

Homolytic Bond Strengths and Formation Rates in Half-Sandwich Chromium Alkyl Complexes: Relevance for Controlled Radical Polymerization**

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Dedicated to Jan Reedijk on the occasion of his retirement

In the past decade, controlled/living radical polymerization (CRP) processes have seen a considerable surge of interest owing, in part, to their relevance to the accessibility of a variety of well-defined polymer structures (e.g. predetermined molecular mass, narrow molecular weight distribution).^[1] We have been interested in the 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. The growing radical chain is trapped by formation of

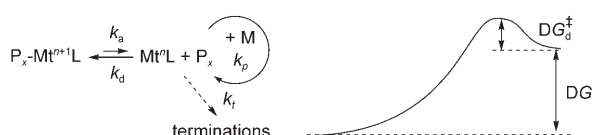
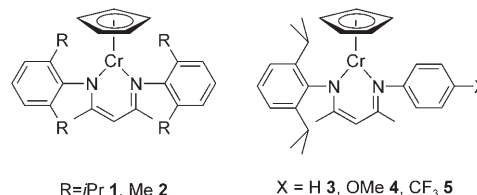


Figure 1. Free-energy profile of controlled radical polymerizations by OMRP. P_x = growing polymer chain, Mt = metal, L = ancillary ligand(s), M = monomer.

a metal–carbon bond to yield a metal-capped polymer chain, which is a dormant organometallic species (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), for which activation is made difficult by the relatively strong bonds established with 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 $[\text{Co}(\text{acac})_2]$ (M_w/M_n as low as 1.1; acac = acetylacetonate).^[8,9] Recent studies 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]



Scheme 1. Compounds used in this study.

In search of other transition-metal complexes capable of controlling the polymerization of less reactive monomers, we have considered the use of half-sandwich β -diketiminato systems of Cr^{II} (Scheme 1). Previous studies have shown that stable Cr^{III} complexes with methyl ligands can be prepared by oxidation of **1** with silver triflate and subsequent 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 from the solvent.^[16] Thus, this metal system shows promise for applications in OMRP. Herein, we show by a combination of

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

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.200801498>.

experimental and computational methods that the Cr^{III}–PVAc bond strength is dramatically influenced by the steric effects 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 on 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 known compound [CpCr^{III}{Ar¹NC(CH₃)CHC(CH₃)NAr²}] with Ar¹ = Ar² = 2,6-*i*Pr₂C₆H₃ (Dipp), Cp = C₅H₅, **1**^[12] 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.

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 a polydispersity index (PDI = M_w/M_n) of 2.5–3.7 and a final polymer with $M_n = 7.9 \times 10^4$ g mol^{−1} (theoretical number-average molecular weight $M_{n(th)} = 1.7 \times 10^4$ g mol^{−1}) 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 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/V-70/**2** = 500/0.8/1) yielded essentially no polymer in 4 h (ca. six 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 following 60 h ($M_n = 1.12 \times 10^4$ g mol^{−1}, $M_w/M_n = 1.68$ at 12 % conversion; $M_{n(th)} = 5.16 \times 10^3$; Table 1), indicating a weak propensity for the Cp[XylNC(CH₃)CHC(CH₃)NXyl]Cr^{III}–PVAc bond to break homolytically.

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

Complex	<i>t</i> [h]	Conv [%]	M_n SEC ^[a]	$M_{n(th)}$ ^[b]	M_w/M_n ^[a]
2 ^[c]	3.5	2	–	–	–
	8	11	10 470	4730	1.81
	18	12	10 200	5160	1.86
	22.5	11	10 740	4730	1.74
	48	12	11 270	5160	1.67
	66	12	11 270	5160	1.68
1 ^[d]	3.5	2	–	–	–
	8	6	23 800	2500	1.36
	24	23	29 800	9900	1.75
	32	34	38 000	14 600	1.74
	46	70	67 300	30 100	1.80

[a] Determined by size exclusion chromatography (SEC). [b] $M_{n(th)} = ([M]_0/[Cr]_0)(M_{mono})_{(conv)}$. [c] VAc/V-70/**2** = 500/0.8/1, 50 °C for 4 h, then 90 °C. [d] VAc/V-70/**1** = 500/0.8/1, 30 °C.

With the idea in mind that the Cr^{III}–PVAc bond dissociation enthalpy (BDE) could be lowered by 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/V-70/**1** = 500/0.8/1), the conversion reached 70 % after only 20 h, but control of the polymerization was poor ($M_n = 5.67 \times 10^4$ g mol^{−1}, $M_w/M_n = 2.5$, $M_{n(th)} = 3.01 \times 10^4$ g mol^{−1}), suggesting that the reversible trapping equilibrium of Figure 1 is not sufficiently displaced toward the dormant state under these conditions. When the reaction was repeated at lower temperature (VAc/V-70/**1** = 500/0.8/1 at 30 °C), the polymerization was slower (Table 1, $k_{app} = 3.3 \times 10^{-6}$ s^{−1}). Although the level of control is not yet ideal (at 70 % conversion $M_n = 6.73 \times 10^4$ g mol^{−1}, $M_w/M_n = 1.80$, $M_{n(th)} = 3.01 \times 10^4$ g mol^{−1}), the continuous growth of M_n demonstrates the occurrence of an OMRP process. When the same experiment was performed in the presence of a larger excess of V-70 (VAc/V-70/**1** = 500:4:1), the polymerization was faster and uncontrolled (PDI > 2.4). This result clearly shows that, contrary to the [Co(porphyrin)]^[22] and [Co(acac)₃]^[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 the nature of the alkyl chain (PS vs. PVAc) on the Cr^{III}–C BDE was probed by DFT calculations on [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 quantum mechanics, thus we avoided the larger Dipp-substituted β -diketiminato system; the steric effects were conveniently probed by the comparison of Ph and Xyl systems. Amongst different rotamers, the lowest energy ones are those in which 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}] complexes and R, as well as full details on the DFT calculations, are given in the Supporting Information.

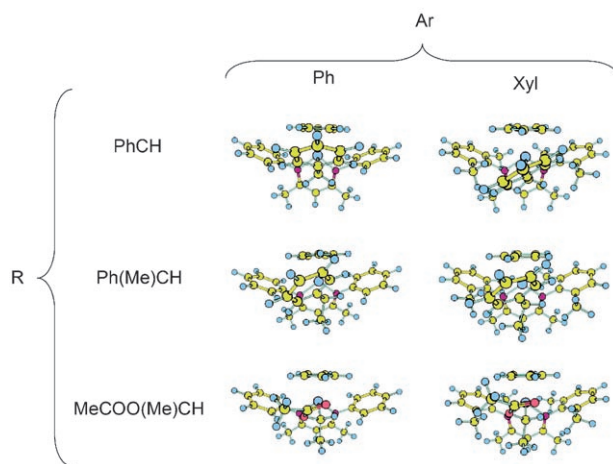


Figure 2. DFT-optimized structures of [CpCr{ArNC(CH₃)CHC(CH₃)NAr}(R)] compounds.

Table 2: Calculated Cr^{III}–C bond dissociation enthalpies (BDE)^[a] and bond lengths^[b] 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

[a] B3LYP/6-31G**; ZPVE and PV corrections on the basis of the ideal gas model. BDE in kcal mol^{−1}. [b] In Å.

The calculated BDEs 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 aryl 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, respectively).

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 aryl substituents lengthens the bond for all R groups. 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 effect is electronic rather than steric and is 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, which shows signs of controlled growth. On the basis of these results, we are now developing new [CpCr^{II}{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 (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 (5.6×10^3 g mol^{−1} 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 aryl 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 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.

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 modulation 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 DippNHC(Me)CHC(Me)Ar (Ar = C₆H₅, *p*-C₆H₄OMe, or *p*-C₆H₄CF₃) were prepared by reacting the appropriate aniline derivative with DippNHC(Me)CHC(Me)O according to the literature procedure for the corresponding Ar = *o*-C₆H₄OMe derivative.^[24]

2: In a glovebox, XylNHC(Me)CHC(Me)NXyl (2.1834 g, 7.124 mmol) in THF (20 mL) was treated with *n*BuLi (2.0 M in pentane, 3.6 mL, 7.2 mmol) at −30 °C. In a separate Schlenk flask, NaCp (2.0 M solution in THF, 3.6 mL, 7.2 mmol) was added to [CrCl₂(tmeda)]^[25] (1.7034 g, 7.124 mmol, tmeda = *N,N,N',N'*-tetramethylethylenediamine) suspended in THF (25 mL) 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 black crystals (1.2185 g, 41.7 % yield).

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

Controlled polymerizations: 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, and three freeze-pump-thaw cycles were carried out. The tube was then placed in a preheated oil bath at the desired temperature. Samples were periodically withdrawn by glass syringe after quenching the solution by cooling with an ice bath. The conversion was calculated by weight difference after removing all

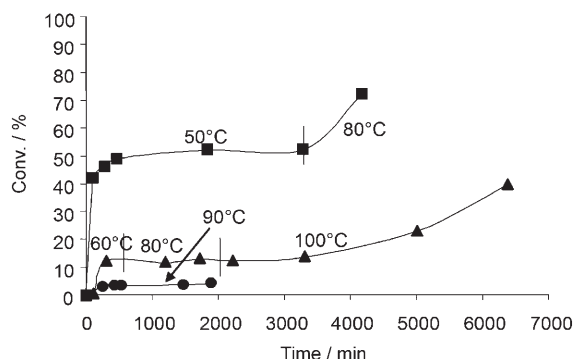


Figure 3. Behavior of complexes **3** (● VAc/V-70/**3** = 250:0.9:1), **4** (▲ VAc/V-70/**4** = 500:0.9:1) and **5** (■ VAc/V-70/**5** = 250:0.9:1) as OMRP traps for PVAc. Further details are given in the Supporting Information.

residual monomer by evaporation under vacuum to constant weight. The polymer residue was directly analyzed by size exclusion chromatography after dissolution in THF.

Received: March 30, 2008

Published online: July 4, 2008

Keywords: chromium · homolytic bond cleavage · poly(vinyl acetate) · polymerization · stereoelectronic effects

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