# Notes

## Upon the Fluxionality of [RhCl(PPh$_3$)(Ph$_2$PO$_2$CCH=CHMe)]

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The fluxional behaviour of [RhCl(PPh$_3$)(Ph$_2$PO$_2$CCH=CHMe)]observed in the n.m.r. spectra is attributed to the rapid equilibrium between two isomers having mutually *cis* and *trans* phosphorus atoms respectively. Thermodynamic parameters for this process are measured and loss of P–P but not Rh–P coupling under fast exchange conditions suggests that $J_{PP}$ has different signs for the two isomers

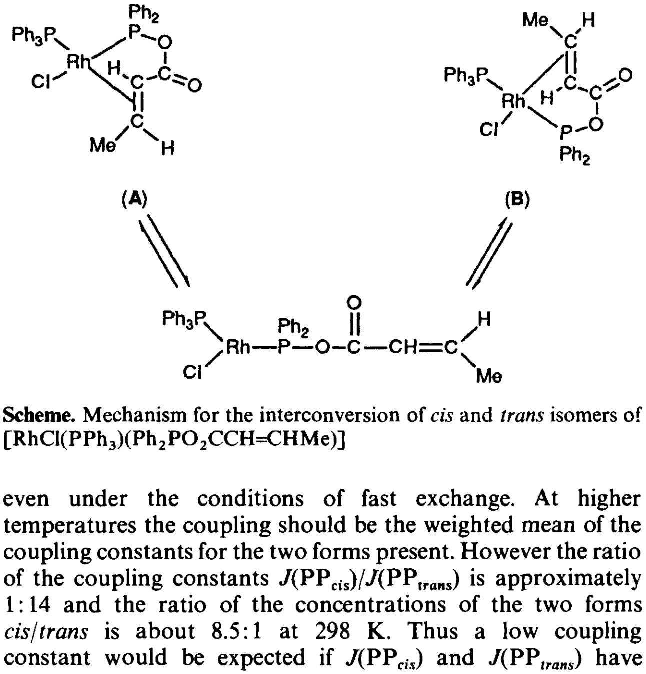
We recently reported[1] that reactions of [RhCl(PPh$_3$)$_3$] with mixed anhydrides of acrylic and diphenylphosphinous acids give complexes of the form [RhCl(PPh$_3$)$_n$(Ph$_2$PO$_2$CCR=CR′R″)] ($n$ = 1, R = R′ = H, R″ = Me or CH=CHMe; $n$ = 2, R = H, R′ = R″ = Me; R = Me, R′ = H, R″ = Ph) and that unusual fluxional behaviour is exhibited in the specific case of [RhCl(PPh$_3$)(Ph$_2$PO$_2$CCH=CHMe)] at room temperature. At low temperature the $^1$H and $^{31}$P n.m.r. spectra both indicate that the complex adopts the structure which has been shown, by *X*-ray crystallography, to be that adopted in the solid state. In this, the mixed anhydride is bound through the phosphorus atom and the double bond. Furthermore the phosphorus atoms, as shown in (**A**) in the Scheme, are in a mutually *cis* configuration. On warming, the resonance of the mixed anhydride exhibits substantial broadening whilst that of the PPh$_3$ remains sharp but loses the mutual phosphorus coupling. Broadening of the resonances from the vinylic protons of the mixed anhydride ligand is also observed. The origin of these effects was obscure, but detailed studies have now been carried out and provide insight into the origins of this fluxional behaviour.

### Results and Discussion

Close examination of the low-temperature $^{31}$P n.m.r. spectrum of [RhCl(PPh$_3$)(Ph$_2$PO$_2$CCH=CHMe)] reveals the presence of a second species, (**B**), which gives rise to two doublets of doublets at δ 116.5 ($J_{RhP}$ = 133.2) and 24.1 p.p.m. ($J_{RhP}$ = 122.2, $J_{PP}$ = 423.2 Hz). The large value of $J_{PP}$ suggests that the complex has mutually *trans* phosphorus atoms and the structure shown in the Scheme. On warming, the resonances of species (**B**) coalesce* with the resonances from the major species present, (**A**), suggesting that it is an isomer of the major species. This observation also leads to the conclusion that the fluxional process involves rapid reversible exchange between (**A**) and (**B**), *i.e.* an end-over-end rotation of the mixed anhydride ligand about an axis approximately bisecting the Cl–Rh–P(Ph$_3$) angle. Such ligand rotations have previously been observed, for example, in chelating ligands containing S and Se.[2]

By measuring the relative concentrations of the *cis* and *trans* forms of [RhCl(PPh$_3$)(Ph$_2$PO$_2$CCH=CHMe)] at different temperatures (223—263 K) it is possible to calculate thermodynamic parameters for the *cis* ⟶ *trans* isomerisation processes as $\Delta G^\circ_{298}$ = 5.3 kJ mol$^{-1}$, $\Delta H^\circ_{298}$ = 3.7 kJ mol$^{-1}$, and $\Delta S^\circ_{298}$ = −5.3 J K$^{-1}$ mol$^{-1}$. It is unusual to be able to compute the values of these thermodynamic parameters since, in general, only one isomer can be observed.[2]

Since the phosphorus atoms remain bound to the rhodium at all times, they would be expected to exhibit mutual coupling even under the conditions of fast exchange. At higher temperatures the coupling should be the weighted mean of the coupling constants for the two forms present. However the ratio of the coupling constants $J(PP_{cis})/J(PP_{trans})$ is approximately 1:14 and the ratio of the concentrations of the two forms *cis*/*trans* is about 8.5:1 at 298 K. Thus a low coupling constant would be expected if $J(PP_{cis})$ and $J(PP_{trans})$ have opposite signs.



Scheme. Mechanism for the interconversion of *cis* and *trans* isomers of [RhCl(PPh$_3$)(Ph$_2$PO$_2$CCH=CHMe)]

It thus appears that the fluxionality of the complex arises because of the close potential energy of the *cis* and *trans* forms which in turn is largely determined by steric factors. If the steric size of the substituents on the double bond is reduced by complexing the mixed anhydride derived from acrylic acid, the resultant complex, [RhCl(PPh$_3$)(Ph$_2$PO$_2$CCH=CH$_2$)], is not fluxional, existing only as the *trans* isomer.[3] On the other hand, increasing the bulk of the co-ordinated anion as in [Rh(O$_2$CCH=CHMe)(PPh$_3$)(Ph$_2$PO$_2$CCH=CHMe)] stabilises the *cis* isomer and neither the *trans* isomer nor the fluxionality is observed.[4]

The intimate mechanism for the *cis*–*trans* isomerisation is not identifiable directly from the n.m.r. spectra but it may involve decomplexation of the double bond as shown in the Scheme. This seems particularly likely since for Ph$_2$PO$_2$CCH=CMe$_2$, which is only slightly more sterically congested than Ph$_2$PO$_2$CCH=CHMe, bidentate binding through the phosphorus atom and the double bond is not observed, rather it is co-ordinated

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* The low concentration of species (**B**) means that it is not possible accurately to measure the coalescence temperature, nor to compute activation parameters for the interchange of the two species.

through the phosphorus atom only in a complex of formula [$RhCl(PPh_3)_2(Ph_2PO_2CCH{=}CMe_2)$].[1]

## Experimental

The complex [$RhCl(PPh_3)(Ph_2PO_2CCH{=}CHMe)$] was prepared as previously described.[1] N.m.r. spectra were collected on a Brüker Associates AM 300 spectrometer in $CD_2Cl_2$.

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## References

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