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► **To cite this version:**

Yohan Champouret, Ulrich Baisch, Rinaldo Poli, Liming Tang, Julia l. Conway, et al.. Homolytic Bond Strengths and Formation Rates in Half-Sandwich Chromium Alkyl Complexes: Relevance for Controlled Radical Polymerization. *Angewandte Chemie International Edition*, 2008, 47 (32), pp.6069-6072. 10.1002/anie.200801498 . hal-03192514

HAL Id: hal-03192514

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Submitted on 8 Apr 2021

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Homolytic bond strengths and formation rates in half-sandwich chromium-alkyl complexes: relevance for controlled radical polymerization**

Yohan Champouret, Ulrich Baisch, Rinaldo Poli,* Liming Tang, Julia L. Conway, Kevin M. Smith,*†

This last decade, controlled/living radical polymerization (CRP) processes have seen a considerable surge of interest due, in part, to their relevance to access to a variety of well-defined polymer structures (e.g. predetermined molecular mass, narrow molecular weight distribution).^[1] We have been interested in one-electron reactivity of transition metal complexes and its relevance in CRP.^[2] One way in which transition metal complexes can be used to control radical polymerization is through a reversible deactivation consisting of the formation of an organometallic dormant species, a metal-capped polymer chain, by trapping the growing radical chain with formation of a metal-carbon bond, see Figure 1. We refer to this particular control mechanism as “organometallic radical polymerization” (OMRP).^[2] One of the outstanding challenges in this area is the possibility to control the polymerization of less reactive monomers (e.g. vinyl chloride, vinylidene dichloride, vinyl acetate, etc.), for which activation is made difficult by the relative strong bonds established with the common radical traps.

Reasonable control for the radical propagation of poly(vinyl acetate) (PVAc) has been achieved on the basis of another control mechanism (degenerative transfer, DT, based on the use of xanthates or dithiocarbamates).^[3, 4] Results obtained by atom transfer radical polymerization (ATRP) have not been nearly as good,^[5-7] while good control was recently achieved in the presence of Co(acac)₂ (M_w/M_n as low as 1.1).^[8, 9] Recent studies carried out partly in one of our laboratories have shown that this process occurs either by DT or

by OMRP depending on the presence of additional ligands such as pyridine or water.^[10, 11]

<Figure 1>

In search for other transition metal complexes capable of controlling the polymerization of less reactive monomers, we have considered the use of half-sandwich β -diketiminato system of Cr^{II}, or the type shown in Scheme 1. Previous studies have shown that stable Cr^{III} complexes with methyl ligands can be prepared by oxidation of **1** with silver triflate, followed by alkylation with methyl lithium,^[12] similar to the preparation of related chromium β -diketiminato organometallic complexes.^[13-15] However, attempts to synthesize half-sandwich Cr^{III} complexes with larger alkyl ligands led to unexpected products presumably resulting from homolysis of the Cr^{III}-alkyl bond and subsequent hydrogen atom abstraction reactions of the solvent.^[16] Thus, this metal system shows promise for applications in OMRP. In this report, we will show by a combination of experimental and computational methods that the Cr^{III}-PVAc bond strength is dramatically influenced by the steric effect of the β -diketiminato aryl substituents and can be tuned to a suitable range for the CRP of the vinyl acetate monomer (VAc). Early reports of the use of Cr^{II} acetate and benzoyl peroxide for controlled radical polymerization were discussed on the basis of what we now call an OMRP mechanism, but the polymerization activity was low for vinyl acetate.^[17-19]

In addition to the already known^[12] compound CpCr^{II}[Ar¹NC-(CH₃)CHC(CH₃)NAr²] with Ar¹ = Ar² = *i*Pr₂C₆H₃ (Dipp), **1**, we have now prepared the analogue with Ar¹ = Ar² = 2,6-Me₂C₆H₃ (Xyl), **2**, as well as asymmetric analogues with Ar¹ = Dipp and Ar² = Ph (**3**), *p*-C₆H₄OMe (**4**), and *p*-C₆H₄CF₃, (**5**). The structures of complexes **2**, **4** and **5** have been confirmed using single crystal X-ray diffraction. Synthetic and structural details are provided in the supporting information.

<Scheme 1>

Initial studies showed that compound **2** traps the growing polystyrene (PS) radical chain inefficiently. Indeed, the V-70-initiated polymerization in the presence of **2** [bulk; styrene/V-70/**2** = 250:0.8:1; V-70 = 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile)] gave PDI = 2.5–3.7, and a final polymer with $M_n = 7.9 \cdot 10^4$ g/mol ($M_{n(th.)} = 1.7 \cdot 10^4$ g/mol) at 65 % conversion (additional data are presented in the Supporting Information). Since the growing PVAc radical is expected to establish a stronger bond than the growing PS radical,^[20, 21] we anticipated a more efficient radical trapping for the growing PVAc radical chain.

In agreement with the above expectation, a preliminary screening of VAc polymerization initiated by V-70 in the presence of **2** at 50°C (VAc/2/V-70 = 500/1/0.8) yielded essentially no polymer in 4 h (ca. 6 half-lives of V-70). Subsequent warming to 90°C yielded an initial polymerization (11% conversion after an additional 4 h), and then essentially no further conversion in the

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[**] RP thanks the ANR (contract No. NT05-2_42140) and IUF for financial support and the CICT (Project CALMIP) for granting free computational time, and KMS thanks NSERC of Canada for financial support and Dr. Brian O. Patrick (UBC) for performing the single crystal X-ray structural determinations and refinements.

following 60 h ($M_n = 1.12 \cdot 10^4$ g/mol, $M_w/M_n = 1.68$ at 12% conversion; $M_{n(th.)} = 5.16 \cdot 10^3$), see Table 1, showing a weak propensity for the Cp[XylNC(CH₃)CHC(CH₃)NXyl]Cr^{III}-PVAc bond to break homolytically.

<Table 1>

With the idea in mind that the Cr^{III}-PVAc BDE could be weakened by a greater ligand steric bulk, we turned our attention to compound **1**. Indeed, when an experiment was carried out with complex **1** at 50°C in the presence of V-70 (VAc/1/V-70 = 500/1/0.8), the conversion reached 70 % after only 20 h, but control of the polymerization was poor ($M_n = 5.67 \cdot 10^4$ g/mol; $M_w/M_n = 2.5$; $M_{n(th.)} = 3.01 \cdot 10^4$ g/mol), suggesting that the reversible trapping equilibrium of Figure 1 is not sufficiently displaced toward the dormant state under these conditions. Upon running the same process at lower temperature (VAc/1/V-70 = 500/1/0.8 at 30°C), the polymerization was slower, see Table 1 ($k_{app} = 3.3 \cdot 10^{-6}$ s⁻¹). Although the level of control is not yet ideal (at 70% conversion: $M_n = 6.73 \cdot 10^4$ g/mol, $M_w/M_n = 1.80$, $M_{n(th.)} = 3.01 \cdot 10^4$ g/mol), the continuous growth of M_n demonstrates the occurrence of an OMRP process. When the same experiment was run in the presence of a larger excess of V-70 (VAc/V-70/1 = 500:1.5:1), the polymerization was faster and uncontrolled. This result clearly shows that, contrary to the Co(porphyrin)^[22] and Co(acac)₂^[10] systems, the present Cr^{II} complex is not capable of mediating an associative DT process, consistent with the absence of vacant sites on the Cr atom in the Cr^{III}-capped dormant chain to promote an associative radical exchange.

The effect of the ligand steric encumbrance (Xyl vs. Dipp) and of the alkyl nature (PS vs. PVAc) on the Cr^{III}-C BDE was probed by DFT calculations on system CpCr^{III}[ArNC(CH₃)CHC(CH₃)NAr](R), where Ar = Ph or Xyl and R = CH₂Ph, CHMePh (a model of the PS growing chain) and CHMeOOCMe (a model of the growing PVAc chain). All calculations were carried out by full QM, thus we avoided the larger Dipp-substituted β-diketiminato system, the steric effects being conveniently probed by the comparison of Ph and Xyl systems. Amongst different rotamers, the lowest energy ones are those where the Ph or OOCMe group is oriented *endo* relative to the Cp ring, as shown in Figure 2. The optimized geometries of the separate CpCr^{III}[ArNC(CH₃)CHC(CH₃)NAr] and R, as well as fuller details on the DFT calculations, are given as supporting information.

<Figure 2>

The calculated BDE's are reported in Table 2. They show, in agreement with the experimental evidence, a stronger Cr^{III}-R bond for the PVAc model than for the PS model, whereas the Cr^{III}-CH₂Ph bond has an intermediate strength. Introducing *o*-Me substituents on the Ph rings of the β-diketiminato ligand considerably weakens the Cr^{III}-R bonds (by 7.5 kcal mol⁻¹ for the secondary CH₂Ph group and by 9.8 and 8.7 kcal mol⁻¹ for the tertiary PS and PVAc models).

<Table 2>

The effect of steric bulk on the Cr^{III}-C BDE is further revealed by trends in the bond lengths. Addition of the *o*-CH₃ groups to the β-diketiminato Ph substituents lengthens the bond for all R. Addition of the *α*-CH₃ group to R (going from benzyl to 1-phenylethyl) also lengthens the bond. Conversely, replacement of Ph with OOCMe (going from the PS to the PVAc model) strengthens the bond, this being an electronic rather than a steric

effect related to the smaller delocalization of the radical spin density. These results are in perfect harmony with the inefficient PS trapping and with an irreversible PVAc trapping by the Xyl system. Extrapolation of the calculated BDEs to the Dipp system rationalizes the reversible trapping observed for the radical polymerization of VAc, showing signs of controlled growth. On the basis of these results, we are now developing new CpCr^{III}[Ar¹NC(CH₃)CHC(CH₃)NAr²] systems with intermediate bulk.

Preliminary experiments in the presence of the isosteric complexes **3-5** indicated that the steric pressure of one Dipp and one Ph substituent does not sufficiently labilize the Cr^{III}-PVAc bond, but revealed an unexpected electronic effect in the radical trapping rate, see Figure 3. Use of compound **3** yielded almost no polymer at 90°C (4% conversion after 30 h), although the M_n and M_w/M_n were low ($5.6 \cdot 10^3$ and 1.15, respectively) in agreement with a controlled process. Compound **4** gave 12% conversion within the initial 5 h at 60°C, then no further increase after 40 h at 80°C. However, further heating to 100°C yielded an increased conversion (40% after an additional 65 h). Finally, in the presence of complex **5** an initial burst of polymerization (41% conversion) occurred within the first 2 h at 50°C, but then conversion reached a plateau at 50% for the next 52 h and subsequent heating to 80°C took the conversion up to 71% after an additional 15 h. It seems that the *para* substituent on the group (X in Scheme 1) has an important effect on the alkyl radical trapping ability of the Cr^{II} complex (barrier to bond formation in Figure 1). While the complexes containing the Xyl, Dipp and Ph substituents (**1**, **2** and **3**) are able to trap the growing PVAc radical chain rather effectively, those containing the *p*-C₆H₄OMe and especially the *p*-C₆H₄CF₃ substituents (**4** and **5**) are much less efficient. The origin of this electronic effect is currently unknown; it is the subject of continuing investigations.

<Figure 3>

In conclusion, we have shown for the first time that a Cr^{II}/Cr^{III} system can provide a platform for controlled radical polymerization of less reactive monomers. The Cr^{III}-C bond strength can be tuned by accurate choice of the steric bulk on the β-diketiminato ligand. However, electronic factors affecting the rate of radical trapping must also be considered for the optimization of the OMRP process.

Experimental Section

Ligands: The symmetric β-diketiminato ligand, XylNHC(Me)-CHC(Me)NXyl (Xyl = 2,6-Me₂C₆H₃) was prepared according to the literature procedure.^[23] The mixed N-aryl β-diketiminato ligands, DppNHC(Me)CHC(Me)Ar (Ar = C₆H₅, *p*-C₆H₄OMe, or *p*-C₆H₄CF₃), were prepared by reacting the appropriate aniline with DppNHC(Me)CHC(Me)O, according to the literature procedure previously used to prepare the corresponding Ar = *o*-C₆H₄OMe derivative.^[24]

Compound 2: In a glovebox, XylNHC(Me)CHC(Me)NXyl (2.1834 g, 7.124 mmol) dissolved in 20 mL of THF was reacted with BuLi (3.6 mL of 2.0 M solution in pentane, 7.2 mmol) at -30 °C. In a separate Schlenk flask, NaCp (3.6 mL of 2.0 M solution in THF, 7.2 mmol) was added to CrCl₂(tmeda)^[25] (1.7034 g, 7.124 mmol) suspended in 25 mL of THF at 25 °C. After 30 min, the yellow solution of the deprotonated ligand was added dropwise to the reaction mixture in the Schlenk flask. After the reaction mixture had stirred overnight at 25 °C, the solvent was removed in vacuo, and the residue was extracted with pentane and filtered through Celite. The solvent was again removed in vacuo, and the residue was extracted into a minimum of pentane, filtered, and cooled to -30 °C overnight to yield 1.2185 g of black crystals (41.7% yield).

Compounds 3-5: Compounds **3**, **4** and **5** were prepared using the same procedure as for compound **2**, above, but using the DppNHC(Me)CHC(Me)NAr ligands, where Ar = C₆H₅, *p*-C₆H₄OMe, or *p*-C₆H₄CF₃, respectively.

Controlled polymerizations. A general procedure was as follows. Under strict exclusion of air and moisture, the reaction components (e.g. metal complex and V-70 for the OMRP runs) were placed in a Schlenk tube equipped with a stirring bar. Freshly distilled monomer and the solvent (when this was used) were added at 0 °C, followed by three freeze-pump-thaw cycles. The tube was then placed in a pre-heated oil bath at the desired temperature. Samples were periodically withdrawn by glass syringe after quenching the solution with an ice-bath. The conversion was calculated by weight difference, after removing all residual monomer by evaporation under vacuum to constant weight. The polymer residue was directly analyzed by size exclusion chromatography after dissolution in THF.

Received: ((will be filled in by the editorial staff))

Published online on ((will be filled in by the editorial staff))

Keywords: Chromium · homolytic bond cleavage · ligand stereoelectronic effects · controlled radical polymerization · OMRP · poly(vinyl acetate)

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Legends

Scheme 1. Compounds used in this study.

Figure 1. Free energy profile of controlled radical polymerizations by OMRP.

Figure 2. DFT-optimized structures of CpCr[ArNC(CH₃)CHC(CH₃)NAr](R) compounds.

Figure 3. Behavior of complexes **3** (circles; VAc/V-70/**3** = 250:0.9:1), **4** (triangles; VAc/V-70/**4** = 500:0.9:1) and **5** (squares; VAc/V-70/**5** = 250:0.9:1) as OMRP traps for PVAc. Further details are given as Supporting Information.

Tables

Table 1. Radical Polymerization of vinyl acetate initiated by V-70 with complexes **2** and **1**.

Complex	t (h)	Conv (%)	M_n^{SEC} ^[a]	$M_n^{(th)}$ ^[b]	M_w/M_n ^[a]
2 ^[c]	3.5	2	-	-	-
	8	11	10470	4730	1.81
	18	12	10200	5160	1.86
	22.5	11	10740	4730	1.74
	48	12	11270	5160	1.67
	66	12	11270	5160	1.68
1 ^[d]	3.5	2	-	-	-
	8	6	23800	2500	1.36
	24	23	29800	9900	1.75
	32	34	38000	14600	1.74
	46	70	67300	30100	1.80

^[a]Determined by size exclusion chromatography (SEC). ^[b] $M_n^{(th)} = ([M]_0/[Cr]_0) \cdot M_{mono} \cdot conv$. ^[c]VAc/2/V-70 = 500/1/0.8; 50°C for 4h, then 90°C.

^[d]VAc/1/V-70/ = 500/1/0.8; 30°C.

Table 2. Calculated Cr^{III}-C Bond Dissociation Enthalpies (BDE)^a in kcal mol⁻¹ and bond lengths in Å for compounds CpCr^{III}[ArNC(CH₃)-CHC(CH₃)NAr](R).

R	Ar = Ph		Ar = Xyl	
	BDE	Cr-C	BDE	Cr-C
CH ₂ Ph	20.8	2.136	13.3	2.146
CH(Me)Ph	11.8	2.173	2.0	2.197
CH(Me)OOCMe	28.4	2.109	19.7	2.124

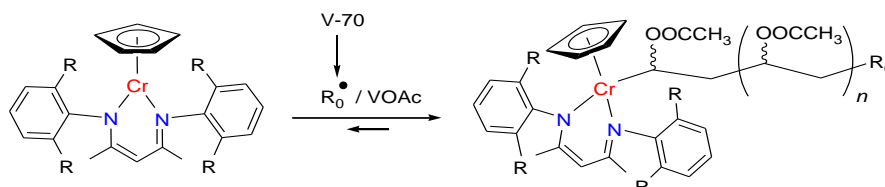
^aB3LYP/6-31G**; ZPVE and PV corrections on the basis of the ideal gas model.

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Chromium(III)-alkyl bonds

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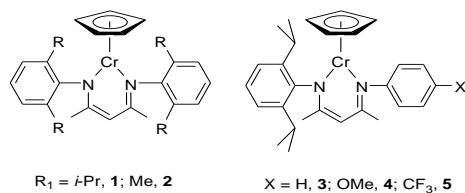
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Homolytic bond strengths and formation rates in half-sandwich chromium-alkyl complexes: relevance for controlled radical polymerization

The steric properties of the aryl substituents in chromium β -ketiminato complexes can be tuned in order to achieve reversible radical trapping of a growing poly(vinyl acetate) radical chain.

Graphical material



Scheme 1

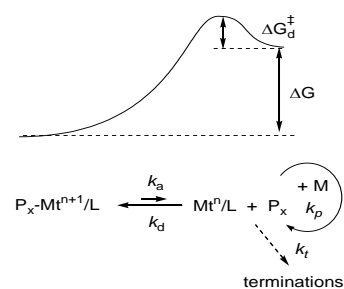


Figure 1

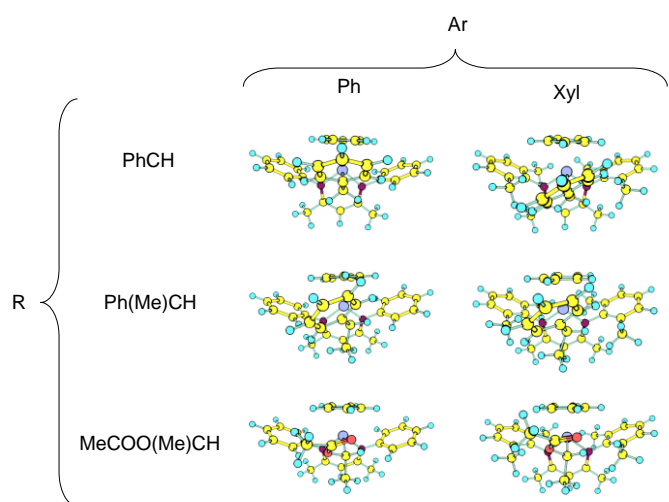


Figure 2

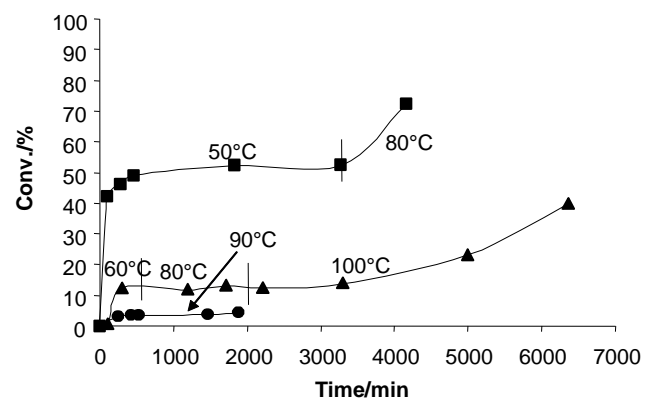


Figure 3