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The role of Brønsted acid catalysis in inter-metal ligand exchange reactions

Ian J. Blackmore, Vernon C. Gibson,* Andrew J. Graham, Matthew Jolly, Edward L. Marshall and Brian P. Ward

Department of Chemistry, Imperial College, South Kensington, London, UK SW7 2AY

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A Brønsted acid is shown to catalyse the inter-metal exchange of mono-anionic (alkoxide and amide) and dianionic (imido) ligands in four-coordinate molybdenum complexes of the type $\mathrm{Mo(NR)_2(X)_2}$ (R = alkyl, aryl; X = alkoxide, amide).

The exchange of ligands between metal centres forms a cornerstone of inorganic synthetic methodology. One of the first documented[1] and most widely used[2] examples is the metathetical exchange of halide for alkyl ligands using Grignard reagents or related main group metal alkyls, a reaction type that extends to mono-anionic ligands such as alkoxide and amide.[3] Exchange reactions involving dianionic oxo, imido and alkylidene ligands are less well documented, but have been observed and utilised synthetically on numerous occasions.[4–7] Here we show that these fundamentally important ligand exchange reactions can be catalysed by a Brønsted acid.

In an earlier study we showed that multiply-bonded oxo and imido ligands are readily exchanged between metal centres in four-coordinate oxo and imido complexes of the type $\mathrm{Mo(O)_2(OR)_2}$ and $\mathrm{Mo(NR')_2(OR)_2}$[5] (Scheme 1). The exchange process was found to proceed most readily where one of the reactants bears a small group such as an oxo unit. For exchange between metal centres carrying sterically more hindered units, especially imido groups, the reaction is much slower, and in some cases may not proceed at all. For example, the exchange of the imido ligands between $\mathrm{Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)_2(OBu^t)_2}$ and $\mathrm{Mo(NBu^t)_2(OBu^t)_2}$ is negligible at room temperature, while the exchange of the mono-anionic *tert*-butoxide and arylamido ligands in $\mathrm{Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)_2(OBu^t)_2}$ and $\mathrm{Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)_2(NH\text{-}2,6\text{-}Pr^i_2C_6H_3)_2}$ does not take place at any discernible rate at temperatures up to 100 °C. This may be rationalised as being a consequence of greater steric crowding in the imido- or amido-bridged dimolybdenum transition state species.

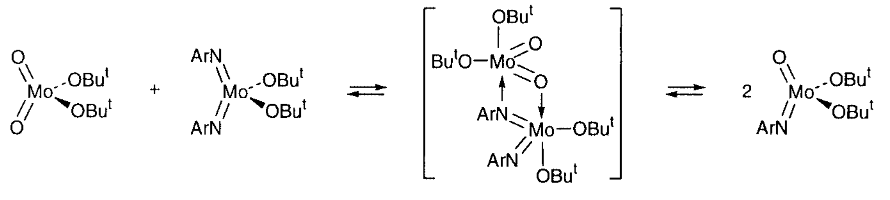
With a view to forging ligand exchange in these more difficult cases, we decided to investigate the effect of a Brønsted acid, since acid catalysis is well known to play a key role in many fundamentally important organic transformations, especially those involving multiply bonded oxygen functions (*e.g.* carboxylic acids and esters).[8] †

The reaction of $\mathrm{Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)_2(OBu^t)_2}$ with $\mathrm{Mo(NBu^t)_2(OBu^t)_2}$ (Scheme 2a), in the presence of 10% $\mathrm{H(Et_2O)_2BAr^F_4}$ ($\mathrm{Ar^F = 3,5\text{-}(CF_3)_2C_6H_3}$), was monitored by ^{1}H NMR spectroscopy in $\mathrm{CD_2Cl_2}$ solvent. The effect of the acid on the rate of ligand exchange was dramatic, increasing from effectively zero at room temperature in the absence of acid, to a steady conversion to equilibrium (K_{eq} = 95(2)) at room temperature ($k = 5.0(1) \times 10^{-6}$ dm^3 mol^{-1} s^{-1}) ‡ in the presence of $\mathrm{H(Et_2O)_2BAr^F_4}$.

Encouraged by this observation, we turned our attention to the exchange of the alkoxide and amide ligands of $\mathrm{Mo(NBu^t)_2(OBu^t)_2}$ and $\mathrm{Mo(NBu^t)_2(NHBu^t)_2}$ (Scheme 2b) which, in the absence of acid, does not proceed at all at room temperature. By contrast, upon addition of 15% $\mathrm{H(Et_2O)_2BAr^F_4}$,§ equilibrium ($K_{eq}$ = 6.0(2)) is attained within 18 h at room temperature ($k = 6.5(2) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}). For the sterically more hindered arylimido/arylamido analogues $\mathrm{Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)_2(OBu^t)_2}$ and $\mathrm{Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)_2(NH\text{-}2,6\text{-}Pr^i_2C_6H_3)_2}$ (Scheme 2c), for which there is no evidence of exchange in the absence of acid to 100 °C, addition of 30% $\mathrm{H(Et_2O)_2BAr^F_4}$§ allows equilibrium ($K_{eq}$ = 1.40(3)) to be reached within 2 days at room temperature ($k = 1.20(3) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}).

The rate of the acid catalysed reaction is slowed in the presence of excess $\mathrm{HOBu^t}$. For example, addition of 1.25 equivalents of $\mathrm{HOBu^t}$ to the imido ligand exchange reaction shown in Scheme 2a slows the ligand exchange process approximately 3-fold.¶ This suggests that $\mathrm{HOBu^t}$ dissociation is implicated in the rate determining step and that the role of the acid may be to protonate the metal-bonded oxygen of the *tert*-butoxide ligand (Scheme 3). This would allow access, *via* dissociation of *tert*-butanol, to a three-coordinate cationic bis(imido)molybdenum alkoxide species. The reduced steric hindrance at the molybdenum centre, combined with the increased electrophilicity of the formally positively charged species, would be expected to favour ligand exchange *via* M–L–M bridges. ||

The site of protonation of $\mathrm{Mo(NR')_2(OR)_2}$ species has been probed through a study of the reaction of $\mathrm{Mo(NBu^t)_2(OBu^t)_2}$ with one equivalent of $\mathrm{H(Et_2O)_2BAr^F_4}$. The ^{1}H NMR spectrum of $\mathrm{Mo(NBu^t)_2(OBu^t)_2}$ consists of two equal intensity singlets at δ 1.28 and δ 1.39. On electronegativity grounds, the higher frequency resonance can be reasonably assigned to the *tert*-butyl protons of the imido ligands. This is corroborated by examination of the per-deuteriated *tert*-butoxide complex, $\mathrm{Mo(NBu^t)_2[OC(CD_3)_3]_2}$ which affords a single resonance at δ 1.39 due to the *tert*-butylimido group. Upon treatment of $\mathrm{Mo(NBu^t)_2[OC(CD_3)_3]_2}$ with one equivalent of $\mathrm{H(Et_2O)_2BAr^F_4}$ two new singlet resonances are observed at δ 1.27 and δ 1.53 in a 1 : 1 ratio, along with a broadened resonance integrating as one hydrogen at δ 3.92 attributable to the ligand bonded proton. The chemical shift of the lower frequency *tert*-butyl signal is consistent with a *tert*-butylamido ligand (*cf.* δ 1.21 for the *tert*-butylamide ligands of $\mathrm{Mo(NBu^t)_2(NHBu^t)_2}$). This confirms



Scheme 1 The inter-metal exchange of multiply-bonded oxo and imido ligands *via* oxo and imido bridges.

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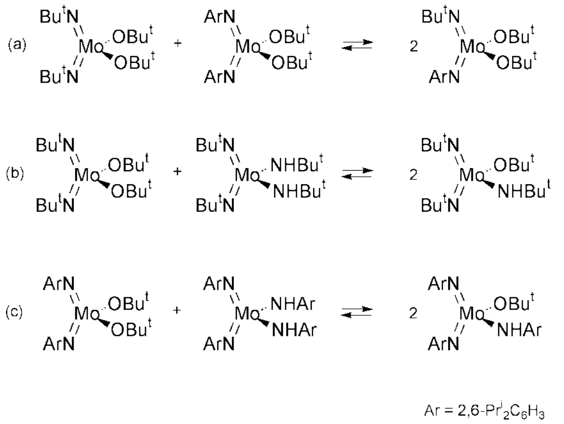
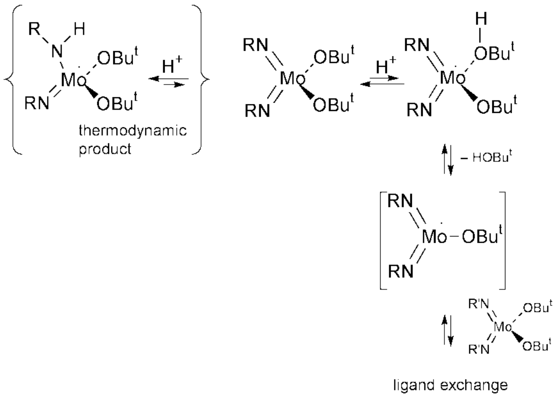


Scheme 2 Exchange of: (a) di-anionic imido ligands, and (b) and (c) mono-anionic alkoxide and amide ligands.



Scheme 3 Possible sites of protonation and proposed mechanistic pathway involving HOBu^t dissociation.

that the thermodynamically preferred site of protonation is the imido nitrogen rather than the alkoxide oxygen. The dependency of the rate of ligand exchange on *tert*-butanol concentration, however, suggests that the proton can migrate to the alkoxide oxygen to generate a metal-bonded *tert*-butanol ligand. This is not unreasonable since protonation/deprotonation of oxygen and nitrogen functions is known to be rapid and reversible.

In the case of the exchange reaction of *tert*-butylamide for *tert*-butoxide ligands (Scheme 2b), addition of acid leads to broadening of the *tert*-butylamide resonance at δ 1.21 suggesting that the nitrogen of the amide ligand is the site of protonation. This accords with the finding by Wilkinson and co-workers that $W(NBu^t)_2(NHBu^t)_2$ is protonated at the *tert*-butylamido nitrogen upon low temperature treatment with HBF_4 in diethyl ether.[10] In a further NMR experiment, *tert*-butylamine (2 equiv.) was added to a mixture of $Mo(NBu^t)_2(NHBu^t)_2/H(Et_2O)_2BAr^F_4$ (15 mol%); the resultant spectrum showed a single *tert*-butyl resonance for the amide ligand at δ 1.15, shifted towards the chemical shift for free *tert*-butylamine (δ 1.10). Addition of a further 4, followed by 6 equiv. of *tert*-butylamine led to a further shift of this resonance towards that of free *tert*-butylamine, indicating that the amide ligands are exchanging rapidly with the free *tert*-butylamine on the timescale of the NMR experiment. In the absence of acid, no such exchange is seen. These observations are consistent with protonation at the amido nitrogen and acid catalysing the exchange of the amide ligand with free amine.

These results highlight the catalytic effect of a Brønsted acid in the exchange between metal centres of mono-anionic and di-anionic ligands, and indicate a potentially much wider role for Brønsted acid catalysis in these and related inorganic transformations. It is also likely that Brønsted acid catalysis could play an important role in metal-mediated transformations of organic substrates. To this end, we are presently investigating the effect of acid on the reactivity of metal oxo and imido species towards unsaturated organic substrates.

Acknowledgements

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Notes and references

† Oxo-alkoxo complexes of the Group 6 metals may be viewed as relatives of organic esters; in the older chemical literature such metal species are refered to as metalate esters.

‡ Rate determined using a second order reversible treatment, see ref. 9.

§ This concentration of acid was chosen to give a conveniently measurable rate of conversion. While there is a clear dependence of the rate of conversion on acid concentration, it has not proved possible to date to determine with precision the order of this dependence.

¶ It has not proved possible to obtain accurate quantitative rate data for this process due to the difficulty in integrating NMR resonances, many of which overlap, in this multi-component mixture. Nevertheless, the gross effect of the added HOBu^t in slowing down the reaction is clear. It should be noted that there is no evidence for adduct formation in these sterically hindered systems, and therefore the suppression of the rate is unlikely to be a result of *tert*-butanol binding to the four-coordinate molybdenum species.

|| The alternative site of protonation, the nitrogen of the imido ligand, would not be expected to enhance the rate of ligand exchange since the resultant amido group would lead to greater steric hindrance at the metal centre and thereby disfavour the formation of M–L–M bridges.

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