

Activation of Dichloromethane by (Phosphane)_nrhodium(I) Complexes – X-ray Structure of [(PEt₃)₂RhCl]₂(μ-Cl)₂(μ-CH₂)

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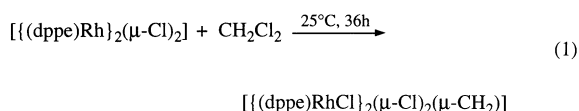
Dichloromethane reacts with dinuclear rhodium complexes [(PR₃)₂Rh]₂(μ-Cl)₂ to give the bridging-methylene complexes [(PR₃)₂RhCl]₂(μ-Cl)₂(μ-CH₂) (PR₃ = PEt₃, PPh₂Me). The structure of the PEt₃ complex has been established by X-ray

diffraction study. The early stages of the reaction of [(C₈H₁₄)₂Rh]₂(μ-Cl)₂ with monophosphanes have been monitored by ³¹P NMR, evidencing chloride bridges cleavage and phosphane redistribution processes.

Activation of dihalomethanes by low oxidation state transition metal complexes has attracted a great deal of interest as a means of generating haloalkyl transition metal derivatives which are versatile precursors for a wide range of useful compounds^[1]. Oxidative addition of diiodo and dibromomethane is well documented, and, although less common, the case of dichloromethane is now well recognized.

Several examples of simple oxidative addition of dichloromethane (CH₂Cl₂) to electron-rich Rh^I complexes of mono or polydentate phosphorus^{[2][3]}, nitrogen^{[4][5][6]}, sulfur^[7], and phosphorus/nitrogen^{[8][9]} ligands have been reported. They usually afford chloromethylrhodium(III) complexes.

However, we found only two examples of double oxidative addition of CH₂Cl₂ on binuclear Rh^I complexes^{[10][11]}. The chloride-bridged rhodium(I) dimer [(dppe)Rh]₂(μ-Cl)₂ [dppe = 1,2-bis(diphenylphosphanyl)ethane] has been reported to react with CH₂Cl₂ to generate a bridging-methylene rhodium(III) complex (eq. 1)^[10].



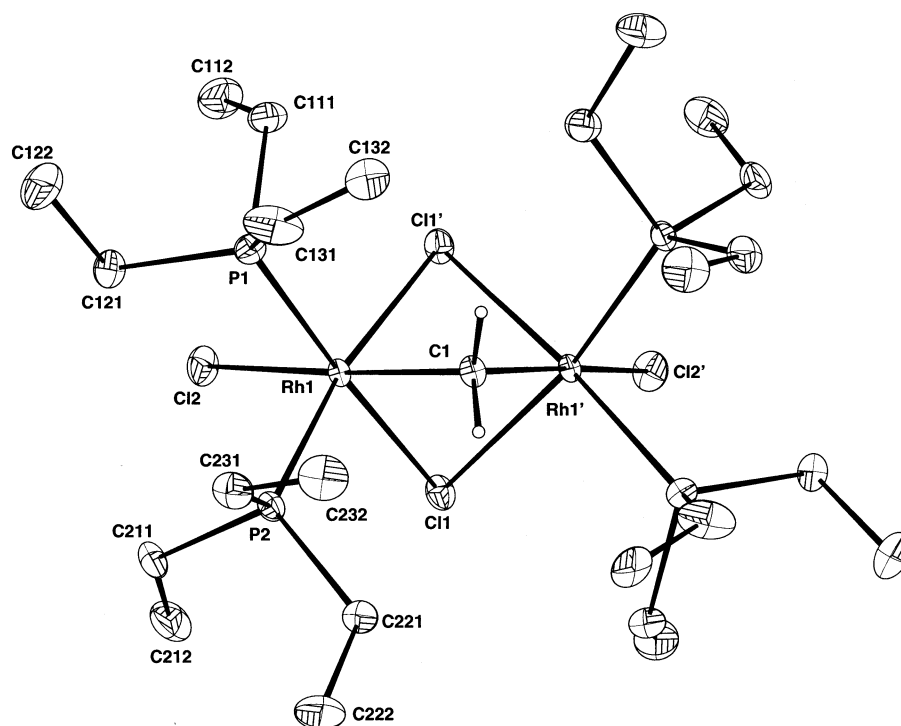
The other example concerns the oxidative addition of *gem*-dichlorocarbons on the binuclear basic complex [(Rh(μ-pz)(CNtBu)₂)₂] (pz = pyrazolate) to give [(Rh(μ-pz)Cl(CNtBu)₂)₂(μ-CHR)]^[11].

In this paper, we report that activation of CH₂Cl₂ to generate methylene-bridged dimers is not limited to dinuclear Rh^I complexes and to Rh^I complexes bearing chelating diphosphanes, and can be obtained from both mononuclear and dinuclear monophosphane rhodium(I) complexes. Furthermore, some insight is given on the intermediates in-

volved in the reaction of monophosphanes with the chloro-bridged dimer [(C₈H₁₄)₂Rh]₂(μ-Cl)₂, **1** (C₈H₁₄ = cyclooctene).

As part of our work on the synthesis of amidorhodium complexes, we have been led to prepare the dimer [(PEt₃)₂Rh]₂(μ-Cl)₂, **2**^{[12][13]}. Compound **2** is prepared in pure form [³¹P{¹H} NMR, δ (THF) = 44.3, J_{P-Rh} = 194 Hz] by treating 4 equivalents of PEt₃ with **1** in THF. It can also be prepared in CH₂Cl₂ by reacting the starting materials for 10 min, followed by immediate evaporation of the solvent. Incidentally, we observed that if the reaction time in CH₂Cl₂ is longer than 10 min, a second complex is formed [³¹P{¹H} NMR, δ (CH₂Cl₂) = 31.1, J_{P-Rh} = 147 Hz] which becomes the only reaction product after 2 h. This new complex was isolated by precipitation with THF. Apart from the expected signals for the triethylphosphane ligands, the ¹H-NMR spectrum exhibits a broad signal at δ = 3.7, which becomes sharper on phosphorus decoupling, and the ¹³C{¹H, ³¹P} NMR spectrum shows a triplet at δ = 38.9 (J_{C-Rh} = 22 Hz, see Experimental Section). These signals could correspond to the methylene bridge of a dinuclear Rh^{III} complex, as suggested by the relatively small J_{P-Rh} coupling constant. This complex was definitely identified as the methylene-bridged dinuclear complex [(PEt₃)₂RhCl]₂(μ-Cl)₂(μ-CH₂) **3** by single crystal X-ray diffraction analysis.

The molecular structure, which has a 2-fold symmetry, is shown in Figure 1. The binuclear structure is built up by two rhodium centers joined by two chloride ligands and a bridging methylene unit the carbon of which is located on the 2-fold axis. This structure is very similar to that of the recently reported [(dppe)RhCl]₂(μ-Cl)₂(μ-CH₂) complex^[10]. As in the dppe compound, each rhodium center has a symmetrical, quasi-octahedral environment and formally can be considered as Rh^{III}. A comparison of important bond distances and bond angles within the

Figure 1. Molecular structure and numbering scheme for $[\{(\text{PEt}_3)_2\text{RhCl}\}_2(\mu\text{-Cl})_2(\mu\text{-CH}_2)]$.

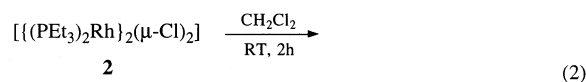
$\text{Rh}_2\text{Cl}_4\text{P}_4\text{CH}_2$ framework for the two complexes is given in Table 1.

Table 1. Comparison of interatomic distances [$\text{\AA}$] and bond angles [$^\circ$] within the $\text{Rh}_2\text{Cl}_4\text{P}_4\text{CH}_2$ framework of $[\{L_2\text{RhCl}\}_2(\mu\text{-Cl})_2(\mu\text{-CH}_2)]$. E.s.d.s. in parentheses refers to the last significant digit

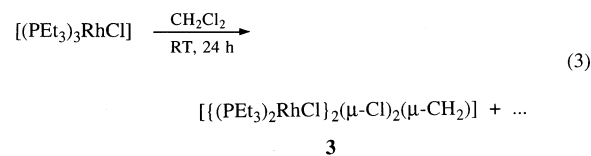
	L = PEt_3	L = dppe
Rh(1)–Cl(1)	2.4458(4)	2.4532(7)
Rh(1)–Cl(1')	2.4618(4)	2.4700(8)
Rh(1)–Cl(2)	2.5310(4)	2.5071(7)
Rh(1)–P(1)	2.2851(4)	2.2587(8)
Rh(1)–P(2)	2.2605(4)	2.2394(8)
Rh(1)–C(1)	2.060(2)	2.057(3)
Cl(1)–Rh(1)–Cl(1')	81.64(2)	82.35(3)
Cl(1)–Rh(1)–Cl(2)	89.69(1)	94.15(3)
Cl(1')–Rh(1)–Cl(2)	87.41(1)	93.07(3)
Cl(1)–Rh(1)–P(1)	174.87(2)	176.65(3)
Cl(1')–Rh(1)–P(1)	93.28(1)	99.23(3)
Cl(2)–Rh(1)–P(1)	89.40(1)	88.72(3)
Cl(1)–Rh(1)–P(2)	89.61(1)	93.74(3)
Cl(1')–Rh(1)–P(2)	169.97(1)	175.99(3)
Cl(2)–Rh(1)–P(2)	97.49(1)	86.30(3)
P(1)–Rh(1)–P(2)	95.51(2)	84.72(3)
Cl(1)–Rh(1)–C(1)	81.95(4)	80.70(7)
Cl(1')–Rh(1)–C(1)	81.55(4)	80.29(7)
Cl(2)–Rh(1)–C(1)	166.99(5)	172.0(1)
P(1)–Rh(1)–C(1)	98.04(4)	96.62(8)
P(2)–Rh(1)–C(1)	92.42(3)	100.02(7)
Rh(1)–Cl(1)–Rh(1')	75.58(1)	76.20(2)
Rh(1)–C(1)–Rh(1')	93.7(1)	95.2(2)

The main differences are observed for the angles around the metal atom. They are certainly related to the larger strain resulting from the chelating coordination of the dppe ligand, as is clearly shown by the P(1)–Rh(1)–P(2) angle which varies from 95.51° in the triethylphosphane complex to 84.72° in the dppe one.

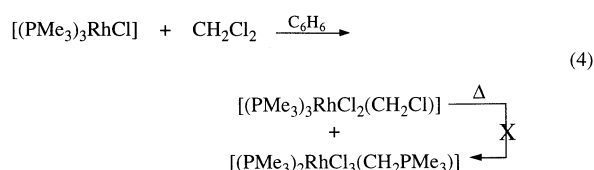
This results (eq. 2) shows that the activation of CH_2Cl_2 by a chloride-bridged rhodium(I) dimer discovered by Fryzuk et al. (eq. 1) is not limited to the case of rhodium(I) complexes with chelating diphosphanes^[10].



More surprisingly, the same methylene-bridged dinuclear rhodium complex **3** is formed as the major product by reaction of the mononuclear complex $[(\text{Et}_3\text{P})_3\text{RhCl}]$ with CH_2Cl_2 for 24 h at room temperature. On the basis of ^{31}P -NMR analysis, some others unidentified (phosphane)rhodium complexes are also formed in small amounts.

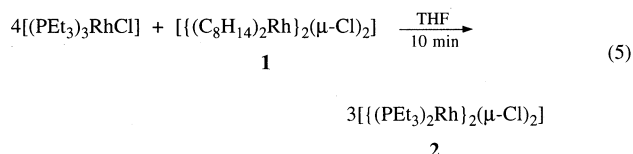


This result (eq. 3) is somewhat surprising in view of the reaction described by Milstein et al. in the case of PMe_3 (eq. 4)^[2].



Indeed PEt_3 and PMe_3 have similar electronic properties ($\text{p}K_{\text{a}}$ 8.69 vs 8.65) and differ by their cone angles, only (132° vs 118°)^[14]. Nevertheless, this reaction may occur via displacement of an equilibrium between $[(\text{PEt}_3)_3\text{RhCl}]$ and $[(\text{PEt}_3)_2\text{Rh}\}_2(\mu\text{-Cl})_2]$, a well-known process in the case of $[(\text{PPh}_3)_3\text{RhCl}]$ ^[15]. The different behaviour of $[(\text{PMe}_3)_3\text{RhCl}]$ may be merely ascribed to the unfavorable dissociation of the smaller phosphane.

In the course of our study of the reaction of PEt_3 (4 equiv.) with $[(\text{C}_8\text{H}_{14})_2\text{Rh}\}_2(\mu\text{-Cl})_2]$ **1**, we made another interesting observation. Indeed, according to literature data^{[16][17][18]}, e.g. in the case of Ph_2PMe ^[18], this reaction was believed to occur by stepwise replacement of the cyclooctene ligands, without cleavage of the chloride bridges, to ultimately yield $[(\text{PEt}_3)_2\text{Rh}\}_2(\mu\text{-Cl})_2]$ (**2**). We surprisingly observed that, after a few min at room temp. in dichloromethane, the very major phosphane complex is $[(\text{PEt}_3)_3\text{RhCl}]$. The reaction rapidly evolves to generate the chloride-bridged dimer **2**, together with the bridging-methylene one **3** which is the only product after 1 h. The observation of $[(\text{PEt}_3)_3\text{RhCl}]$ as the only phosphane complex (no free PEt_3) at the early stage of the reaction implies the presence of unreacted **1** and suggests a subsequent redistribution of the phosphane ligands. This was demonstrated independently by reacting $[(\text{PEt}_3)_3\text{RhCl}]$ (4 equiv.) with **1** (1 equiv.) in THF, affording quantitatively $[(\text{PEt}_3)_2\text{Rh}\}_2(\mu\text{-Cl})_2]$ (^{31}P NMR) (eq. 5).



The above results led us to reinvestigate the previously reported reaction of PPh_2Me (4 equiv.) with **1**^[18] by ^{31}P -NMR monitoring at the early stage of the reaction at room temperature. In THF, the reaction is very fast. Within 5 min the main reaction product is $[(\text{PPh}_2\text{Me})_2\text{Rh}\}_2(\mu\text{-Cl})_2]$ and only traces of other complexes {among which $[(\text{PPh}_2\text{Me})_3\text{RhCl}]$ } are observable. In CH_2Cl_2 , however, a mixture of 5 complexes is observed after 5–10 min. The major product is $[(\text{PPh}_2\text{Me})_3\text{RhCl}]$ (^{31}P NMR: $\delta = 31.8$, dt, $J_{\text{P-Rh}} = 187$ Hz, $J_{\text{P-P}} = 42$ Hz and $\delta = 16.5$, dd, $J_{\text{P-Rh}} = 139$ Hz, $J_{\text{P-P}} = 42$ Hz). Among the four others complexes, only two could be identified. On the basis of literature data^[18], one is $[(\text{PPh}_2\text{Me})(\text{C}_8\text{H}_{14})\text{Rh}\}_2(\mu\text{-Cl})_2]$ (^{31}P NMR $\delta = 40.4$, $J_{\text{P-Rh}} = 187$ Hz) while the other is the expected $[(\text{PPh}_2\text{Me})_2\text{Rh}\}_2(\mu\text{-Cl})_2]$ (^{31}P NMR: $\delta = 34.0$, $J_{\text{P-Rh}} = 196$ Hz). Among the two other minor complexes, one gives a broad doublet (^{31}P NMR: $\delta = 32.8$, $J_{\text{P-Rh}} = 194.5$ Hz) and the second a spin figure which resembles that of a tris(phosphane)rhodium(I) complex (^{31}P NMR: $\delta = 22.8$, dt, $J_{\text{P-Rh}} = 150$ Hz, $J_{\text{P-P}} = 24$ Hz and $\delta = 10.6$, dd, $J_{\text{P-Rh}} = 96$ Hz, $J_{\text{P-P}} = 24$ Hz). After 20 min, all the above signals have evolved to leave those of the dinuclear complex $[(\text{PPh}_2\text{Me})_2\text{Rh}\}_2(\mu\text{-Cl})_2]$, exclusively. Then this signal progressively vanishes to cleanly leave a doublet (^{31}P NMR: $\delta = 17.7$, $J_{\text{P-Rh}} = 148$ Hz) attributed to the methylene-

bridged $[(\text{PPh}_2\text{Me})_2\text{RhCl}\}_2(\mu\text{-Cl})_2(\mu\text{-CH}_2)]$ (**4**) which can be readily isolated. This CH_2Cl_2 activation appears to be slower than in the case of $[(\text{PEt}_3)_2\text{Rh}\}_2(\mu\text{-Cl})_2]$, probably as a consequence of the lower electron-donating ability of PPh_2Me ($\text{p}K_{\text{a}} = 4.57$) as compared to that of PEt_3 ^[14].

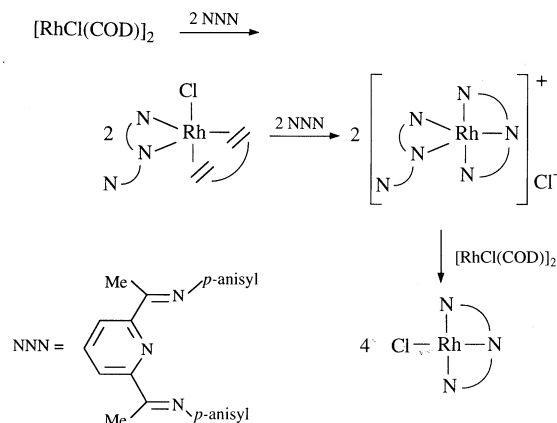
It is thus clear that when $[(\text{C}_8\text{H}_{14})_2\text{Rh}\}_2(\mu\text{-Cl})_2]$ **1** is treated with 4 equivalents of PR_3 (either PEt_3 or PPh_2Me), cleavage of chloride bridges occurs, followed by phosphane redistribution, affording the dinuclear complexes $[(\text{PR}_3)_2\text{Rh}\}_2(\mu\text{-Cl})_2]$. In both cases, these complexes activate CH_2Cl_2 to give the methylene-bridged complexes $[(\text{PR}_3)_2\text{RhCl}\}_2(\mu\text{-Cl})_2(\mu\text{-CH}_2)]$.

As a complement, we also studied the reaction of **1** with only 2 equivalents of either PEt_3 or PPh_2Me , again by ^{31}P -NMR monitoring at the early stage of the reaction at room temperature. Indeed, the authors who previously reported on the reaction with PPh_2Me indicated that the NMR spectra were recorded several hours after mixing the reactants^[18].

In both cases, after 5–10 min mixing the reactants in THF at room temperature, the tetrasubstituted $[(\text{PR}_3)_2\text{Rh}\}_2(\mu\text{-Cl})_2]$ and the disubstituted $[(\text{C}_8\text{H}_{14})(\text{PR}_3)\text{Rh}\}_2(\mu\text{-Cl})_2]$ complexes are present as the two major products. In the case of PPh_2Me , three others complexes are also observable, two of them giving rise to doublets (^{31}P NMR: $\delta = 40.0$, $J_{\text{P-Rh}} = 187$ Hz and $\delta = 33.2$, $J_{\text{P-Rh}} = 195$ Hz) and the third one (minor) giving a spin figure corresponding to a tris(phosphane)rhodium complex, as previously observed with 4 equivalents of PPh_2Me (vide supra). After 2 h, only the doublet corresponding to the expected $[(\text{C}_8\text{H}_{14})(\text{PR}_3)\text{Rh}\}_2(\mu\text{-Cl})_2]$ is present.

Thus, although the cleavage of the chloride bridges could not be clearly evidenced in the case of two equivalents of phosphane, these results indicate that reaction of monophosphanes with $[(\text{C}_8\text{H}_{14})_2\text{Rh}\}_2(\mu\text{-Cl})_2]$ always involves substitution of the four cyclooctene ligands, followed by redistribution of the phosphane with unreacted starting complex.

It must be noted that a *related* ligand redistribution process has been recently evidenced by NMR in the special case of terdentate nitrogen ligands^[5].



The resulting complex has also been shown to react with CD_2Cl_2 at 298 K to yield the corresponding chloro-

methyl complex $[\text{RhCl}_2(\text{CD}_2\text{Cl})(\{2,6\text{-C}(\text{Me})=\text{N-}p\text{-anisyl}\}_2\text{C}_5\text{H}_3\text{N})]^{[5]}$.

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Experimental Section

General: All reactions were performed under argon using standard Schlenk techniques. $[(\text{C}_8\text{H}_{14})_2\text{Rh}]_2(\mu\text{-Cl})_2$ **1** was prepared according to the literature procedure^[19]. – C, H analyses: Perkin-Elmer 2400 apparatus. – NMR: Bruker AC 200 (monitoring of reactions), AMX 400 (isolated complexes) (400.1, 162.0, 100.6, and 12.6 MHz, for ^1H , ^{31}P , ^{13}C , and ^{103}Rh , respectively). For ^1H NMR, CD_2Cl_2 as solvent, $\delta_{\text{H}} = 5.33$; for ^{31}P NMR, H_3PO_4 as external standard; for ^{13}C NMR, CD_2Cl_2 as solvent, $\delta_{\text{C}} = 52.9$; for ^{103}Rh NMR, CD_2Cl_2 as solvent, rhodium metal as external standard.

$[(\text{PEt}_3)_2\text{RhCl}]_2(\mu\text{-Cl})_2(\mu\text{-CH}_2)$ **(3)**: Triethylphosphane (0.37 ml, 2.51 mmol) was added to a solution of $[(\text{C}_8\text{H}_{14})_2\text{Rh}]_2(\mu\text{-Cl})_2$ (0.450 g, 0.63 mmol) in CH_2Cl_2 (20 ml). After 2 h stirring at room temp., the solvent was evaporated under reduced pressure. The resulting powder was washed with THF (20 ml) and dried in vacuo (0.401 g, 77%). – ^1H NMR: $\delta = 1.25$ (m, 36 H, $\text{CH}_3\text{CH}_2\text{P}$), 2.00 (m, 12 H, $\text{CH}_3\text{CH}_2\text{P}$), 2.15 (m, 12 H, $\text{CH}_3\text{CH}_2\text{P}$), 3.69 (bs, 2 H, CH_2). – $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 34.4$, d, $J_{\text{P-Rh}} = 147$ Hz. – $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ NMR: $\delta = 8.12$ (s, CH_3CH_2), 18.20 (s, CH_3CH_2), 38.88 (t, $J_{\text{C-Rh}} = 22$ Hz, CH_2). – $^{103}\text{Rh}\{^1\text{H}\}$ NMR: $\delta = 1696$ (t). – $\text{C}_{25}\text{H}_{62}\text{Cl}_4\text{P}_4\text{Rh}_2$ (834.3): calcd. C 35.99, H 7.49; found C 35.32, H 7.43.

$[(\text{PPh}_2\text{Me})_2\text{RhCl}]_2(\mu\text{-Cl})_2(\mu\text{-CH}_2)$ **(4)**: The same procedure as above was followed using PPh_2Me (41 μl ; 0.217 mmol) and $[(\text{C}_8\text{H}_{14})_2\text{Rh}]_2(\mu\text{-Cl})_2$ (0.039 g; 0.054 mmol) in CH_2Cl_2 (0.7 ml) and 6 h stirring at room temp. (0.045 g; 71%). – ^1H NMR: $\delta = 1.53$ ($\text{A}_3\text{XMX}'\text{A}'_3$ spin system with a broad line symmetrically flanked by two sharp lines separated by 10.8 Hz, 12 H, CH_3P), 4.25 (bs, 2 H, CH_2), 6.9–7.6 (m, 40 H, aromatic H). – $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 20.31$, d, $J_{\text{P-Rh}} = 148.7$ Hz. – $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ NMR: $\delta = 14.90$ (q, $J_{\text{C-H}} = 133$ Hz, CH_3P), 56.78 (tt, $J_{\text{C-H}} = 143$ Hz, $J_{\text{C-Rh}} = 18$ Hz, CH_2), 127–133 (aromatic C). – $^{103}\text{Rh}\{^1\text{H}\}$ NMR: $\delta = 1847$ (t). – $\text{C}_{53}\text{H}_{54}\text{Cl}_4\text{P}_4\text{Rh}_2$ (1162.5): calcd. C 54.76, H 4.68; found C 54.25, H 4.49.

X-ray Crystallographic Analysis of $[(\text{PEt}_3)_2\text{RhCl}]_2(\mu\text{-Cl})_2(\mu\text{-CH}_2)$ (3): X-ray quality crystals were obtained by slow diffusion of THF vapors into a concentrated CH_2Cl_2 solution of the complex. The data were collected on a Stoe Imaging Plate Diffraction System (IPDS) equipped with an Oxford Cryosystems cooler device. The crystal-to-detector distance was 80 mm. 115 exposures (2 min per exposure) were obtained with $0 < \varphi < 149.5^\circ$ and with the crystals rotated through 2° in φ . Coverage of the unique set was over 99% complete to at least 24° . Crystal decay was monitored by measuring 200 reflexions per image. The final unit cell parameters were obtained by the least-squares refinement of 5000 reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collection.

The structure was solved by direct methods (SIR92)^[20] and refined by least-squares procedures on F_o . One of the methyl of an ethyl group attached to P(1) is distributed statistically over two positions. The coordinates for these disordered carbon atoms were refined applying geometrical restraints to maintain reasonable C–C distances and C–C–C bond angles. H atoms were located on

difference Fourier maps, but they were introduced in calculation in idealized positions [$d(\text{CH}) = 0.96 \text{ \AA}$] and their atomic coordinates were recalculated after each cycle. They were given isotropic thermal parameters 20% higher than those of the carbon to which they are attached. Only the H atoms attached to the C methylene carbon were refined with an isotropic thermal parameter. Least-squares refinements were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = w' \{1 - [\Delta F/6\sigma(F_o)]^2\}^2$ where $w' = 1/\sum_1^n A_r T_r(x)$ with 3 coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$ where x was $F_o/F_c(\text{max})^{[21]}$. Models reached convergence with $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$, having values listed in Table 1. Criteria for a satisfactory complete analysis were the ratios of rms shift to standard deviation less than 0.1 and no significant features in final difference maps. Details of data collection and refinement are given in Table 2.

Table 2. Crystal and collection data for compound **3** · 2 CH_2Cl_2

Crystal Parameters	
formula	$\text{C}_{25}\text{H}_{62}\text{Cl}_4\text{P}_4\text{Rh}_2 \cdot 2 \text{CH}_2\text{Cl}_2$
fw [g]	1004.15
shape (color)	box (yellow)
size [mm]	$0.50 \times 0.40 \times 0.30$
crystal system	orthorhombic
space group	<i>Pnan</i>
<i>a</i> [Å]	13.1328(9)
<i>b</i> [Å]	17.479(2)
<i>c</i> [Å]	18.734(2)
<i>V</i> [Å ³]	4300.5(6)
<i>Z</i>	4
<i>F</i> (000)	2052
ρ (calcd) [g·cm ^{−3}]	1.551
μ (Mo- <i>K</i> α) [cm ^{−1}]	14.238
Data collection	
Diffractometer	IPDS Stoe
monochromator	graphite
radiation	Mo- <i>K</i> α ($\lambda = 0.71073$)
detector distance [mm]	80
Scan mode	
φ range [°]	$0 < \varphi < 149.5$
φ incr. [°]	1.3
exposure time [min]	2
2θ range [°]	$4.9 < 2\theta < 47.9$
no. of rflns collected	19755
no. of unique rflns	3308
merging factor <i>R</i> (int)	0.0353
reflections used [$I > 2\sigma(I)$]	2737
Refinement	
<i>R</i>	0.0186
<i>R</i> _w	0.0213
Weighting scheme	Chebyshev
Coefficient .Ar	1.39, −0.222, 1.22
(Δ/s) _{max}	0.009
Δr _{max}	0.39
Δr _{min}	−0.35
GOF	1.102

The calculations were carried out with the CRYSTALS package programs^[22] running on a PC. The drawing of the molecule was realized with the help of CAMERON^[23]. The atomic scattering factors were taken from International Tables for X-ray Crystallography^[24]. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100808. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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