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$Al(OPr^i)_3$-catalysed halogen exchange processes of relevance to atom transfer radical polymerization: the effect depends on the metal electronic structure

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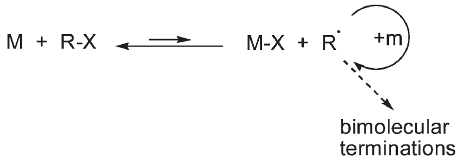
Whether or not tri(isopropoxo)aluminium catalyses halogen exchange for an ATRP catalyst depends on the number of valence electrons.

Since its discovery in 1995,[1,2] 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).

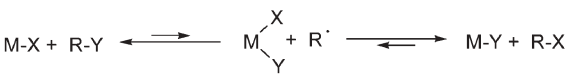
The role of species M, a transition metal complex capable of increasing its formal oxidation state and coordination number by one unit, is to catalyse the chain growth from the dormant species. Thus, ATRP depends critically on transition metal catalysis and a number of studies have been devoted to understanding its mechanistic details.[3,4]

It has been shown that the addition of certain Lewis acids, most notably $Al(OPr^i)_3$, in conjunction with a number of catalysts such as $RuCl_2(PPh_3)_3$,[5] $CpFeX(CO)_2$ (X = Br, I),[6] $NiBr_2(PPh_3)_2$,[7] $Ni(PPh_3)_4$,[8] $ReIO_2(PPh_3)_2$,[9] and CuBr/bipy,[10] 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.[4] Parallel work has shown that $Al(OPr^i)_3$ has no effect on the halogen exchange rate between the $RuCl_2(PPh_3)_3$ catalyst and a bromide initiator, RBr.[11] This is a relevant observation, because the simplest possible halogen exchange mechanism involves the ATRP intermediates, Scheme 2. Thus, the fact that $Al(OPr^i)_3$ accelerates ATRP but not halogen exchange appears rather puzzling.

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 $Al(OPr^i)_3$.[12–14] We wish to report here, using $CpMoX_2(Pr^i_2dad)$ (X = Cl, I; Pr^i_2dad = $Pr^iN{=}CH{-}CH{=}NPr^i$) as a case study, that $Al(OPr^i)_3$ *does* catalyse the halogen exchange process for an ATRP catalyst, and to rationalize the difference relative to $RuCl_2(PPh_3)_3$.[11]



Scheme 1



Scheme 2

The accelerating effect of $Al(OPr^i)_3$ on the $CpMoCl_2(Pr^i_2dad)$-catalysed ATRP of methyl acrylate (MA), initiated by ethyl 2-iodopropionate (IEA) was shown previously.[14] In order to gain insight into the $Al(OPr^i)_3$ mechanism of action for this ATRP process, a number of EPR investigations were carried out as shown in Fig. 1. Warming the solution of the complex under typical ATRP conditions, with or without the IEA initiator, but in the absence of $Al(OPr^i)_3$, did not yield any spectral change (a). In the presence of 1 equiv. of $Al(OPr^i)_3$, a new peak assigned to the new complex CpMoICl (Pr^i_2dad) became evident (b), revealing the catalytic activity of $Al(OPr^i)_3$ on the halide exchange.† 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, $CpMoI_2(Pr^i_2dad)$ (d). The latter has been isolated and fully characterized.‡

Complex $CpMoI_2(Pr^i_2dad)$ 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_{app} is 5.0×10^{-5} min^{-1} with no $Al(OPr^i)_3$ and 1.9×10^{-3} min^{-1} with 1 equiv. of $Al(OPr^i)_3$ [*cf.* 3.7×10^{-4} min^{-1} for the $CpMoCl_2$ (Pr^i_2dad)-catalyzed process].[14] Thus, k_{app} 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 Fig. 2. The measured (SEC) $\bar{M}_n$ are only slightly lower than theory, indicating the possible intervention of catalyzed chain transfer.§ Unlike the $CpMoCl_2(Pr^i_2dad)$-catalyzed process,[14] nothing indicates an initiator efficiency factor *f* lower than 1.

The observed catalytic action of $Al(OPr^i)_3$ on both the ATRP of MA (the dormant species being a $-CH_2-CH(I)-COOMe$ terminated polymer) with either $CpMoCl_2(Pr^i_2dad)$ or $CpMoI_2$–(Pr^i_2dad), and on the halogen exchange between $CpMoCl_2$ (Pr^i_2dad) and $CH_3CH(I)COOEt$, provides persuasive evidence that the processes involve the same intermediates (Scheme 2).

Now the interesting question is why the $RuCl_2(PPh_3)_3$ system

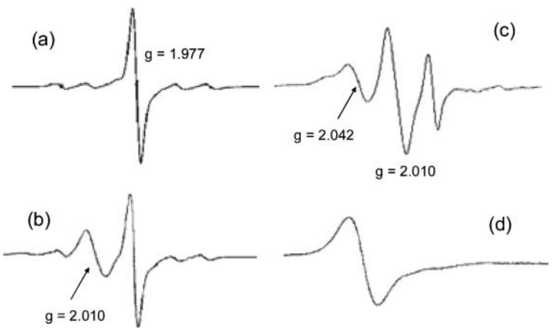


Fig. 1 EPR study of complex $CpMoCl_2(Pr^i_2dad)$ in toluene. (a) After 1 h at 80 °C with 1 equiv. of IEA (spectrum of dichloride complex); (b) as in (a) plus 1 equiv. of $Al(OPr^i)_3$; (c) with NaI (10 equiv.) in THF, 20 min at 50 °C; (d) same as (c) after 2 h (spectrum of $CpMoI_2(Pr^i_2dad)$).

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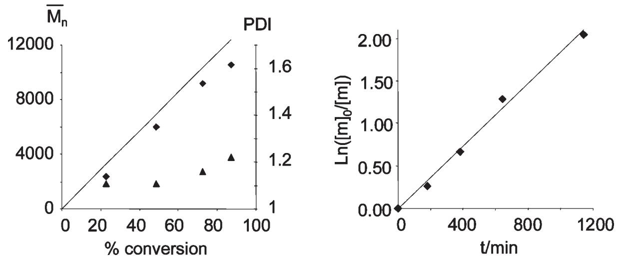

Fig. 2 Left: $\bar{M}_n$ (diamonds) and PDI (triangles) against conversion for PMA obtained from CpMoI$_2$(^{i}Pr$_2$–dad)/Al(O^{i}Pr)$_3$/IEA (MA/Mo/IEA/Al = 165/1/1/1) in toluene (30% v/v) at 80 °C. The line corresponds to the theoretical $\bar{M}_n$. Right: first order kinetics.

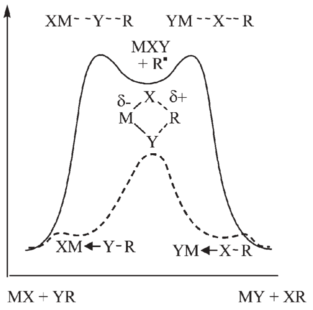

Fig. 3 Ideal reaction coordinate for the atom transfer and halogen exchange processes involving an ATRP catalyst [M]–X and a dormant polymer chain R–Y.

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 Al(OPr^i)$_3$. Complexes of type RuX$_2$L$_3$ have a 16-electron configuration and are in principle capable of coordinating 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 (S$_N$i), see Fig. 3.

Complexes of type CpMoX$_2$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¶ were carried out on the model systems RuCl$_2$(PH$_3$)$_3$ and CpMoCl$_2$(PH$_3$)$_2$ (a model of CpMoCl$_2$(PMe$_3$)$_2$, which also acts an ATRP catalyst)[12] and on their adducts with RCl [R = CH$_3$, CH(CH$_3$)COOCH$_3$] as models of initiators or dormant polymer chains.

As expected, the interaction of either RCl molecule with the 17-electron Mo complex turned out to be repulsive. No stable local minimum for a 19-electron CpMoCl$_2$(PH$_3$)$_2$(RCl) complex could be optimized. Conversely, addition of RCl to RuCl$_2$(PH$_3$)$_3$ afforded stable adducts, as shown in Fig. 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 ΔG°_{298} = 7.3 and 3.9 kcal mol^{-1} for R = CH$_3$ and CH(CH$_3$)COOCH$_3$, respectively]. Isomeric adducts where RCl occupies a position *trans* to a Cl ligand are also local minima, but slightly higher in energy.

The Lewis acidic Al(OPr^i)$_3$ can in principle interact only with nucleophilic centers, such as the negatively polarized halogen ligands. Therefore, it seems logical that the presence of Al(OPr^i)$_3$ would have no effect on the S$_N$i 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 MXY 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 S$_N$i) leading to halogen exchange.

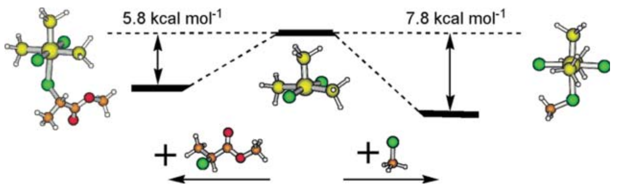

Fig. 4 DFT study of the RCl addition to RuCl$_2$(PH$_3$)$_3$ (R = CH$_3$, CH(CH$_3$)COOCH$_3$).

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Notes and references

† The same phenomenon was observed for the Cl–Br exchange using BrEA.

‡ Cyclic voltammetry (THF): irreversible oxidation at $E_{p,a}$ = 0.17 V. Single crystals used for the X-ray investigation were obtained by slowly cooling a saturated toluene solution to −30 °C. Crystal data: C$_{13}$H$_{21}$I$_2$N$_2$Mo, M = 555.06, orthorhombic, a = 12.4552(3), b = 17.2336(6), c = 7.7943(2) Å, U = 1673.03(8) Å^3, T = 110(2) K, space group *Pnma* (no. 62), Z = 4, μ(Mo–Kα) = 4.462 mm^{-1}, 6813 reflections measured, 1983 unique (R_{int} = 0.0338) which were used in all calculations. The final $wR(F^2)$ was 0.0478 (all data). The data have been deposited at the Cambridge Crystallographic Data Centre. CCDC 243377. See http://www.rsc.org/suppdata/cc/b4/b409992c/ for crystallographic data in .cif or other electronic format.

§ The growth of PDI at high conversions in the presence of transfer to monomer is well understood, see ref. 15

¶ Geometry optimizations were carried out at the B3LYP level. The LANL2DZ basis, augmented with an *f* polarization function (α = 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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