Stereo- and Regiospecific Conversions of $Rh_2X_6(PR_3)_3$ Molecules to $Rh_2X_6(PR_3)_4$ and $RhX_3(PR_3)_3$ Molecules

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Studies by ^{31}P NMR spectroscopy have shown that the face-sharing bioctahedral molecules $Rh_2X_6(PR_3)_3$ (X = Cl, Br; PR_3 = PEt_3, PPr_3, PBu_3) exist exclusively as the 1,2,6-isomers and are converted by addition of 1 molar equiv of PR'_3 (R' may be R) exclusively to the 1,3,6,8-$Rh_2X_6(PR_3)_3(PR'_3)$ isomer, with the entering PR'_3 occupying the 6- (or 8-) position. Moreover, the edge-sharing 1,3,6,8-$Rh_2X_6(PR_3)_4$ type molecules react further with trialkylphosphine to produce exclusively *mer*-$RhX_3(PR_3)_3$ products, even though, as is also demonstrated, the *fac*-$RhX_3(PR_3)_3$ isomers are thermodynamically preferred.

Introduction

It is known that, in general, the following reversible interconversions of mononuclear MX_3L_3 (MONO), edge-sharing bioctahedral $M_2X_6L_4$ (ESBO), and face-sharing biooctahedral $M_2X_6L_3$ (FSBO) compounds can take place, as shown in the following reactions:

$$M_2X_6L_3 \underset{-L}{\overset{+L}{\rightleftharpoons}} M_2X_6L_4 \underset{-2L}{\overset{+2L}{\rightleftharpoons}} 2MX_3L_3 \qquad (1)$$

$$3M_2X_6L_4 \rightleftharpoons 2M_2X_6L_3 + 2MX_3L_3 \qquad (2)$$

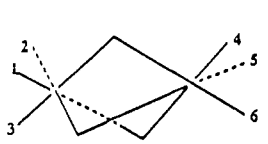
This type of chemistry has been most thoroughly studied for the complexes of molybdenum,[1] and in a limited way for M = W.[2] In the case of tungsten, the strength of the W–W bonding in both the FSBO and the ESBO is so great that conversion to the MONO does not appear to take place. In the molybdenum compounds paramagnetism broadens the ^1H NMR signals and obliterates the ^{31}P signals entirely (at room temperature); hence, there were few structural details accessible by NMR spectroscopy.

We have chosen to study processes of the above type by employing rhodium, for two principal reasons.

(1) The impossibility of forming metal–metal bonds in either of the dinuclear species means that all three types of compound are accessible. At each step, the total number of metal to ligand bonds is conserved, but two M–X_b bonds are replaced by one M–X_t and one M–P bond. These changes should be approximately thermoneutral.

(2) The rhodium systems offer important advantages for NMR investigation. First, the compounds are fully diamagnetic so that sharp $^{31}P\{^1H\}$ signals are seen. Second, ^{103}Rh (100% abundant) has a nuclear spin of $^1/_2$ so that each ^{31}P signal is split into a doublet. Moreover, the magnitude of the coupling is unambiguously diagnostic of whether the phosphorus atom is trans to X or trans to another P. It has already been shown[3] that J_{Rh-P} for a phosphine trans to a halide is in the range of 103–120 Hz, while that for a phosphine trans to another phosphine is in the range of 70–90 Hz.

It might also be added that, as reported earlier,[4] structural information by X-ray crystallography was available for a number of ESBO and FSBO compounds. This same paper defines the numbering schemes for ligand positions in these two classes of compounds. For the reader's convenience, these are shown here again:



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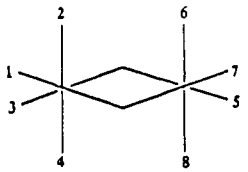

II

In this paper, we describe $^{31}P\{^1H\}$ studies of the type reactions shown above, whereby we have been able to show that, for rhodium compounds, they systematically proceed with strict stereo- and regiospecificity. Moreover, they appear to be under kinetic control, and the specificity can be accounted for in a very straightforward way.[5]

Experimental Section

General Data. All operations were performed in an atmosphere of argon and solvents employed were carefully dried and freshly distilled. The 1,2,6-$Rh_2X_6(PR_3)_3$ compounds were prepared as previously described.[4] Phosphines were purchased from Strem Chemicals and stored under argon.

The $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 operating at 81 MHz in 10-mm tubes. Chemical shifts, in ppm, are referenced to an external standard of 85% phosphoric acid. Coupling constants are given in Hz and are Rh–P couplings unless otherwise specified.

In this paper we shall employ numbers for some of the compounds. For those whose preparation and structure were described in our previous paper,[4] we shall use the same numbers. Thus, the complete list of numbers is as follows: 1,2,6-$Rh_2Cl_6(PEt_3)_3$ (**1**); 1,3,6,8-$Rh_2Cl_6(PEt_3)_4$ (**2**); 1,2,6-$Rh_2Cl_6(PPr^n_3)_3$ (**3**); 1,2,6-$Rh_2Br_6(PEt_3)_3$ (**4**); 1,2,6-$Rh_2Br_6(PPr^n_3)_3$ (**5**); 1,2,6-$Rh_2Cl_6(PBu^n_3)_3$ (**6**).

Reaction between 1 and PR_3 (1 equiv; R_3 = Et_3, Me_3, and Me_2Ph). Formation of 1,3,6,8-$Rh_2Cl_6(PEt_3)_3(PR_3)$. A dichloromethane solution of **1** was prepared at room temperature, transferred to the NMR tube, and purged with argon. After the solution was cooled to −50 °C, 1 equiv of triethylphosphine was introduced with a microsyringe. This reaction appeared to be complete within the time required to record the spectrum. In recording the $^{31}P\{^1H\}$ spectrum about 300 scans were accumulated

(1) Poli, R.; Gordon, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 6723 and earlier references cited therein.
(2) Chacon, S. T.; Chisholm, M. H.; Streib, W. E.; Van der Sluys, W. *Inorg. Chem.* **1989**, *28*, 5.
(3) (a) Grim, S. O.; Ference, R. A. *Inorg. Chim. Acta* **1970**, *4*, 277. (b) Mann, B. E.; Masters, C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1972**, 704. (c) Grim, S. O.; Satek, L. C. *J. Coord. Chem.* **1974**, *3*, 307.
(4) Cotton, F. A.; Kang, S.-J.; Mandal, S. K. *Inorg. Chim. Acta* **1992**, *206*, 29.
(5) Cotton, F. A.; Eglin, J. L.; Kang, S.-J.; *J. Am. Chem. Soc.* **1992**, *114*, 4015.

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over a period of 10 min. Following this, the solvent was evaporated at 0 °C. Red crystals suitable for the X-ray diffraction study were obtained by slow diffusion of hexane into a chloroform solution of the product. The other phosphines (PMe_3 and PMe_2Ph) were added in a similar way to the dichloromethane solution of **1** at −60 °C. $^{31}P\{^1H\}$ NMR: 1,3,6,8-$Rh_2Cl_6(PEt_3)_4$, δ 45.2 (d, 2P, J = 115 Hz), 10.8 (d, 2P, J = 81 Hz); 1,3,6,8-$Rh_2Cl_6(PEt_3)_3(PMe_3)$, δ 45.2 (d, 2P, J = 115 Hz), 3.7 (4d, 2P, $J_{P-P',trans}$ = 617, J = 80 Hz); 1,3,6,8-$Rh_2Cl_6(PEt_3)_3(PMe_2Ph)$, δ 47.0 (d, 2P, J = 115 Hz), 6.2 (4d, 2P, $J_{P-P',trans}$ = 615 Hz, J = 80 Hz).

Disproportionation of 1,3,6,8-$Rh_2Cl_6(PEt_3)_4$ (2). A dichloromethane solution of **2** was prepared at −20 °C, transferred to an NMR tube, and purged with argon. The NMR tube was sealed under vacuum. Disproportionation was studied at −20 °C and +20 °C by recording NMR spectra periodically. The products of disproportionation are 1,2,6-$Rh_2Cl_6(PEt_3)_3$ and *mer*-$RhCl_3(PEt_3)_3$.

Reaction between 2 and PEt_3 (2 equiv). Formation of *mer*-$RhCl_3(PEt_3)_3$. A dichloromethane solution of **2** was prepared at room temperature, transferred to an NMR tube, and purged with argon. To this solution slightly more than 2 equiv of triethylphosphine were added with a microsyringe. The reaction appeared to be complete within the time needed to record the spectrum at room temperature, and about 500 scans were accumulated over a period of 15 min. $^{31}P\{^1H\}$ NMR: *mer*-$RhCl_3(PEt_3)_3$, δ 26.9 (2t, 1P, J = 112 Hz, $J_{P-P,cis}$ = 23 Hz), 11.3 (2d, 2P, J = 83 Hz, $J_{P-P,cis}$ = 24 Hz).

Thermal Treatment of 1,3,6,8-$Rh_2Cl_6(PEt_3)_4$ (2). Solid 1,3,6,8-$Rh_2Cl_6(PEt_3)_4$ was placed in a Schlenk tube and heated under dynamic vacuum at ca. 150 °C. After 1 day, the residue was dissolved in dichloromethane. The $^{31}P\{^1H\}$ NMR spectrum of the resulting solution showed only the presence of 1,2,6-$Rh_2Cl_6(PEt_3)_3$.

Isomerization of *mer*-$RhCl_3(PEt_3)_3$. A dichloromethane solution of *mer*-$RhCl_3(PEt_3)_3$ was prepared from the reaction of 1,2,6-$Rh_2Cl_6(PEt_3)_3$ with slightly more than 3 equiv of triethylphosphine. The solution was transferred to an NMR tube which was then sealed. The isomerization was followed by periodically recording the $^{31}P\{^1H\}$ NMR spectrum. This isomerization is very slow (less than 10% conversion after 4 days at room temperature). $^{31}P\{^1H\}$ NMR: *fac*-$RhCl_3(PEt_3)_3$, δ 29.2 (d, 3P, J = 112 Hz). The same process can be observed in acetone solution.

Thermal Treatment of $RhCl_3(PEt_3)_3$. Solid $RhCl_3(PEt_3)_3$ (either the *mer* or *fac* isomer) was placed in a Schlenk tube and heated under dynamic vacuum at ca. 150 °C. After $1^1/_2$ days, the residue was dissolved in dichloromethane. The $^{31}P\{^1H\}$ NMR spectrum of the resulting solution showed only the presence of 1,2,6-$Rh_2Cl_6(PEt_3)_3$.

Reaction of 3 with PR_3 (R_3 = Pr^n_3, Et_3, and Me_2Ph). Formation of 1,3,6,8-$Rh_2Cl_6(PPr^n_3)_3(PR_3)$. 1,2,6-$Rh_2Cl_6(PPr^n_3)_3$ was dissolved in dichloromethane, and the resulting solution was transferred to an NMR tube. The solution was cooled to −50 °C and treated with 1 equiv of PR_3. The reactions were followed by $^{31}P\{^1H\}$ NMR spectroscopy. $^{31}P\{^1H\}$ NMR: 1,3,6,8-$Rh_2Cl_6(PPr^n_3)_4$, δ 39.3 (d, 2P, J = 115 Hz), 4.4 (d, 2P, J = 81 Hz); 1,3,6,8-$Rh_2Cl_6(PPr^n_3)_3(PEt_3)$, δ 39.2 (d, 2P, J = 114 Hz), 6.2 (4d, 2P, $J_{P-P',trans}$ = 585 Hz, J = 80 Hz); 1,3,6,8-$Rh_2Cl_6(PPr^n_3)_3(PMe_2Ph)$; δ 38.8 (d, 2P, J = 115 Hz), 1.5 (4d, 2P, $J_{P-P',trans}$ = 610 Hz, J = 81 Hz).

Reaction between 4 and PR_3 (1 equiv; R_3 = Et_3, Me_3, and Me_2Ph). Formation of 1,3,6,8-$Rh_2Br_6(PEt_3)_3(PR_3)$. A dichloromethane solution of **4** was prepared at room temperature, transferred to the NMR tube, purged with argon. This solution was treated with 1 equiv of PR_3 at −65 °C. The resulting solution was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The conversion of **4** to the ESBO was 70–90% complete after 600 scans, taken over about 20 min. $^{31}P\{^1H\}$ NMR: 1,3,6,8-$Rh_2Br_6(PEt_3)_4$, δ 46.0 (d, 2P, J = 115 Hz), 4.5 (d, 2P, J = 82 Hz); 1,3,6,8-$Rh_2Br_6(PEt_3)_3(PMe_3)$, δ 46.0 (d, 2P, J = 115 Hz), −1.5 (4d, 2P, $J_{P-P',trans}$ = 595 Hz, J = 82 Hz); 1,3,6,8-$Rh_2Br_6(PEt_3)_3(PMe_2Ph)$, δ 46.0 (d, 2P, J = 115 Hz), −0.5 (4d, 2P, $J_{P-P',trans}$ = 587 Hz, J = 82 Hz).

Isomerization of 1,2,6-$Rh_2Br_6(PEt_3)_3$ (4). A 1,2-dibromoethane solution of **4** was prepared at room temperature and transferred to an NMR tube. This NMR tube was sealed to exclude oxygen, maintained at 20 °C, and periodically monitored by $^{31}P\{^1H\}$ NMR spectroscopy. A dichloromethane solution of **4** was also prepared, and possible isomerization of this solution at −20 and −60 °C was tracked by $^{31}P\{^1H\}$ NMR spectroscopy, but no additional signal was detected in this temperature range.

Reaction between 4 and PEt_3 (3 equiv). Formation of *mer*-$RhBr_3(PEt_3)_3$. A dichloromethane solution of **4** was treated with slightly more than 3 equivalents of triethylphosphine at room temperature, and the reaction monitored by $^{31}P\{^1H\}$ NMR spectroscopy. $^{31}P\{^1H\}$ NMR:

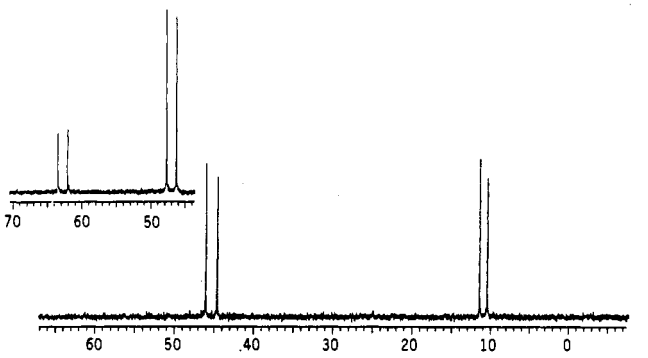


Figure 1. $^{31}P\{^1H\}$ NMR spectra: Upper, compound **1**; lower, compound **1** after addition of PEt_3.

δ 23.0 (2t, 1P, J = 109 Hz, $J_{P-P',cis}$ = 23 Hz), 2.2 (2d, 2P, J = 83 Hz, $J_{P-P',cis}$ = 23 Hz).

Disproportionation of 1,3,6,8-$Rh_2Br_6(PEt_3)_4$. A dichloromethane solution of 1,3,6,8-$Rh_2Br_6(PEt_3)_4$ was prepared at −20 °C, transferred to an NMR tube, and purged with argon. The NMR tube was sealed under vacuum. Disproportionation was studied at −40 °C by recording the NMR spectrum periodically. The products of disproportionation are 1,2,6-$Rh_2Br_6(PEt_3)_3$ and *mer*-$RhBr_3(PEt_3)_3$.

Thermal Treatment of 1,3,6,8-$Rh_2Br_6(PEt_3)_4$ and $RhBr_3(PEt_3)_3$. Solid 1,3,6,8-$Rh_2Br_6(PEt_3)_4$ or $RhBr_3(PEt_3)_3$ was placed in a Schlenk tube and heated under dynamic vacuum at ca. 70 °C. After 1 day, the residue was dissolved in dichloromethane. The $^{31}P\{^1H\}$ NMR spectrum of the resulting solutions showed only the presence of 1,2,6-$Rh_2Br_6(PEt_3)_3$.

Reaction between 5 and PR_3 (1 equiv; R_3 = Pr^n_3, Me_3, and Me_2Ph). Formation of 1,3,6,8-$Rh_2Br_6(PPr^n_3)_3(PR_3)$. 1,2,6-$Rh_2Br_6(PPr^n_3)_3$ was dissolved in dichloromethane, and the resulting solution was transferred into an NMR tube. The solution was cooled to −60 °C, treated with 1 equiv of PR_3, and these reactions tracked by $^{31}P\{^1H\}$NMR spectroscopy. $^{31}P\{^1H\}$NMR: 1,3,6,8-$Rh_2Br_6(PPr^n_3)_4$, δ 37.0 (d, 2P, J = 115 Hz), −3.8 (d, 2P, J = 82 Hz); 1,3,6,8-$Rh_2Br_6(PPr^n_3)_3(PMe_3)$, δ 37.0 (d, 2P, J = 115 Hz), −7.5 (4d, 2P, $J_{P-P',trans}$ = 597 Hz, J = 82 Hz); 1,3,6,8-$Rh_2Br_6(PPr^n_3)_3(PMe_2Ph)$, δ 38.4 (d, 2P, J = 115 Hz), −4.5 (4d, 2P, $J_{P-P',trans}$ = 570 Hz, J = 82 Hz).

Reaction of 6 with PR_3 (R_3 = Bu^n_3, Me_3, and Me_2Ph). Formation of 1,3,6,8-$Rh_2Cl_6(PBu^n_3)_3(PR_3)$. A dichloromethane solution of 1,2,6-$Rh_2Cl_6(PBu^n_3)_3$ was prepared at room temperature, transferred to the NMR tube, and purged with argon. After the solution was cooled to −30 °C, 1 equiv of PR_3 was introduced with a microsyringe. The reactions were then monitored by $^{31}P\{^1H\}$ NMR spectroscopy. $^{31}P\{^1H\}$ NMR: 1,3,6,8-$Rh_2Cl_6(PBu^n_3)_4$, δ 42.8 (d, 2P, J = 115 Hz), 7.1 (d, 2P, J = 79 Hz); 1,3,6,8-$Rh_2Cl_6(PBu^n_3)_3(PMe_3)$, δ 44.7 (d, 2P, J = 116 Hz), 9.8 (4d, 2P, $J_{P-P',trans}$ = 619 Hz, J = 82 Hz); 1,3,6,8-$Rh_2Cl_6(PBu^n_3)_3(PMe_2Ph)$, δ 44.7 (d, 2P, J = 116 Hz), 6.5 (4d, 2P, $J_{P-P',trans}$ = 611 Hz, J = 81 Hz).

Results and Discussion

Reactions of 1,2,6-$Rh_2X_6(PR_3)_3$ Compounds with one PR'_3. Figure 1 shows the spectrum of 1,2,6-$Rh_2Cl_6(PEt_3)_3$ (**1**) and the spectrum that results immediately upon addition of 1 molar equiv of PEt_3 at −50 °C. The new spectrum is that of **2**, 1,3,6,8-$Rh_2Cl_6(PEt_3)_4$. The spectrum of **1** shows two doublets, in an intensity ratio of 1:2, each with a splitting characteristic of a phosphorus atom trans to a halogen atom. (For numerical values, see the Experimental Section.) The reaction of **1** with PEt_3 goes to completion; the signals due to **1** disappear completely and are replaced by the spectrum of **2**, with no signals other than those expected for **2**.

The spectrum of **2** identifies it uniquely and unequivocally; no other one of the nine possible isomers of an $M_2X_6L_4$ compound[4] is consistent with this spectrum. There are two doublets of equal intensity but different splitting. In the one centered at ca. 45 ppm the splitting is large (as it was for both signals in **1**) thus identifying the responsible PEt_3 ligands as (1) equivalent and (2) trans to Cl. Moreover, there is no further splitting by other phosphorus atoms. Hence, these two phosphines must be bonded to the same rhodium atom. The only way to satisfy all of these criteria is to put these two phosphine ligands in mutually cis

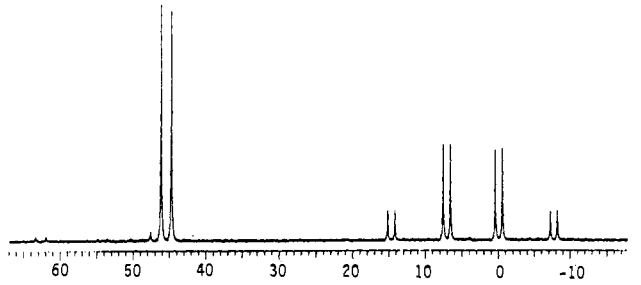


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of **1** + PMe_3.

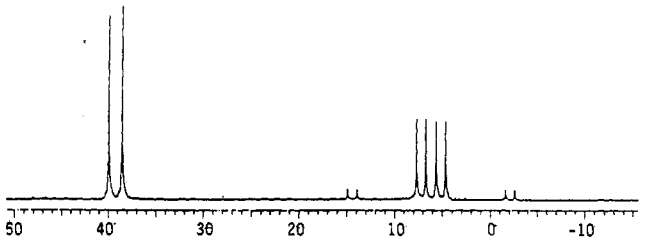
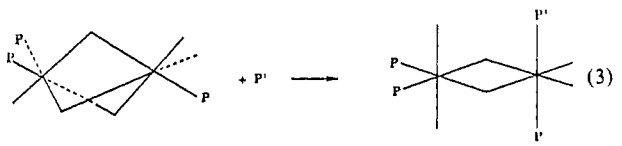


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of **3** + PEt_3.

equatorial positions (1 and 3) on one rhodium atom. The other signal, at ca. 11 ppm, has a splitting indicative of P trans to P, and thus there must be two PEt_3 ligands trans to each other on the other rhodium atom. Only by putting them in the two axial positions (6 and 8) can this be accomplished. Thus, the product of the reaction of the 1,2,6-$Rh_2Cl_6(PEt_3)_3$ FSBO with 1 molar equiv of PEt_3 is solely the 1,3,6,8-$Rh_2Cl_6(PEt_3)_4$ ESBO. As reported previously,[4] when a solution obtained in this way was evaporated, the solid obtained proved to be just this compound, by X-ray crystallography.

Figure 2 shows the spectrum obtained immediately after addition of 1 molar equiv of PMe_3 to **1**. Evidently, a trace of **1** remains, but there is essentially complete conversion of 1,2,6-$Rh_2Cl_6(PEt_3)_3$ to one, and only one, new compound. Once again, the NMR spectrum provides a unique and unequivocal identification of this product. There is again a doublet at ca. 45 ppm with a splitting indicative of two PEt_3 ligands each trans to Cl. Thus, on one rhodium atom we have the two equatorial positions (1 and 3) occupied by PEt_3 ligands. Now, however, instead of another doublet with a small splitting, we have a quartet of doublets, with a small splitting within each doublet. The only possible explanation for this is that two different phosphines occupy the axial positions on the second rhodium atom. The quartet structure is that expected for an ABX system with J_{AB} comparable in magnitude to the difference in the chemical shifts of A and B.

As can be seen from the data listed in the Experimental Section, the reaction of **1** with 1 molar equiv of PMe_2Ph also proceeds cleanly to give just one product, the NMR spectrum of which is qualitatively the same as that just described for the reaction product with PMe_3. We can summarize the results of all these reactions just discussed by eq 3, where P′ may, or may not, represent the same phosphine as P.



The reactions of **3** with 1 mol of PEt_3 and PMe_2Ph were examined and the results are again completely consistent with eq 3. In the product with P = PPr^n_3 and P′ = PEt_3 the chemical shift difference is so small that the quartet has a rather different appearance (Figure 3), but the interpretation is the same.

The reactions of **4** and **5** with PMe_3, PEt_3, and PMe_2Ph, and of **6** with PBu^n_3, PMe_3, and PMe_2Ph, also proceeded in exactly

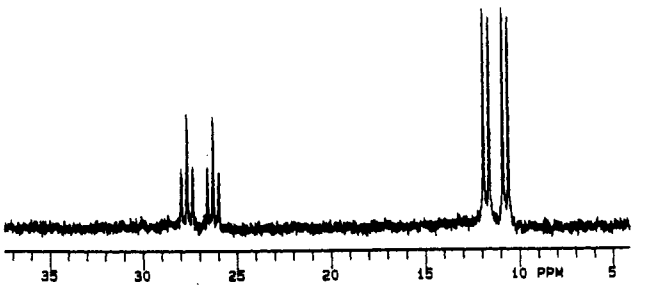
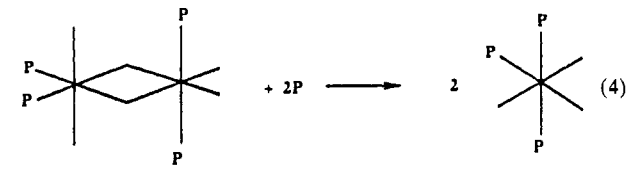


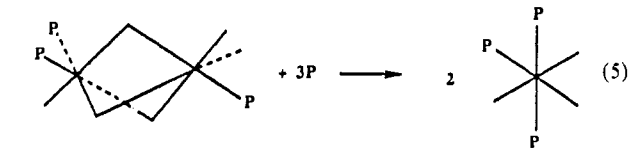
Figure 4. $^{31}P\{^1H\}$ NMR spectrum of **2** + 2PEt_3.

the same way as those just discussed for **1** and **3**. The spectral are all very similar to those shown in Figures 1 and 2. The numerical values characterizing these spectra are given in the Experimental Section.

Treatment of 1,3,6,8-$Rh_2Cl_6(PEt_3)_4$ with 2PEt_3. The reaction of **2** with 2 molar equiv of PEt_3 was shown to proceed cleanly and completely to give a product whose $^{31}P\{^1H\}$ NMR spectrum is shown in Figure 4. It is clear that the sole product is *mer*-$RhCl_3(PEt_3)_3$. The multiplet at 25–28 ppm can be described as a doublet (J_{Rh-P} = 112 Hz) split into triplets by P–P coupling (J_{P-P} = 24 Hz) while the multiplet of twice this intensity at ca. 11 ppm is a doublet (J_{Rh-P} = 83 Hz) each member of which is further split into a doublet by the P–P coupling. The reaction can be described by eq 4.



Treatment of 4 with 3PEt_3. When the FSBO compound 1,5,6-$Rh_2Br_6(PEt_3)_3$ was treated with 3 molar equiv of PEt_3, it was converted entirely to *mer*-$RhBr_3(PEt_3)_3$, whose $^{31}P\{^1H\}$ NMR spectrum is practically the same as that of its chloro analog except for displacements of the chemical shifts. The reaction is described by eq 5.



Disproportionation of ESBO Molecules. When a CH_2Cl_2 solution of one of the 1,3,6,8-$Rh_2X_6(PR_3)_4$ compounds is allowed to stand, disproportionation occurs according to eq 2. The rate of disproportion is greater for X = Br than for X = Cl. In the latter case the process is slow below −30 °C (less than 20% after 2 days) whereas disproportionation is observable for the bromide compounds even below −50 °C.

Reversal of Reaction 1. As indicated in eq 1, the addition of more phosphine to an FSBO compound converts it to an ESBO compound, which can, in turn be split by more phosphine to give the MONO compound. The data we have summarized so far have confirmed this and also revealed that each step is highly stereospecific. We have found that it is also possible to reverse these reactions by heating the solid ESBO and MONO compounds so as to volatilize the liberated phosphine. These reverse reactions go to completion and give exclusively the 1,2,6-$Rh_2X_6(PR_3)_3$ compounds, which can be identified and shown to be pure by ^{31}P NMR spectroscopy.

Stability of 1,2,6-FSBO Isomers. At no time has any evidence been seen for the conversion of a 1,2,6-FSBO isomer into the alternative 1,3,6-isomer. We previously[4] suggested a reason for this preference, namely, that weakening of both Rh-X bonds to any one μ-X ligand is unfavorable. Thus, the nonobservation of

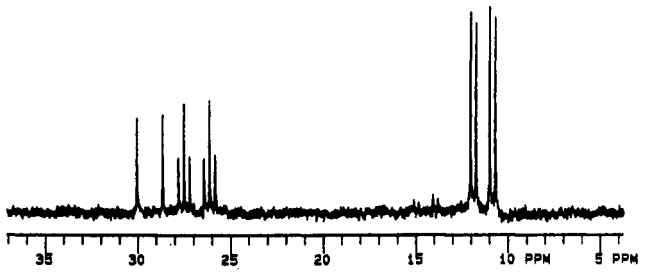


Figure 5. The spectrum observed after a solution of *mer*-$RhCl_3(PEt_3)_3$ in acetone had been kept at 22 °C for 6 days.

a 1,3,6-FSBO could be due to the fact that, even when present in equilibrium with the dominant 1,2,6-isomer, it is at a mole fraction too small (<2%) to be detected. However, as will be explained later, even if the 1,3,6-isomer is not excluded purely on thermodynamic grounds, it may be impossible for mechanistic reasons for it to be obtained from the 1,2,6-isomer under the mild conditions employed in all the solution studies reported here.

Isomerization of *mer*-$RhX_3(PR_3)_3$. When solutions of *mer*-$RhCl_3(PEt_3)_3$ in dichloromethane or acetone were allowed to stand at about 22 °C, slow conversion to the *fac* isomer was observed. The ^{31}P NMR spectrum of such a reaction mixture at an intermediate stage in acetone are shown in Figure 5. The fact that the reactions of $Rh_2X_6(PR_3)_3$ and $Rh_2X_6(PR_3)_4$ with sufficient phosphine to convert them entirely to $RhX_3(PR_3)_3$ always produced exclusively *mer*-$RhX_3(PR_3)_3$ shows that these reactions are kinetically rather than thermodynamically controlled.

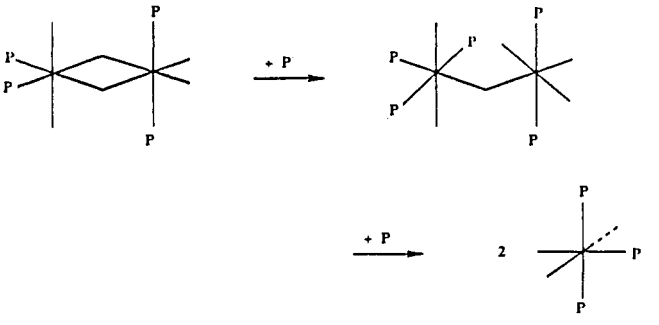
Mechanistic Explanation for the Observations. It is now necessary to provide an explanation for the remarkable stereospecificity of all the observed interconversions, including the counterthermodynamic formation of *mer*-$RhX_3(PR_3)_3$ instead of the *fac* isomer. There is a simple way to do this based on only a few plausible postulates, namely postulates 1–3.

(1) Bridge bonds trans to R_3P ligands, being distinctly weaker than those trans to X ligands (see ref 4) will be preferentially broken.

(2) The insertion of the additional PR_3 will occur either in concert with Rh–(μ-X) bond cleavage or so soon thereafter that no five-coordinate Rh center will exist long enough to undergo fluxional reorganization. In any event, the incoming PR_3 occupies the same coordination site previously occupied by the μ-X ligand before the Rh–(μ-X) bond was broken.

(3) In case there is more than one type of weakened Rh–(μ-X) bond, the one leading to the more symmetrical distribution of the PR_3 ligands in the product will be the one opened.

In the light of the postulates, it is obvious that the stereochemistry shown in eq 3 is the only one possible. Turning to the overall transformation represented in eq 4, we can take it in two steps, as shown in eq 6, whereby we see that the postulates again unambiguously require the observed stereochemical result. Finally, the transformation in eq 5 is accounted for by the reasonable assumption that it proceeds by the successive occurrence of the transformations shown in eqs 3 and 6. It must be noted that the final step in eq 6 is not in accord with the postulates, but it is the only way that one can get from the intermediate to the final products. There is also no direct evidence for the intermediate, and thus it must be admitted that the two step process described by eq 6 is highly speculative.



(6)

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