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# Al(OPr<sup>i</sup>)<sub>3</sub>-catalysed halogen exchange processes of relevance to atom transfer radical polymerization: the effect depends on the metal electronic structure

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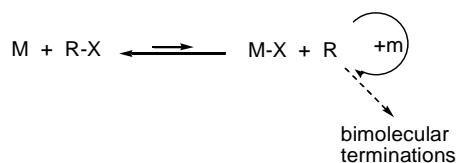
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## Whether tri(isopropoxo)aluminium catalyses or not halogen exchange for an ATRP catalyst depends on the number of valence electrons.

Since its discovery in 1995,<sup>1,2</sup> Atom Transfer Radical Polymerisation (ATRP) has become the most actively investigated controlled radical polymerization process. With this technique, the bimolecular terminations are reduced in importance relative to the chain propagation by involving the reactive radicals in a rapid and thermodynamically favourable atom transfer equilibrium by the action of a halogenated spin trap M-X, producing halogen-terminated dormant chains R-X (Scheme 1).

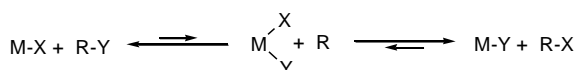
The role of species M, a transition metal complex capable of



Scheme 1.

increasing its formal oxidation state and coordination number by one unit, is to catalyse the chain growth from the dormant species. Thus, ATRP depends critically on transition metal catalysis and a number of studies have been devoted to understanding its mechanistic details.<sup>3,4</sup>

It has been shown that the addition of certain Lewis acids, most notably Al(OPr<sup>i</sup>)<sub>3</sub>, in conjunction with a number of catalysts such as RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>,<sup>5</sup> CpFeX(CO)<sub>2</sub> (X = Br, I),<sup>6</sup> NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>,<sup>7</sup> Ni(PPh<sub>3</sub>)<sub>4</sub>,<sup>8</sup> ReIO<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>,<sup>9</sup> and CuBr/bipy,<sup>10</sup> results in faster polymerisations and also narrower MW distributions for the resulting polymer. The detailed mechanism of action of this additive, however, is not completely understood, though it appears to be confined to the atom transfer step rather than to the free radical chain propagation.<sup>4</sup> Parallel work has shown that Al(OPr<sup>i</sup>)<sub>3</sub> has no effect on the halogen exchange rate between the RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> catalyst and a bromide initiator, RBr.<sup>11</sup> This is a relevant observation, because the simplest possible halogen exchange mechanism involves the ATRP intermediates, Scheme 2. Thus, the fact that Al(OPr<sup>i</sup>)<sub>3</sub> accelerates ATRP but not halogen exchange appears rather puzzling.



Scheme 2.

We have recently shown that a family of half-sandwich Mo(III) complexes catalyzes the ATRP of styrene and acrylates, and that this is accelerated by Al(OPr<sup>i</sup>)<sub>3</sub>.<sup>12-14</sup> We wish to report here, using CpMoX<sub>2</sub>(Pr<sup>i</sup><sub>2</sub>dad) (X = Cl/I; Pr<sup>i</sup><sub>2</sub>dad = Pr<sup>i</sup>N=CH-CH=NPr<sup>i</sup>) as a case study, that Al(OPr<sup>i</sup>)<sub>3</sub> does catalyse the halogen exchange process for an ATRP catalyst, and to rationalize the difference relative to RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>.<sup>11</sup>

The accelerating effect of Al(OPr<sup>i</sup>)<sub>3</sub> on the CpMoCl<sub>2</sub>(Pr<sup>i</sup><sub>2</sub>dad)-catalysed ATRP of methyl acrylate (MA), initiated by ethyl 2-iodopropionate (IEA) was shown previously.<sup>14</sup> In order to gain insight on the Al(OPr<sup>i</sup>)<sub>3</sub> mechanism of action for this ATRP process, a number of EPR investigations were carried out as shown in Figure 1. Warming the solution of the complex under typical ATRP conditions, with or without the IEA initiator, but in the absence of Al(OPr<sup>i</sup>)<sub>3</sub>, did not yield any spectral change, (a). In the presence of 1 equiv of Al(OPr<sup>i</sup>)<sub>3</sub>, a new peak assigned to the new complex CpMoClI(Pr<sup>i</sup><sub>2</sub>dad) became evident (b), revealing the catalytic activity of Al(OPr<sup>i</sup>)<sub>3</sub> on the halide exchange.<sup>†</sup> The nature of the mixed halogen species is proven by the exchange with NaI in THF, which leads, through the same complex (c), to the corresponding diiodide, CpMoI<sub>2</sub>(Pr<sup>i</sup><sub>2</sub>dad) (d). The latter has been isolated and fully characterized.<sup>§</sup>

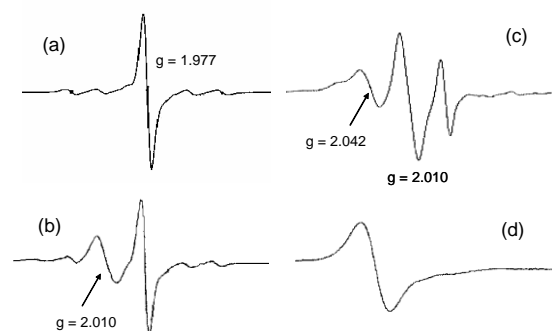
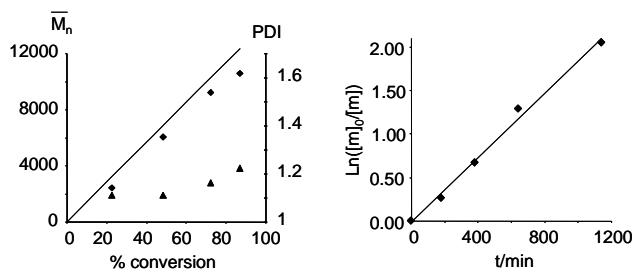


Fig. 1 EPR study of complex CpMoCl<sub>2</sub>(Pr<sup>i</sup><sub>2</sub>dad) in toluene. (a) after 1 h at 80°C with 1 equiv. of IEA (spectrum of dichloride complex); (b) as in (a), plus 1 equiv. of Al(OPr<sup>i</sup>)<sub>3</sub>; (c) with NaI (10 equiv.) in THF, 20 min at 50°C; (d) same as (c), after 2 h (spectrum of CpMoI<sub>2</sub>(Pr<sup>i</sup><sub>2</sub>dad))

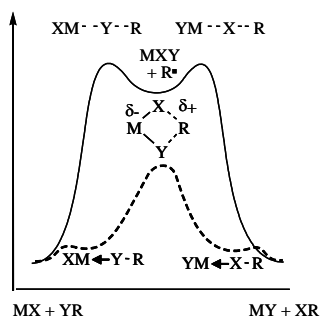
Complex CpMoI<sub>2</sub>(Pr<sup>i</sup><sub>2</sub>dad) is a better ATRP catalyst than the dichloride analogue. Under the same experimental conditions (MA/Mo/IEA = 165/1/1 in toluene, 30% v/v, 80°C) the apparent polymerization rate constant *k*<sub>app</sub> is 5.0x10<sup>-5</sup> min<sup>-1</sup> with no Al(OPr<sup>i</sup>)<sub>3</sub> and 1.9x10<sup>-3</sup> min<sup>-1</sup> with 1 equiv of Al(OPr<sup>i</sup>)<sub>3</sub> [cf. 3.7x10<sup>-4</sup> min<sup>-1</sup> for the CpMoCl<sub>2</sub>(Pr<sup>i</sup><sub>2</sub>dad)-catalyzed process].<sup>14</sup> Thus, *k*<sub>app</sub> increases by a factor of 5 on going from the dichloride to the diiodide catalyst. For the Al-containing polymerization, a conversion of 87% was achieved in 19 h, leading to a PMA with PDI = 1.22 (as low as 1.11 at intermediate conversions), see Figure 2. The measured (SEC) *M*<sub>n</sub> are only slightly lower than theory, indicating the possible intervention of catalyzed chain transfer.<sup>‡</sup> Unlike the CpMoCl<sub>2</sub>(Pr<sup>i</sup><sub>2</sub>dad)-catalyzed process,<sup>14</sup> nothing indicates an initiator efficiency factor *f* lower than 1.

The observed catalytic action of Al(OPr<sup>i</sup>)<sub>3</sub> on both the ATRP of MA (the dormant species being a -CH<sub>2</sub>-CH(I)-COOMe terminated polymer) with either CpMoCl<sub>2</sub>(Pr<sup>i</sup><sub>2</sub>dad) or CpMoI<sub>2</sub>(Pr<sup>i</sup><sub>2</sub>dad), and on the halogen exchange between CpMoCl<sub>2</sub>(Pr<sup>i</sup><sub>2</sub>dad) and CH<sub>3</sub>CH(I)COOEt, provides persuasive evidence that the processes involve the same intermediates (Scheme 2).



**Fig. 2.** Left:  $\bar{M}_n$  (diamonds) and PDI (triangles) against conversion for PMA obtained from  $\text{CpMoCl}_2(\text{Pr}_2\text{-dad})/\text{Al}(\text{O}^i\text{Pr})_3/\text{IEA}$  (MA/Mo/IEA/Al = 165/1/1/1) in toluene (30% v/v) at 80 °C. The line corresponds to the theoretical  $\bar{M}_n$ . Right: first order kinetics.

Now the interesting question is why the  $\text{RuCl}_2(\text{PPh}_3)_3$  system exhibits a selective acceleration of ATRP with no effect on halogen exchange. The logical explanation is that a second halogen exchange pathway, at lower energy, is viable for the Ru complex, but not for the Mo complex, and that this second pathway is not catalyzed by  $\text{Al}(\text{O}^i\text{Pr})_3$ . Complexes of type  $\text{RuX}_2\text{L}_3$  have a 16-electron configuration and are in principle capable to coordinate an additional 2-electron donor ligand. We can therefore easily imagine an equilibrium involving coordination of the halogenated dormant species to the Ru(II) centre, enhancing the C atom electrophilicity and triggering an internal nucleophilic substitution ( $\text{S}_{\text{Ni}}$ ), see Figure 3.



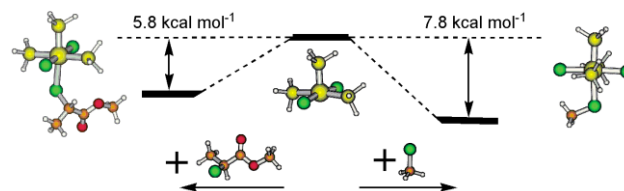
**Fig. 3.** Ideal reaction coordinate for the atom transfer and halogen exchange processes involving an ATRP catalyst  $[\text{M}]\text{-X}$  and a dormant polymer chain  $\text{R-Y}$ .

Complexes of type  $\text{CpMoX}_2\text{L}_2$ , on the other hand, have a 17-electron configuration, thus addition of a 2-electron donor would lead to an unstable 19-electron complex. In order to obtain supporting evidence for this hypothesis, DFT calculations<sup>6</sup> were carried out on the model systems  $\text{RuCl}_2(\text{PH}_3)_3$  and  $\text{CpMoCl}_2(\text{PH}_3)_2$  (a model of  $\text{CpMoCl}_2(\text{PMe}_3)_2$ , which also acts an ATRP catalyst)<sup>12</sup> and on their adducts with  $\text{RCl}$  [ $\text{R} = \text{CH}_3$ ,  $\text{CH}(\text{CH}_3)\text{COOCH}_3$ ] as models of initiators or dormant polymer chains.

As expected, the addition of either  $\text{RCl}$  molecule to the 17-electron Mo complex turned out repulsive. No stable local minimum for a 19-electron  $\text{CpMoCl}_2(\text{PH}_3)_2(\text{RCl})$  complex could be optimized. Conversely, addition of  $\text{RCl}$  to  $\text{RuCl}_2(\text{PH}_3)_3$  afforded stable adducts, as shown in Figure 4. These adducts are in fact lower in energy than the sum of the separated molecules, though a large negative entropy results in a positive free energy at 298 K for the addition process [calculated  $\Delta G^\circ_{298} = 7.3$  and  $3.9 \text{ kcal mol}^{-1}$  for  $\text{R} = \text{CH}_3$  and  $\text{CH}(\text{CH}_3)\text{COOCH}_3$ , respectively]. Isomeric adducts where  $\text{RCl}$  occupies a position trans to a Cl ligand are also local minima, but slightly higher in energy.

The Lewis acidic  $\text{Al}(\text{O}^i\text{Pr})_3$  can in principle interact only with nucleophilic centers, such as the negatively polarized halogen ligands. Therefore, it seems logical that the presence of  $\text{Al}(\text{O}^i\text{Pr})_3$  would have no effect on the  $\text{S}_{\text{Ni}}$  mechanism. The question remains of how this additive catalyzes the atom transfer process. A possibility that should be considered is a greater Lewis acid-base interaction with the halogen lone pairs in the

$\text{MX} \cdot \text{Y}$  intermediate (Scheme 2) and also in the transition state that leads to it, where these atoms are more negatively polarized relative to the organic initiator/dormant chain. Additional calculations are in progress to verify this hypothesis, as well as to probe the entire reaction coordinate for the different mechanisms (atom transfer and  $\text{S}_{\text{Ni}}$ ) leading to halogen exchange.



**Fig. 4.** DFT study of the  $\text{RCl}$  addition to  $\text{RuCl}_2(\text{PH}_3)_3$  ( $\text{R} = \text{CH}_3$ ,  $\text{CH}(\text{CH}_3)\text{COOCH}_3$ )

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## Notes and references

† The same phenomenon was observed for the Cl/Br exchange using  $\text{BrEA}$ .

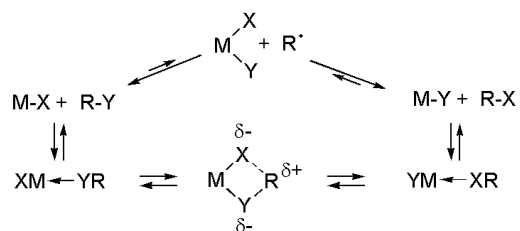
§ Cyclic voltammetry (THF): irreversible oxidation at  $E_{\text{p,a}} = 0.17 \text{ V}$ . A single crystals used for the X-ray investigation were obtained by slowly cooling a saturated toluene solution to  $-30^\circ\text{C}$ . Crystal data:  $\text{C}_{13}\text{H}_{21}\text{I}_2\text{N}_2\text{Mo}$ ,  $M = 555.06$ , orthorhombic,  $a = 12.4552(3)$ ,  $b = 17.2336(6)$ ,  $c = 7.7943(2) \text{ \AA}$ ,  $U = 1673.03(8) \text{ \AA}^3$ ,  $T = 110(2) \text{ K}$ , space group  $\text{Pnma}$  (no. 62),  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 4.462 \text{ mm}^{-1}$ , 6813 reflections measured, 1983 unique ( $R_{\text{int}} = 0.0338$ ) which were used in all calculations. The final  $wR(F^2)$  was 0.0478 (all data). The data have been deposited with the Cambridge Crystallographic Data Centre (number CCDC-243377)

‡ The growth of PDI at high conversions in the presence of transfer to monomer is well understood, see K. Matyjaszewski, *ACS Symposium Series* 1998, **685**, 2.

& Geometry optimizations were carried out at the B3LYP level. The LANL2DZ basis, augmented with an  $f$  polarization punction ( $\alpha = 0.8$ ) was used for Mo and Ru. All other atoms were described with 6-31G\* bases. No symmetry constraints were used and all normal modes had positive frequencies for all converged geometries.

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Graphical Content Entry



Text for graphical abstract:

Tri(isopropoxo)aluminium is found to catalyse halogen exchange between metal complex and organic halide initiator, as well as ATRP, when using a 17-electron half-sandwich molybdenum(III) compound.