DALTON

Tertiary phosphine ligand-exchange reactions involving the M$\equiv$M quadruply bonded complexes $M_2Cl_4L_4$, where L = PMe_3, PEt_3, $PBu^n{}_3$ or PMe_2Ph*

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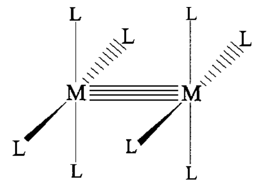
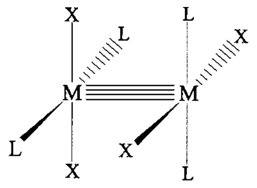
The reactions between $M_2Cl_4L_4$ complexes and an excess of L or L′ (PMe_3, PEt_3, $PBu^n{}_3$, PMe_2Ph or $PMePh_2$) have been studied in [$^2H_8$]toluene by $^{31}P-\{^1H\}$ NMR spectroscopy. The substitutions proceed in a stepwise manner wherein L′ displaces L, except for L′ = $Me_2PCH_2CH_2PMe_2$ (dmpe) which yields Mo_2Cl_4(dmpe-*P*)$_4$. No tertiary phosphine in this series is capable of displacing PMe_3 from a $M_2Cl_4(PMe_3)_4$ complex but by spin magnetization transfer the degenerate exchange involving $Mo_2Cl_4(PMe_3)_4$ and PMe_3 (added in excess) can be detected. The complexes $Mo_2Cl_4(PMe_3)_4$ and $Mo_2Cl_4(PEt_3)_4$ in benzene showed no PMe_3 for PEt_3 scrambling at +50 °C over several days despite the fact that $Mo_2Cl_4(PMe_3)_{4-n}(PEt_3)_n$, where $n = 2$ or 3, are kinetically inert to ligand redistribution. In the presence of [$^2H_5$]pyridine $Mo_2Cl_4(PMe_3)_4$ and $Mo_2Cl_4(PEt_3)_4$ underwent tertiary phosphine scrambling at 25 °C and in neat [$^2H_5$]pyridine $Mo_2Cl_4(PMe_3)_4$ revealed the formation of an equilibrium concentration of $Mo_2Cl_4(PMe_3)_3$(py) (py = pyridine) and free PMe_3. Under similar conditions $Mo_2Cl_4(PEt_3)_4$ yielded an equilibrium mixture of $Mo_2Cl_4(PEt_3)_3$(py) and $Mo_2Cl_4(PEt_3)_2(py)_2$ and free PEt_3. From kinetics the $\Delta H^\ddagger$ values are positive in the range +24 to +34 kcal mol^{-1} and the $\Delta S^\ddagger$ values range from +12 to +28 cal K^{-1} mol^{-1}. Collectively the data reported are consistent with an interchange dissociative mechanism, I_d, wherein M−P bond breaking contributes significantly to the rate-determining step with related values of $\Delta H^\ddagger$ being larger for M = W than M = Mo. The rate dependence on the entering ligand is clearly evident from temperature-dependent studies and leads to varying $\Delta S^\ddagger$ values. The I_d mechanism is proposed to involve pre-equilibria between $M_2Cl_4L_4$ and the entering L′ in an axial site followed by rate-determining M−L displacement. In neat [$^2H_5$]pyridine this may be viewed as a solvent-assisted displacement. The present results are discussed in terms of earlier studies from which researchers inferred a simple dissociative process, D, involving M−PR_3 bond rupture as the first and rate-determining step.

Compounds containing multiple bonds between metal atoms comprise an important class of species in modern co-ordination chemistry.[1] The structures and bonding in these complexes have been extensively studied as have their attendant spectroscopies. Also the redox reactivity of the dinuclear center has proved to be of interest in terms of developing multielectron substrate activation.[2] Within this class of compounds those containing M$\equiv$M quadruple bonds are particularly noteworthy as their discovery led to the recognition of the δ bond, a bond not found in main group chemistry. Compounds with M$\equiv$M quadruple bonds without exception contain a M−M valence configuration $\sigma^2\pi^4\delta^2$ where only one δ orbital is used in M−M bonding. That is to say they are diamagnetic and the other δ type M−M orbital is used in metal–ligand bonding. Thus these complexes have two square-planar ML_4 units joined by the M$\equiv$M quadruple bond in an eclipsed manner as depicted in **1**. The eclipsed geometry is the one that allows for the formation of the δ^2 bond and members of this series of d^4–d^4 dinuclear complexes include $M_2(\mu-O_2CR)_4$, M_2(porphyrin)$_2$, where M = Mo and W, and R = alkyl or aryl, and $M_2X_8{}^{n-}$ where M = Mo or W, X = halide, $n = 4$ and M = Tc or Re, X = halide and $n = 2$.[1] In addition for M = Mo and W there is an important group of complexes of the formula $M_2X_4L_4$ where X = alkyl, alkynyl or halide and L = a neutral donor ligand such as a tertiary phosphine PR'_3 or pyridine, py. These typically adopt a structure depicted by **2** which is presumably favored by steric considerations. The use of chelating diphosphines such as $Ph_2PCH_2CH_2PPh_2$ and related arsines leads to so-called α and β isomers shown in **3a** and **3b**, respectively.[3] The latter have attracted certain attention because the α isomer is a kinetic product of the reaction between $M_2X_8{}^{4-}$ and the chelating phosphine or arsine and the β isomer is the thermodynamic product. In the β isomer there is often a twist about the M−M axis so that the two four-co-ordinate metal atoms are not eclipsed. The latter phenomenon has drawn attention with respect to the energetics of



1



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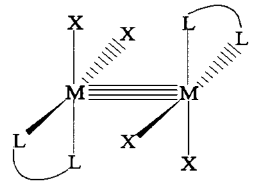
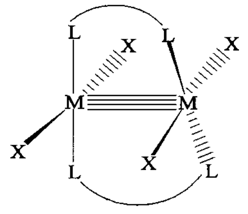


3a



3b

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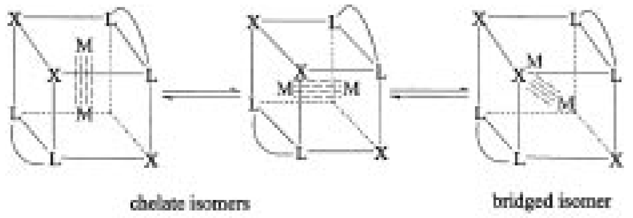
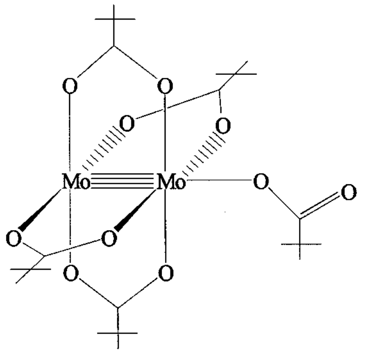
[*] Dedicated to Professor Fred Basolo, from whom we learned much about substitution reactions at metal centers, on the occasion of his 75th birthday.

Non-SI unit employed: cal = 4.184 J.



chelate isomers **4a**

bridged isomer **4b**



5

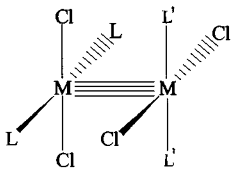
the δ–δ interactions and the assignment of the $\delta \longrightarrow \delta^*$ electronic transitions.[4] The conversion of the α into the β isomers, **3a** and **3b**, has also been extensively studied and evidence in favor of an 'internal flip' mechanism has been presented.[5] In this mechanism the M–M axis is reoriented about one of three positions within the pseudo-cubic arrangement of ligands as shown in **4**.

Remarkably little attention has been paid to the mechanisms of ligand substitution reactions at M≡M quadruply bonded complexes. In comparing the reactivity of $M_2(O_2CR)_2(MeCN)_4^{2+}$ complexes we noted that the MeCN ligands were extremely labile for M = Mo compared to M = Rh and we suggested that this might be due to electronic factors associated with their respective M–M electronic configurations: M = Mo, $\sigma^2\pi^4\delta^2$; *vs.* M = Rh, $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$.[6] The latter configuration may be viewed as electronically saturated in a similar manner to octahedral cobalt(III) and rhodium(III) complexes that have a t_{2g}^6 electronic configuration and are chemically inert. Their substitution reactions proceed *via* dissociative or interchange dissociative mechanisms.[7] By contrast the Mo_2^{4+} center with its electronic configuration $\sigma^2\pi^4\delta^2$ has low-lying empty metal d-based molecular orbitals available for nucleophilic attack. The lability of $Mo_2(O_2CR)_4$ complexes has also been noted in their facile carboxylate exchange reactions in solution[6,8] and the $Mo_2(O_2CBu^t)_5^-$ anion, which has the solid-state molecular structure shown in **5**, is fluxional on the NMR time-scale at room temperature in [$^2H_8$]toluene.[9]

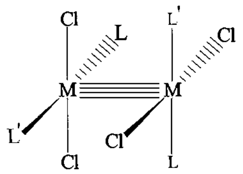
While we were inclined to view the lability of the Mo_2^{4+} center in terms of its ability to enter into associative exchange processes with ligands such as carboxylates which have additional lone pairs, we were aware of the work of Andersen and co-workers[10] who had studied the phosphine exchange reactions shown in equation (1), where L = PMe_3 or PMe_2Ph. These

$$Mo_2Me_4(PEt_3)_4 + L \longrightarrow Mo_2Me_4(PEt_3)_3L + PEt_3 \quad (1)$$

workers also examined the reaction between $Mo_2Me_4(PMe_2Ph)_4$ and PMe_3 and PEt_3 and found substitution of PMe_2Ph by PMe_3 but not by PEt_3.[10a] [They also examined the reaction between $Mo_2X_2(O_2CBu^t)_2(PMe_2Et)_2$ ($X = CH_2CMe_3$ or $OSiMe_3$) and PMe_3 and determined $\Delta H^\ddagger = 22.2$ and 24.7 kcal mol^{-1} for $X = CH_2Bu^t$ and $OSiMe_3$, respectively, with $\Delta S^\ddagger = 15$ cal K^{-1} mol^{-1} in both instances.[10b]] From studies of the kinetics of reaction (1) with an excess of L they found that the reaction was first order in [Mo_2] and zeroth order in [L] when L was present in 10–30 mole excess. They observed no rate dependence on the entering ligand at −50 °C in [$^2H_8$]toluene and for L = PMe_2Ph they determined $\Delta H^\ddagger = 21$ kcal mol^{-1} and $\Delta S^\ddagger = 18$ cal K^{-1} mol^{-1}. From a comparison of reactions involving $Mo_2Me_4(PEt_3)_4$ and $Mo_2Me_4(PMe_2Ph)_4$ with PMe_3 they observed a rate dependence on the leaving group. These observations led Andersen and co-workers.[10a] to conclude that the substitution of one tertiary phosphine by another was proceeding by a dissociative process and that it was favored when a bulky phosphine was replaced by a less bulky phosphine at the Mo_2^{4+} center.



6a



6b

Clearly the conclusions drawn by us, based only on qualitative substitutional behavior, are in opposition to the quantitative studies of Andersen and co-workers. Being mindful 'to never trust in science to the principle of exclusion',[11] we have now examined the reactions of phosphine interchange (2), in

$$M_2Cl_4L_4 + L'(\text{excess}) \longrightarrow ? \quad (2)$$

[$^2H_8$]toluene, where M = Mo or W, L = PEt_3, PBu^n_3 or PMe_2Ph and L′ = PMe_3, PMe_2Ph, $PMePh_2$, $Me_2PCH_2CH_2PMe_2$ (=dmpe) or pyridine. We have also examined the degenerate exchange reaction where L = L′ and studied the reactions between $Mo_2Cl_4L_4$ and $Mo_2Cl_4L'_4$ in both toluene and pyridine. From the results of the present studies we suggest that the phosphine exchange reactions (2) do not proceed *via* a simple dissociative mechanism but rather by an interchange dissociative mechanism wherein the entering phosphine is within the co-ordination sphere of the M_2^{4+} center.

Results and Discussion

General procedures

Studies of reactions (2) were monitored by ^{31}P-{^1H} NMR spectroscopy. The samples of $Mo_2Cl_4L_4$ were prepared in a helium filled dry-box. The sample was weighed and dissolved in 600 µl [$^2H_8$]toluene in a J. Young® NMR tube. In the case of PMe_3, which is very volatile, 15 equivalents were added employing a gas-line manifold. Other L′ were added by microliter syringe from stock solutions in [$^2H_8$]toluene. No new compounds of formula $M_2Cl_4L_{4-n}L'_n$ were isolated in this study but they were characterized by their ^{31}P-{^1H} NMR spectra and with simulated spectra. (Compounds of this type have been isolated and fully characterized previously.[12])

In studies of the rate of phosphine substitution (2) we monitored the disappearance of the ^{31}P signal due to $M_2Cl_4L_4$. In most instances the stepwise appearance of $Mo_2Cl_4L_3L'$, $Mo_2Cl_4L_2L'_2$, $M_2Cl_4LL'_3$ and $M_2Cl_4L'_4$ could be seen in addition to the liberation of L. A $M_2Cl_4L_2L'_2$ compound can exist in one of two isomeric forms as shown in **6a** and **6b**. Compounds **6a** are characterized by A_2B_2 spin systems whereas **6b** are AA′BB′ and, in the case of M = W, the spin system is further complicated by ^{183}W, $I = \frac{1}{2}$, 14.3% natural abundance. The reactions have been monitored as a function of the excess of L′ (15–30 equivalents) and as a function of temperature.

At this point it is worth commenting on some specific aspects of these studies.

$Mo_2Cl_4(PMe_2Ph)_4$ + PMe_3. Within the temperature range 35 to 60 °C the formation of the complex $Mo_2Cl_4(PMe_2Ph)_3(PMe_3)$ is clearly evident in this reaction as shown in Fig. 1. The

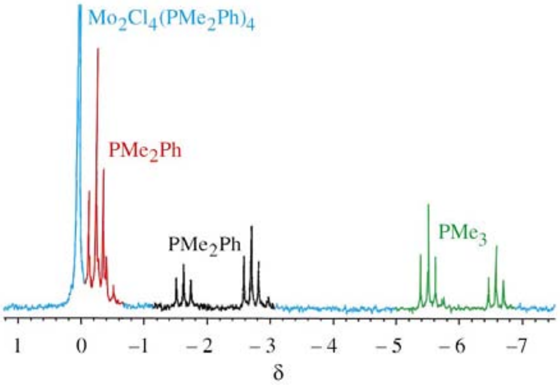


Fig. 1 The $^{31}P-\{^1H\}$ NMR spectrum of $Mo_2Cl_4(PMe_2Ph)_3(PMe_3)$: $^2J_{PP} = 174$, $^3J_{PP} = 19$ Hz

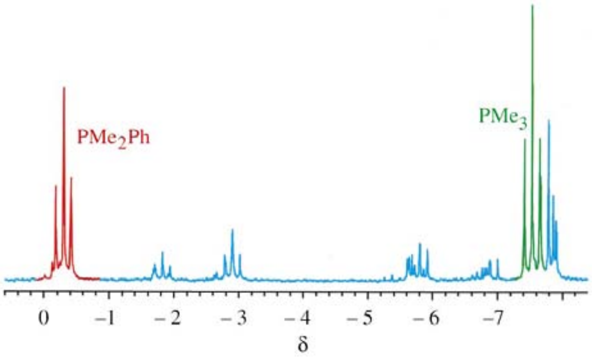


Fig. 2 The $^{31}P-\{^1H\}$ NMR spectrum of $Mo_2Cl_4(PMe_2Ph)_2(PMe_3)_2$, A_2B_2 isomer: $^3J_{AB} = 19$ Hz

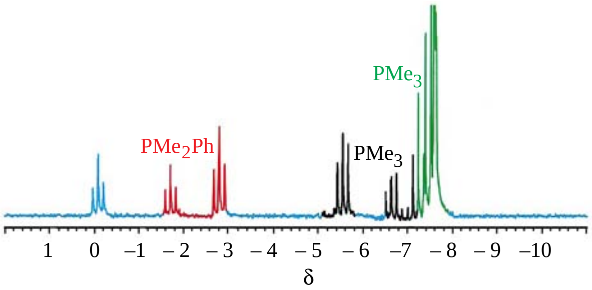


Fig. 3 The $^{31}P-\{^1H\}$ NMR spectrum of $Mo_2Cl_4(PMe_2Ph)(PMe_3)_3$: $^2J_{PP} = 174$, $^3J_{PP} = 19$ Hz

starting complex $Mo_2Cl_4(PMe_2Ph)_4$ appears as a singlet and the formation of $Mo_2Cl_4(PMe_2Ph)_3(PMe_3)$ is noted by a PMe_2Ph triplet close in chemical shift to that of the starting complex due to the two mutually *trans* PMe_2Ph ligands. The other molybdenum center has *trans* Mo−PMe_3 and Mo−PMe_2Ph groups with the former being upfield of the latter. Each ^{31}P nucleus gives rise to a doublet of triplets due to ^{31}P–^{31}P coupling and as can be seen from Fig. 1 the doublet of triplets shows some second-order character as the chemical shift separation of the Mo−*P*Me_3 and Mo−*P*Me_2Ph ^{31}P nuclei differ by only *ca.* 4 ppm. The ^{31}P NMR spectrum has been simulated by GNMR Version 3.6 employing the J_{pp} values listed in the figure caption.

With time the signals due to $Mo_2Cl_4(PMe_2Ph)_3(PMe_3)$ disappear as those due to $Mo_2Cl_4(PMe_2Ph)_2(PMe_3)_2$ grow in. These are shown in Fig. 2. At this point no starting complex $Mo_2Cl_4(PMe_2Ph)_4$ remains and free PMe_2Ph and PMe_3 are both present (not shown in Fig. 2). The signals shown in red and green are due to the $Mo_2Cl_4(PMe_2Ph)_2(PMe_3)_2$ complex and conform to an A_2B_2 spin system indicating the formation of a compound of type **6a**. Other resonances shown in Fig. 2 represent $Mo_2Cl_4(PMe_2Ph)_3(PMe_3)$ (as described before) and $Mo_2Cl_4(PMe_2Ph)(PMe_3)_3$. The third substitution product $Mo_2Cl_4(PMe_2Ph)(PMe_3)_3$ is shown in Fig. 3 and has features similar to that described for the first substitution complex, namely two 'leaning' doublets of triplets and one triplet due to the mutually *trans* Me_3P−Mo−PMe_3 phosphorus nuclei. The latter resonance is close and partially overlaps with the ^{31}P signal of the product $Mo_2Cl_4(PMe_3)_4$. Confirmation of these assignments was obtained by $^{31}P-\{^1H\}$–$^{31}P-\{^1H\}$ correlation spectroscopy (COSY). The final spectrum is shown in Fig. 4 and is again simple consisting of a singlet due to $Mo_2Cl_4(PMe_3)_4$ along with the singlets due to free PMe_3 and the displaced PMe_2Ph.

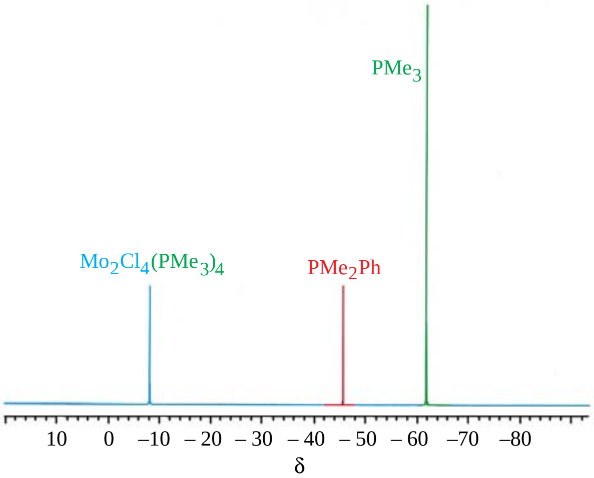


Fig. 4 The $^{31}P-\{^1H\}$ NMR spectrum of the fourth substitution product $Mo_2Cl_4(PMe_3)_4$ and free PMe_2Ph and PMe_3

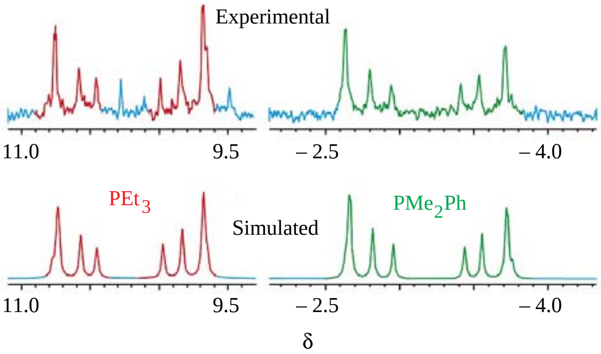


Fig. 5 Experimental (top) and simulated (bottom) $^{31}P-\{^1H\}$ NMR spectra of $W_2Cl_4(PEt_3)_2(PMe_2Ph)_2$, AA′BB′ isomer: $^2J_{PP} = 144$, $^3J_{PP} = 28$ Hz. The observed resonances shown in blue arise from $W_2Cl_4(PEt_3)(PMe_2Ph)_3$

The reactions between $M_2Cl_4(PEt_3)_4$ with PMe_2Ph proceed in a similar stepwise manner but the complexes $M_2Cl_4(PEt_3)_2(PMe_2Ph)_2$ are of the type **6b** and as shown in Fig. 5 this gives rise to two sets of multiplets which are second order, each being half of an AA′BB′ spin system.

The most plausible explanation for the formation of isomer **6a** (the A_2B_2 spin system, Fig. 2) in reaction (2) employing L′ = PMe_3 and the formation of **6b**, when L′ = PMe_2Ph, is that the *trans* effect of PMe_3 > PMe_2Ph[13] whereas in the substitution of PEt_3 by PMe_2Ph we obtain the thermodynamic isomer based on relief of steric strain. Note that in the presence of an excess of PMe_2Ph, even if the *trans* effect of PEt_3 > PMe_2Ph, the second observable product would be $Mo_2Cl_4(PMe_2Ph)_2(PEt_3)_2$ having the configuration **6b**.

The reactions between $Mo_2Cl_4L_4$ (L = PEt_3 or PMe_2Ph) and $Me_2PCH_2CH_2PMe_2$ in [$^2H_8$]toluene were unique amongst the series studied in that we did not observe a stepwise substitution but rather saw the formation of a compound that we formulate as Mo_2Cl_4(dmpe-*P*)$_4$ as the complex $Mo_2Cl_4L_4$ decreases in concentration. The progress of a typical reaction is shown in Fig. 6. Regrettably we were not able to isolate the compound

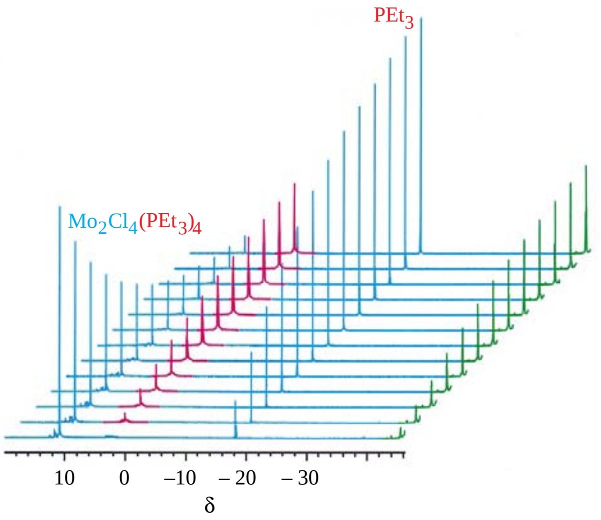


Fig. 6 The $^{31}P-\{^1H\}$ NMR spectrum of $Mo_2Cl_4(PEt_3)_4$ with excess of dmpe at 5 °C over 8 h. The formation of $Mo_2Cl_4(dmpe\text{-}P)_4$ is seen by the growth of the red (co-ordinated) and green (dangling) ^{31}P signals

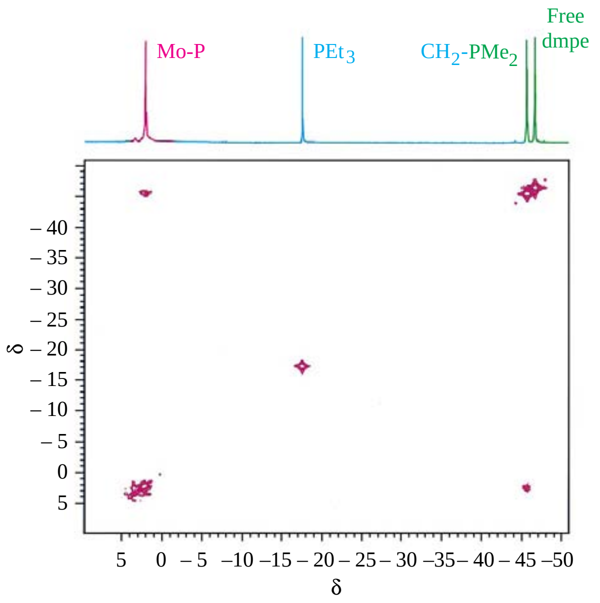


Fig. 7 The $^{31}P-\{^1H\}-^{31}P-\{^1H\}$ COSY NMR spectrum of $Mo_2Cl_4(dmpe\text{-}P)_4$ at 25 °C

formulated as $Mo_2Cl_4(dmpe\text{-}P)_4$ by bench-top reaction procedures because a subsequent reaction leads to an insoluble dark blue material. Upon heating the complex formulated as $Mo_2Cl_4(dmpe\text{-}P)_4$ in $[^2H_8]$toluene at 50 °C in the presence of an excess of dmpe and the liberated L ($L = PEt_3$ or PMe_2Ph), the solution becomes pale orange and by $^{31}P-\{^1H\}$ NMR spectroscopy no simple Mo-containing compound could be formulated. In the presence of an excess of dmpe it seems likely that the $M\equiv M$ bond is cleaved upon heating. We must therefore confine our remarks to (*i*) examining the evidence for the existence of $Mo_2Cl_4(dmpe\text{-}P)_4$ and (*ii*) the kinetic data pertaining to its formation.

Table 1 Rate constants for the reactions $M_2Cl_4L_4 + L' \longrightarrow M_2Cl_4L_3L' + L$, where $L = PEt_3$ and $L' = PMe_3$ or PMe_2Ph

		$10^5\ k_{obs}/s^{-1}$	
Complex	T/K	PMe_3	PMe_2Ph
$Mo_2Cl_4(PEt_3)_4$	268	2.91(5)	2.39(3)
	273	7.24(5)	6.42(5)
	278	18.6(5)	16.0(5)
	283	48.5(9)	40.3(8)
	288	116.9(10)	70.7(10)
$W_2Cl_4(PEt_3)_4$	308	2.71(5)	2.74(5)
	313	6.08(5)	6.02(5)
	317	13.2(5)	13.0(5)
	324	38.0(5)	32.5(5)
	329	82.7(8)	70.0(7)
	331	121.0(10)	95.2(10)

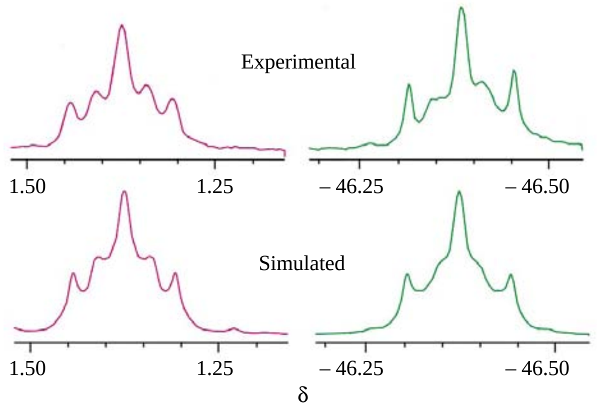


Fig. 8 Experimental (top) and simulated (bottom) $^{31}P-\{^1H\}$ NMR spectra of $Mo_2Cl_4(dmpe\text{-}P)_4$

The $^{31}P-\{^1H\}$ NMR spectrum of $Mo_2Cl_4(dmpe\text{-}P)_4$ formed in the reaction between $Mo_2Cl_4(PEt_3)_4$ and an excess (15 equivalents) of dmpe is shown in Fig. 7. Note that the $^{31}P-\{H\}-^{31}P-\{H\}$ COSY spectrum indicates the two ^{31}P signals at $\delta \approx -46.1$ and 1.8 are coupled and are in the integral ratio 1:1. The former signal, δ −46.1, is close to that of free dmpe, while the latter is typical of a bound PMe_2Ph $^{31}P-\{^1H\}$ signal. A careful examination of the signals at δ −46.1 and 1.8 reveals that both are a part of a complex spin system. For the purpose of simulation we assumed an $AA'A''A'''BB'B''B'''$ spin system with the observed and simulated spectra being shown in Fig. 8. It is also worthy of mention that the color of the solution is dark blue, typical of a $MoCl_4L_4$ compound, where $L = PMe_3$, PEt_3, PMe_2Ph or $PBu^n{}_3$. Although there is to our knowledge no known compound of the type $M_2Cl_4(dmpe\text{-}P)_4$ there are mononuclear complexes containing dmpe-*P* and related diphosphine ligands.[14] We thus rest our case for the existence of the compound $Mo_2Cl_4(dmpe\text{-}P)_4$ in solution. The data pertaining to the kinetics of its formation will be discussed along with related data for other studies of reaction (2).

Reaction (2) was also studied for L′ = pyridine (or $[^2H_5]$pyridine). For $Mo_2Cl_4L_4$, where $L = PEt_3$ or PMe_2Ph, we observed some pyridine for L substitution. Indeed, from variable temperature studies we were able to monitor the equilibria (3a) and (3b). A $Mo_2Cl_4L(py)_3$ complex could be detected but only in

$$Mo_2Cl_4L_4 + py\ (solvent) \rightleftharpoons Mo_2Cl_4L_3(py) + L \qquad (3a)$$

$$Mo_2Cl_4L_3(py) + py\ (solvent) \rightleftharpoons Mo_2Cl_4L_2(py)_2 + L \qquad (3b)$$

very low concentrations. [The compounds $Mo_2X_4(py)_4$ are known for X = Cl or Br.[15]] We were able to obtain the thermodynamic parameters $\Delta H°$ and $\Delta S°$ from Arrhenius plots. For $L = PEt_3$, $\Delta H° = 5.2(4)$ kcal mol^{-1} and $\Delta S° = 11(1)$ cal K^{-1} mol^{-1} and for $L = PMe_2Ph$, $\Delta H° = 5.3(1)$ kcal mol^{-1} and $\Delta S° = 6(4)$ cal K^{-1} mol^{-1}, which, of course, indicates that (*i*) the $Mo-PR_3$ bond is thermodynamically favored over Mo–py and (*ii*) that PMe_2Ph is slightly favored relative to PEt_3. The latter could be understandable in terms of steric factors, as judged by Tolman's cone angles.[16] It should also be noted that the compound $Mo_2Cl_4(py)_4$ is known.[15] Finally we note that in neat $[^2H_5]$pyridine even $Mo_2Cl_4(PMe_3)_4$ shows evidence of the equilibrium (3a) at room temperature. The signal for the free PMe_3 is slightly broadened, indicative of the reversible nature of (3a) on the NMR time-scale.

Table 2 Activation parameters for the reactions $M_2Cl_4L_4 + L' \longrightarrow M_2Cl_4L_3L' + L$

M	L	L′	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal K^{-1} mol^{-1}
Mo	PEt_3	PMe_3	27.9(4)	25(1)
		PMe_2Ph	25.8(5)	17(2)
		dmpe	24.5(4)	12(2)
	PMe_2Ph	PMe_3	33.1(5)	27(2)
W	PEt_3	PMe_3	32.3(4)	25(1)
		PMe_2Ph	29.9(5)	18(2)
W	PBu_3	PMe_3	33.1(5)	26(1)
		PMe_2Ph	32.7(6)	22(2)

Kinetics of the disappearance of $M_2Cl_4L_4$ in reaction (2)

The reactions were monitored by ^{31}P-{^1H} NMR spectroscopy for three half-lives with 15 to 30 equivalents of L′. The rates of reaction showed no dependence on [L′]. The rate of disappearance of $M_2Cl_4L_4$ obeyed first-order kinetics. A summary of rate data is presented in Table 1.

The first and most apparent trend is that $k_{obs}(Mo) > k_{obs}(W)$. This is consistent with the view that bond breaking is important in the rate-determining step as it is well recognized that metal–ligand bonds to third-row transition elements are stronger than those to second-row elements. [In our previous studies of the binding of Lewis bases such as PBu^n_3 or CN^- to $M_2(OR)_6$ compounds the difference in M−L bond energies were small, *ca.* 3 kcal mol^{-1}, and in the order W−L > Mo−L.][17] In the present study this is seen in the magnitude of the $\Delta H^‡$ values listed in Table 2. Consistently we observe that $\Delta H^‡(W) > \Delta H^‡(Mo)$ by *ca.* 3 kcal mol^{-1}. Comparable rates of substitution are seen for M = W with a *ca.* 40 °C higher temperature than for M = Mo for a given ligand set. The second important factor that is evident from an inspection of the rate data in Table 1 is the influence of the leaving group. For example, the less bulky L = PMe_2Ph is replaced more slowly than L = PEt_3.

Both of the above findings are consistent with the work of Andersen and co-workers.[10] However, the third observation that can be seen from the data in Table 1 is that k_{obs} is influenced by the entering ligand L′. This is masked in some instances by the fact that there are isokinetic temperatures. For example, at −5 °C $Mo_2Cl_4(PEt_3)_4$ reacts at essentially the same rate with PMe_3 as it does with PMe_2Ph and dmpe. However, at +15 °C the rates differ quite markedly, certainly well outside the limits of experimental error. This difference of rate dependence with temperature owes its origin to differing entropies of activation. One should also note that a similar difference is seen in substitution reactions of $W_2Cl_4L_4$ complexes. This provides the first piece of evidence that substitution is not proceeding *via* a **simple** dissociative mechanism and that reactive $[M_2Cl_4L_3]^‡$ species, solvated by [$^2H_8$]toluene, are not present in solution.

Having established the rates of substitution for $Mo_2Cl_4L_4$ complexes we are able to test for the hypothetical dissociative process as proposed by Andersen, by carrying out reactions involving the mixing of $Mo_2Cl_4L_4$ and $Mo_2Cl_4L'_4$. So for example at +50 °C in [$^2H_8$]toluene a dissociative mechanism would lead to ligand scrambling and the formation of $Mo_2Cl_4L_{4-n}L'_n$ complexes, readily detectable by ^{31}P-{^1H} NMR spectroscopy. When $Mo_2Cl_4(PMe_2Ph)_4$ and $Mo_2Cl_4(PEt_3)_4$ were heated in [$^2H_8$]toluene at 45 °C for 15 h the scrambled products $Mo_2Cl_4(PMe_2Ph)_{4-n}(PEt_3)_n$ were seen to be formed. This might at first be viewed as evidence for the D mechanism. However, given that the Mo−PMe_2Ph and Mo−PEt_3 bonds have a very similar energy [as seen in the $\Delta H°$ values determined for reaction (3a)], any free tertiary phosphine, which could arise by decomposition, could catalyse the scrambling of the ligands. However, in the reactions between $Mo_2Cl_4(PEt_3)_4$ and $Mo_2Cl_4(PMe_3)_4$, and, $Mo_2Cl_4(PMe_2Ph)_4$ and $Mo_2Cl_4(PMe_3)_4$, no such scrambling was observed at +50 °C, in [$^2H_8$]toluene over 15 h.

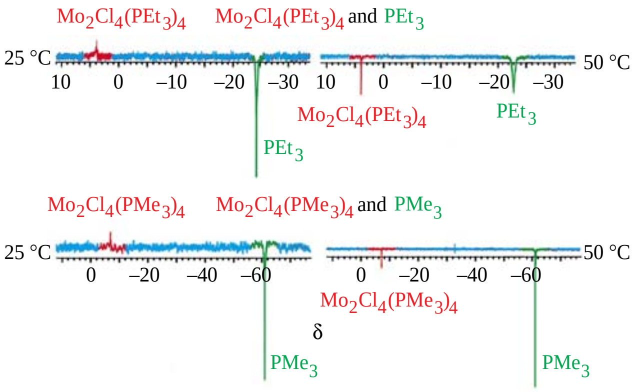


Fig. 9 Difference ^{31}P-{^1H} NMR spectra of spin magnetization transfer experiments involving $Mo_2Cl_4L_4$ and L, where L = PEt_3 (top) and PMe_3 (bottom) at 25 and 50 °C, shown left and right, respectively

In these reactions the $Mo_2Cl_4L_4$ complexes, where L = PEt_3 or PMe_2Ph, would act as 'traps' for any free PMe_3. The ligand scrambling reaction would thus be quenched by the formation of $Mo_2Cl_4(PEt_3)_3(PMe_3)$ and the liberation of an equivalent of PEt_3 which, as we have stated earlier, is not capable of displacing a Mo−PMe_3 bond in $Mo_2Cl_4(PMe_3)_4$. The trace amount of PMe_3 that might have been present in such a solution mixture would go unnoticed in that the concentration of $Mo_2Cl_4(PEt_3)_3(PMe_3)$ would be very low.

Given that in [$^2H_5$]pyridine $Mo_2Cl_4(PMe_3)_4$ enters into the equilibrium (3a), we carried out the reaction between $Mo_2Cl_4(PEt_3)_4$ and $Mo_2Cl_4(PMe_3)_4$ in this solvent. Upon mixing we observed scrambling. At room temperature (25 °C) we observed $Mo_2Cl_4(PMe_3)_4$, free PEt_3, $Mo_2Cl_4(PEt_3)(PMe_3)(py)_2$ and $Mo_2Cl_4(PEt_3)_3(py)$ and $Mo_2Cl_4(PEt_3)_2(py)_2$. Upon heating to 60 °C for 15 h and returning the sample to 25 °C we observed free PEt_3, $Mo_2Cl_4(PMe_3)_4$, $Mo_2Cl_4(PEt_3)(PMe_3)(py)_2$, $Mo_2Cl_4(PMe_3)_2(PEt_3)(py)$, $Mo_2Cl_4(PMe_3)_3(py)$ and $Mo_2Cl_4(PMe_3)_2(py)_2$. For the compound $Mo_2Cl_4(PMe_3)_2(PEt_3)(py)$ the two PMe_3 ligands are on adjacent metal atoms as determined by ^{31}P-{^1H} NMR spectroscopy. From the latter we conclude that pyridine facilitates ligand scrambling by what may be viewed as a solvent-assisted dissociative process for the Mo−PR_3 ligands. The lack of any detectable free PMe_3 in the above reaction mixture reflects its higher affinity for the Mo_2 center relative to PEt_3.

Since pyridine is itself a good nucleophile one might wonder what is meant by the term solvent-assisted dissociation of the Mo−PR_3 bonds. Also one might speculate that a different reaction pathway is possible in this solvent. We thus returned to investigate further the reaction (2) carried out in [$^2H_8$]toluene where L = L′, *i.e.* the degenerate replacement of one tertiary phosphine by itself.

Spin magnetization transfer experiments

The reactions involving $Mo_2Cl_4L_4$ with an excess of L in [$^2H_8$]toluene were studied as a function of temperature for both L = PEt_3 and PMe_3. Irradiation at the frequency of the free phosphine and inspection of the co-ordinated L signal by difference spectroscopy reveals at 25 °C a positive enhancement of it as shown in Fig. 9. This is not consistent with L exchange since this would give rise to a negative difference spectrum. The only explanation for a positive difference spectrum arises from nuclear Overhauser enhancement (NOE)[18] wherein a significant concentration of free L is within the co-ordination sphere of the $Mo_2Cl_4L_4$ complex. This is actually to be expected since all M_2^{4+} quadruply bonded complexes have a weak affinity to bind ligands in the axial position, *i.e.* along the M−M axis.[1] Thus, we ascribe the positive difference spectrum to the equilibrium (4). The equilibrium (4) must be kinetically labile as

$$Mo_2Cl_4L_4 + L\ (\text{excess}) \rightleftharpoons Mo_2Cl_4L_4L_n; \quad n = 1 \text{ or } 2 \qquad (4)$$

we see no direct evidence for $Mo_2Cl_4L_4L_n$ species where $n = 1$ or 2.

Upon heating to +50 °C there are unequivocal negative difference spectra (see Fig. 9) indicative of significant ^{31}P site exchange between the free and the co-ordinated ligands on the NMR time-scale. This is a particularly important observation for $L = PMe_3$ since this tertiary phosphine is otherwise inert to substitution by other R_3P ligands. Also in the lack of reactivity observed between $Mo_2Cl_4(PEt_3)_4$ and $Mo_2Cl_4(PMe_3)_4$ at 50 °C in [$^2H_8$]toluene it could be argued that Mo–PMe_3 bond dissociation does not occur unless pyridine is present.

Conclusion

While much of the present work corroborates the findings of Andersen and co-workers,[10] we do see certain differences. For reaction (2) the importance of bond breaking is clearly evident from the relative rates of reactions for related molybdenum and tungsten complexes. Also the notion that substitution proceeds to release steric strain at the dimetal center finds support in that PMe_3 is resistant to substitution by PEt_3 and PMe_2Ph. However, we have found that $PMePh_2$ will displace one ligand to form $Mo_2Cl_4L_3(PMePh_2)$ where $L = PEt_3$, PMe_2Ph or PBu^n_3. Here a more bulky phosphine with a Tolman cone angle of 136° replaces one with an angle of 132 ($L = PEt_3$ and PBu^n_3) and 122° ($L = PMe_2Ph$).[16] The kinetics of this last reaction clearly indicates the existence of the equilibrium (5) ($L = PEt_3$, PBu^n_3 or PMe_2Ph) (see Experimental section).

$$M_2Cl_4L_4 + PMePh_2 \rightleftharpoons M_2Cl_4L_3(PMePh_2) + L \quad (5)$$

Evidence against a simple dissociative mechanism involving the equilibrium (6) comes from a number of observations. (1) In

$$Mo_2Cl_4L_4 \rightleftharpoons Mo_2Cl_4L_3 + L \quad (6)$$

our studies of the rates of substitution, equation (2), we see that there is an influence of the entering ligand L′. This manifests itself principally in the differing entropies of activation. (2) The kinetic lability of $Mo_2Cl_4(PMe_3)_4$ to enter into PMe_3 scrambling in [$^2H_8$]toluene in the presence of free PMe_3 (as evidenced by spin magnetization transfer) is in marked contrast to its inertness to phosphine scrambling in the presence of $Mo_2Cl_4(PEt_3)_4$ in toluene. (3) The pyridine-promoted phosphine scrambling is understandable in terms of the pyridine-assisted dissociation of PR_3 ligands, equations (3a) and (3b). (4) The reaction with dmpe, which proceeds from $Mo_2Cl_4L_4$ directly to Mo_2Cl_4(dmpe-*P*)$_4$, indicates that once one of the chelating phosphine bonds accesses an equatorial site by displacement of L then the complex is labilized toward dissociation of additional L. This most readily can be accounted for by an equilibrium of type (4) since the unco-ordinated PMe_2 group can rapidly and reversibly occupy the axial site. Thus the position of the equilibrium (4) is effectively displaced to the right.

We therefore conclude that the phosphine exchange occurs by an interchange dissociative mechanism, I_d, wherein the entering ligand effectively moves from an axial site to an equatorial position as the latter M–PR_3 bond breaks. [In studies of the H_2O exchange in Mo_2^{4+} (aq) Sykes and co-workers[19] compared the relative lability of H_2O exchange in the axial position *versus* that in the equatorial position to that seen for V^V–oxo (aq) ion.]

Bearing in mind ‘to never trust in science to the principle of exclusion’[11] we would finally like to suggest that substitution reactions at M_2^{4+} (M≡M) centers are in general unlikely to proceed *via* a limiting dissociative reaction pathway since these complexes are unsaturated. The situation is somewhat akin to substitution at square-planar platinum(II).[20] However, the relative importance of bond breaking and bond forming will surely be greatly influenced by the nature of the entering and leaving ligands, the solvent and overall charge on the complex. The greater kinetic lability of $Mo_2Me_4L_4$ compared with $Mo_2Cl_2L_4$ can be understood in terms of the effective charge at the Mo_2 center as the electron donating properties of Me are greater than those of Cl.

Experimental

All manipulations were carried out using standard Schlenk-line and glove-box techniques under an atmosphere of argon or nitrogen. The deuteriated solvents, [$^2H_8$]toluene and [$^2H_5$]pyridine, were freeze–pump–thaw degassed and stored under nitrogen over molecular sieves (4 Å) prior to use. Standard solutions of PMe_2Ph, $PMePh_2$, dmpe and pyridine were prepared using [$^2H_8$]toluene and stored under argon. Pyridine was dried over sodium, distilled, degassed and stored under nitrogen over molecular sieves (4 Å) prior to use. The ^{31}P-{^1H} NMR spectra were recorded on a Varian I400 spectrometer at 166.9 MHz and referenced externally relative to 85% H_3PO_4. Simulations of such spectra were performed using GNMR V3.6 software. The chemical shifts and coupling constants were optimized by assignment iteration, a least-squares iteration procedure that produces a fit between the observed experimental spectra and calculated peak positions. The dimolybdenum compounds $Mo_2Cl_4(PMe_2Ph)_4$, $Mo_2Cl_4(PEt_3)_4$ and $Mo_2Cl_4(PMe_3)_4$ were prepared from $Mo_2(O_2CMe)_4$ by the general procedure described.[21] The ditungsten complexes $W_2Cl_4(PEt_3)_4$, $W_2Cl_4(PBu_3)_4$ and $W_2Cl_4(PMe_3)_4$ were prepared from the reduction of WCl_4 by the general procedure described.[22] The phosphine ligands PMe_3, PEt_3, PBu^n_3, PMe_2Ph and $PMePh_2$ were purchased from Aldrich and the diphosphine ligand dmpe from Strem.

General sample preparation for measurement of kinetics

For all the rate determinations the disappearance of the $M_2Cl_4L_4$ complex was monitored over at least three half-lives under pseudo-first-order conditions. Linear plots of ln *k versus* $1/T$ were obtained thus indicating that the reaction was first order in [$M_2Cl_4L_4$]. This was true for all cases except where $L' = PMePh_2$, where after approximately one half-life the plot levelled out and an equilibrium situation was obtained. Both before and after each experiment the temperature of the NMR machine was calibrated using neat methanol (<25 °C) or neat ethylene glycol (>25 °C), with an equilibration time of at least 15 min and the acquisition of at least three spectra. The temperature before and after each experiment did not vary by more than 0.4 °C.

The samples were generally prepared using J. Young® NMR tubes in a helium glove-box. The $M_2Cl_4L_4$ complex was weighed using an analytical balance accurate to 0.1 mg. The stock [$^2H_8$]toluene solutions of the phosphine ligands were then added *via* a microlitre syringe, except in the case of PMe_3, which was volatile enough to be transferred using a calibrated gas manifold. For $Mo_2Cl_4(PEt_3)_4$ it was imperative that the samples were prepared and maintained at a low temperature (generally −78 °C) prior to the measurements. This is easily achieved in the case of PMe_3 which was condensed into a J. Young® NMR tube at −196 °C, however in the case of the other phosphine ligands the $Mo_2Cl_4(PEt_3)_4$ complex must be weighed in the helium box and capped with a small rubber septum through which the phosphine [$^2H_8$]toluene solutions could be injected whilst keeping the NMR sample at −78 °C.

The pulse width and T_1 of the ^{31}P nuclei were determined by standard techniques as outlined in the Varian manual. A delay time (d_1) of at least $5T_1$ was then used during the acquisition of the ^{31}P-{^1H} NMR data to ensure full relaxation and thus accurate measurement of the integration.

The standard deviations in the measurements of k_{obs} were determined by taking three measurements at one temperature, *e.g.* for $Mo_2Cl_4(PMe_2Ph)_4$ with 15 equivalents of PMe_3 at 40 °C

Table 3 Summary of ^{31}P-{^1H} NMR data for the compounds under discussion

Compound	δ, *J*/Hz
PMe_3	−61.0 (s)
dmpe	−46.3 (s)
PMe_2Ph	−45.8 (s)
PBu_3	−31.1 (s)
$PMePh_2$	−23.6 (s)
PEt_3	−18.7 (s)
$Mo_2Cl_4(PEt_3)_4$	9.8 (s)
$Mo_2Cl_4(PEt_3)_3(PMe_3)$	−7.3 (m, 1P, PMe_3, $^2J = 164$, $^3J = 18$), 10.1 (m, 1P, PEt_3, $^2J = 164$, $^3J = 18$), 10.7 (m, 2P, PEt_3, $^3J = 18$)
$Mo_2Cl_4(PEt_3)_2(PMe_3)_2$ (AA′BB′)	−7.0 (m, 2P, PMe_3) and 11.1 (m, 2P, PEt_3)
(A_2B_2)	−8.3 (t, 2P, PMe_3) and 11.2 (t, 2P, PEt_3), $^3J(AB) = 18.1$
$Mo_2Cl_4(PMe_3)_4$	−7.2 (s)
$Mo_2Cl_4(PEt_3)_3(PMe_2Ph)$	−3.5 (dt, 1P, PMe_2Ph, $^2J = 153$, $^3J = 18$), 9.6 (t, 2P, PEt_3, $^3J = 18$), 11.5 (dt, 1P, PEt_3, $^2J = 153$, $^3J = 18$)
$Mo_2Cl_4(PEt_3)_2(PMe_2Ph)_2$ (AA′BB′)	−3.8 (m, 2P, PMe_2Ph) and 12.2 (m, 2P, PEt_3), $^2J(AB) = {}^2J(A'B') = 154$, $^3J(AA') = 18$, $^3J(AB') = {}^3J(A'B) = 19$, $^3J(BB') = 20$
$Mo_2Cl_4(PEt_3)(PMe_2Ph)_3$	−2.8 (t, 2P, PMe_2Ph, $^3J = 19$), −3.7 (dt, 1P, PMe_2Ph, $^2J = 156$, $^3J = 20$), 11.5 (dt, 1P, PEt_3, $^2J = 156$, $^3J = 20$)
$Mo_2Cl_4(PMe_2Ph)_4$	−2.9 (s)
$Mo_2Cl_4(dmpe\text{-}P)_4$[a] (AA′A″A‴BB′B″B‴)	−46.1 (m, 4P) and 1.8 (m, 4P, Mo−P), $^2J(AA') = {}^2J(A''A''') = 174$, $^3J(AA'') = {}^3J(AA''') = {}^3J(A'A'') = {}^3J(A'A''') = 19$, $^3J(AB) = {}^3J(A'B') = {}^3J(A''B'') = {}^3J(A'''B''') = 22$
$Mo_2Cl_4(PMe_2Ph)_4$	0.4 (s)
$Mo_2Cl_4(PMe_2Ph)_3(PMe_3)$[b]	−5.8 (dt, 1P, PMe_3, $^2J = 174$, $^3J = 19$), −2.8 (dt, 1P, PMe_2Ph, $^2J = 174$, $^3J = 19$), 0.3 (t, 2P, PMe_2Ph, $^3J = 19$)
$Mo_2Cl_4(PMe_2Ph)_2(PMe_3)_2$ (A_2B_2)	−7.0 (t, 2P, PMe_3) and −0.3 (t, 2P, PMe_2Ph), $^3J(AB) = 19$
$Mo_2Cl_4(PMe_2Ph)(PMe_3)_3$	−7.1 (t, 2P, PMe_3, $^3J = 19$ Hz), −5.8 (dt, 1P, PMe_3, $^2J = 175$, $^3J = 20$), −2.1 (dt, 1P, PMe_2Ph, $^2J = 175$, $^3J = 20$)
$W_2Cl_4(PEt_3)_4$[c]	6.5 (s)
$W_2Cl_4(PEt_3)_3(PMe_3)$	−10.0 (dt, 1P, PMe_3, $^2J = 150$, $^3J = 28$), 8.1 (dt, 1P, PEt_3, $^2J = 150$, $^3J = 28$), 8.6 (t, 2P, PEt_3, $^3J = 28$)
$W_2Cl_4(PEt_3)_2(PMe_3)_2$ (AA′BB′)	−8.2 (m, 2P, PMe_3) and 10.2 (m, 2P, PEt_3), $^2J(AB) = {}^2J(A'B') = 153$, $^3J(AA') = {}^3J(AB') = {}^3J(A'B) = 27$
$W_2Cl_4(PEt_3)_3(PMe_2Ph)$	−5.8 (dt, 1P, PMe_2Ph, $^2J = 143$, $^3J = 28$), 7.9 (dt, 1P, PEt_3, $^2J = 143$, $^3J = 28$), 9.0 (t, 2P, PEt_3, $^3J = 28$)
$W_2Cl_4(PEt_3)_2(PMe_2Ph)_2$ (AA′BB′)	−3.1 (m, 2P, PMe_2Ph) and 10.2 (m, 2P, PEt_3), $^2J(AB) = {}^2J(A'B') = 144$, $^3J(AA') = {}^3J(AB') = {}^3J(A'B) = 27$
$W_2Cl_4(PEt_3)_3(PMePh_2)$	−0.2 (dt, 1P, $PMePh_2$, $^2J = 144$, $^3J = 28$), 7.8 (dt, 1P, PEt_3, $^2J = 144$, $^3J = 28$), 8.2 (t, 2P, PEt_3, $^3J = 28$)
$W_2Cl_4(PBu_3)_4$	4.5 (s)
$W_2Cl_4(PBu_3)_3(PMe_3)$	−10.2 (dt, 1P, PMe_3, $^2J = 150$, $^3J = 29$), 5.1 (dt, 1P, PBu_3, $^2J = 150$, $^3J = 29$), 6.0 (t, 2P, PBu_3, $^3J = 29$)
$W_2Cl_4(PBu_3)_3(PMe_2Ph)$	−4.5 (dt, 1P, PMe_2Ph, $^2J = 143$, $^3J = 28$), 7.1 (dt, 1P, PBu_3, $^2J = 143$, $^3J = 28$), 7.7 (t, 2P, PBu_3, $^3J = 28$)
$W_2Cl_4(PBu_3)_2(PMe_2Ph)_2$ (AA′BB′)	−1.1 (m, 2P, PMe_2Ph) and 7.0 (m, 2P, PBu_3), $^2J(AB) = {}^2J(A'B') = 144$, $^3J(AA') = {}^3J(AB') = {}^3J(A'B) = 27$
$W_2Cl_4(PBu_3)_3(PMePh_2)$	−3.0 (dt, 1P, $PMePh_2$, $^2J = 144$, $^3J = 28$), 0.2 (dt, 1P, PBu_3, $^2J = 143$, $^3J = 28$), 6.0 (t, 2P, PBu_3, $^3J = 28$)
$Mo_2Cl_4(PEt_3)_3(py)$	8.5 (d, 2P, PEt_3, $^3J = 20$), 21.8 (t, 1P, PEt_3, $^3J = 20$)
$Mo_2Cl_4(PEt_3)_2(py)_2$	20.2 (s)
$Mo_2Cl_4(PMe_2Ph)_3(py)$	1.7 (d, 2P, PMe_2Ph, $^3J = 22$), 9.2 (t, 1P, PMe_2Ph, $^3J = 22$)
$Mo_2Cl_4(PMe_2Ph)_2(py)_2$	6.8 (s)
$Mo_2Cl_4(PMe_3)_3(py)$[d]	−9.2 (d, 2P, PMe_3, $^3J = 22$), −4.1 (t, 1P, PMe_3, $^3J = 22$)
$Mo_2Cl_4(PMe_3)_2(py)_2$	0.2 (s, PMe_3)
$Mo_2Cl_4(PEt_3)(PMe_3)(py)_2$	−0.8 (d, 1P, PMe_3, $^3J = 24$), 20.8 (d, 1P, PEt_3, $^3J = 24$)
$Mo_2Cl_4(PEt_3)(PMe_3)_2(py)$	3.0 (t, 1P, PMe_3, $^3J = 21$), 8.8 (dd, 1P, PMe_3, $^2J = 163$, $^3J = 21$), 11.0 (dd, 1P, PEt_3, $^2J = 163$, $^3J = 21$)
$Mo_2Cl_4(PEt_3)_2(PMe_3)(py)$	3.2 (t, 1P, PMe_3 $^3J = 22$), 9.2 (d, 2P, PEt_3, $^3J = 22$)
$Mo_2Cl_4(PMe_2Ph)_3(py)$	−1.1 (d, 2P, $^3J = 21$), 9.6 (t, 1P, $^3J = 21$)
$Mo_2Cl_4(PMe_2Ph)_2(PMe_3)(py)$	−1.5 (t, 1P, PMe_3, $^3J = 22$), 3.2 (d, 2P, PMe_2Ph, $^3J = 22$)
$Mo_2Cl_4(PEt_3)_3(PMe_2Ph)$	−3.5 (dt, 1P, PMe_2Ph, $^2J = 153$, $^3J = 18$), 9.6 (t, 2P, PEt_3, $^3J = 18$), 11.5 (dt, 1P, PEt_3, $^2J = 153$, $^3J = 18$)
$Mo_2Cl_4(PEt_3)_2(PMe_2Ph)_2$ (AA′BB′)	−3.8 (m, 2P, PMe_2Ph) and 12.2 (m, 2P, PEt_3), $^2J(AB) = {}^2J(A'B') = 154$, $^3J(AA') = 18$, $^3J(AB') = {}^3J(A'B) = 19$, $^3J(BB') = 20$
(A_2B_2)	−3.3 (t, 2P, PMe_2Ph) and 12.4 (t, 2P, PEt_3), $^3J(AB) = 19$
$Mo_2Cl_4(PEt_3)(PMe_2Ph)_3$	−2.8 (t, 2P, PMe_2Ph, $^3J = 19$), −3.7 (dt, 1P, PMe_2Ph, $^2J = 156$, $^3J = 20$), 11.5 (dt, 1P, PEt_3, $^2J = 156$, $^3J = 20$)

[a] A through A‴ represent the co-ordinated arm of the dmpe-*P* and B through B‴ the dangling arm. The compound $Mo_2Cl_4(dmpe\text{-}P)_4$ is a complex spin system, AA′A″A‴BB′B″B‴, which was simulated using GNMR V3.6. It was assumed that there was no coupling between B, B′, B″ and B‴, *i.e.* between the 'dangling' phosphine ligands. [b] The leaning observed for the two sets of doublet of triplets for the complex is due to second-order effects which were simulated using GNMR V3.6. [c] The ^{31}P-{^1H} NMR spectrum has complicated tungsten satellites which can be simulated using GNMR V3.6. This is clearly evident in the starting material $W_2Cl_4(PEt_3)_4$, which unlike its molybdenum analogue has complex satellites as ^{183}W has 14.3% natural abundance, *e.g.* $^1J(^{183}WP) = 238$, $^2J(^{183}WP) = 51$, $^3J(PP) = 29$ Hz, with zero coupling to the spin-inactive tungsten and no $^2J(PP)$ coupling as the *trans* phosphine ligands are magnetically equivalent due to symmetry. [d] Upon the addition of neat [$^2H_5$]pyridine to $Mo_2Cl_4(PMe_3)_4$ only a small amount of $Mo_2Cl_4(PMe_3)_3(py)$ and free PMe_3 were observed. Heating the sample to 60 °C did result in a further small liberation of PMe_3 but the concentrations were so small that equilibrium constant measurements were not possible.

$k_{obs} = 4.91 \times 10^{-5}$, 4.96×10^{-5}, 4.96×10^{-5} s^{-1}, and then calculating the standard deviation by standard mathematical techniques. In this case the standard deviation was 0.03×10^{-5} s^{-1}, thus the value is reported as $4.94(3) \times 10^{-5}$ s^{-1}. Errors in the fit of the Eyring plots were determined using non-linear regression analysis performed using SIGMA PLOT 3.0.

Reaction of $Mo_2Cl_4(PEt_3)_4$ with L′ (PMe_3, PMe_2Ph or dmpe). The sample temperature was maintained at −78 °C prior to the experiment. The rate of disappearance of $Mo_2Cl_4(PEt_3)_4$ was monitored in the temperature range −5 to 15 °C at 5 °C intervals *via* ^{31}P-{^1H} NMR spectroscopy. The NMR data are given in Table 3.

The compound [$Mo_2Cl_4(dmpe\text{-}P)_4$] is a complex spin system, AA′A″A‴BB′B″B‴, which was simulated using GNMR V3.6. It was assumed that there was no coupling between B, B′, B″ and B‴, *i.e.* between the 'dangling' phosphine ^{31}P nuclei.

Reaction of $M_2Cl_4L_4$ with PMe_3 (M = Mo, L = PMe_2Ph; M = W, L = PEt_3 or PBu^n_3). A J. Young® NMR tube was charged with $M_2Cl_4L_4$ (0.0086 mmol) and [$^2H_8$]toluene (600 µl). The blue solution was then cooled to −196 °C using liquid nitrogen and the NMR tube evacuated. Trimethylphosphine (0.14 mmol) was then condensed into the NMR tube *via* a calibrated gas-transfer manifold. The reaction was then allowed to attain room temperature and the rate of disappearance of

$[M_2Cl_4L_4]$ was monitored *via* $^{31}P\text{-}\{^1H\}$ NMR spectroscopy in the temperature range 35 to 60 °C for M = W and −5 to 15 °C for M = Mo at 5 °C intervals. The NMR data are given in Table 3.

The leaning observed for the two sets of doublet of triplets for the complex $Mo_2Cl_4(PMe_2Ph)_3(PMe_3)$ is due to second-order effects which were simulated using GNMR V3.6.

Reaction of $Mo_2Cl_4L_4$ with dmpe, where L = PMe_2Ph or $PBu^n{}_3$. A NMR tube was charged with $Mo_2Cl_4L_4$ (0.017 mmol) and dmpe (600 µl, 0.22 M, 0.17 mmol). The NMR machine was warmed to 50 °C and calibrated with neat ethylene glycol. After the desired temperature was attained the sample was inserted and the reaction followed by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy (data in Table 3).

Note that not all the $Mo_2Cl_4(PMe_3)_4$ complex was consumed; even at 60 °C only a small amount of $Mo_2Cl_4(dmpe\text{-}P)_4$ and PMe_3 were formed. Further, prolonged heating at 60 °C resulted in the cleavage of the Mo≣Mo quadruple bond as the color changes from deep blue to pale red and the only peaks identified in the $^{31}P\text{-}\{^1H\}$ NMR spectrum were due to free PMe_3 and free dmpe.

Reaction of $Mo_2Cl_4(PMe_3)_4$ with L′ (PMe_2Ph, $PMePh_2$ or PEt_3). A J. Young® NMR tube charged with $Mo_2Cl_4(PMe_3)_4$ (4.5 mg, 0.007 mmol) and L′ (772 µl of 0.22 M, 0.17 mmol) was heated at 50 °C for 15 h with no observable change detected in the $^{31}P\text{-}\{^1H\}$ NMR spectrum (data in Table 3).

Reaction of $W_2Cl_4L_4$ with L′, where L = PEt_3 or $PBu^n{}_3$ and L′ = PMe_2Ph or $PMePh_2$. A J. Young® NMR tube was charged with $W_2Cl_4L_4$ (0.0107 mmol) and L′ (600 µl, 0.22 M, 0.17 mmol) to afford a green solution. The disappearance of $W_2Cl_4L_4$ was monitored over at least three half-lives by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy in the temperature range 35 to 60 °C at 5 °C intervals, unless otherwise stated.

The $^{31}P\text{-}\{^1H\}$ NMR spectra of these ditungsten complexes have complicated tungsten satellites which can be simulated using GNMR V3.6. This is clearly evident for the starting material $W_2Cl_4(PEt_3)_4$, which unlike its molybdenum analogue has complex satellites as ^{183}W has 14.3% natural abundance.

Reaction of $Mo_2Cl_4L_4$ with pyridine, where L = PEt_3, PMe_2Ph or PMe_3. Upon addition of neat $[^2H_5]$pyridine (600 µl) to $Mo_2Cl_4L_4$ (0.037 mmol) pyridine/phosphine exchange was observed to varying degrees depending upon L and the temperature. The equilibria, where L = PEt_3 or PMe_2Ph, were examined using a 2.36 M solution of pyridine in $[^2H_8]$toluene (600 µl, 0.471 mmol) by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy over the temperature range 20 to 80 °C at 10 °C intervals. The sample was allowed to equilibrate at each temperature for at least 25 min.

A reversible equilibrium was found to be in effect and K_1 values were calculated at various temperatures and from an Arrenhius plot the $\Delta H°$ and $\Delta S°$ of the reaction could be calculated: $K_1 = [Mo_2Cl_4L_3(py)][L]/[Mo_2Cl_4L_4][py]$; for L = PEt_3, $\Delta H_1° = 5.3(4)$ kcal mol^{-1}, $\Delta S_1° = 11(1)$ cal K^{-1} mol^{-1}; for L = PMe_2Ph, $\Delta H_1° = 5.2(4)$ kcal mol^{-1}, $\Delta S_1° = 11(1)$ cal K^{-1} mol^{-1}. The NMR data are given in Table 3.

Upon the addition of neat $[^2H_5]$pyridine to $Mo_2Cl_4(PMe_3)_4$ only a small amount of $Mo_2Cl_4(PMe_3)_3(py)$ and free PMe_3 were observed. Heating the sample to 60 °C did result in a further small liberation of PMe_3 but the concentrations were so small that equilibrium constant measurements were not possible.

Reaction of $Mo_2Cl_4(PEt_3)_4$ with $Mo_2Cl_4(PMe_3)_4$ in pyridine. A J. Young® NMR tube was charged with $Mo_2Cl_4(PEt_3)_4$ (5.4 mg, 0.0067 mmol), $Mo_2Cl_4(PMe_3)_4$ (6.0 mg, 0.0094 mmol) and $[^2H_5]$-pyridine (600 µl). From $^{31}P\text{-}\{^1H\}$ NMR spectroscopy it was determined that PEt_3, $Mo_2Cl_4(PMe_3)_4$, $Mo_2Cl_4(PEt_3)_4$, $Mo_2Cl_4(PEt_3)_3(py)$, $Mo_2Cl_4(PEt_3)(PMe_3)(py)_2$ and $Mo_2Cl_4(PEt_3)_2(py)_2$ were formed at room temperature. The reaction was then monitored by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy at 25 °C and no change was observed over 48 h. The sample was then heated at 60 °C for 24 h, after which time the new products $Mo_2Cl_4(PEt_3)(PMe_3)_2(py)$, $Mo_2Cl_4(PEt_3)_2(PMe_3)(py)$ and $Mo_2Cl_4(PMe_3)_2(py)_2$ could be identified in the $^{31}P\text{-}\{^1H\}$ NMR spectrum.

Reaction of $Mo_2Cl_4(PMe_2Ph)_4$ and $Mo_2Cl_4(PMe_3)_4$ in pyridine. A J. Young® NMR tube was charged with $Mo_2Cl_4(PMe_2Ph)_4$ (8.8 mg, 0.01 mmol), $Mo_2Cl_4(PMe_3)_4$ (6.0 mg, 0.009 mmol) and $[^2H_5]$pyridine (600 µl). Upon mixing, PMe_2Ph, $Mo_2Cl_4(PMe_3)_4$, $Mo_2Cl_4(PMe_2Ph)_4$ and $Mo_2Cl_4(PMe_2Ph)_3(py)$ could be identified in the $^{31}P\text{-}\{^1H\}$ NMR spectrum at room temperature. After heating at 55 °C for 24 h $Mo_2Cl_4(PMe_2Ph)_2(PMe_3)(py)$ could also be identified in the $^{31}P\text{-}\{^1H\}$ NMR spectrum.

Reaction of $Mo_2Cl_4(PMe_2Ph)_4$ and $Mo_2Cl_4(PEt_3)_4$ in toluene. A J. Young® NMR tube charged with $Mo_2Cl_4(PMe_2Ph)_4$ (6.5 mg, 0.007 mmol), $Mo_2Cl_4(PEt_3)_4$ (5.8 mg, 0.08 mmol) and $[^2H_8]$toluene (600 µl) was heated at 40 °C for 24 h, after which time $Mo_2Cl_4(PMe_3)_4$, $Mo_2Cl_4(PMe_2Ph)_4$, $Mo_2Cl_4(PEt_3)_3(PMe_2Ph)$, $Mo_2Cl_4(PEt_3)_2(PMe_2Ph)_2$ (AA′BB′), $Mo_2Cl_4(PEt_3)_2(PMe_2Ph)_2$ (A_2B_2) and $Mo_2Cl_4(PEt_3)(PMe_2Ph)_3$ were determined in the $^{31}P\text{-}\{^1H\}$ NMR spectrum.

Reaction of $Mo_2Cl_4(PMe_3)_4$ and $Mo_2Cl_4L_4$ in toluene, where L = PEt_3 or PMe_2Ph. A J. Young® NMR tube charged with $Mo_2Cl_4L_4$ (0.0107 mmol), $Mo_2Cl_4(PMe_3)_4$ and $[^2H_8]$toluene (600 µl) was heated at 50 °C for 15 h with no observable change detected in the $^{31}P\text{-}\{^1H\}$ NMR spectrum.

Spin transfer magnetization $^{31}P\text{-}\{^1H\}$ NMR experiment with $Mo_2Cl_4L_4$ and L (PMe_3 or PEt_3). A J. Young® NMR tube was charged with $Mo_2Cl_4L_4$ (0.012 mmol), L (0.05 mmol) and $[^2H_8]$toluene (600 µl). The sample was then irradiated at the frequency corresponding to the free phosphine at various temperatures (25 to 60 °C). The corresponding blank spectrum in which neither peak was irradiated was also acquired. From the subtraction of the blank from the irradiated spectrum a difference NOE spectrum was obtained.

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