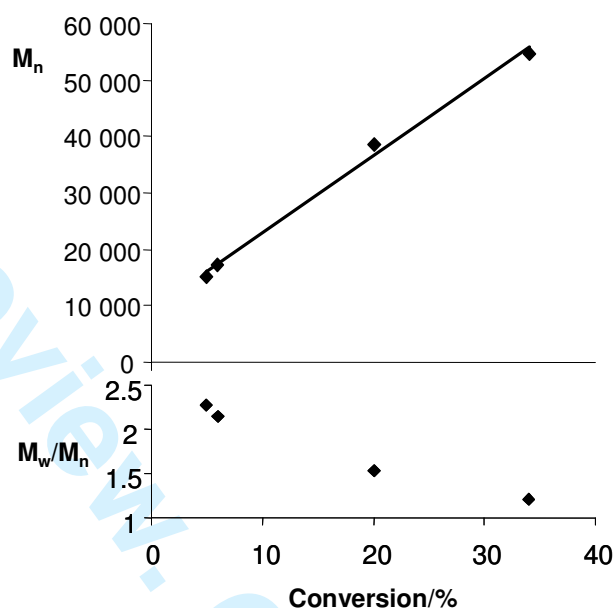
polymerization rate and degree of control. However, a steric bulk increase on going from **1** to **2** and then to **3** and **4** did not produce any significant labilization of the Cr<sup>III</sup>-PVAc bond since the polymerization did not proceed in any of these cases beyond 12% conversion for experiments carried out at 90°C, see Figure 2. Indeed, the polymerization essentially stops in each case after an initial burst of monomer consumption, within the first 5-10 hours.



**Figure 2.** Conversion as a function of time for the VAc polymerization initiated by V-70 in the presence of compounds **1-5**. Conditions: VAc/V-70/Cr<sup>II</sup> = 500:0.8:1. T = 50°C for 4 h, then 90°C.

On the other hand, new polymerization experiments with compound **5**, run at higher temperatures, gave a lower apparent polymerization rate constant., only 34% conversion after 84 h at 90°C. The  $M_n$  value increased linearly with conversion and the  $M_w/M_n$  decreased to reach a value of only 1.21 for the final sample (see Figure 3), although the  $M_n$  was much greater than expected (54 800 vs. 14 600). A polymerization process that takes place rapidly under mild conditions (30°C)<sup>16</sup> cannot become slower at a higher temperature while maintaining the same mechanism. It is

more logical to think of a deactivation process (*vide infra*).



**Figure 3.** Number average molecular weight and polydispersity index for the PVAc obtained in the presence of compound **5**. Conditions are as in Figure 2.

**(c) Design of a single-component chromium reagent as OMRP initiator.**

Well-defined  $\text{Cr}^{\text{III}}\text{-R}$  complexes could serve as single-component OMRP reagents if they possessed a Cr-alkyl bond that was sufficiently weakened by steric interactions to readily undergo homolysis.<sup>12, 13</sup> To date, the success of synthetic routes to  $\text{CpCr}(\text{nacnac})\text{X}$  complexes has depended on the degree of steric bulk in the target molecule. For the 2,6- $i\text{Pr}_2$  substituted system,  $\text{CpCr}(\text{nacnac}^{\text{dipp,dipp}})\text{Cl}$  was difficult to prepare by salt metathesis, and did not react cleanly with Grignard reagents.<sup>14</sup> In contrast, reducing the size of the ortho substituents in the nacnac ligands was found to greatly improve both the synthesis and salt metathesis reactivity.<sup>15, 43</sup> For example,  $\text{CpCr}(\text{nacnac}^{\text{xy1,xy1}})\text{Me}$  was readily prepared from  $\text{CpCr}(\text{nacnac}^{\text{xy1,xy1}})\text{Cl}$  with  $\text{MeMgI}$ .<sup>15</sup>

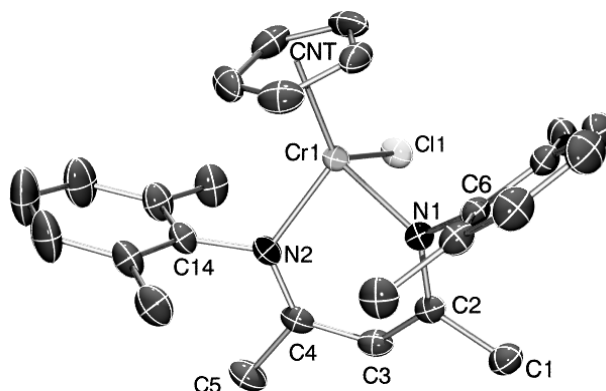
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4 Synthesis of the corresponding  $\text{CpCr}(\text{nacnac}^{\text{dipp,dipp}})\text{Me}$  had necessitated the use of the  
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7 corresponding  $\text{Cr}^{\text{III}}$  triflate complex.<sup>14</sup>  
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10 Isolated  $\text{CpCr}(\text{nacnac}^{\text{xy1,xy1}})\text{Me}$  does not serve as an effective single-component  
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12 OMRP reagent. When 16.1 mg of this  $\text{Cr}^{\text{III}}$  methyl complex was dissolved in 4 mL of  
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14 neat vinyl acetate, only a 9% mass conversion was observed after 48 hours at room  
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16 temperature. The resulting polymer had both a high  $M_n$  (83900 compared to 9140  
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18 expected  $M_n$ ) and a high PDI of 3.4. The lack of steric pressure on the small methyl  
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20 ligand and the relative instability of the  $\text{CH}_3\cdot$  radical should make the  $\text{Cr}^{\text{III}}\text{-CH}_3$  BDE  
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22 high and the homolytic dissociation unfavorable. Initiation to form  $\text{CH}_3\cdot$  and the  $\text{Cr}^{\text{II}}$   
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24 radical trap will thus be inefficient at room temperature. However, the observation of  
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26 a small amount of uncontrolled polymerization leading to high  $M_n$  is consistent with  
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28 the slow release of  $\text{CH}_3\cdot$  radicals which then react rapidly in neat vinyl acetate.<sup>44</sup>  
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36 For an efficient single component OMRP reagent, a  $\text{Cr}^{\text{III}}$  alkyl complex is  
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38 required that has a low  $\text{Cr-R}$  BDE and that generates a  $\text{R}\cdot$  radical capable of reacting  
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40 rapidly with vinyl acetate. The steric pressure exerted by the neopentyl ligand has  
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42 often been used to encourage not only intramolecular deprotonation reactions,<sup>17-20</sup> but  
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44 also metal-alkyl bond homolysis.<sup>21-23</sup> While several classes of even-electron  
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46 monomeric chromium neopentyl complexes are known for  $\text{Cr}^{\text{II}}$ ,<sup>31, 45</sup>  $\text{Cr}^{\text{IV}}$ ,<sup>46, 47</sup> and  
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48  $\text{Cr}^{\text{VI}}$ ,<sup>48-50</sup> well-defined  $\text{Cr}^{\text{III}}$  neopentyl complexes are relatively unexplored.<sup>51</sup>  
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55 The synthesis of compound  $\text{CpCr}(\text{nacnac}^{\text{xy1,xy1}})\text{Cl}$  (**6**) was achieved by reacting  
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57  $\text{CrCl}_3$  with one equivalent of  $\text{Li}(\text{nacnac}^{\text{xy1,xy1}})$ , followed by one equivalent of  $\text{NaCp}$  to  
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59 yield an air stable crystalline solid. The geometry of **6** (Figure 4) can be described as a  
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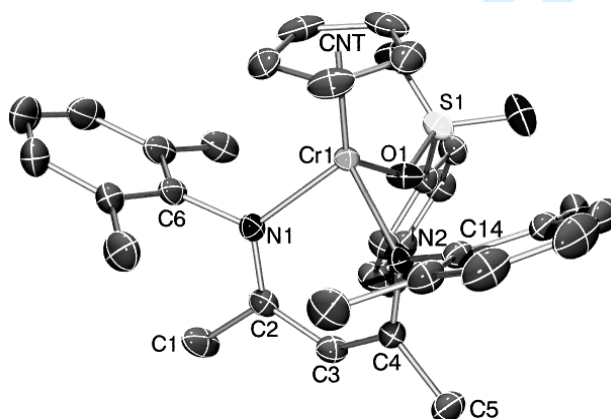
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4 “three-legged piano stool” and is ubiquitous of half-sandwich Cr<sup>III</sup> complexes. The  
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6 Cr–Cl bond length of 2.3082(5) Å is similar to that found in CpCr(nacnac<sup>dipp,dipp</sup>)Cl,<sup>14</sup>  
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8 as well as other cyclopentadienyl Cr<sup>III</sup> complexes with terminal Cl groups, like  
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10 CpCr(acac)Cl and Cp\*Cr(acac)Cl (Cr–Cl of 2.299(1) and 2.307(1) Å, respectively).<sup>52</sup>  
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12 It is also similar to the Cr–Cl distance in 6-coordinate Cr<sup>III</sup> nacnac complexes with  
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14 terminal Cl ligands (2.346(1) Å for Cr(nacnac<sup>Ph,Ph</sup>)Cl<sub>2</sub>(THF)<sub>2</sub><sup>53</sup> and 2.2947(12) Å for  
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16 Cr(nacnac<sup>dipp,dipp</sup>)(O<sub>2</sub>CMe)Cl(THF)<sup>54</sup>), while 5-coordinate Cr<sup>III</sup> nacnac complexes  
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18 display shorter Cr–Cl bond lengths (2.233(2) Å and 2.2294(14) for the terminal  
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20 chloride ligands in [Cr(nacnac<sup>dipp,dipp</sup>)Cl(μ-Cl)]<sub>2</sub> and Cr(nacnac<sup>dipp,dipp</sup>)[(OCPh)<sub>2</sub>CH]Cl,  
21  
22 respectively).<sup>54</sup> Unlike the geometries of **2** and **3**, the Cr atom deviates significantly  
23  
24 from the plane of the nacnac ligand, toward the Cl atom. The Cr in **6** lies 0.615(3) Å  
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26 out of the imaginary plane defined by the N1–C2–C4–N2 atoms, which is smaller  
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28 than the 0.72 Å out-of-plane distortion previously observed for the bulkier  
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30 CpCr(nacnac<sup>dipp,dipp</sup>)Cl.<sup>14</sup> Relative to the Cr<sup>II</sup> structures, the Cr–CNT distance is  
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32 slightly shorter, whereas the Cr–N distances are not significantly different.  
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**Figure 4.** Thermal ellipsoid diagram (50%) of compound **6**. All H atoms are omitted and only one Cp orientation is shown for clarity. Selected bond lengths (Å):

Cr(1)–N(1), 2.018(2); Cr(1)–N(2), 2.020(2); Cr(1)–CNT, 1.92(2); Cr(1)–Cl(1), 2.3082(5). Selected bond angles (deg): N(1)–Cr(1)–N(2), 90.47(7); N(1)–Cr(1)–Cl(1), 94.28(5); N(2)–Cr(1)–Cl(1), 93.14(5); CNT–Cr(1)–N(1), 124.8(4); CNT–Cr(1)–N(2), 125.0(4); CNT–Cr(1)–Cl(1), 120.34(6); CNT–(CrN<sub>2</sub>)<sup>a</sup>, 160.5(4). <sup>a</sup>Angle between the CNT–Cr vector and the CrN<sub>2</sub> plane.

While **6** is a useful precursor to CpCr(nacnac<sup>xy1,xy1</sup>)Me,<sup>15</sup> attempts to install more sterically demanding alkyl ligands once again required the use of a better leaving group. The reaction of compound **6** with one equivalent of AgOTs provides compound **7** in high yields as an air stable crystalline solid (Figure 5). Preliminary reactions between **6** and AgOTf or AgOTs had indicated that the Cr<sup>III</sup> tosylate was less air sensitive and more crystalline than the Cr<sup>III</sup> triflate complex. The Cr–O bond length in **7**, 1.9839(15) Å, is slightly shorter than the 2.030(1) observed for the CpCr(nacnac<sup>dipp,dipp</sup>)(OTf),<sup>14</sup> which may be attributable to the lower electron withdrawing power of the *para*-tolyl substituent compared to CF<sub>3</sub>, the decreased steric demand of the 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> substituted nacnac, or both.

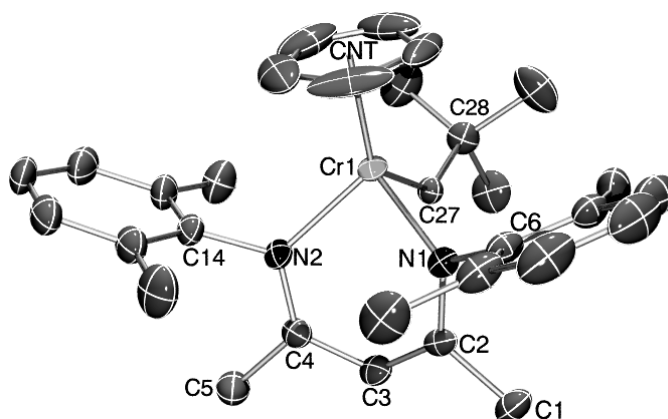


**Figure 5.** Thermal ellipsoid diagram (50%) of compound **7**. All H atoms are omitted for clarity. Selected bond lengths (Å): Cr(1)–N(1), 2.0038(16); Cr(1)–N(2), 2.0019(17); Cr(1)–CNT, 1.896; Cr(1)–O(1), 1.9839(15). Selected bond angles (deg): N(1)–Cr(1)–N(2), 90.17(7); N(1)–Cr(1)–O(1), 91.45(7); N(2)–Cr(1)–O(1), 92.48(7);

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4 CNT–Cr(1)–N(1), 125.74; CNT–Cr(1)–N(2), 123.82; CNT–Cr(1)–O(1), 123.32;  
5 Cr(1)–O(1)–S(1), 135.77(9).  
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10 The reaction of compound **7** with one-half equivalent of  
11 Mg(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>·1.05(1,4-dioxane) gave CpCr(nacnac<sup>xy1,xy1</sup>)Np (**8**), where Np =  
12 neopentyl, CH<sub>2</sub>CMe<sub>3</sub>. The use of the halide-free dialkyl Mg reagent was required to  
13 avoid unwanted substitution of the tosylate ligand in **7** with a halide prior to alkylation  
14 to form **8**. Complex **8** was found to be highly soluble in non-polar solvents, similar to  
15 the previously reported CpCr(nacnac<sup>xy1,xy1</sup>)Me.<sup>14, 15</sup> The structural characterization of **8**  
16 has been achieved by single crystal X-ray diffraction (Figure 6). The Cr–C(27) bond  
17 is significantly elongated in **8** (2.136(3) Å) compared to the 2.076(2) Å observed  
18 previously for the corresponding Cr<sup>III</sup> methyl complex.<sup>15, 43</sup> The Cr–N bond lengths in  
19 **8** are also slightly longer, and the Cr–C(27)–C(28) angle is 135.1(2)°, indicative of the  
20 strain imposed by the <sup>t</sup>Bu substituent of the neopentyl ligand. Solutions of **8** are  
21 purple, exhibiting strong bands in the UV-visible spectrum at 404 nm and 567 nm.  
22 The strong absorbance around 550 nm seems characteristic of CpCr(nacnac)(alkyl)  
23 complexes: the increase in absorbance at 530 nm due to formation of  
24 CpCr(nacnac)Me was used to monitor the kinetics of iodomethane activation with  
25 CpCr(nacnac) complexes **1–3**.<sup>15</sup> Although **8** was stable in solution to allow for  
26 recrystallization from hexanes, decomposition took place upon dilution (necessary for  
27 UV/Vis characterization) to yield CpCr(nacnac<sup>xy1,xy1</sup>), **1**. The decrease in stability of **8**  
28 at high dilution is consistent with the facile homolytic Cr–C bond cleavage,  
29 paralleling the reactivity of other neopentyl complexes,<sup>21–23</sup> with formation of  
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compound **1** and an extremely reactive neopentyl radical, and indicated the potential for complex **8** to be used as a single component reagent to initiate and control the radical polymerization of vinyl acetate.

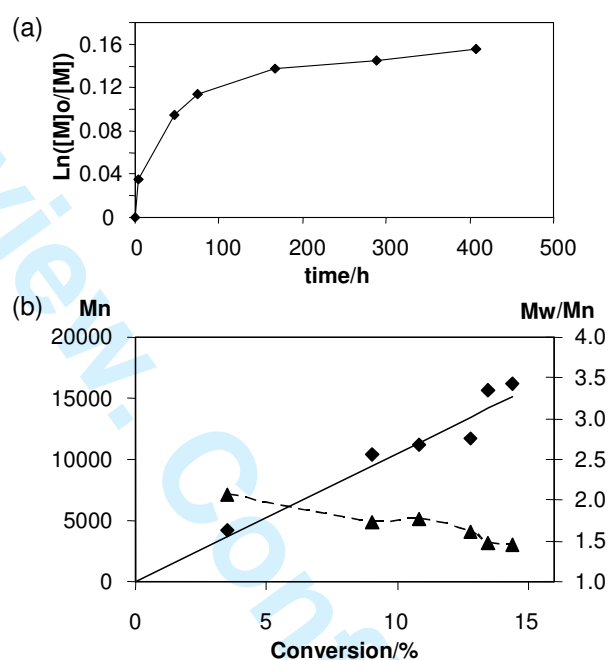


**Figure 6.** Thermal ellipsoid diagram (50%) of compound **8**. Compound **8** has two independent molecules in the crystal lattice, only one is shown and all H atoms are omitted for clarity. Selected bond lengths (Å): Cr(1)–N(1), 2.046(2); Cr(1)–N(2), 2.051(2); Cr(1)–CNT, 1.949; Cr(1)–C(27), 2.136(3). Selected bond angles (deg): N(1)–Cr(1)–N(2), 89.71(9); N(1)–Cr(1)–C(27), 93.50(10); N(2)–Cr(1)–C(27), 93.63(10); CNT–Cr(1)–N(1), 123.03; CNT–Cr(1)–N(2), 122.29; CNT–Cr(1)–C(27), 125.39; Cr(1)–C(27)–C(28), 135.1(2).

#### (d) OMRP of VAc with complex **8**

Polymerizations of VAc in the presence of complex **8** (VAc/**8** = 1200:1) at room temperature gave a linearly growing  $M_n$  up to a monomer conversion of 14% after 400 h ( $M_{n,SEC} = 16200$  vs. the expected value of 15100,  $M_w/M_n = 1.46$ ), see Figure 7. These results contrasts with the uncontrolled polymerization observed with  $CpCr(nacnac^{xyl,xyl})Me$  under the same conditions, as discussed above. There is no visible induction period and the good agreement between the observed and calculated  $M_n$  demonstrates the increased initiator efficiency compared with the OMRP reactions

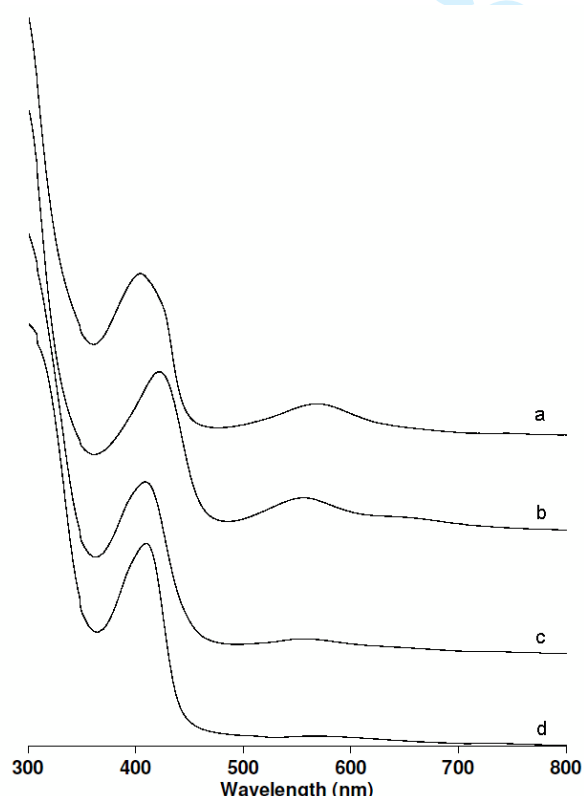
with the V-70 initiator. However, the progressive decrease of the polymerization rate constant (decreasing slope in Figure 7a) suggests that partial deactivation of the growing chains occurs, which also causes the broad molecular weight distribution.



**Figure 7.** (a)  $\ln([VAc]_0/[VAc])$  as a function of time for the VAc polymerization initiated by compound **8**. Conditions: VAc/**8** = 1200:1. T = room temp. (b) Variation of the  $M_{n,SEC}$  (diamonds) and  $M_w/M_n$  (triangles) as a function of conversion; the solid line represents  $M_{n,th}$ .

Spectroscopic analysis of the polymerization reaction of vinyl acetate with **8** revealed absorbance peaks at 422 nm and 556 nm, at a reaction time of 10 min, indicating that **8** had been completely consumed, presumably being transformed into the  $CpCr(nacnac^{xyl,xyl})(PVAc)$  dormant species. This is again in contrast to the previously discussed reaction of  $CpCr(nacnac^{xyl,xyl})Me$  in vinyl acetate, where after 48 hours the absorbance peak of the  $Cr^{III}$  methyl starting material was still evident at 546 nm. Throughout the progress of the polymerization reaction initiated by **8**, the

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4 UV/Vis spectrum further evolved to yield a shift of the major band toward higher  
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6 frequency (412 nm), while the 556 nm band decreased in intensity, see Figure 8. This  
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8 spectral evolution parallels the observed decrease in polymerization rate (Figure 7).  
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10 After 400 h of polymerization process, the sample was heated at 70°C for 3.5 h to  
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12 produce a colour change from purple to green (incident light) and orange (transmitted  
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14 light) with the higher energy absorption band increasing in intensity and the 556 nm  
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16 band disappearing and being replaced by a less intense band at 575 nm. The results  
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18 suggested that, even though the rate of polymerization had slowed down significantly  
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20 (see Figure 7), there was still some  $\text{CpCr}^{\text{III}}(\text{nacnac}^{\text{xyl,xyl}})(\text{PVAc})$  compound present  
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22 after 400 h of polymerization, which underwent further reactivity once heated.  
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**Figure 8.** Evolution of the UV/Vis properties during the VAc polymerization controlled by compound **8** (conditions as shown in Figure 7). (a) Initial spectrum of compound **8**; (b) after 10 min of polymerization; (c) after 400 h of polymerization; (d) after warming to 70°C (spectrum of the decomposition product).

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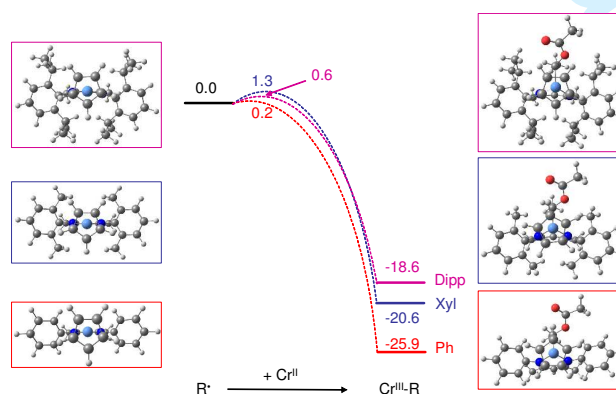
It is striking to compare the behaviour of the polymerization initiated by compound **8** on one side (14% in 400 h at room temperature, Figure 7) with that initiated by the 1/V-70 mixture (5% in 50 h at 90°C, Figure 2), both leading in principle to the same OMRP equilibrium. This clearly proves that the  $\text{CpCr}^{\text{III}}(\text{nacnac}^{\text{xyl,xyl}})(\text{PVAc})$  dormant chain can be reversibly reactivated under mild conditions to sustain the OMRP of vinyl acetate, but it also suffers irreversible thermal deactivation, even at room temperature at a slow rate, and much faster at more elevated temperatures.

It is interesting to compare the relatively slow polymer growth in the presence of the  $\text{CpCr}(\text{nacnac}^{\text{xyl,xyl}})$  system and the previously reported<sup>16</sup> faster polymer growth in the presence of the  $\text{CpCr}(\text{nacnac}^{\text{dipp,dipp}})$  system (70% conversion in 46 h at 30°C). This difference confirms the previously proposed steric effect on the homolytic bond dissociation energy, which is further investigated at the theoretical level in the next section.

#### (e) DFT study of the OMRP trapping processes

The previous communication reported geometry optimizations at the full QM level using density functional theory (DFT) for  $\text{CpCr}^{\text{II}}(\text{nacnac}^{\text{Ar,Ar}})$  and  $\text{CpCr}^{\text{III}}(\text{nacnac}^{\text{Ar,Ar}})(\text{CHMeOOCMe})$  (a model of the OMRP dormant chain), leading to the calculation of the  $\text{Cr}^{\text{III}}\text{-C}$  BDE values of 28.4 and 19.7 kcal/mol for Ar = Ph and Xyl, respectively.<sup>16</sup> This shows a tremendous steric effect of the nacnac aryl

substituents on the Cr<sup>III</sup>-C bond fragility, which is also reflected in the optimized Cr<sup>III</sup>-C distances (2.109 and 2.124 Å, respectively). Calculations of the Ar = dipp system were not carried out because too time consuming at the full QM level. We now report QM/MM results for the same systems as well as for the bulkier dipp system in terms of both energetics and radical trapping barriers. The energetic results and views of the optimized structures are shown in Figure 9, whereas the essential bonding parameters are given in Table 2. All optimized geometries are available in the Supporting Information in the form of Cartesian coordinates. The calculations were carried out with imposition of the experimentally determined spin state ( $S = 3/2$  for the alkylchromium(III) complexes and  $S = 2$  for the chromium(II) trapping species), leading to calculated structure in excellent agreement with those determined crystallographically for complexes **1** and **5**. The calculated Cr-C bond lengths for the cyclopentadienyl ligand are longer than those observed experimentally:<sup>55</sup> the CNT-Cr distances for the Cr<sup>II</sup> Xyl and Dipp nacnac complexes were 2.022 and 2.016 Å for **1** and **5**, respectively.



**Figure 9.** Optimized geometries and QM/MM relative energies (in kcal/mol) of geometry-optimized CpCr<sup>II</sup>(nacnac<sup>Ar,Ar</sup>) and CpCr<sup>III</sup>(nacnac<sup>Ar,Ar</sup>)(CHMeOOCMe) for

Ar = Ph, Xyl and Dipp.

**Table 2.** Selected bond distances (Å) and angles (°) for the B3LYP//UFF optimized geometries.

Complex	CpCr <sup>II</sup> (nacnac <sup>Ar,Ar</sup> )			TS			CpCr <sup>III</sup> (nacnac <sup>Ar,Ar</sup> )(R) <sup>a</sup>			
	Ar	Ph	Xyl	Dipp	Ph	Xyl	Dipp	Ph	Xyl	Dipp
<i>Distances</i>										
CNT-Cr	2.081	2.081	2.070	2.072	2.080	2.079	2.070	2.081	2.096	
Cr-N	2.014	2.009	2.028	2.021	2.024	2.051	2.018	2.033	2.062	
	2.014	2.009	2.030	2.020	2.021	2.040	2.024	2.034	2.088	
Cr-C	-	-	-	4.290	3.440	3.396	2.091	2.115	2.139	
<i>Angles</i>										
CNT-Cr-N	133.3	133.6	132.3	134.2	131.7	131.9	121.6	123.5	123.8	
	133.2	133.6	133.9	133.3	131.0	132.1	124.4	124.5	124.5	
CNT-Cr-C				108.7	106.0	101.4	117.6	114.9	114.1	
CNT-(CrN <sub>2</sub> ) <sup>b</sup>	175.8	179.5	178.5	178.6	161.4	167.5	141.8	143.3	143.7	
N-Cr-N	93.3	92.7	93.8	92.4	91.6	93.4	92.3	90.1	91.7	
N-Cr-C	-	-	-	77.5	92.2	92.3	97.5	100.2	102.0	
				75.1	91.4	89.1	97.2	97.8	94.8	

<sup>a</sup> R = CHMeOOCMe. <sup>b</sup> Angle between the CNT-Cr vector and the CrN<sub>2</sub> plane

The energetic results in terms of DBE(Cr<sup>III</sup>-C) for the Ph and Xyl systems are quite close to those previously obtained at the full QM level, although the steric labilization exerted by the four Me groups is predicted as less severe by the QM/MM calculations relative to the full QM level. The present calculation uses a polarized SDD basis set for the Cr atom, which is considered as more balanced than the LANL2DZ basis set without polarization functions previously used in the full QM calculations.<sup>16</sup> The presence of a steric effect is confirmed on going from the Xyl to the Dipp substituents, where the four *i*Pr groups induce a further Cr<sup>III</sup>-C bond labilization by 2.0 kcal/mol relative to four Me groups. This labilization is accompanied by a significant lengthening of the Cr<sup>III</sup>-C bond, in the order Ph (2.091 Å)

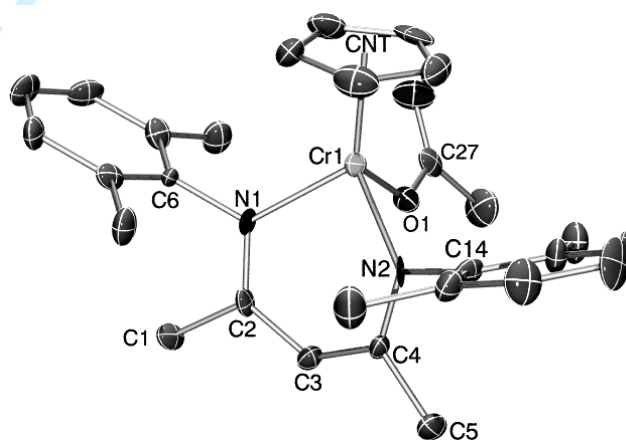
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4 < Xyl (2.115 Å) < Dipp (2.139 Å).  
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7 We have also optimized the transition state leading from the  $\text{CpCr}^{\text{II}}(\text{nacnac}^{\text{Ar,Ar}})$   
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9 complex plus free radical to the OMRP dormant species. The coordination geometry  
10 is quite close to that of the  $\text{Cr}^{\text{II}}$  complex with a rather long  $\text{Cr}^{\text{II}}\text{-C}$  distance, *i.e.* the  
11 transition state is early for the radical trapping process, consistent with the very low  
12 calculated energy barrier. The barrier is lowest, as expected, for the less encumbered  
13 Ph derivative, whereas the most encumbered Dipp system yields a lower barrier than  
14 the Xyl system with intermediate steric demand. Although the barrier for trapping  
15 the radical is very low for all three systems, the unexpectedly lower barrier for the  
16 Dipp derivative may be attributable to the structure of the  $\text{Cr}^{\text{II}}$  complex. The  
17 calculated ground state structure of  $\text{CpCr}(\text{nacnac}^{\text{dipp,dipp}})$  faithfully reproduces the  
18 slight bowing of the N-aryl substituents out of the plane defined by the nacnac ligand  
19 that was observed in the X-ray structure of 1.<sup>14</sup> As suggested by a helpful reviewer,  
20 this sterically-induced initial deformation of the  $\text{Cr}^{\text{II}}$  Dipp complex may permit a  
21 slightly lower energy approach of the alkyl radical compared to  $\text{CpCr}(\text{nacnac}^{\text{xyl,xyl}})$   
22 which does not display this distortion.  
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#### 50 (f) Isolation of the deactivated complex

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52 As discussed above, UV-vis analysis of the  $\text{Cr}^{\text{III}}$  neopentyl compound in vinyl  
53 acetate suggested that while **8** was consumed within minutes at room temp, a  
54 subsequent thermal decomposition reaction occurred and that this is accelerated by  
55 heating. To determine the ultimate fate of the organochromium complex, the  
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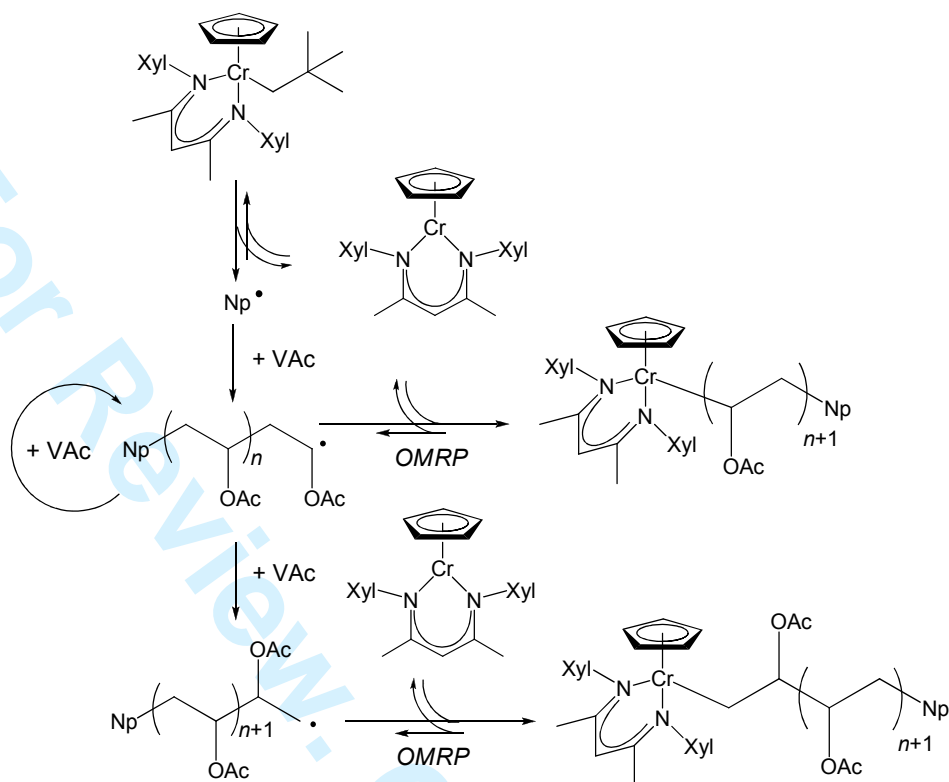
thermolized reaction mixture of 35.8 mg of **8** in 4 mL of vinyl acetate was evacuated and the unknown Cr species was extracted from the PVAc with diethyl ether. After filtration, concentration, and storage at  $-35\text{ }^{\circ}\text{C}$  for two weeks, 7.9 mg of X-ray quality crystals of  $\text{CpCr}(\text{nacnac}^{\text{xy1,xy1}})\text{OC}(\text{O})\text{Me}$  (**9**) (Figure 10) were obtained, corresponding to a 23% isolated yield based on **8**.



**Figure 10.** Thermal ellipsoid diagram (50%) of **9**. All H atoms are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ): Cr(1)–N(1), 2.010(5); Cr(1)–N(2), 2.004(6); Cr(1)–C(1), 1.914; Cr(1)–O(1), 1.952(5); C(27)–O(1), 1.278(9); C(27)–O(2), 1.230(9). Selected bond angles (deg): N(1)–Cr(1)–N(2), 90.7(2); N(1)–Cr(1)–O(1), 92.7(2); N(2)–Cr(1)–O(1), 88.6(2); C(1)–Cr(1)–N(1), 124.94; C(1)–Cr(1)–N(2), 123.34; C(1)–Cr(1)–O(1), 125.92; Cr(1)–O(1)–C(27), 133.6(5).

The independent synthesis of **9** was achieved by the reaction of **6** with one equivalent of  $\text{AgOAc}$ , with UV-visible spectroscopic analysis confirming that **9** was the thermal decomposition product of the polymerization reaction. Upon reexamination of the V-70 initiated OMRP experiments, UV-vis spectroscopy confirmed that the  $\text{Cr}^{\text{III}}$  acetate complex was a common termination pathway for all of the Cr mediated vinyl acetate polymerization reactions conducted at elevated

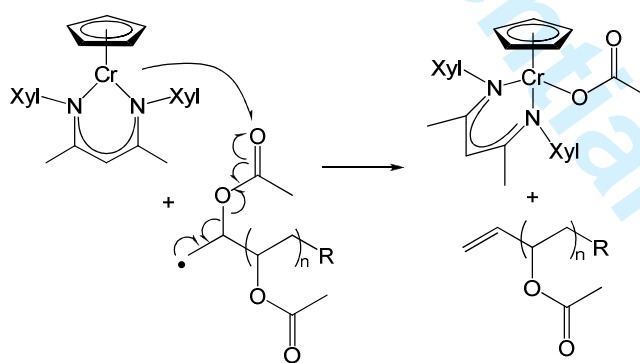
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4 temperatures. Suspicions arose about the possibility of Cr<sup>III</sup> acetate formation by  
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6 oxidative addition of a =CH-OC(O)CH<sub>3</sub> moiety from the polymer chain. However, a  
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8 control experiment showed no signs of reactivity for compound **1** towards  
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10 commercially obtained PVAc upon heating to 50°C for 24 h. Similarly, prolonged  
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12 heating of **1** in vinyl acetate does not result in any change in the UV/Vis spectrum of **1**.  
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15 These results suggested a more complicated mechanism for the formation of  
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17 CpCr(nacnac)OAc. The proposed mechanism for the formation of **9** is that of  
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19 β-acetate elimination arising from a 2,1-insertion (head-to-head) of the monomer, as  
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21 shown in Scheme 3. Head-to-head insertion is known to be particularly problematic  
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23 for the radical polymerization of vinyl acetate, due to the relatively poor  
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25 regioselectivity of radical addition.<sup>1,5</sup> Note that the 2,1-insertion step may lead to the  
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27 generation of a dormant species with a presumably stronger Cr<sup>III</sup>-C bond, which could  
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29 also contribute for a gradual slow down of the polymerization process.  
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Scheme 3

Elimination of  $\beta$ -acetate groups has been well documented as a decomposition mode in attempts to copolymerize ethylene and vinyl acetate with Ni and Pd catalysts.<sup>2, 3</sup> We point out, however, that the  $\beta$ -acetate elimination process from the newly formed dormant species is not likely to follow a classical  $\beta$ -elimination mechanism, because this requires an open coordination site on Cr capable of accepting the two additional electrons furnished by the incoming acetate group. While the metal is electronically unsaturated (15 electrons) and metal-based orbitals are indeed available, the latter are however half-occupied because of the ubiquitous spin quartet configuration of half-sandwich Cr<sup>III</sup>. Expansion to a 17-electron configuration would require an energetically costly (for Cr<sup>III</sup>) electron pairing process.<sup>56-58</sup> A likely

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4 alternative is acetate group transfer from the  $\beta$ -C atom of the radical chain to the Cr  
5 center, as shown in Scheme 4. Unfortunately, we were unable to observe vinyl chain  
6 end resonances in the  $^{13}\text{C}$  NMR spectrum of the polymer isolated from thermolysis of  
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10 end resonances in the  $^{13}\text{C}$  NMR spectrum of the polymer isolated from thermolysis of  
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12 **8** in vinyl acetate to provide additional support for the mechanism proposed in  
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14 Scheme 4. Homolytic bond rupture followed by atom (or group) transfer has been  
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16 observed for R-Co(porphyrin) complexes where the coordination geometry has no *cis*  
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18 vacant site available to accommodate the migrating atom or group.<sup>59</sup> It is quite  
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20 vacant site available to accommodate the migrating atom or group.<sup>59</sup> It is quite  
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22 possible that, following a 2,1-insertion, the resulting  $\text{CH}_2$ -terminated radical  
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24 undergoes competitive  $\beta$ -acetate transfer as shown in Scheme 4 or  $\text{Cr}^{\text{III}}$ -C bond  
25  
26 formation as shown in Scheme 3, thus yielding a mixture of acetate complex and a  
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28 less active  $\text{Cp}(\text{nacnac}^{\text{xyl,xyl}})\text{Cr}-\text{CH}_2\text{CH}(\text{OAc})\text{-PVAc}$  dormant species. Only upon  
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30 warming the latter can be reactivated and eventually be completely transformed into  
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32 the final acetate product.  
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Scheme 4

## Conclusions

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7 The present study has revealed a more complex situation than previously  
8 appreciated for the OMRP of vinyl acetate mediated by half-sandwich Cr<sup>II</sup> complexes  
9 of type CpCr(nacnac). The new data reported here confirm the sterical labilization of  
10 the Cr<sup>III</sup>-PVAc bond, with the more encumbering nacnac<sup>dipp,dipp</sup> ligand resulting in a  
11 faster apparent rate constant for polymer growth than the nacnac<sup>xy1,xy1</sup> ligand. However,  
12 the relatively stronger bond of Cp(nacnac<sup>xy1,xy1</sup>)Cr-PVAc is still sufficiently labile to  
13 sustain the OMRP of vinyl acetate even at room temperature. On the other hand, an  
14 irreversible deactivation process comes into play, slowly at room temperature and  
15 faster upon warming, to yield a new material now firmly identified as the acetate  
16 complex, CpCr(nacnac<sup>xy1,xy1</sup>)OAc.  
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43 Conway for obtaining single crystals of **3** and **7**, respectively, suitable for X-ray  
44 diffraction.  
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**Supporting Information Available:** A listing of the Cartesian coordinates and final

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4 energies of all calculated complexes, UV-visible spectra of complexes **1**, **2**, **3**, **6**, **7**, **8**,  
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7 and **9**, and complete crystallographic data for complexes **2**, **3**, **6**, **7**, **8**, and **9**. This  
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9 material is available free of charge via the Internet at <http://pubs.acs.org>.  
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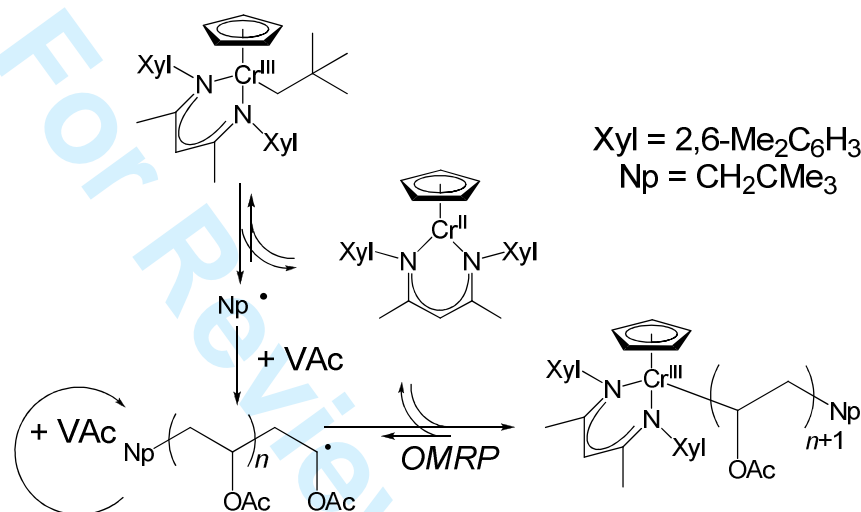
## 16 References

- 17  
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19 1 Chen, E. Y.-X., *Chem. Rev.* **2009**, *109*, 5157-5214.  
20 2 Williams, B. S.; Leatherman, M. D.; White, P. S.; Brookhart, M., *J. Am. Chem. Soc.* **2005**, *127*,  
21 5132-5146.  
22 3 Berkefeld, A.; Drexler, M.; Möller, H. M.; Mecking, S., *J. Am. Chem. Soc.* **2009**, *131*,  
23 12613-12622.  
24 4 (a) Ito, S.; Munakat, K.; Nakamura, A.; Nozaki, K., *J. Am. Chem. Soc.* **2009**, *131*, 14606. (b)  
25 Nakamura, A.; Ito, S.; Nozaki, K. *Chem. Rev.* **2009**, *109*, 5215-5244.  
26 5 Satoh, K.; Kamigaito, M., *Chem. Rev.* **2009**, *109*, 5120-5156.  
27 6 Poli, R., *Angew. Chem., Int. Ed. Engl.* **2006**, *45*, 5058-5070.  
28 7 Debuigne, A.; Poli, R.; Jérôme, C.; Jérôme, R.; Detrembleur, C., *Prog. Polym. Sci.* **2009**, *34*,  
29 211-239.  
30 8 Smith, K. M., *Coord. Chem. Rev.* **2006**, *250*, 1023-1031.  
31 9 Furstner, A., *Chem. Rev.* **1999**, *99*, 991-1046.  
32 10 Wessjohann, L. A.; Scheid, G., *Synthesis* **1999**, 1-36.  
33 11 Takai, K.; Nitta, K.; Fujimura, O.; Utimoto, K., *J. Org. Chem.* **2002**, *54*, 4732-4734.  
34 12 Takai, K.; Matsukawa, N.; Takahashi, A.; Fujii, T., *Angew. Chem., Int. Ed. Engl.* **1998**, *37*,  
35 152-155.  
36 13 Wessjohann, L. A.; Schmidt, G.; Schrekker, H. S., *Tetrahedron* **2008**, *64*, 2134-2142.  
37 14 Doherty, J. C.; Ballem, K. H. D.; Patrick, B. O.; Smith, K. M., *Organometallics* **2004**, *23*,  
38 1487-1489.  
39 15 MacLeod, K. C.; Conway, J. L.; Tang, L.; Smith, J. J.; Corcoran, L. D.; Ballem, K. H. D.;  
40 Patrick, B. O.; Smith, K. M., *Organometallics* in press (doi: 10.1021/om900788c).  
41 16 Champouret, Y.; Baisch, U.; Poli, R.; Tang, L.; Conway, J. L.; Smith, K. M., *Angew. Chem., Int.*  
42 *Ed. Engl.* **2008**, *47*, 6069-6072.  
43 17 Schrock, R. R., *Acc. Chem. Res.* **1979**, *12*, 98-104.  
44 18 Foley, P.; Dicosimo, R.; Whitesides, G. M., *J. Am. Chem. Soc.* **1980**, *102*, 6713-6725.  
45 19 Pamplin, C.; Legzdins, P., *Acc. Chem. Res.* **2003**, *36*, 223-233.  
46 20 Mindiola, D. J., *Acc. Chem. Res.* **2006**, *39*, 813-821.  
47 21 Tsou, T.-T.; Loots, M.; Halpern, J., *J. Am. Chem. Soc.* **1982**, *104*, 623-624.  
48 22 Wayland, B. B.; Poszmik, G.; Mukerjee, S., *J. Am. Chem. Soc.* **1994**, *116*, 7943-7944.  
49 23 Fernandez, I.; Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J., *Organometallics* **2008**, *27*, 109-118.  
50 24 Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J.,  
51  
52  
53  
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50  
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52  
53  
54  
55  
56  
57  
58  
59  
60
- Organometallics* **1996**, *15*, 1518-1520.
- 25 Armarego, W. L. F.; Perrin, D. D., *Purification of Laboratory Chemicals*. ed.; Butterworth  
Heinemann, 4th ed.: 1996.
- 26 Budzelaar, P. H. M.; De Gelder, R.; Gal, A. W., *Organometallics* **1998**, *17*, 4121-4123.
- 27 Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W., *J.*  
*Am. Chem. Soc.* **2001**, *123*, 8738-8749.
- 28 Gong, S. G.; Ma, H. Y., *Dalton Trans.* **2008**, 3345-3357.
- 29 Panda, T.; Gamer, M.; Roesky, P., *Organometallics* **2003**, *22*, 877-878.
- 30 (a) Andersen, R. A.; Wilkinson, G., *J. Chem. Soc., Dalton Trans.* **1977**, 809-811. (b) Dryden, N.  
H.; Legzdins, P.; Trotter, J.; Yee, V. C., *Organometallics* **1991**, *10*, 2857-2870.
- 31 Hao, S. K.; Song, J. I.; Berno, P.; Gambarotta, S., *Organometallics* **1994**, *13*, 1326-1335.
- 32 (a) Baker, M. V.; Field, L. D.; Hambley, T. W. *Inorg. Chem.* **1988**, *27*, 2872-2876. (b) Schubert,  
E. M. *J. Chem. Educ.* **1992**, *69*, 62..
- 33 *SAINT*, version 7.03A. ed.; Bruker Analytical X-ray System: Madison, WI, USA, 1997-2003.
- 34 *SADABS. Bruker Nonius area detector scaling and absorption correction - V2.10*. ed.; Bruker  
AXS Inc.: Madison, Wisconsin, USA, 2003.
- 35 Altomare, A.; Burla, M.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni,  
A.; Polidori, G.; Spagna, R., *J. Appl. Cryst.* **1999**, *32*, 115-119.
- 36 Sheldrick, G. M., *SHELXTL, version 5.1*. ed.; Bruker AXS, Inc.: Madison WI, 1997.
- 37 Farrugia, L. J., *J. Appl. Crystallogr.* **1997**, *32*, 565.
- 38 Frisch, M. J., *et al.*, *Gaussian 03, Revision D.01*. ed.; Gaussian, Inc.: Wallingford CT, 2004.
- 39 Becke, A. D., *J. Chem. Phys.* **1993**, *98*, 5648-5652.
- 40 Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff, W. M., *J. Am. Chem. Soc.*  
**1992**, *114*, 10024-10035.
- 41 Ehlers, A. W.; Boehme, M.; Dapprich, S.; Gobbi, A.; Hoellwarth, A.; Jonas, V.; Koehler, K. F.;  
Stegmann, R.; Veldkamp, A.; Frenking, G., *Chem. Phys. Lett.* **1993**, *208*, 111-114.
- 42 Fan, H. J.; Adhikari, D.; Saleh, A. A.; Clark, R. L.; Zuno-Cruz, F. J.; Cabrera, G. S.; Huffman, J.  
C.; Pink, M.; Mindiola, D. J.; Baik, M. H., *J. Am. Chem. Soc.* **2008**, *130*, 17351-17361.
- 43 Huang, Y. B.; Jin, G. X., *Dalton Trans.* **2009**, 767-769.
- 44 Solution phase measurements give the bimolecular rate constant for the reaction of methyl  
radical with vinyl acetate as  $1.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , while the same reaction with the more  
stabilized benzyl radical has  $k = 14 \text{ M}^{-1} \text{ s}^{-1}$ : (a) Zytowski, T.; Fischer, H. *J. Am. Chem. Soc.*  
**1996**, *118*, 437-439. (b) Fischer, H.; Radom, L. *Angew. Chem. Int. Ed.* **2001**, *40*, 1340-1371.
- 45 Hermes, A. R.; Morris, R. J.; Girolami, G. S., *Organometallics* **1988**, *7*, 2372-2379.
- 46 Mowat, W.; Shortland, A. J.; Hill, N. J.; Wilkinson, G., *J. Chem. Soc., Dalton Trans.* **1973**,  
770-778.
- 47 Schulzke, C.; Enright, D.; Sugiyama, H.; Leblanc, G.; Gambarotta, S.; Yap, G. P. A.; Thompson,  
L. K.; Wilson, D. R.; Duchateau, R., *Organometallics* **2002**, *21*, 3810-3816.
- 48 Meijboom, N.; Schaverien, C. J.; Orpen, A. G., *Organometallics* **1990**, *9*, 774-782.
- 49 Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B., *J. Chem. Soc., Dalton*  
*Trans.* **1995**, 2111-2123.
- 50 Coles, M. P.; Gibson, V. C.; Clegg, W.; Elsegood, M. R. J.; Porrelli, P. A., *J. Chem. Soc., Chem.*  
*Commun.* **1996**, 1963-1964.
- 51 The metallacylobutane  $\text{Cp}^*\text{Cr}(\text{pyridine})(\text{CH}_2)_2\text{CMe}_2$  has been prepared via the route

- 1  
2  
3  
4 developed for the analogous CH<sub>2</sub>SiMe<sub>3</sub> reactions: Heintz, R. A.; Leelasubcharoen, S.;  
5 Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H., *Organometallics* **1998**, *17*, 5477-5485.  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
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53  
54  
55  
56  
57  
58  
59  
60
- 52 Heinemann, O.; Jolly, P. W.; Krüger, C.; Verhovnik, G. P. J., *J. Organometal. Chem.* **1998**, *553*,  
477-479.
- 53 Kim, W.-K.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H.,  
*Organometallics* **1998**, *17*, 4541-4543.
- 54 Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J., *Eur. J.*  
*Inorg. Chem.* **2001**, 1895-1903.
- 55 Gallant, A. J.; Smith, K. M.; Patrick, B. O., *Chem. Commun.* **2002**, 2914-2915.
- 56 Poli, R., *Chem. Rev.* **1996**, *96*, 2135-2204.
- 57 Fettinger, J. C.; Mattamana, S. P.; Poli, R.; Rogers, R. D., *Organometallics* **1996**, *15*,  
4211-4222.
- 58 Mattamana, S. P.; Poli, R., *Organometallics* **1997**, *16*, 2427-2433.
- 59 De Bruin, B.; Dzik, W. I.; Li, S.; Wayland, B. B., *Chem. Eur. J.* **2009**, *15*, 4312-4320.

## Graphical Abstract for Table of Contents



Symmetric  $\text{CpCr}[(\text{ArNCMe})_2\text{CH}]$  complexes ( $\text{Ar} = 2,6\text{-diisopropylphenyl}$ ,  $2,6\text{-xylyl}$ ,  $2,4,6\text{-mesityl}$  or  $2,6\text{-diethylphenyl}$ ) and a mixed-aryl nacnac complex  $\text{CpCr}[\text{ArNC}(\text{Me})\text{CHC}(\text{Me})\text{NAr}']$  ( $\text{Ar} = 2,6\text{-diisopropylphenyl}$  and  $\text{Ar}' = 2,6\text{-xylyl}$ ) have been studied as moderators for the polymerization of vinyl acetate initiated by V-70. The isolated, structurally-characterized  $\text{Cr}^{\text{III}}$  neopentyl complex  $\text{CpCr}[(\text{XylNCMe})_2\text{CH}](\text{CH}_2\text{CMe}_3)$  has been used to polymerize vinyl acetate at room temperature, while elevated temperatures lead to deactivation via formation of the  $\text{Cr}^{\text{III}}$  acetate.