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Pairwise ligand exchange reactions in tetrahedral and pseudo-tetrahedral transition metal complexes†

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Ligand exchange reactions between various transition-metal complexes of the form [Mo(Q)$_2$X$_2$], [M(Q)CpX$_2$] and [Mo(Q)$_2$CpX], where Q and X are di-anionic and mono-anionic ligands, respectively, and M is Nb or Ta, have been studied. The formal electron count at the metal, and also the steric and electronic properties of the supporting ligands, are found to influence exchange rates, while ligand steric and electronic properties affect equilibrium constants.

Introduction

The exchange of anionic ligands between electropositive metal centres forms a cornerstone of inorganic synthetic methodology. One of the best known and most widely exploited examples is the metathetical exchange of a halide ligand for a group such as alkyl or aryl using main group compounds such as Grignard reagents or their alkali metal relatives.[1,2] Analogous processes are also widely documented for transition-metal species, usually involving mono-anionic groups such as halide, alkoxide or amide, *etc.*[3–7] More recently examples involving dianionic groups such as oxo, imido or alkylidene have been described.[8–15]

Some time ago we initiated a programme of study to learn more about these fundamentally important and synthetically useful transformations.[16] A potential challenge in studying this type of process for transition metals is the enormous variety, not only of metals, but also of coordination numbers and ligand combinations available; the task is then one of selecting a suitable coordination geometry, ligand types and metals which would allow the factors contributing to the exchange process to be delineated.

Following initial observations of relatively clean and facile exchange processes in some molybdenum and niobium systems, we decided to focus on pseudo-tetrahedral complexes of the type [M(Q)$_2$X$_2$] and [M′(Q)X$_3$] where X is a mono-anionic ligand such as halide, alkoxide, amide or even cyclopentadienyl and where Q is a dianionic group such as oxo, imido or alkylidene. This coordination geometry offers several advantages: (i) a wide variety of closely related derivatives can be readily synthesised, (ii) a tetrahedral or pseudo-tetrahedral geometry is maintained in the reactants and products,‡ and (iii) the steric and electronic environment around the metal can be varied in a controlled manner through appropriate choice of Q and X ligands. An additional facet of this system is that it has the potential to allow competitive effects between the ligands to be assessed since there exists a direct competition between the ligands for the available d$_\pi$-symmetry metal orbitals in a tetrahedral geometry.[17]

The three systems forming the basis of this study are shown in Fig. 1. Their steric and electronic characteristics are worth pointing out at this stage. Firstly, the two systems containing the cyclopentadienyl moiety tend to be more sterically hindered; this is partly due to the fact that five ligand (carbon) atoms are interacting with the metal centre compared with only one donor atom for an oxo or imido group. Secondly, the electron count of the complexes effectively increases in the order I < II < III. For example, if the Cp ligand is considered to contribute five electrons, and the dianionic Q and monianionic X ligands their minimum quota of two and one electrons (as neutral ligands) respectively, the electron count proceeds from 12 to 14 to 16 for Classes I through III. It has to be recognised, however, that for ligand donor atoms possessing lone pairs of electrons (which is the case for both the Q and X ligands discussed here), additional electron density will usually be donated to the metal centre *via* p$_\pi$ to d$_\pi$ donation depending on the electronegativity of the donor atom and the availability of empty metal d-orbitals of suitable symmetry.§ Such ligands inevitably lead to increased electron density at the metal centre over and above the minimum electron count provided by the ligand set. Nevertheless, the trend of increasing electron count from Classes I through III is clear.

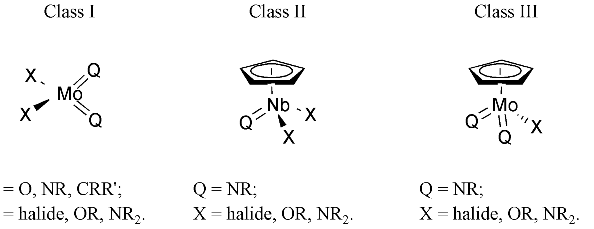

Fig. 1 Generalised representations of the three classes of ligand exchange systems.

Earlier investigations

In a previous study we examined the exchange of the oxo and imido ligands in four-coordinate molybdenum complexes of Class I. For the reactants Mo(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(O^{t}Bu)$_2$ and Mo(O)$_2$(O^{t}Bu)$_2$ (eqn. (1)), the exchange reaction was found to proceed cleanly and at a convenient rate for a kinetic study by NMR spectroscopy. However, the rate data for this reaction were later found to be difficult to reproduce, and appeared to be sensitive to the drying procedure for the glassware and different batches of solvent. This led us to suspect that a proton source, possibly derived from moisture, may be influencing the reaction rate which, in turn, led us to examine more generally the effect of proton acid catalysis on the pairwise ligand exchange process. In a subsequent investigation, a clear role for acid in

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† Electronic supplementary information (ESI) available: Experimental procedures for synthesis of new compounds and for NMR-scale ligand exchange reactions as well as ^{1}H NMR spectroscopic data characterising products of these reactions. See http://www.rsc.org/suppdata/dt/b3/b308062e/

‡ X-Ray crystal structure determinations on representative examples of [Mo(Q)$_2$X$_2$] and [Nb(Q)CpX$_2$] compounds, including [Mo(O)$_2$(O^{t}Bu)$_2$] and [Nb(N^{t}Bu)Cp(OCMe$_2$CF$_3$)$_2$], reveal mononuclear structures: M. Jolly, PhD thesis, University of Durham, 1994.

§ For tetrahedral and pseudo-tetrahedral metal complexes, it is possible to form only three p$_\pi$–d$_\pi$ bonds and so the ligands are effectively in competition for the available metal orbitals.

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catalysing the exchange reaction was established.[18] It also appeared that the oxo–imido exchange reaction shown in eqn. (1) may be particularly sensitive due to the propensity

$$\underset{\mathbf{1}}{[Mo(O)_2(O^tBu)_2]} + \underset{\mathbf{3}}{[Mo(NAr)_2(O^tBu)_2]} \rightleftharpoons 2\,\underset{\mathbf{B_{1,3}}}{[Mo(O)(NAr)(O^tBu)_2]} \qquad (1)$$

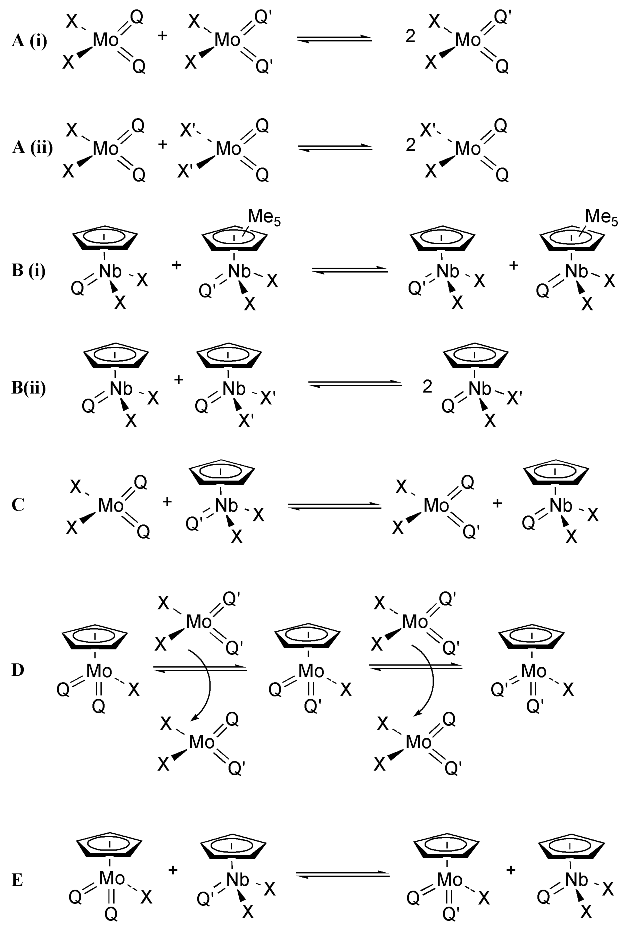
{Ar = 2,6-$^iPr_2C_6H_3$}

of $[Mo(O)_2(O^tBu)_2]$ to undergo autocatalytic decomposition upon exposure to trace amounts of moisture. The product of bulk decomposition of $[Mo(O)_2(O^tBu)_2]$ is a blue solid,[19] the so-called 'molybdenum blues', which comprise Mo(v) oxo–hydroxide cluster species.[20] Although a blue solid is not observed during the exchange reaction, it is possible that trace decomposition could occur with the generation of a proton source which then affects the rate of the exchange reaction. We report here the results of a further kinetic study on this system using more rigorous drying procedures, along with a study of exchange reactions involving a wide variety of tetrahedral and pseudo-tetrahedral species of types I to III.

Results

Introduction

Eight main classes of exchange reaction have been addressed; these are outlined in Scheme 1. Type A entails exchange between two different $[Mo(Q)_2X_2]$ (Class I) species; either of their dianionic (Type A(i)) ligands or their monoanionic (Type A(ii)) ligands. Similar exchange processes (Types B(i) and B(ii)) may be envisaged between two species of the type $[M(Q)(\eta^5\text{-}C_5R_5)X_2]$ (Class II) {where R = H or Me and M is a metal from Group 5, namely Nb or Ta}. We have also studied dianionic ligand exchange reactions between Class I and Class II compounds (C), between Class I and compounds of the type $[Mo(Q)_2(\eta^5\text{-}C_5R_5)X]$ (Class III, D) and between compounds of Classes II and III (E).



Scheme 1 Ligand exchange reactions employed in the present study.

Table 1 Species of the type $[Mo(Q)_2X_2]$

	$(Q)_2$			
X_2	$(O)_2$	$(N^tBu)_2$	$(NAr)_2$	$(NAr)(CHCMe_2Ph)$
$(O^tBu)_2$	**1**[17]	**2**	**3**[17]	**4**[21]
$(O^tBu^{F3})_2$	**5**	**6**		**7**[21]
$(O^tBu^{F6})_2$	**8**	**9**		**10**[21]
$(O^iPr)_2$		**11**		
Cl_2		**12**[22]		
$(NH^tBu)_2$		**13**[23]		

Ar = 2,6-$^iPr_2C_6H_3$; $^tBu^{F3}$ = $C(CH_3)_2(CF_3)$; $^tBu^{F6}$ = $C(CH_3)(CF_3)_2$. Syntheses of uncited compounds are described in the present work.

Table 2 Species of the type $[M(Q)(\eta^5\text{-}C_5R_5)X_2]$

	(Q)		
X_2	(NAr)	(N^tBu)	(NMe)
Cl_2	Cp **14**[24] Cp* **15**;[24] Ta **15a**[24]	**16**[24]	Cp **17**[24] Cp* **18**[24]
$(O^tBu)_2$		**19**	
$(O^tBu^{F3})_2$		**20**	
$(O^tBu^{F3})_2$		**21**	
$(O^iPr)_2$		**22**	
Br_2		**23**	
$(NH^tBu)_2$		**24**[25]	
$(Pyrrolyl)_2$		**25**	

Ar = 2,6-$^iPr_2C_6H_3$; $^tBu^{F3}$ = $C(CH_3)_2(CF_3)$; $^tBu^{F6}$ = $C(CH_3)(CF_3)_2$; pyrrolyl = (NC_4H_4); M = Nb except where stated otherwise. Syntheses of uncited compounds are described in the present work.

Table 3 Other reactants

$[Mo(N^tBu)_2CpCl]$	**26**[26]
$[Mo(O)_2Cl_2(DME)]$	**27**[27,28]
$[Mo(N^tBu)_2Cl_2(DME)]$	**28**[27,28]

DME = 1,2-Dimethoxyethane.

For convenience, the starting species involved in the ligand exchange reactions studied are labelled with numerals and grouped together in Tables 1–3. Similarly, mixed ligand species produced by the pairwise exchange process are labelled with capital letters and subscripts to indicate the two starting species from which the product is derived (Tables 4 and 5).

The ligand exchange reactions were monitored by ^1H NMR spectroscopy. This is an advantageous technique since the species involved in, and synthesised by, these exchange reactions tend to afford clean ^1H NMR spectra with sharp and readily assignable resonances (see for examples Figs. 2 and 5). Thus accurate concentrations of all the solution species can be determined at all times by comparison of the integrals of selected peaks, chosen for maximum clarity and comparability.

A(i): Dianionic ligand exchange between complexes of the form $[Mo(Q)_2X_2]$

The exchange reaction shown in eqn. (1)[16] has been reinvestigated. At room temperature in C_6D_6, a 0.048 mol dm^{-3} solution of a mixture of **1** and **3** equilibrated over *ca.* 4 weeks to give a mixture of **1**, **3** and $\mathbf{B_{1,3}}$ with an equilibrium constant, K_{eq}(298 K), of 1.37 (Fig. 2). The plot arising from a second order treatment of the data[29] (see Experimental section) is shown in Fig. 3, affording a rate constant, k_1(298 K), of 7.32 × 10^{-6} dm^3 mol^{-1} s^{-1}. The effect of temperature on rate constant for this reaction was probed over the temperature range 20–60 °C; the data are collected in Table 6. From a plot of

Table 4 Mixed dianionic ligand species produced by ligand exchange reactions

Q, Q′ (a) [Mo(Q)(Q′)X$_2$]	(X)$_2$ or X (O^{t}Bu)$_2$	 (O^{t}Bu^{F3})$_2$	 (O^{t}Bu^{F6})$_2$
(O)(N^{t}Bu)	**A**$_{1,2}$	**D**$_{5,6}$	**E**$_{8,9}$
(O)(NAr)	**B**$_{1.3}$		
(N^{t}Bu)(NAr)	**C**$_{2,3}$^{a}		
(b) [Mo(Q)(Q′)CpX]	Cl		
(N^{t}Bu)(NAr)	**E′**$_{3,26}$		
(NAr)(NAr)	**F′**$_{3,E'/C,E'}$		
(N^{t}Bu)(NMe)	**G′**$_{17,26}$		
(c) [Mo(Q)(Q′)X$_2$(DME)]	Cl$_2$		
(O)(N^{t}Bu)	**H′**$_{27,28}$		

Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; ^{t}Bu^{F3} = C(CH$_3$)$_2$(CF$_3$); ^{t}Bu^{F6} = C(CH$_3$)(CF$_3$)$_2$; DME = 1,2-dimethoxyethane. ^{a} Or **C**$_{3,26}$ or **C**$_{3,19}$ or **C**$_{3,E'}$.

Table 5 Mixed monoanionic ligand species produced by ligand exchange reactions

(X)(X′) (a) [Mo(Q)$_2$(X)(X′)]	(Q)$_2$ or Q (O)$_2$	 (^{t}BuN)$_2$	 (NAr)(CHCMe$_2$Ph)
(O^{t}Bu)(O^{t}Bu^{F3})	**F**$_{1,5}$	**I**$_{2,6}$	**L**$_{4,7}$
(O^{t}Bu)(O^{t}Bu^{F6})	**G**$_{1,8}$	**J**$_{2,9}$	**M**$_{4,10}$
(O^{t}Bu^{F3})(O^{t}Bu^{F6})	**H**$_{5,8}$	**K**$_{6,9}$	**N**$_{7,10}$
(O^{t}Bu)(O^{i}Pr)		**O**$_{2,11}$	
Cl(O^{t}Bu)		**P**$_{2,12}$	
Cl(NH^{t}Bu)		**Q**$_{12,13}$	
(O^{t}Bu)(NH^{t}Bu)		**R**$_{2,13}$	
(b) [M(Q)Cp(X)(X′)]	(NAr)	(N^{t}Bu)	(NMe)
(Cl)(Cl)		Cp* **S**$_{16,18/5,16}$	Cp*, Ta **T**$_{15a,17}$
(O^{t}Bu)(O^{t}Bu)	**U**$_{3,19}$		
(O^{t}Bu)(O^{t}Bu^{F3})		**V**$_{19,20}$	
(O^{t}Bu)(O^{t}Bu^{F6})		**W**$_{19,21}$	
(O^{t}Bu^{F3})(O^{t}Bu^{F6})		**X**$_{20,21}$	
(O^{t}Bu)(O^{i}Pr)		**Y**$_{19,22}$	
(Cl)(Br)		**Z**$_{16,23}$	
Cl(O^{t}Bu)		**A′**$_{2,12/16,19}$	
Cl(NH^{t}Bu)		**B′**$_{12,13/16,24}$	
(O^{t}Bu)(NH^{t}Bu)		**C′**$_{2,13/19,24}$	
Cl(pyrrolyl)		**D′**$_{16,25}$	

Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; ^{t}Bu^{F3} = C(CH$_3$)$_2$(CF$_3$); ^{t}Bu^{F6} = C(CH$_3$)(CF$_3$)$_2$; pyrrolyl = (NC$_4$H$_4$). M = Nb unless stated otherwise.

Table 6 Second-order rate constants obtained from ligand exchange reactions between **1** and **3** at various temperatures

T/K	$k_{1,T}$/dm^3 mol^{-1} s^{-1}
293	7.32×10^{-6}
313	2.47×10^{-5}
323	3.75×10^{-5}
333	3.18×10^{-4}

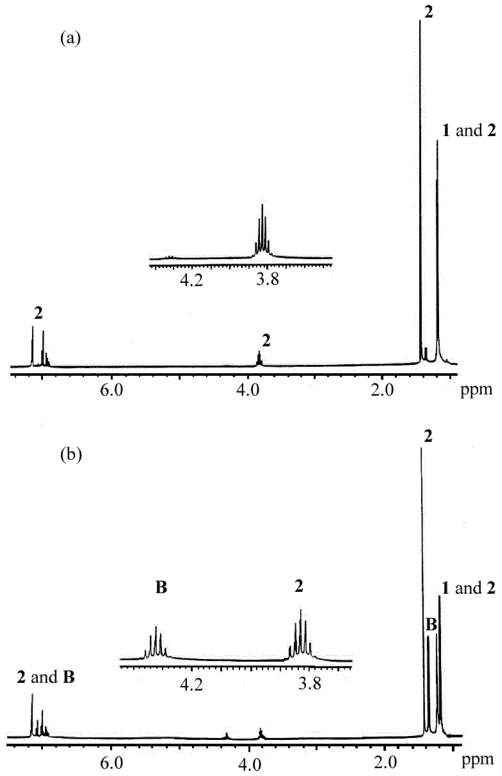


Fig. 2 ^{1}H NMR spectra of the reaction between [Mo(O)$_2$(O^{t}Bu)$_2$] (**1**) and [Mo(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(O^{t}Bu)$_2$] (**3**) to give [Mo(O)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$] (**B**$_{1,3}$) after (a) 1 h and (b) at equilibrium (4 weeks).

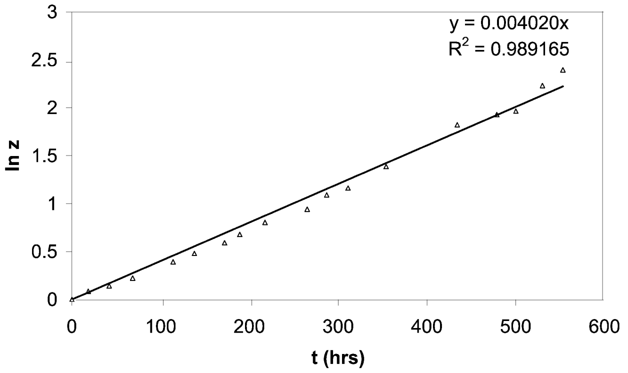


Fig. 3 Second-order reversible kinetic plot for the reaction between **1** and **3** to yield **B**$_{1,3}$ $\{z = [x(a - 2x_e) + ax_e]/[a(x_e - x)]\}$.

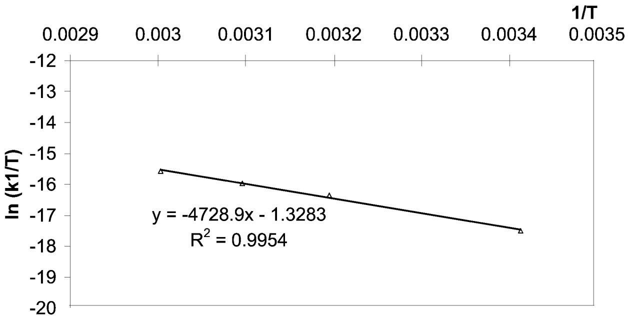


Fig. 4 Plot of ln(k_1/T) *vs.* (1/T) for the ligand exchange reaction between **1** and **3**.

ln(k_1/T) *vs.* 1/T[30] (Fig. 4), the following activation parameters were obtained: $\Delta H^{\neq}_{298}$ = 39.3 kJ mol^{-1}; $\Delta S^{\neq}$ = −208.6 J K^{-1} mol^{-1}; $\Delta G^{\neq}_{298}$ = 101.5 kJ mol^{-1}.

Exchange of oxo groups with *tert*-butyl imido groups has also been probed through the reaction of **1** with **2** to yield **A**$_{1,2}$; this proceeds much more rapidly than for O/NAr exchange (hours at room temperature). The product-favouring equilibrium [K_{eq}(298 K) > 100] allows for a preparative-scale synthesis of **A**$_{1,2}$, although it is found to be extremely sensitive to oxygen and/or moisture. A rate constant, k_1(298 K), of 1.06×10^{-3} dm^3 mol^{-1} s^{-1} was calculated for the exchange process; in this case, since the equilibrium so strongly favours the product, a non-reversible treatment may be used.[29]

Table 7 Summary of equilibrium constants and times to equilibrium for exchange of monoanionic ligands in [Mo(Q)$_2$X$_2$] systems

Entry	Reactants (a) [Mo(O)$_2$X$_2$]	K_{eq}(298 K)	Time to equilibrium (R.T.)
1	X = O^{t}Bu, **1** and X = O^{t}Bu^{F3}, **5**	5–15	<5 min
2	X = O^{t}Bu, **1** and X = O^{t}Bu^{F6}, **8**	30–80	<5 min
3	X = O^{t}Bu^{F3}, **5** and X = O^{t}Bu^{F6}, **8**	5–15	<5 min
	(b) [Mo(NAr)(CHCMe$_2$Ph)X$_2$]		
4	X = O^{t}Bu, **4** and X = O^{t}Bu^{F3}, **7**	11.0	<<5 min
5	X = O^{t}Bu, **4** and X = O^{t}Bu^{F6}, **10**	120	<<5 min
6	X = O^{t}Bu^{F3}, **7** and X = O^{t}Bu^{F6}, **10**	8.0	<5 min
	(c) [Mo(N^{t}Bu)$_2$X$_2$]		
7	X = O^{t}Bu, **2** and X = O^{t}Bu^{F3}, **6**	7.0	5–10 min
8	X = O^{t}Bu, **2** and X = O^{t}Bu^{F6}, **9**	50	5–10 min
9	X = O^{t}Bu^{F3}, **6** and X = O^{t}Bu^{F6}, **9**	7.0	15 min
10	X = O^{t}Bu, **2** and X = O^{i}Pr, **11**	3.0	<5 min
11	X = Cl, **12** and X = O^{t}Bu, **2**	$>10^4$	<5 min ($k_1 > 7.7$ dm^3 mol^{-1} s^{-1})
12	X = Cl, **12** and X = NH^{t}Bu, **13**	$>10^4$	<5 min ($k_1 > 7.7$ dm^3 mol^{-1} s^{-1})
13	X = O^{t}Bu, **2** and X = NH^{t}Bu, **13**	20	15 d ($k_1 = 5.2 \times 10$–5 dm^3 mol^{-1} s^{-1})

Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; ^{t}Bu^{F3} = C(CH$_3$)$_2$(CF$_3$); ^{t}Bu^{F6} = C(CH$_3$)(CF$_3$)$_2$.

In order to probe the effect of changes to the ancilliary alkoxide ligands, similar experiments were performed using the trifluoro-*tert*-butoxide (reaction of **5** with **6** to give **D**$_{5,6}$) and hexafluoro-*tert*-butoxide (reaction of **8** with **9** to give **E**$_{8,9}$) analogues of **1** and **2**. Substitution of three and six fluorines on each *tert*-butyl group had little effect on the rate of exchange in the case of the trifluoro-*tert*-butoxide system [k_1(298 K) = 1.3×10^{-3} *vs.* 1.06×10^{-3} dm^3 mol^{-1} s^{-1}] but a more marked effect in the case of the hexafluoro-*tert*-butoxide system [k_1(298 K) = 5.4×10^{-4} dm^3 mol^{-1} s^{-1}]; in both cases the equilibrium constant strongly favoured the products [K_{eq}(298 K) > 100].

The exchange of arylimido and *tert*-butylimido ligands between **2** and **3** to give the mixed imido product **C**$_{2,3}$,[16] although proceeding visibly at room temperature, was extremely slow and proceeded at a more convenient rate by heating the mixture to 60 °C. At this temperature, equilibrium [K_{eq}(333 K) = 25] was attained within 5 days. The relatively high equilibrium constant once again allows for a preparative-scale synthesis of the mixed ligand product (**C**$_{2,3}$). A sample of this compound in C$_6$D$_6$ at room temperature revealed very slow appearance (by NMR) of resonances attributable to **2** and **3** confirming the equilibrium nature of the exchange reaction.

We have also briefly investigated oxo/imido exchange between [Mo(Q)$_2$Cl$_2$(DME)] species (DME = 1,2-dimethoxyethane). Although such compounds do not fall under the umbrella of 'pseudo-tetrahedral' metal complexes, the potential lability of the bidentate donor could feasibly allow them to access four-coordinate species. [Mo(N^{t}Bu)$_2$Cl$_2$(DME)] (**28**) and [Mo(O)$_2$Cl$_2$(DME)] (**27**) were found to exchange oxo and imido ligands to form [Mo(O)(N^{t}Bu)Cl$_2$(DME)] (**H′**$_{27,28}$) over 3 days at room temperature. The equilibrium mixture was highly product-rich [K_{eq}(298 K) ≈ 200] and a second order non-reversible kinetic treatment afforded a rate constant, k_1(298 K), of 2.3×10^{-4} dm^3 mol^{-1} s^{-1}. The high value of K_{eq} allows the synthesis of **H′**$_{27,28}$ on a preparative scale; it was obtained in moderate yield as a pale green solid after crystallisation from diethyl ether at −78 °C.

As a further demonstration of the slower ligand exchange reactivity of these six-coordinate complexes, [Mo(N^{t}Bu)-Cl$_2$(DME)] and [Mo(NAr)$_2$Cl$_2$(DME)] were mixed and heated to 60 °C for several weeks. No reaction was observed, in contrast to (NAr)/(N^{t}Bu) exchange in the tetrahedral [Mo(Q)$_2$X$_2$] system which reaches equilibrium in 5 days at this temperature.

A(ii) Monoanionic ligand exchange between compounds of the form [Mo(Q)$_2$(X)$_2$]

The exchange of *tert*-butoxide ligands (substituted with 0, 3 or 6 fluorines) has been probed in the system [Mo(O)$_2$(OR)$_2$]; the data are collected in Table 7. In the cases of (O^{t}Bu)/(O^{t}Bu^{F3}) exchange (reaction of **1** with **5** to give **F**$_{1,5}$; entry 1), (O^{t}Bu)/(O^{t}Bu^{F6}) exchange (reaction of **1** with **8** to give **G**$_{1,8}$; entry 2) and (O^{t}Bu^{F3})/(O^{t}Bu^{F6}) exchange (reaction of **5** with **8** to give **H**$_{5,8}$; entry 3), equilibrium was achieved extremely rapidly (<5 min) at room temperature. Due to broadening in the ^{1}H NMR spectra of these mixtures, a result of intermetal alkoxide exchange of the type seen in the Mo(O)$_2$(O^{t}Bu)$_2$/Mo(N^{t}Bu)$_2$-(O^{t}Bu)$_2$ system (*vide supra*), accurate determination of equilibrium constants was not possible. However, estimates could be made, giving a value for K_{eq}(298 K) in the range 5–15 for entries 1 and 3 and 30–80 for exchange of O^{t}Bu/O^{t}Bu^{F6} exchange (entry 2).

A similar series of experiments has been carried out using systems supported by other dianionic ligand sets. In the case where (Q)$_2$ = (NAr)(C(H)CMe$_2$Ph), exchange of (O^{t}Bu) and (O^{t}Bu^{F3}) (reaction of **4** with **7** to yield **L**$_{4,7}$; entry 4) proceeded extremely rapidly (<5 min at −80 °C) to yield a mixture with an equilibrium constant, K_{eq}(298 K), of 11.0. Exchange of (O^{t}Bu) and (O^{t}Bu^{F6}) (reaction of **4** with **10** to give **M**$_{4,10}$; entry 5) yielded a mixture much richer in products [K_{eq}(298 K) = 120]. This reaction was also very rapid, as was (O^{t}Bu^{F3})/(O^{t}Bu^{F6}) exchange (reaction of **7** with **10** to yield **N**$_{7,10}$; entry 6) [K_{eq}(298 K) = 8.0]. These rapid ligand exchange reactions involving molybdenum alkylidene species have been exploited to control *cis–trans* selectivity in ring-opening metathesis polymerisation reactions.[31]

Where (Q)$_2$ = (N^{t}Bu)$_2$, the reactions are slightly slower than for those outlined above; however the results are still broadly comparable. Additionally, with this supporting imido ligand, exchange of other monoanionic ligands, specifically: chloride with *tert*-butoxide (reaction of **12** with **2** to give **A′**$_{2,12}$; entry 11), chloride with *tert*-butylamide (reaction of **12** with **13** to give **B′**$_{12,13}$; entry 12), and *tert*-butoxide with *tert*-butylamide (reaction of **2** with **13** to give **C′**$_{2,13}$; entry 13) has been probed. These reactions tend to favour strongly the mixed-ligand products and, in all but the last case, to be extremely rapid. A second-order reversible treatment of the results (*vide supra*) afforded a rate constant, k_1(298 K) of 5.2×10^{-5} dm^3 mol^{-1} s^{-1}.

Table 8 Reaction parameters and kinetic data for the exchange of alkoxide ligands in [Nb(N^{t}Bu)CpX$_2$] systems

Ligands exchanged	Reactants	Product	K_{eq}(298 K)^a	k_1/dm^3 mol^{-1} s^{-1}	Time to equilibrium; temp.
O^{t}Bu/O^{i}Pr	**19** + **22**	$\mathbf{Y}_{19,22}$	4.0	2.8 × 10^{-4}	48 h; R.T.
O^{t}Bu/O^{t}Bu^{F3}	**19** + **20**	$\mathbf{V}_{19,20}$	6.7 (333 K)	4.1 × 10^{-5}	10 d; 60 °C
O^{t}Bu/O^{t}Bu^{F6}	**19** + **21**	$\mathbf{W}_{19,21}$	43 (333 K)	1.9 × 10^{-5}	70 d; 60 °C
O^{t}Bu^{F3}/O^{t}Bu^{F6}	**20** + **21**	$\mathbf{X}_{210,21}$	7.0 (373 K)	5.8 × 10^{-6}	100 d; 100 °C
Cl/Br	**16** + **23**	$\mathbf{Z}_{16,23}$	N/R	>7.7	5 min; R.T.
Cl/O^{t}Bu	**16** + **19**	$\mathbf{A}'_{16,19}$	N/R	1.3 × 10^{-2}	2 h; R.T.
Cl/NH^{t}Bu	**16** + **24**	$\mathbf{B}'_{16,24}$	N/R	9.7 × 10^{-4}	24 h; R.T.
Cl/NC$_4$H$_4$	**16** + **25**	$\mathbf{D}'_{16,25}$	15	2.5 × 10^{-1}	20 min; R.T.
O^{t}Bu/NH^{t}Bu	**19** + **24**	$\mathbf{C}'_{19,24}$	15 (est.) (373 K)	*ca.* 8 × 10^{-7}	20% complete after 60 d; 100 °C

^{t}Bu^{F3} = C(CH$_3$)$_2$(CF$_3$); ^{t}Bu^{F6} = C(CH$_3$)(CF$_3$)$_2$; N/R = non-reversible. ^{a} Unless stated otherwise.

B(i) Exchange of dianionic ligands between compounds of the form [M(Q)CpX$_2$] {M = Nb, Ta}

We have previously described the exchange reaction between [Nb(NMe)Cp*Cl$_2$] (**18**) and [Nb(N^{t}Bu)CpCl$_2$] (**16**) to give [Nb(N^{t}Bu)Cp*Cl$_2$] ($\mathbf{S}_{16,18}$) and [Nb(NMe)CpCl$_2$] (**17**).[16] This equilibrium lies far to the left [K_{eq}(373 K) = 0.18] and requires several days (*ca.* 10) at 100 °C for the reaction to equilibrate.

In order to eliminate the possibility of the observed products arising from inter-metal exchange of the cyclopentadienyl ligands, [Ta(NAr)Cp*Cl$_2$] (**15a**) and [Nb(NMe)CpCl$_2$] (**17**) were mixed together in a 'double-crossover' experiment.[16] The products obtained consisted solely of [Ta(NMe)Cp*Cl$_2$] ($\mathbf{T}_{15a,17}$) and [Nb(NAr)CpCl$_2$] (**14**) demonstrating unambiguously that inter-metal imido-ligand exchange was taking place. Ring exchange would result in formation of [Ta(NAr)CpCl$_2$] and [Nb(NMe)Cp*Cl$_2$] which are not observed in the ^{1}H NMR spectrum of the product mixture. An equilibrium constant could not be calculated for this reaction since the ^{1}H NMR spectroscopic resonances attributable to $\mathbf{T}_{15a,17}$ were not discernable, owing to overlap.

The effect on rate of increasing the size of the ligands is once again seen from the reaction of [Nb(NAr)Cp*Cl$_2$] (**15**) with [Nb(N^{t}Bu)CpCl$_2$] (**16**) to give [Nb(N^{t}Bu)Cp*Cl$_2$] ($\mathbf{S}_{15,16}$) and [Nb(NAr)CpCl$_2$] (**14**). This reaction required several weeks at 140 °C to attain equilibrium, unlike the analogous (N^{t}Bu)/(NMe) exchange reaction above which required 10 days at 100 °C. The temperature required to drive the reaction towards equilibrium is so high that some decomposition occurs, and therefore an accurate K_{eq} could not be determined. The third possible imido/imido exchange reaction in the [Nb(NR)Cp/Cp*Cl$_2$] system is (NAr)/(NMe), *i.e.* the reaction of **15** with **17** to give **18** and **14**. As might be anticipated, this exchange has a rate intermediate between the two already discussed, taking *ca.* two weeks at 140 °C to reach equlibrium.

B(ii) Exchange of monoanionic ligands between compounds of the form [Nb(Q)CpX$_2$]

In a similar manner to the [Mo(Q)$_2$X$_2$] systems discussed earlier, alkoxide/alkoxide ligand exchange has been studied between niobium centres supported by an imido ligand and a cyclopentadienyl ring. The results are collected in Table 8. A stack plot showing the progress (*via* ^{1}H NMR spectroscopy) of the reaction between **19** and **20** to give $\mathbf{V}_{19,20}$ is shown in Fig. 5.

Unlike the [Mo(Q)$_2$X$_2$] systems, the exchange reactions in these half-sandwich niobium species are sufficiently slow to allow a second-order reversible kinetic treatment to calculate rate constants; these are also given in Table 8.

Ligand exchange reactions involving halides are the fastest in this class. For example, chloride for bromide exchange proceeded to completion within 5 min (reaction of **16** with **23** to give $\mathbf{Z}_{16,23}$), and chloride exchanged with *tert*-butoxide (reaction of **16** with **19** to give $\mathbf{A}'_{16,19}$) within 2 h at room temperature. Both equilibria lie strongly to the side of the products (no reactants are detectable by NMR spectroscopy). In this case, the reaction was slow enough to study its kinetics by NMR spectroscopy. A standard second-order non-reversible treatment gave a rate constant, k_1(298 K) of 1.27 × 10^{-2} dm^3 mol^{-1} s^{-1}.

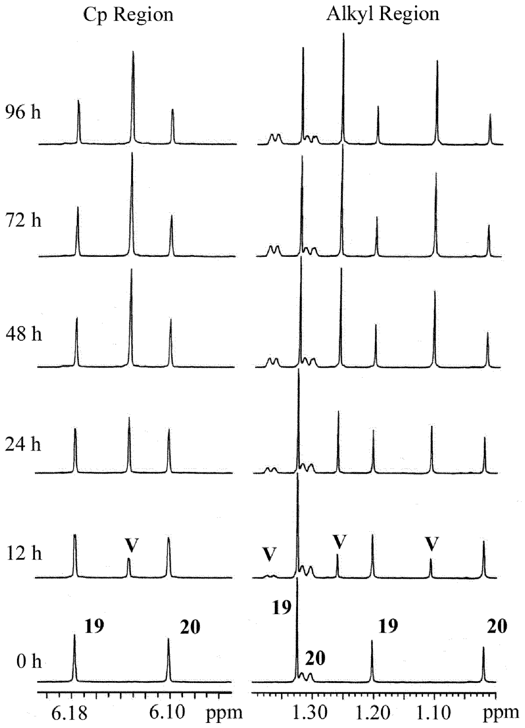


Fig. 5 Stack plot of the ^{1}H NMR spectra of the reaction between [Nb(N^{t}Bu)Cp(O^{t}Bu)$_2$] (**19**) and [Nb(N^{t}Bu)Cp(O^{t}Bu^{F3})$_2$] (**20**) to give [Nb(N^{t}Bu)Cp(O^{t}Bu)(O^{t}Bu^{F3})] ($\mathbf{V}_{19,20}$) at 60 °C.

Chloride/*tert*-butylamide exchange (reaction of **16** with **24** to form $\mathbf{B}'_{16,24}$) was also found to lie completely over to the side of product, and was significantly slower (as might be expected for the more bulky amide ligand), requiring 24 h at room temperature to reach completion; this afforded a second-order rate constant of 9.7 × 10^{-4} dm^3 mol^{-1} s^{-1}. By contrast, the exchange reaction of a planar amide such as η^1-pyrollyl with chloride (reaction of **16** with **25** to form $\mathbf{D}'_{16,25}$) was fast. In this case, an equilibrium was established (K_{eq}(298 K) = 15) within 20 min at room temperature, giving a rate constant of 2.5 × 10^{-1} dm^3 mol^{-1} s^{-1}.

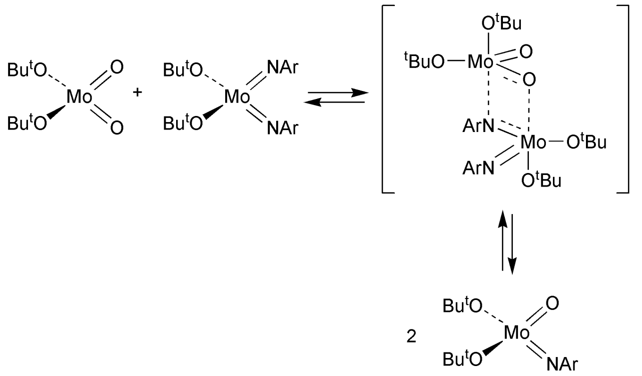
As was observed in the [Mo(Q)$_2$X$_2$] case, the slowest exchange was seen for (O^{t}Bu)/(NH^{t}Bu) (reaction of **19** with **24** to give $\mathbf{C}'_{19,24}$). No reaction was apparent at ambient temperature, even over several days. At 60 °C, traces of **C**′ were observed after two weeks; at 100 °C, the reaction had proceeded to *ca.* 20% conversion after 60 days. Assuming an equilbrium constant, K_{eq}(373 K), for this reaction of 15, as found for the analogous molybdenum reaction (*vide supra*), a rate constant, k_1(373 K), of 8 × 10^{-7} dm^3 mol^{-1} s^{-1} can be estimated.

C Exchange of dianionic ligands betweeen [Mo(Q)$_2$X$_2$] and [Nb(Q)CpX$_2$]

The reaction between [Mo(NAr)$_2$(O^{t}Bu)$_2$] (**3**) and [Nb(N^{t}Bu)Cp(O^{t}Bu)$_2$] (**19**) to give [Mo(N^{t}Bu)(NAr)(O^{t}Bu)$_2$] ($\mathbf{C}_{3,19}$) and [Nb(NAr)Cp(O^{t}Bu)$_2$] ($\mathbf{U}_{3,19}$)[16] was only observed upon heating to 110 °C and a temperature of 140 °C was required to reach equilibrium [K_{eq}(413 K) = 0.25 in 7 days]. This result is directly comparable with (NAr)/(N^{t}Bu) exchange between Nb centres (reaction of **15** and **16**; see above) with an equilibrium favouring the reactants.

D Exchange of dianionic ligands between [Mo(Q)$_2$X$_2$] and [Mo(Q)$_2$CpX]

It was anticipated from the foregoing results that the still more hindered and (formally) more electron-rich system [Mo(Q)$_2$CpX] might be expected to exchange ligands yet more slowly than complexes of the form [Nb(Q)CpX$_2$]. Accordingly, [Mo(N^{t}Bu)$_2$CpCl] (**26**) and [Mo(NAr)$_2$(O^{t}Bu)$_2$] (**3**) were mixed and heated to 60 °C. After 48 h, only trace reaction had occurred so the temperature was increased to 100 °C. This yielded an equilbrium mixture of **3**, $\mathbf{C}_{3,26/3,E'}$, **2**, **26**, $\mathbf{E'}_{3,26}$ and $\mathbf{F'}_{3,C/C,E'}$ *after 6 months* as shown in Scheme 2. The presence of both $\mathbf{C}_{3,26/3,E'}$ and **2** at equilibrium demonstrates that [Mo(NAr)$_2$(O^{t}Bu)$_2$] can exchange both of its imido ligands.



Scheme 2 Inter-metal exchange of oxo and imido ligands *via* an associative mechanism.

E Exchange of dianionic ligands between [Mo(Q)$_2$CpX] and [Nb(Q)CpX$_2$]

In the reaction between [Mo(N^{t}Bu)$_2$CpCl] (**26**) and [Nb(NAr)CpCl$_2$] (**14**), only small traces of the products of inter-metal imido ligand exchange, namely [Mo(N^{t}Bu)(NAr)CpCl] and [Nb(N^{t}Bu)CpCl$_2$] (**16**), were present after 3 months at 100 °C. Imido ligand exchange was observed between [Mo(N^{t}Bu)$_2$CpCl] (**26**) and [Nb(NMe)CpCl$_2$] (**17**) over a period of one week at 100 °C (in CDCl$_3$). However, the only resonances in the product mixture were found to correspond to [Nb(N^{t}Bu)CpCl$_2$] (**16**); the remainder of the material had precipitated from solution.

Discussion

A(i): Dianionic ligand exchange between complexes of the form [Mo(Q)$_2$X$_2$]

It can be seen that the values of the thermodynamic activation parameters for the reaction betweeen **1** and **3** differ somewhat from those previously reported.[16] Nevertheless, the strongly negative entropy of activation remains consistent with the associative mechanism originally proposed (Scheme 3) and the results reported here compare well with those obtained from the pairwise exchange of oxo and imido groups in rhenium(VII) compounds.[32]

The more rapid exchange of oxo groups with *tert*-butyl imido moieties (reaction of **1** and **2**) is to be expected given this proposed associative mechanism; additionally the alkyl-substituted imido nitrogen might be expected to be more basic, and hence show a greater propensity for bridging, than would an aryl-substituted imido nitrogen. An additional feature of (^{t}BuN)/(O) exchange is the much more pronounced favouring of the mixed ligand product over reactants which is more in line with observations by Espenson on Re(VII) systems.[32]

An interesting facet of this equilibrating mixture is the significant broadening of the ^{t}BuO resonances in the ^{1}H NMR spectrum assigned to the dioxo species **1** (at δ 1.15) and the mixed species $\mathbf{A}_{1,2}$ (at δ 1.25). This is attributed to intermetal exchange of the alkoxide ligands at a rate comparable to the NMR timescale. Consistently, cooling a sample of the equilibrium mixture in D$_3$CC$_6$D$_5$ to −10 °C caused significant sharpening of the resonances. We can envisage three distinct (O^{t}Bu) exchange processes as outlined in Fig. 6. Intuitively, the exchange rates would be expected to increase in the order $k_a < k_b < k_c$, purely on steric grounds (assuming these exchange processes to have a similar associative transition state to that proposed for the dianionic ligand exchange reaction) and it is merely fortuitous that k_c is comparable to the NMR timescale. Determination of these rate constants has not proved possible since they are complicated functions of relaxation time (T_1), population and shift difference ($\Delta\delta$) of the three species and also of the rate constant of oxo/imido ligand exchange (k_1).[33]

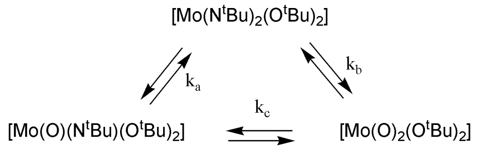
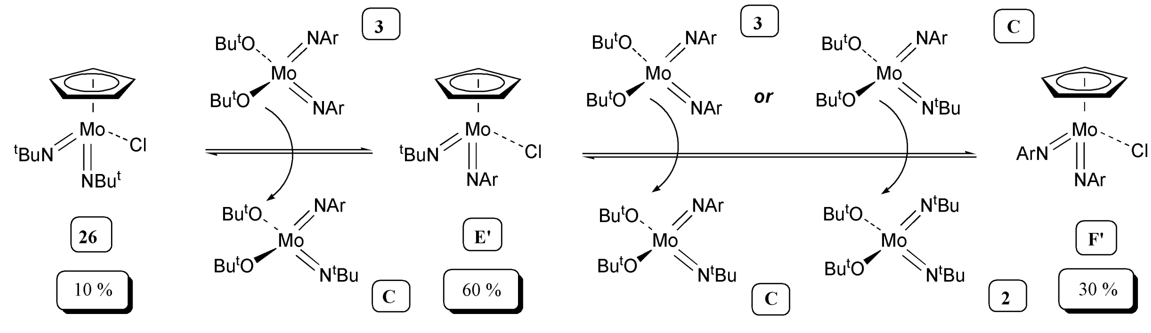


Fig. 6 Multi-site intermetal alkoxide exchange.

It may be seen that the ancilliary alkoxide ligands in the system [Mo(O)$_2$(OR)$_2$]/[Mo(NR)$_2$(OR)$_2$] have a relatively small effect on both rate and equilibrium constants. This may be explained in terms of a trade-off between increasing M=O and M=N multiple bond strengths, along with enhanced steric interactions, upon increased fluorination (slowing the exchange rate) *vs.* increasing electrophilicity of the metal centres as more



Scheme 3 Imido-ligand exchange reaction between [Mo(N^{t}Bu)$_2$CpCl] (**26**) and [Mo(NAr)$_2$(O^{t}Bu)$_2$] (**3**). Percentage values indicate equilibrium composition of [Mo(Q)$_2$CpX] species.

fluorines are added to the butoxide ligands (potentially favouring the formation of oxo/imido bridges).

The more crowded [Mo(Q)Cl$_2$(DME)] species exchange their dianionic ligands significantly more slowly than their four-coordinate counterparts; again consistent with the proposed associative mechanism.

A(ii) Monoanionic ligand exchange between compounds of the form [Mo(Q)$_2$(X)$_2$]

Immediately noticeable is the much faster rate of exchange for the monoanionic *vs.* dianionic ligand cases. This is not surprising in view of the lower bond multiplicities for the monoanionic ligands compared to their dianionic counterparts. The trends in K_{eq}(298 K) for this class of exchange is also not unexpected since it might be anticipated that the mixed ligand product would be most favoured where the two ligands have maximum difference in steric bulk and/or electronic properties. All of the exchange reactions summarised in Table 7 follow this trend. It is presumed that exchange of (O^{t}Bu) and (NH^{t}Bu) (entry 13) is so slow on steric grounds.

B(i) Exchange of dianionic ligands between compounds of the form [M(Q)CpX$_2$] {M = Nb, Ta}

Dianionic ligand exchanges in [M(Q)CpX$_2$] systems are significantly slower than for their [Mo(Q)$_2$X$_2$] counterparts (days to weeks at 100 °C or higher *vs.* weeks at room temperature or a few days at 60 °C). This is a predictable consequence of the associative transition state proposed for these reactions. Compounds of the form [M(Q)CpX$_2$] have a higher formal electron count than those of the type [Mo(Q)$_2$X$_2$] and, given the presence of a cyclopentadienyl ring, more bulk around the immediate vicinity of the metal centre. Both of these factors would reduce the propensity of the system to form a bimolecular adduct, hence retarding the reaction rate and requiring more forcing conditions to achieve reasonable rates of reaction. Additionally, it has previously been shown in a theoretical study that compounds of the form [M(Q)$_2$X$_2$] {M = Mo or W} should be more active for olefin metathesis (the transition state for which is analogous to that shown in Scheme 2) than those of the form [M(Q)X$_4$].[34]

The equilibrium in these half-sandwich systems appear to be largely dominated by steric effects. For example, the reaction of **16** with **18** strongly favours the reactants, presumably due to unfavourable steric interactions between the N^{t}Bu group and pentamethylcyclopentadienyl ligand of $\mathbf{S_{16,18}}$. Although it did not prove possible to determine an accurate equilibrium constant for the reaction of **15** with **16** (due to partial decomposition), reactants are clearly favoured here also, presumably due to greater steric hindrance between N^{t}Bu and Cp* in $\mathbf{S_{15,16}}$ than between NAr and Cp* in **15**. The propensity of pentamethylcyclopentadienyl to reside on the metal centre supported by the least bulky imido moiety is also reflected in the slight product bias of the equilibrium produced in the reaction of **15** with **17**.

B(ii) Exchange of monoanionic ligands between compounds of the form [Nb(Q)CpX$_2$]

Exchange of ligands between the niobium centers of [Nb(Q)CpX$_2$] species is found to be slower than for molybdenum complexes of the type [Mo(Q)$_2$X$_2$]. This can be explained on steric grounds. Expectedly, the exchange of mono-anionic ligands in the half-sandwich system is much faster than imido/imido ligand exchange. Broadly similar trends to those observed in the [Mo(Q)$_2$X$_2$] system are found, with comparable equilibrium constants (in the range 1–10) except for the vastly sterically and electronically different (O^{t}Bu) and (O^{t}Bu^{F6}) ligands which give a much greater bias towards the mixed ligand product. In this [Nb(Q)CpX$_2$] system a trend towards slower reaction rate is observed as the size of the exchanging alkoxides is increased. A supplementary factor could be F–F lone-pair repulsions in the proposed bridged dimeric transition states. Both effects would lead to a slower rate of exchange with increasing fluorine substitution, a trend which is clearly evident in the first four entries of Table 8. This reactivity trend was not so readily apparent in the [Mo(Q)$_2$X$_2$] system since all those reactions were fast (<15 min to equilibrium in all cases).

The substantial rate acceleration observed for Cl/η^1-NC$_4$H$_4$ exchange when compared to Cl/NH^{t}Bu exchange may be explained in terms of the spatial anisotropy of the pyrollyl ligand leading to reduced steric interactions in the bimolecular transition state. However, electronic effects cannot be ruled out: for example, the nitrogen lone-pair is involved in the π-system of the pseudo-aromatic ring and thus the metal centre will be more electrophilic and thus more susceptible to forming a bimolecular adduct. It is not possible to determine with any degree of certainty whether steric or electronic effects dominate in this case.

Examination of the data given in Table 8 reveals a strong correlation between the rate of intermetal ligand exchange and the size of the two exchanging ligands. Rates decrease in the order: Cl/Br > Cl/O^{t}Bu > Cl/NH^{t}Bu > O^{t}Bu/O^{i}Pr > O^{t}Bu/O^{t}Bu^{F3} > O^{t}Bu/O^{t}Bu^{F6} > O^{t}Bu^{F3}/O^{t}Bu^{F6} > O^{t}Bu/NH^{t}Bu. Remarkably, this series spans some seven orders of magnitude in rate constant. This simple steric argument accords well with an associative mechanism leading to a bimolecular transition state.

One other factor worthy of note is the differences in the equilibrium constant, K_{eq}. This seems to be largest (and hence the mixed ligand product most favoured) when the two exchanging substituents are electronically and/or sterically most disparate *e.g.* (O^{t}Bu)/Cl. Very similar ligands such as (O^{t}Bu)/(O^{i}Pr) give a K_{eq} close to the statistical value of 4.0 (for an A + B ⟶ 2C reaction) or 1.0 (for an A + B ⟶ C + D reaction).

C and D Exchange of dianionic ligands between [Mo(Q)$_2$X$_2$] and [Nb(Q)CpX$_2$] or [Mo(Q)$_2$CpX]

Dianionic ligand exchange between [Mo(Q)$_2$X$_2$] and [Nb(Q)CpX$_2$] (Class C) is considerably faster than that between the niobium centres of [Nb(Q)CpX$_2$]. For example, (NAr)/(N^{t}Bu) exchange between Nb and Mo centres takes only 7 days at 140 °C as opposed to several weeks for the half-sandwich niobium system. This result is expected given the less crowded environment around the four-coordinate molybdenum centre.

Conversely, the more hindered and (formally) electron-rich system, [Mo(Q)$_2$CpX], would be expected to exchange ligands more slowly with [Mo(Q)$_2$X$_2$] than for exchange between [Nb(Q)CpX$_2$] and [Mo(Q)$_2$X$_2$]. This is indeed observed, forming the equilibria shown in Scheme 3 (after 6 months at elevated temperature). Detailed study of this reaction is non-trivial since there are no fewer than six metal-containing species at equilibrium. However, since exchange reactions involving compounds of the type [Mo(Q)$_2$CpX] are observed to be the slowest of all those studied, it is believed that an exchange reaction between two species of this type (*e.g.* reaction of $\mathbf{E'_{3,26}}$ with itself to give **26** and $\mathbf{F'_{E',E'}}$) can be discounted. Exchange of chloride and *tert*-butoxide also seems not to occur since a mixture of [Mo(N^{t}Bu)$_2$(O^{t}Bu)$_2$] (**2**) and [Mo(N^{t}Bu)$_2$CpCl] (**26**) was not observed to produce even slight traces of [Mo(N^{t}Bu)$_2$(O^{t}Bu)Cl] ($\mathbf{P_{2,26}}$) or [Mo(N^{t}Bu)$_2$Cp(O^{t}Bu)] over several months at 100 °C. It is thus proposed that products $\mathbf{E'_{3,26}}$ and $\mathbf{F'_{3,C/C,E'}}$ must arise by exchange between [Mo(Q)$_2$X$_2$] and [Mo(Q′)$_2$CpX] species.

E Exchange of dianionic ligands between [Mo(Q)$_2$CpX] and [Nb(Q)CpX$_2$]

From the results discussed in the foregoing sections, it would be anticipated that this class of reaction would be the slowest of all those investigated. In general, this is the case; however the relatively rapid progress of the reaction between **17** and **26** deserves mention. Here, it is likely that the insolubility of one of the products, [Mo(N^{t}Bu)(NMe)CpCl] (**G′**$_{17,26}$), drives the reaction irreversibly to the product **16**. However, it should also be noted that this exchange of less bulky imido ligands would be expected to proceed faster than the (NAr)/(N^{t}Bu) exchange in any case. Interestingly, imido ligand exchange reactions in this class are only observable with the least bulky ancilliary ligand available, namely chloride. For all the other classes, we have also been able to observe exchange reactions with more bulky ancillary ligands such as *tert*-butoxide.

Summary and conclusions

Exchange reactions involving monoanionic and dianionic ligands have been probed for a series of pseudo-tetrahedral complexes whose electronic and steric parameters have been systematically modified. It has been found that the rates of such exchange reactions decrease in the order [Mo(Q)$_2$X$_2$]/[Mo(Q)$_2$X$_2$] (**A**) > [Mo(Q)$_2$X$_2$]/[Nb(Q)CpX$_2$] (**C**) > [Nb(Q)CpX$_2$]/[Nb(Q)CpX$_2$] (**B**) > [Mo(Q)$_2$X$_2$]/[Mo(Q)$_2$CpX] (**D**) > [Nb(Q)CpX$_2$]/[Mo(Q)$_2$CpX] (**E**) for both monanionic (where studied) and dianionic ligand exchange. This correlates directly with the greater steric demands around the metal as we move through Class I to Class III (Fig. 1) and also with the higher formal electron count of the complex along the same series. Additionally, monoanionic ligands exchange faster than their dianionic counterparts, a consequence of the greater metal–ligand bond strengths for dianionic ligand systems. Subsidiary to this effect, exchange reactions of less bulky ligands (*e.g.* oxo or chloride) tend to proceed faster than those of more bulky moieties (*e.g.* arylimido or *tert*-butylamide). These observations, combined with a strongly negative $\Delta S^{\neq}$ value, lend support to the proposition that the mechanism for these reactions, not unlike that proposed for olefin metathesis by Herrison and Chauvin,[35] involves a bimolecular adduct transition state, the formation of which is the rate-determining step.

Experimental

Experimental procedures for the synthesis of new compounds and for NMR-scale ligand exchange reactions as well as ^{1}H NMR spectroscopic data for the products of these reactions may be found in the ESI.†

Kinetic measurements

Wherever possible data were collected over the first three half-lives of the reaction (*i.e.* to *ca.* 90% conversion). All experiments were carried out at least three times to ensure reproducibility and in order to estimate errors. Saturation kinetics, where one reagent is used in vast excess, are not ideally suited to the use of NMR spectroscopy due to difficulties in obtaining accurate integrals of minor species. Standard second order kinetic treatments were employed throughout. C$_6$D$_6$ was a suitable solvent for virtually all the complexes studied and was used throughout except where otherwise stated.

The kinetics of an equilibrium of the form shown in eqn. (2) may be studied by means of the second-order reversible integrated rate eqn. (3).[29]

$$\mathrm{A}+\mathrm{B}\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}2\mathrm{C}\quad\text{with }[\mathrm{A}]_0=[\mathrm{B}]_0 \qquad (2)$$

$$\ln\left(\frac{x(a-2x_\mathrm{e})+ax_\mathrm{e}}{a(x_\mathrm{e}-x)}\right)=k_1\left(\frac{2a(a-x_\mathrm{e})}{x_\mathrm{e}}\right)t$$

$$\{a=[\mathrm{A}]_0=[\mathrm{B}]_0;\ x=\text{amount of reactants consumed at time } t\ i.e.\ 0.5[\mathrm{C}]_t\ \ x_\mathrm{e}=\text{amount of reactants consumed at equilibrium } i.e.\ 0.5[\mathrm{C}]_\mathrm{e}\} \qquad (3)$$

$$\mathrm{A}+\mathrm{B}\xrightarrow{k_1}2\mathrm{C}\quad\text{with }[\mathrm{A}]_0=[\mathrm{B}]_0 \qquad (4)$$

This treatment has been used for determination of the rate constants of most of the reactions in the present work; plotting ln$z$ *vs.* t {where $z=(x(a-2x_\mathrm{e})+ax_\mathrm{e})/a(x_\mathrm{e}-x)$} *e.g.* Fig. 3. In cases where the equilibrium strongly favours the products (eqn. (4)), *i.e.* where $K_\mathrm{eq}>100$, a non-reversible approach with two reactants, in both of which the reaction is first order, may be used (eqn. (5)).[29] The effect of temperature on rate constant may be used (by means of Transition State Theory) to obtain thermodynamic activation parameters for the reaction using eqn. (6).[30]

$$\frac{1}{a-x}=k_1t$$

$$\{a\ =\ [\mathrm{A}]_0=[\mathrm{B}]_0;\ x=\ \text{amount of reactants consumed at time } t\ i.e.\ 0.5[\mathrm{C}]_t\} \qquad (5)$$

$$\ln\left(\frac{k_1}{T}\right)=\ln\left(\frac{k_\mathrm{B}}{h}\right)+\frac{\Delta S^{\neq}}{RT} \qquad (6)$$

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