

The Demonstration of the Trigonal Twist Mechanism in $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$

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NOESY has been used to demonstrate that, unexpectedly, $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ undergoes intramolecular ligand exchange, probably *via* the trigonal twist mechanism; it is shown how heteronuclear coupling in the NOESY experiment can yield valuable mechanistic information.

After the demonstration of facile intermolecular PPh_3 exchange for the PPh_3 *trans* to hydride in $[\text{RhH}_2\text{Cl}(\text{PPh}_3)_3]$,¹ it is common to assume intermolecular tertiary phosphine exchange in related compounds. The alternative mechanism of intramolecular ligand exchange *via* a trigonal twist is often ignored. Although the trigonal twist mechanism was suggested 45 years ago,² it has only been unambiguously demonstrated in a very narrow group of compounds containing two or three bidentate oxygen ligands,³ of the type XYMO_4 , *e.g.* $\text{PhClSn}(\text{PhCH}_2\text{COCHCOMe})_2$,⁴ or MO_6 , *e.g.* $\text{Al}(\text{Pr}^i\text{COCHCOCH}_2\text{Ph})_3$.⁵ It is then a major extrapolation to assume that the same mechanism occurs for a ML_3 group, where the ligands are monodentate and strongly covalent in character, rather than chelating and semi-ionic in the compounds previously studied. A two-dimensional ^{31}P NOESY investigation of $[\text{Cr}(\text{CO})_3(\text{CS})\{\text{P}(\text{OMe})_3\}_3]$ has been interpreted in terms of the trigonal twist mechanism.⁶

In the course of investigating the fluxionality of a number of monomeric ruthenium hydrides, we observed that for $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ **1**, both the hydride ligands and the

inequivalent PPh_3 ligands exchange with approximately the same rate. Magnetization transfer, using the DANTE pulse sequence to invert the ^{31}P NMR signals was used to demonstrate that at 61.7°C, the two chemically equivalent PPh_3 groups exchange with the unique PPh_3 ligand in $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ without exchanging with added PPh_3 . Similarly, magnetization transfer was used at 60.5°C to demonstrate exchange between the hydride ligands. The mechanisms of the reaction comes directly from a ^1H NOESY investigation of the hydride signals, see Fig. 1. Each hydride signal consists of a doublet of doublets of triplets from coupling to the other hydride, the unique PPh_3 , and the two equivalent PPh_3 ligands. Intermolecular exchange of the hydride and PPh_3 ligands can be immediately eliminated. Such exchange would give rise to cross peaks within the diagonal peaks. This can be analysed with the assistance of a spin-state diagram (Fig. 2). For example, if the unique P_aPh_3 group exchanges intermolecularly, the incoming PPh_3 ^{31}P nucleus may have α or β spin, and a cross peak will be observed between lines in the multiplets only differing by the spin of P_a ,

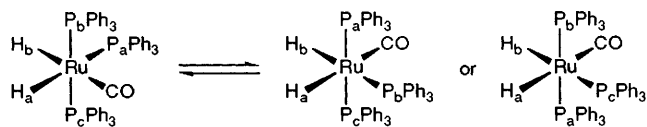
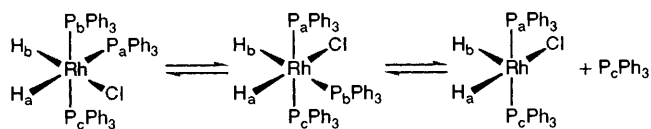
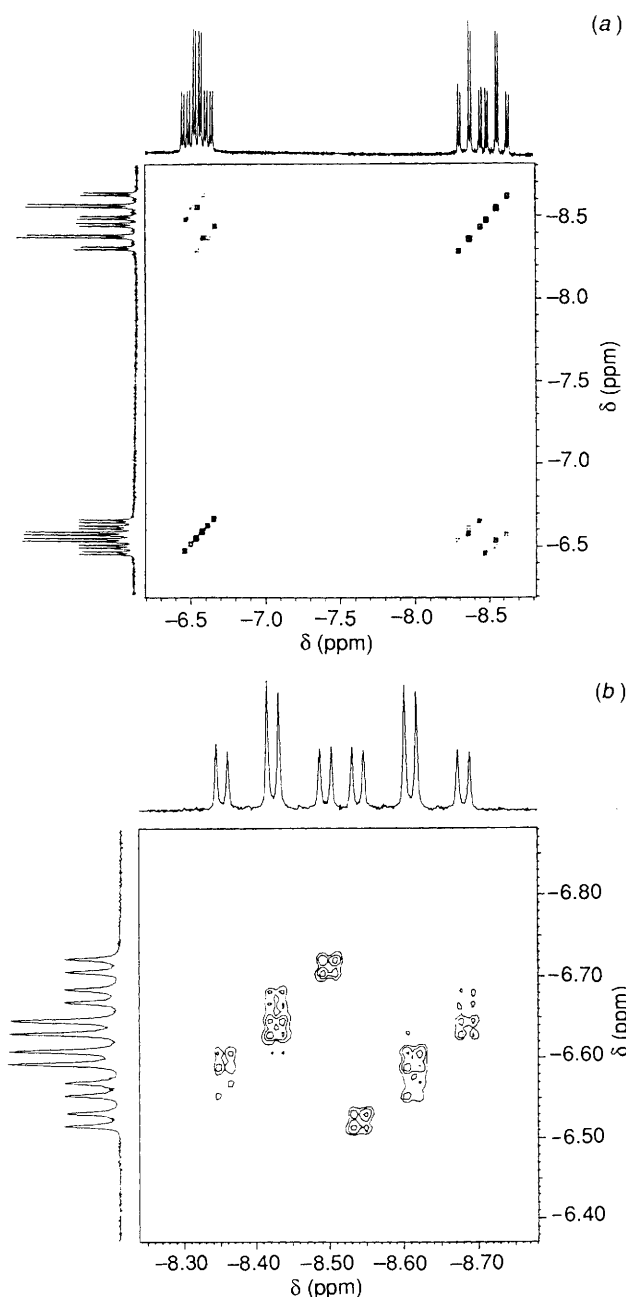
Scheme 1 The trigonal twist mechanism in $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ Scheme 2 An alternative mechanism for *trans*- PPh_3 exchange in $[\text{RhH}_2\text{Cl}(\text{PPh}_3)_3]$ 

Fig. 1 (a) A NOESY NMR spectrum of the hydride signals of $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ at 49.1°C in $[\text{2H}_8]$ toluene. A mixing delay of 0.2 s was used. (b) An expansion of the signal from (a) over the cross peaks centred at $\delta = -8.44$ (x axis) and $\delta = -6.54$ (y axis).

(a) Schematic representation of the multiplet at $\delta = -6.54$, H_a

| Line number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|--------------|----------|----------|----------|----------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|----------|----------|----------|---------|
| H_a | — | — | — | — | — | — | — | — | — | — | — | — | — | — | — | — |
| H_b | α | β | α | β | α | β | α | β | α | β | α | β | α | β | α | β |
| P_a | α | α | β | β | α | α | β | β | α | α | β | β | α | α | β | β |
| P_b | α | α | α | α | $\alpha\beta$ | $\alpha\beta$ | $\alpha\beta$ | $\alpha\beta$ | $\alpha\beta$ | $\alpha\beta$ | $\alpha\beta$ | $\alpha\beta$ | β | β | β | β |
| P_c | α | α | α | α | $\beta\alpha$ | $\beta\alpha$ | $\beta\alpha$ | $\beta\alpha$ | $\beta\alpha$ | $\beta\alpha$ | $\beta\alpha$ | $\beta\alpha$ | β | β | β | β |

(b) Schematic representation of the multiplet at $\delta = -8.44$, H_b

| Line number | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 |
|--------------|----------|----------|---------------|---------------|----------|---------|----------|----------|----------|---------------|---------------|----------|----------|----------|----------|----------|
| H_a | α | β | α | β | α | β | α | β | α | β | α | β | α | β | α | β |
| H_b | — | — | — | — | — | — | — | — | — | — | — | — | — | — | — | — |
| P_a | β | β | β | β | β | β | α | α | α | α | α | α | α | α | α | α |
| P_b | α | α | $\alpha\beta$ | $\alpha\beta$ | β | β | α | α | α | $\alpha\beta$ | $\alpha\beta$ | β | β | β | β | β |
| P_c | α | α | $\beta\alpha$ | $\beta\alpha$ | β | β | α | α | α | $\beta\alpha$ | $\beta\alpha$ | β | β | β | β | β |

Fig. 2 A representation of the coupling of the multiplets of the hydride signals. The α and β refer to the spin states of the nuclei.

e.g. lines 1 and 3, or lines 17 and 25.[†] Rearrangement of the five-coordinate intermediate would lead to additional lines. PPh_3 exchange is observed for $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$, where the lowest energy process is intermolecular exchange of the unique PPh_3 ligand.⁷ Similarly, intermolecular exchange of the axial PPh_3 ligands, P_b and P_c , may be excluded. Intermolecular hydride exchange may similarly be rejected as this would in effect exchange the spins of all the phosphorus nuclei. Intermolecular carbonyl exchange was also excluded by synthesizing $[\text{RuH}_2(^{13}\text{CO})(\text{PPh}_3)_3]$, by the treatment of $\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3$ with ^{13}CO . A ^1H NOESY experiment again failed to show cross peaks attributable to ^{13}CO exchange.

Two types of intramolecular exchange may be considered, pairwise ligand exchange, and the trigonal twist. Pairwise hydride exchange, perhaps *via* a $[\text{Ru}(\eta^2\text{-H}_2)(\text{CO})(\text{PPh}_3)_3]$ intermediate, can be eliminated as this would leave the ^{31}P spin unaffected giving rise to pairwise exchange of lines between H_a and H_b , e.g. lines 5, 6 with 27 or 28,[‡] but not with 17 as is observed. Exchange of P_aPh_3 and the CO ligands produces the same result. The exchange of other pairs of ligands produces different isomers.[§] The only single mechanism is the trigonal twist shown in Scheme 1 which produces the same isomer as the starting one.

The mechanism in Scheme 1 requires P_a , P_b or P_c , and the CO exchanging. This results in the exchanges observed in the NOESY spectrum, which can be deduced from Fig. 2 by exchanging the spin of P_a with P_b or P_c .[¶] In order to obtain the exchange observed in the NOESY spectrum, it is necessary that the sign of $^2J(^{31}\text{P}_a, ^1\text{H}_b)$ is opposite to that of the other $^2J\{^{31}\text{P}, ^1\text{H}(\text{hydride})\}$. By using COSY-90 at 21°C , it has been proved that $^2J(^{31}\text{P}_a, ^1\text{H}_b)$ is of opposite sign to $^2J(^{31}\text{P}_a, ^1\text{H}_a)$,

[†] PPh_3 exchange would interchange lines $1 \leftrightarrow 3$; $2 \leftrightarrow 4$; $3 \leftrightarrow 1$; $4 \leftrightarrow 2$; $5, 6 \leftrightarrow 9, 10$; $7, 8 \leftrightarrow 11, 12$; $16 \leftrightarrow 14$; $17 \leftrightarrow 25$; $18 \leftrightarrow 26$; $19, 20 \leftrightarrow 27, 28$; $21, 22 \leftrightarrow 29, 30$; $23 \leftrightarrow 31$; and $24 \leftrightarrow 32$.

[‡] Pairwise $\text{H}_a \leftrightarrow \text{H}_b$ exchange exchanges lines $1 \leftrightarrow 25$; $2 \leftrightarrow 26$; $3 \leftrightarrow 17$; $4 \leftrightarrow 18$; $5, 6 \leftrightarrow 27, 28$; $7, 8 \leftrightarrow 29, 30$; $9, 10 \leftrightarrow 19, 20$; $11, 12 \leftrightarrow 21, 22$; $13 \leftrightarrow 31$; $14 \leftrightarrow 32$; $15 \leftrightarrow 23$; $16 \leftrightarrow 24$.

[§] For example, exchange of CO and P_bPh_3 followed by exchange of CO and P_aPh_3 produces the same result.

[¶] The predicted line exchanges are $1 \leftrightarrow 25$; $2 \leftrightarrow 26$; $3 \leftrightarrow 27, 28$; $4 \leftrightarrow 29, 30$; $5, 6 \leftrightarrow 17, 27$; $7, 8 \leftrightarrow 18, 29$; $9, 10 \leftrightarrow 20, 31$; $11, 12 \leftrightarrow 22, 32$; $13 \leftrightarrow 19, 20$; $14 \leftrightarrow 21, 22$; $15 \leftrightarrow 23$; and $16 \leftrightarrow 24$.

and ${}^2J({}^{31}\text{P}_{\text{b,c}}, {}^1\text{H}_{\text{a}})$ is of the same sign as ${}^2J({}^{31}\text{P}_{\text{b,c}}, {}^1\text{H}_{\text{b}})$. The cross peaks corresponding to a flip of the spin of the other hydride arises from the short T_1 of the hydrides.||

This work provides conclusive evidence for the lowest energy exchange mechanism in $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ being intramolecular and provides strong evidence for the occurrence of the trigonal twist mechanism. The evidence for the occurrence of the trigonal twist mechanism is not conclusive but the alternative is improbable, *e.g.* involving two consecutive pairwise exchange mechanisms without permitting pairwise exchange of the hydride or PPh_3 ligands. This contrasts with work on $[\text{RhH}_2\text{Cl}(\text{PPh}_3)_3]$, where it was assumed that the lowest energy mechanism of exchanging $\text{P}_{\text{b}}\text{Ph}_3$ or $\text{P}_{\text{c}}\text{Ph}_3$ with free PPh_3 is direct intermolecular exchange.⁸ As a consequence of the present work the exchange could occur *via* a trigonal twist, exchanging PaPh_3 , and PcPh_3 , followed by the

established facile exchange of the PPh_3 which is *trans* to hydride, see Scheme 2.

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|| T_1 was determined at 41 °C for all coordinated atoms. They are 0.45 ± 0.04 s (H_{a}), 0.46 ± 0.04 s (H_{b}), 1.19 ± 0.01 s (${}^{13}\text{C}$), 1.72 ± 0.01 s (${}^{31}\text{P}_{\text{b}}$, ${}^{31}\text{P}_{\text{c}}$).
