Nucleophilic Attack on a Ligand as a Pre-requisite for Ligand Replacement. Kinetics and Mechanism of the Replacement of PMe_2Ph by $P(OMe)_3$ in $[Ru(S_2CH)(PMe_2Ph)_3\{P(OMe)_3\}]^+$

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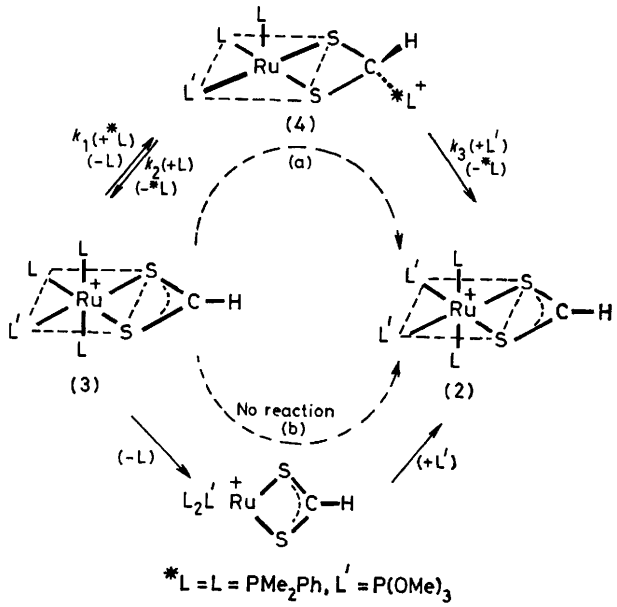
Summary Kinetic data reveal that nucleophilic attack of added PMe_2Ph on the dithioformato carbon atom of the title complex catalyses the substitution of PMe_2Ph by $P(OMe)_3$ to give $[Ru(S_2CH)(PMe_2Ph)_2\{P(OMe)_3\}_2]^+$; the structure of one of the intermediates is inferred from the isolation of $[Ru\{S_2C(H)PMe_2Ph\}(PMe_2Ph)_2\{P(OMe)_2Ph\}]^+$.

WE have shown[1] previously that the purple, five-co-ordinate complex $[Ru\{S_2C(H)PMe_2Ph\}(PMe_2Ph)_3][PF_6]$ (**1**) containing a phosphonium-adduct of a dithioformato ligand, reacts with an excess of $P(OMe)_3$ to give the dithioformato species $[Ru(S_2CH)(PMe_2Ph)_2\{P(OMe)_3\}_2]PF_6$ (**2**). More recently we have isolated $[Ru(S_2CH)(PMe_2Ph)_3\{P(OMe)_3\}]PF_6$ (**3**) by mixing equimolar amounts of (**1**) and $P(OMe)_3$ in methanol. A kinetic study of the conversion of (**3**) into (**2**) has revealed a novel mechanism which illustrates how nucleophilic attack on a ligand can considerably alter the ligand substitution patterns normally observed for octahedral complexes. The results are summarized in the Scheme.

The classical dissociative mechanism [pathway (b)] can be discarded on the basis that complex (**3**) is inert towards ligand substitution under ambient conditions even in the presence of an excess of $P(OMe)_3$. In contrast, the addition



SCHEME. (a) Phosphine-catalysed pathway. (b) Classical ligand dissociative pathway.

TABLE. ^{1}H N.m.r. data for complexes (**1**)—(**5**).[a-d]

Complex	Formula	δ		
		S_2CPMe_2–	Ru–PMe_2–	Ru–$P(OMe)_3$
(**1**)	$[Ru\{S_2C(H)L\}L_3]^+$	2·05 (d, 13·0)	1·52 (pt, 9·0)	
(**2**)	$[Ru(S_2CH)L_2L'_2]^+$		1·87 (vt, 7·5)	3·82 (pt, 10·8)
(**3**)	$[Ru(S_2CH)L_3L']^+$		1·77 (d, 9·0) 1·69 (vt, 7·8) 1·52 (vt, 7·2)	3·81 (d, 10·5)
(**4**)	$[Ru\{S_2C(H)L\}L_2L']^+$	2·10 (d, 13·0)	obscured by (**3**)	3·65 (d, 12·0)
(**5**)	$[Ru\{S_2C(H)L\}L_2L'']^+$	2·07 (d, 13·0)	1·55 (pt, 9·0) 1·43 (pt, 8·4)	3·78 (d, 12·0)

[a] In CD_2Cl_2 as solvent. [b] Except for (**4**) all compounds in the Table were isolated in pure form and gave satisfactory microanalytical results. [c] L = PMe_2Ph, L' = $P(OMe)_3$ and L'' = $P(OMe)_2Ph$. [d] pt = partial triplet, vt = 'virtual' (1:2:1) triplet, d = doublet. Coupling constants (in Hz) appear in parentheses.

of either PMe_2Ph or a mixture of PMe_2Ph and $P(OMe)_3$ to complex (**3**) results in different chemical reactions as manifested by the respective increase and decrease of optical density observed in the u.v.–vis. region at λ = 430 nm. The former reaction can be rationalised in terms of an equilibration between complexes (**3**) and (**4**), the rate of which obeys the rate law (1) where $k_1 + k_2 = 0{\cdot}1$ l mol^{-1} s^{-1} and no $P(OMe)_3$ is present. With both $P(OMe)_3$

$$k_{obs} = 0{\cdot}1[PMe_2Ph];\ 1 \times 10^{-3}\ \text{M} \leqslant [PMe_2Ph] \leqslant 2 \times 10^{-2}\ \text{M} \quad (1)$$

and PMe_2Ph present in the reaction solution (**2**) is formed and the rate law takes the form (2) where $k_1 = 0{\cdot}02$ l mol^{-1} s^{-1}. Since the concentration of $P(OMe)_3$ does not

$$k_{obs} = 0{\cdot}02[PMe_2Ph];\ \begin{cases} 1 \times 10^{-3}\ \text{M} \leqslant [PMe_2Ph] \leqslant 2 \times 10^{-2}\ \text{M} \\ 1 \times 10^{-4}\ \text{M} \leqslant [P(OMe)_3] \leqslant 1 \times 10^{-1}\ \text{M} \end{cases} \quad (2)$$

feature in rate law (2) it can be deduced that step k_1 is rate-limiting as a result of the rapid scavening of reaction intermediate (**4**) by $P(OMe)_3$ to form (**2**) (step k_3). The equilibrium constant for the equilibrium shown in the Scheme can be calculated as $K = k_1/k_2 = 0{\cdot}02/0{\cdot}08 = 0{\cdot}25$ from the kinetic data contained in rate laws (1) and (2).

A ^{1}H n.m.r. spectrum obtained upon adding 1 mol. equiv. of PMe_2Ph to (**3**) shows an equilibrium mixture of approximately 80% of (**3**) and 20% of another species which we infer to be (**4**). The ratio of (**3**) and (**4**) at equilibrium is not affected by further additions of PMe_2Ph and this ratio is in fair agreement with the equilibrium constant calculated independently from the above-mentioned kinetic measurements. Although (**4**) could not be isolated from the equilibrium mixture, its structure can be inferred from the doublet observed at δ 2·1 (J 13 Hz) which is characteristic of PMe_2Ph[1] and PMe_3[2] bonded to the carbon atom of a dithioformato ligand. Complexes (**1**) and (**5**) display similar ^{1}H n.m.r. features (Table) and can therefore be viewed as structural analogues of (**4**). An X-ray diffraction study of (**1**) shows an approximate square pyramidal arrangement of ligands around Ru with the two sulphur atoms co-ordinated in the basal plane.[1] The two PMe_2Ph ligands in (**5**) are magnetically non-equivalent (Table) indicating that $P(OMe)_2Ph$ is bonded *trans* to sulphur. A similar bonding arrangement is proposed for (**4**).

Since reaction step k_3 of the Scheme is non-rate-determining very little mechanistic detail is available for this pathway.

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[1] T. V. Ashworth, M. Laing, and E. Singleton, *J. Chem. Soc., Chem. Commun.*, 1976, 875.
[2] W. Bertleff and H. Werner, *Chem. Ber.*, 1980, **113**, 267.