Intermetal Exchange of Oxo, Imido and Alkylidene Ligands[†]

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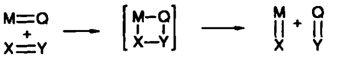
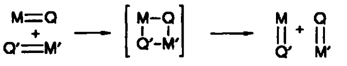
Oxo, imido and alkylidene ligand-exchange reactions occur readily between the co-ordinatively unsaturated centres of MQ_2X_2 (M = Mo or W; Q = O, NR or CHR′; X = OBu^t) and $M(\eta\text{-}C_5R''_5)QX_2$ (M = Nb or Ta; Q = NR or CHR′; X = Cl or OBu^t) compounds (R = $C_6H_3Pr^i_2$-2,6, R′ = CMe_2Ph or Bu^t, R″ = H or Me); a kinetic study of the reaction between $MoO_2(OBu^t)_2$ and $Mo(NR)_2(OBu^t)_2$ indicates that the exchange proceeds *via* a four-centre transition state.

The exchange of multiply bonded ligands *via* reactions with unsaturated reagents, according to the general equation (1), is


(1)

well documented,[1] and in the case where XY = alkene, Q = alkylidene, forms the basis of the technologically important olefin metathesis process.[2] Much less well known is the exchange of multiply bonded ligands *between metals* as represented by equation (2). This offers a potentially useful synthetic


(2)

approach to new transition-metal compounds containing multiple bonds to oxygen, nitrogen or carbon, and in the past has been most dramatically exploited by Schrock and co-workers[3] to prepare new tungsten alkylidene complexes of the type $[WQ(CHCMe_3)Cl_2(PR_3)_2]$ (Q = O or NPh). In this reaction the alkylidene unit is transferred from $[Ta(CHCMe_3)Cl_3(PR_3)_2]$ to the tungsten centres of $[WQ(OCMe_3)_4]$ (Q = O or NPh) and, at the same time, is accompanied by a redistribution of the anionic one-electron (Cl) and neutral two-electron (PR_3) ligands. To date few other examples of this process have been documented. Here, we describe a series of reactions [Scheme 1 (i)–(vii)] in which intermetal transfer of oxo, imido and alkylidene ligands may be observed directly, thus allowing the factors facilitating such exchange processes to be delineated for the first time. Most of the starting compounds have been prepared *via* previously reported procedures (or modifications thereof),‡,§ and the reactions have been followed by ^1H NMR spectroscopy (C_6D_6) on samples in flame-sealed tubes.

The intermetal exchange of imido ligands is shown by the reaction of $[Nb(\eta\text{-}C_5H_5)(NBu^t)Cl_2]$ with $[Nb(\eta\text{-}C_5Me_5)(NMe)Cl_2]$ according to equation (i). The room-temperature ^1H NMR spectrum of the starting mixture is shown in Fig. 1(*a*); no reaction occurs at this temperature but after warming at 100 °C for 11 d the two new imido species $[Nb(\eta\text{-}C_5Me_5)(NBu^t)Cl_2]$ and $[Nb(\eta\text{-}C_5H_5)(NMe)Cl_2]$ are clearly evident [Fig. 1(*b*)]. Prolonged warming does not lead to any further change in the ratio of the products, the equilibrium lying in favour of the reactants [$K_{100\,°C}$ = 0.18(2), ΔG° = 1.3(1) kcal mol^{-1}]; this presumably reflects the less favourable combination of C_5Me_5 and NBu^t ligands in the $[Nb(\eta\text{-}C_5Me_5)(NBu^t)Cl_2]$ product.

In order to confirm that the apparent exchange of imido ligands was not a consequence of C_5H_5/C_5Me_5 ring transfer, $[Nb(\eta\text{-}C_5H_5)(NMe)Cl_2]$ was treated with the tantalum species $[Ta(\eta\text{-}C_5Me_5)(NR)Cl_2]$ (R = $C_6H_3Pr^i_2$-2,6) [equation (ii)] to afford $[Ta(\eta\text{-}C_5Me_5)(NMe)Cl_2]$ and $[Nb(\eta\text{-}C_5H_5)(NR)Cl_2]$ as the sole products; the absence of $[Ta(\eta\text{-}C_5H_5)(NR)Cl_2]$ or $[Nb(\eta\text{-}C_5Me_5)(NMe)Cl_2]$, the expected products arising from ring exchange, rules out the possibility of ring transfer accounting for the exchange process.

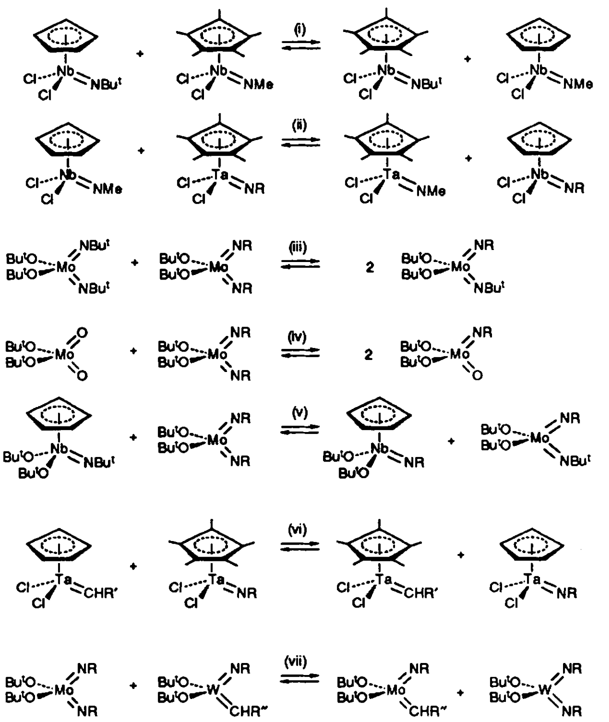
Imido ligand exchange proceeds at *room temperature* for the four-co-ordinate species $Mo(NBu^t)_2(OBu^t)_2$ and $Mo(NR)_2(OBu^t)_2$ [equation (iii) $K_{60\,°C}$ *ca.* 25], and even more rapidly for the oxo–imido ligand exchange shown in equation (iv) [$K_{25\,°C}$ = 0.08]. The latter reaction has been monitored over the temperature range 20–50 °C¶ and the kinetic data are in agreement with a second-order reversible reaction,[9] affording the activation parameters: $\Delta H^{\ddagger}$ = 20.6(4) kcal mol^{-1}, $\Delta S^{\ddagger}$ =

[†] *Non-SI unit employed:* cal = 4.184 J.

‡ $[M(\eta\text{-}C_5R_5)(NR')Cl_2]$ from ref. 4; $[Ta(\eta\text{-}C_5H_5)(CHCMe_2Ph)Cl_2]$ *via* a minor modification of the procedure described[5] for $[Ta(\eta\text{-}C_5H_5)(CHCMe_3)Cl_2]$ using $Mg(CH_2CMe_2Ph)Cl$; $[W(NC_6H_3Pr^i_2\text{-}2,6)(CHCMe_3)(OBu^t)_2]$ from ref. 6.

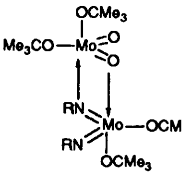
§ (*a*) Procedure for $MoO_2(OBu^t)_2$. To a mixture of MoO_2Cl_2 (1.59 g, 8.0 mmol) and LiOBu^t (1.29 g, 16.0 mmol) was added dropwise cold (−78 °C) Et_2O (100 cm^3). The resulting mixture was allowed to warm to room temperature and stirred for 2 h. Filtration, followed by removal of the volatiles *in vacuo*, gave $MoO_2(OBu^t)_2$ as a colourless oil. Yield 0.79 g, 36%. The product may be purified by recrystallisation from Et_2O at −50 °C to give a white solid that melts upon warming to room temperature. It has also been prepared[7] by treatment of $Mo_2(OBu^t)_6$ with O_2 and shown to be monomeric in benzene solution. (*b*) Procedure for $Mo(NR)_2(OBu^t)_2$ (R = $C_6H_3Pr^i_2$-2,6). To a mixture of $Mo(NR)_2Cl_2$(dme) (4.25 g, 7.0 mmol) and LiOBu^t (1.12 g, 14.0 mmol) was added dropwise cold (−78 °C) Et_2O (80 cm^3). The resulting mixture was allowed to warm to room temperature and stirred for 14 h. Filtration, followed by removal of the volatiles *in vacuo*, yielded an orange solid. This was purified by recrystallisation from Et_2O at −78 °C to give orange crystals of $Mo(NR)_2(OBu^t)_2$. Yield 3.27 g, 69%. NMR (C_6D_6): ^1H (400 MHz), δ 7.01 (d, 2, H_m, J_{HH} = 7.80), 6.93 (t, 1, H_p, J_{HH} = 7.80), 3.84 (spt, 2, C*H*Me$_2$, J_{HH} = 6.80), 1.42 (s, 18, $OCMe_3$) and 1.19 (d, 12, CH*Me*$_2$, J_{HH} = 6.80 Hz); $^{13}C\text{-}\{^1H\}$, δ 153.9 (C_{ipso}), 142.8 (C_o), 127.0 (C_p), 122.9 (C_m), 80.2 (O*C*Me$_3$), 32.1 (OC*Me*$_3$), 28.6 (*C*HMe$_2$) and 23.7 (CH*Me*$_2$) (Found: C, 65.00; H, 8.80; N, 4.60. Calc. for $C_{32}H_{52}MoN_2O_2$: C, 64.85; H, 8.85; N, 4.75%). This compound has also been prepared by Schrock.[8]

¶ Typically $MoO_2(OBu^t)_2$ (12 mg, 0.04 mmol) and $Mo(NR)_2(OBu^t)_2$ (25 mg, 0.04 mmol) were mixed in C_6D_6 in an NMR tube and frozen immediately. The tube was sealed under dry nitrogen and kept frozen until the kinetic run commenced. The reaction was monitored by integration of the methine septets at δ 3.84 and 4.33. Errors have been estimated from an average of three determinations.



Scheme 1 R = 2,6-$Pr^i_2C_6H_3$, R′ = CMe_2Ph, R″ = Bu^t

$-19(2)$ J K^{-1} mol^{-1} and $\Delta G^{\ddagger}$ (298 K) $= 26.2(5)$ kcal mol^{-1}. The negative entropy change for this process is consistent with an ordered transition state, involving bridged oxo and imido ligands (below) and in general keeping with the four-centre mechanism believed to operate for exchange reactions with unsaturated reagents.[1]



In order to test whether exchange is also possible between the four-co-ordinate molybdenum and half-sandwich niobium centres, the *tert*-butoxide derivative [Nb(η-C_5H_5)(NBu^t)(OBu^t)$_2$] was prepared and treated with Mo(NR)$_2$(OBu^t)$_2$ [equation (v)]. This reaction proceeded to give the anticipated products at a rate intermediate for the four-co-ordinate Mo ⟷ Mo and half-sandwich Nb ⟷ Nb imido-exchange reactions. These observations give a qualitative indication that the process is most favourable for very low-electron-count, low-co-ordinate complexes,* and furthermore explains why exchange is not observed between the metal centres of 18-electron species such as MoO(NPh)(dtc)$_2$ (dtc = dithiocarbamate).[10]

Finally, the exchange of alkylidene for imido ligands has been observed according to the reactions shown in equations (vi) and (vii). Alkylidene exchange in the half-sandwich tantalum system requires warming at 120 °C for several days, whereas exchange in the four-co-ordinate system occurs cleanly at 60 °C over a similar period of time.

In summary, the exchange of multiply bonded oxo, imido and alkylidene ligands can occur quite readily at co-ordinatively unsaturated metal centres, and offers a viable synthetic strategy to new compounds containing multiply bonded ligands; this may be particularly beneficial for technologically useful alkylidene complexes.

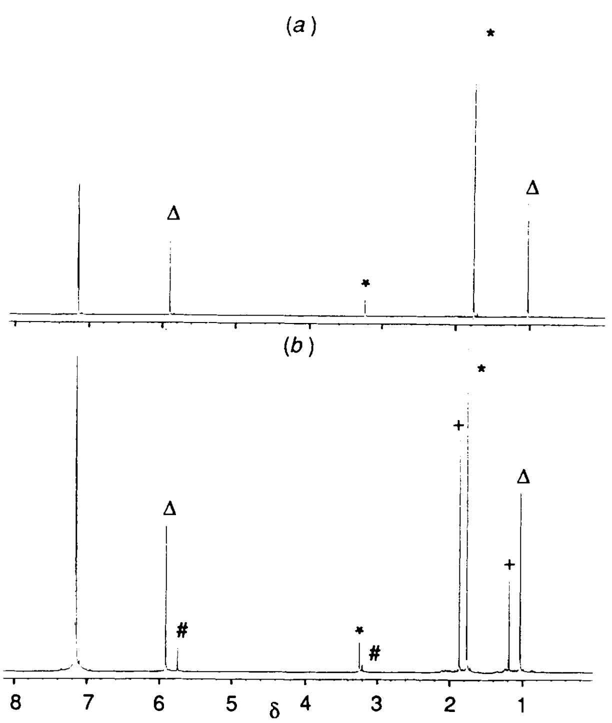


Fig. 1 400 MHz ^1H NMR spectra for the reaction of [Nb(η-C_5H_5)(NBu^t)Cl_2] with [Nb(η-C_5Me_5)(NMe)Cl_2]: (*a*) immediately after unfreezing; (*b*) after 11 d at 100 °C {Δ, [Nb(η-C_5H_5)(NBu^t)Cl_2]; *, [Nb(η-C_5Me_5)(NMe)Cl_2]; #, [Nb(η-C_5H_5)(NMe)Cl_2]; +, [Nb(η-C_5Me_5)(NBu^t)Cl_2]}. Resonances assigned by comparison with data from authentic samples

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* The tetrahedral molybdenum compounds are formally 14-electron species owing to a competition between the two multiply bonded groups for the available metal d_π orbitals, ensuring that one of the ligands can form only a double bond to the metal centre; the half-sandwich niobium imido compounds are formally 16-electron species.