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Synthesis and X-ray Structural Characterization of $\text{RhCl}_2(\text{PMe}_2\text{Ph})_2(\text{C}_3\text{Ph}_3)$, the Product of an Oxidative Addition-Ligand Elimination Reaction

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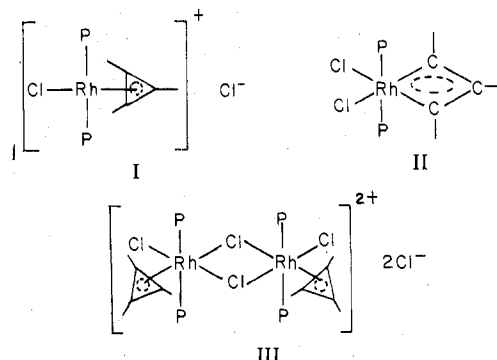
The Vaska complexes $\text{Rh}(\text{CO})\text{Cl}(\text{PR}_3)_2$ ($\text{R}_3 = \text{Me}_3, \text{Me}_2\text{Ph}, \text{MePh}_2$) react with triphenylcyclopropenium salts to generate blue-green rhodiacyclic complexes via oxidative cleavage of the C-C bond. All reactions are accompanied by loss of carbon monoxide. The molecular structure of one such oxidative addition-ligand elimination adduct has been determined by a three-dimensional single-crystal X-ray diffraction study. The title compound crystallizes in the monoclinic space group $C2/c$ with four molecules in a unit cell which measures $a = 19.190$ (7) Å, $b = 11.892$ (6) Å, $c = 14.346$ (4) Å, and $\beta = 93.88$ (2)°. The structure was solved by heavy-atom techniques and refined by full-matrix, mixed iso/anisotropic least-squares analysis to a conventional R value of 0.041 for the 2550 independent observed ($I > 2\sigma(I)$) reflections. The Rh(III) adduct displays pseudooctahedral symmetry with trans phosphines, cis chloride ligands, and a bidentate propenyl-1,3-diyl group. Key bond distances include Rh-P = 2.354 (1) Å, Rh-Cl = 2.472 (1) Å, and Rh-C(propenyl) = 2.000 (4) Å. Structural parameters are compared to the electronically equivalent $[\text{IrCl}(\text{CO})(\text{PMe}_3)_2(\text{C}_3\text{Ph}_3)]^+$ cation; the $\text{M}(\text{C}_3\text{Ph}_3)^+$ units in the two structures are noted to be essentially identical. Comparison of Rh(III)-C(sp²) bond lengths in similar complexes suggests a weak but real π component to the Rh-C(propenyl) bond.

Introduction

Oxidative cleavage of the C-C bond of a strained cyclic hydrocarbon is the most reliable of several known synthetic routes to metallocyclic complexes in the cases where the metal possesses a high propensity to undergo oxidative addition. This reaction has been demonstrated for both saturated¹ and unsaturated ring systems² and is sometimes coupled to small molecule insertions.^{1,2e,f} In our laboratory we have been concentrating on the unsaturated cyclopropenes and cyclopropenium ions. The latter species can be stabilized in a η^3 configuration in $(\eta^3\text{-C}_3\text{R}_3)\text{Ni}(\text{CO})\text{Br}$,³ will ring-open, undergo insertion of CO, and be stabilized as a coordinated $\text{C}_3\text{R}_3\text{CO}$ cyclic ketone in $(\eta^3\text{-C}_3\text{R}_3\text{CO})\text{Co}(\text{CO})_3$,⁴ or will ring-open to form a four-membered metallocycle as in $[\text{Ir}(\text{CO})\text{Cl}(\text{PMe}_3)_2(\text{C}_3\text{Ph}_3)]^+$.^{2a,b} The latter reaction of $\text{Ir}(\text{CO})\text{Cl}(\text{PMe}_3)_2$ and $\text{C}_3\text{Ph}_3^+\text{BF}_4^-$ to form the cationic oxidative addition adduct $[\text{Ir}(\text{CO})\text{Cl}(\text{PMe}_3)_2(\text{C}_3\text{Ph}_3)]^+$ was one of the first authenticated cases of oxidative cleavage of the C-C bond.

Our extension of this iridium work into rhodium chemistry has resulted in a similar oxidative cleavage of the cyclopropenium C-C bond but with several unexpected developments. In contrast to the straightforward reaction with $\text{Ir}(\text{CO})\text{Cl}(\text{PMe}_3)_2$, $\text{C}_3\text{Ph}_3^+\text{X}^-$ ($\text{X} = \text{Cl}, \text{PF}_6$) reacts with $\text{Rh}(\text{CO})\text{Cl}(\text{PR}_3)_2$ complexes with facile evolution of carbon monoxide and a dramatic color change from yellow to blue-green. These observations led us to believe that the rhodium reaction proceeded differently from that of iridium and, as a consequence, to undertake a full single-crystal X-ray

diffraction study to ascertain the mode of reaction. Since the blue-green complex is diamagnetic (inference from NMR), several structural possibilities arise: viz, the η^3 -cyclopropenylrhodium(I) complex, I, and the metallocyclic Rh(III) adduct, II. However, only a few rhodium-containing, green compounds are known,⁵ and these are Rh(II) species which are expected to be paramagnetic unless dimeric. This consideration suggests the possibility of a dimeric structure such as III. Preliminary results of the X-ray study, which have been communicated,⁶ show that II represents the correct formu-



lation. In this paper we wish to present the results of our completed X-ray study together with some additional synthetic findings which add insights into the subtle differences which exist between the iridium and rhodium analogues of the Vaska

complexes $M(\text{CO})\text{Cl}(\text{PR}_3)_2$ and which become evident in their reactions with C_3Ph_3^+ .

Experimental Section

All solvents used in the experiments were commercially available reagent-grade stock; they were stored over molecular sieves and used without further purification. The rhodium complexes $\text{Rh}(\text{CO})\text{Cl}(\text{PR}_3)_2$, $\text{R}_3 = \text{Ph}_3, \text{Ph}_2\text{Me}, \text{PhMe}_2, \text{Me}_3$, and the cyclopropenium salts⁸ $\text{C}_3\text{Ph}_3^+\text{X}^-$, $\text{X} = \text{Cl}$, and PF_6^- , were prepared by published techniques. All reactions were carried out in Schlenk apparatus under an inert nitrogen atmosphere. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer as KBr pellets. Proton NMR spectra were run on a Perkin-Elmer R-20-B spectrometer.

Synthesis of $\text{RhCl}_2(\text{PMe}_2\text{Ph})_2(\text{C}_3\text{Ph}_3)$. A slurry of 0.50 g of $\text{Rh}(\text{CO})\text{Cl}(\text{PMe}_2\text{Ph})_2$ (1.13 mmol) and 0.50 g of $\text{C}_3\text{Ph}_3^+\text{Cl}^-$ (1.65 mmol) in approximately 40 mL of degassed CH_2Cl_2 was stirred under N_2 . The *sym*-triphenylcyclopropenium chloride dissolved during the course of the chemical reaction. After 1 h the reaction was complete; the solution changed from a heterogeneous yellow slurry to a homogeneous blue-green solution. Although no carbon monoxide evolution was visibly evident, infrared analysis of the filtered solution showed no carbonyl bands. If reactants are mixed stoichiometrically, weak carbonyl bands are observed at 2080 cm^{-1} due to some Rh(III) impurity or decomposition product and at 1960 cm^{-1} due to unreacted starting material. The solution volume was reduced to 5 mL and cooled overnight at about 0°C . Filtration of this solution yielded the green-black microcrystalline product. Additional material can be obtained by total evaporation of solvent and recrystallization of the residue from hot benzene. The new complex is only sparingly soluble in CH_2Cl_2 , CHCl_3 , and C_6H_6 and insoluble in hexane and ether. Total yield is about 80%. Infrared analysis showed a transparent carbonyl region while the IR-active E' mode of the C_3Ph_3^+ ring, at 1411 cm^{-1} in the starting material,⁹ had disappeared and had been replaced by a strong band at 1340 cm^{-1} . The NMR was rather uninformative due to the low solubility of the complex. Weak but unshifted signals were observed in the phenyl and methyl regions indicative of the presence of the PMe_2Ph group and the diamagnetism of the complex.

Reactions with $\text{C}_3\text{Ph}_3^+\text{PF}_6^-$. Similar reactions were carried out between the rhodium complexes $\text{Rh}(\text{CO})\text{Cl}(\text{PR}_3)_2$, $\text{R}_3 = \text{Ph}_3, \text{Ph}_2\text{Me}, \text{PhMe}_2, \text{Me}_3$, and the $\text{C}_3\text{Ph}_3^+\text{PF}_6^-$ salt. With the exception of the PPh_3 analogue which did not react, all reactions followed the same pattern as the $\text{C}_3\text{Ph}_3^+\text{Cl}^-$ salt; that is, they led to blue-green solutions, evolved CO, and produced blue-green oils from which no solid product could be isolated. Qualitatively, the rates of these reactions were noted to vary systematically with the steric/electronic effects of the phosphines with $\text{PMe}_3 > \text{PPhMe}_2 > \text{PPh}_2\text{Me}$. All attempts to crystallize these oils have thus far failed.

X-ray Data Collection and Reduction. Crystals suitable for single-crystal X-ray diffraction work were obtained by the Soxhlet extraction technique from CH_2Cl_2 . Preliminary Weissenberg and precession photographs displayed monoclinic C_{2h} ($2/m$) Laue symmetry and gave the approximate unit cell dimensions. Systematic absences of $h + k = 2n + 1$ for $\{hkl\}$ data and $l = 2n + 1$ for $\{h0l\}$ data defined the space group as either Cc (No. 9, C_2^4) or $C2/c$ (No. 15, C_{2h}^6). Successful solution and refinement confirmed the centrosymmetric choice.

The crystal selected for intensity data collection was a prism with dimensions $0.30 \times 0.32 \times 0.40\text{ mm}$. Data were collected on a Enraf-Nonius CAD-4 diffractometer using general procedures outlined previously.¹⁰ Refined unit-cell parameters together with the specifics related to the collection of this data set are given in Table I. Three standard reflections measured periodically during the course of the data collection showed no significant changes.

Intensities and their standard deviations were calculated using the following formulas:

$$I = S(C - RB)$$

$$\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$$

where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time (2.0), B is the total background count, and the parameter p (0.05) is a factor introduced to downweight intense reflections. The data set totaled 3135 independent reflections of which 2550 had $I > 2\sigma(I)$ and were used in the refinement. The data were corrected for Lorentz and polarization effects in the usual way. No absorption correction was

Table I. Experimental Data for Single-Crystal Study of $\text{RhCl}_2(\text{PMe}_2\text{Ph})_2(\text{C}_3\text{Ph}_3)$

A. Unit Cell Parameters at $23 \pm 1^\circ\text{C}$	
$a = 19.190$ (7) Å	space group: $C2/c$ (No. 15, C_{2h}^6)
$b = 11.982$ (6) Å	$Z = 4$
$c = 14.346$ (4) Å	mol wt 717.5
$\beta = 93.88$ (2) $^\circ$	$\rho(\text{calcd}) = 1.46\text{ g cm}^{-3}$
$V = 3266\text{ Å}^3$	$\rho(\text{obsd}) = 1.45\text{ g cm}^{-3}$
B. Measurement of Intensity Data	
radiation: Mo $K\alpha$ (graphite monochromated)	
crystal-to-detector distance: 21 cm	
counter aperture width: 2.0 mm	
incident-beam collimator diameter: 2.0 mm	
takeoff angle: 5.8°	
scan technique: $\theta-2\theta$	
scan rate: variable, $4-20^\circ/\text{min}$	
scan range: $2\theta(\text{Mo } K\alpha_1) - 0.9^\circ$ to $2\theta(\text{Mo } K\alpha_2) + 0.9^\circ$	
background: stationary-crystal stationary-counter background	
counts were taken at each end of the scan range. The ratio of scan time to background time was 2.0.	
range of data: $0^\circ < 2\theta(\text{Mo } K\alpha) < 50^\circ$	

applied in light of the symmetric shape of the crystal and the low molar absorption coefficient (7.501 cm^{-1}).^{11a}

Structure Determination and Refinement.¹² The structure was solved by conventional heavy-atom techniques. Iterative Fourier and least-squares analyses located all nonhydrogen atoms. Initially the least-squares calculations were carried out in the noncentrosymmetric Cc space group as suggested by the statistical analysis of the normalized structure factor amplitudes calculated from a Wilson plot. It soon became evident that the bond distances and angles computed on the basis of such a noncentrosymmetric model were unreasonable. At this time ($R_1 = 0.074$) the Cc space group was rejected in favor of the centrosymmetric $C2/c$ model which requires the molecule to possess twofold symmetry. This refinement proved much more satisfactory and led to more realistic bond distances and angles while retaining compact thermal parameters indicative of an ordered system. Final isotropic refinement converged at residuals of $R_1(F) = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.077$ and $R_2(F) = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.128$ where $w = 1/\sigma(F)$. At this point anomalous dispersion corrections^{11b} for Rh, Cl, and P were applied, and the temperature factors on Rh, Cl, P, and C(1,2) were converted to anisotropic form. Mixed iso/anisotropic refinement was then continued to convergence at $R_1 = 0.050$ and $R_2 = 0.082$. A Fourier difference map revealed the positions of some but not all of the hydrogen atoms so coordinates were calculated on the basis of idealized methyl and phenyl groups. These hydrogen atoms with constant positional and thermal parameters (5.0 Å^2) were included in the last stages of refinement. Final discrepancy indices were $R_1 = 0.041$ and $R_2 = 0.062$, and the final "goodness of fit" was defined as $\text{GOF} = [\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2} = 1.99$, where NO is the number of observations and NV is the number of variable parameters.

During the final cycle of refinement, no parameter shifted by more than 0.14σ where σ refers to the estimated standard deviation of the parameter. The final Fourier difference map showed no peaks greater than 0.87 e/Å^3 (less than 0.15 times the value of a typical carbon atom) and gave no indication of disorder in the centrosymmetric model.

The positional and thermal parameters from the output of the final least-squares analysis are presented in Table II, interatomic bond distances and angles not involving hydrogen are collected in Table III, and equations of weighted least-square planes are summarized in Table IV. The table of observed and calculated structure factor amplitudes is available as supplementary material.

Results and Discussion

The results of the single-crystal X-ray diffraction study displayed in Figure 1 show that $\text{Rh}(\text{CO})\text{Cl}(\text{PMe}_2\text{Ph})_2$ has oxidatively cleaved the C-C bond of the C_3Ph_3^+ cation to generate an octahedral Rh(III) complex which contains a (1,2,3-triphenylpropenylum-1,3-diyl)rhodium metallocycle. In the process carbon monoxide has been eliminated and replaced by the chloride counterion. This facile loss of carbon monoxide was unexpected in light of the previous chemistry demonstrated by Weaver and co-workers^{2a,b} on the iridium analogue and, to our knowledge, represents the first example

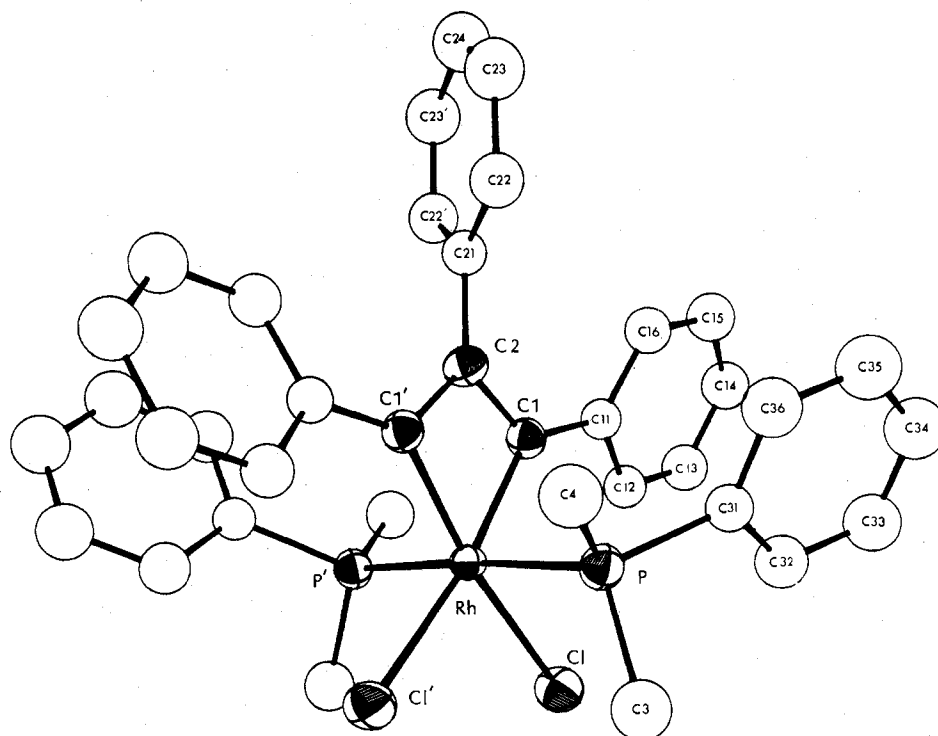


Figure 1. Overall molecular structure of the $\text{RhCl}_2(\text{PMe}_2\text{Ph})_2(\text{C}_3\text{Ph}_3)$ metallocycle showing the atomic labeling scheme.

Table II. Final Atomic Parameters with Estimated Standard Deviations^a

A. Positional Parameters						
atom	x	y	z	B, Å ²		
Rh	0.00000	0.16275 (3)	0.25000	2.08 ^b		
Cl	0.06040 (5)	0.01371 (8)	0.16644 (7)	3.24 ^b		
P	0.09067 (5)	0.15664 (8)	0.36886 (7)	2.62 ^b		
C(1)	0.0396 (2)	0.3043 (3)	0.2001 (3)	2.35 ^b		
C(2)	0.0000	0.3799 (5)	0.2500	2.57 ^b		
C(3)	0.0723 (3)	0.2246 (4)	0.4779 (3)	4.23 (9)		
C(4)	0.1136 (3)	0.0134 (4)	0.4060 (3)	4.08 (9)		
C(11)	0.0936 (2)	0.3315 (3)	0.1370 (3)	2.69 (7)		
C(12)	0.1282 (2)	0.4359 (4)	0.1426 (3)	3.37 (8)		
C(13)	0.1777 (2)	0.4615 (4)	0.0795 (3)	4.00 (9)		
C(14)	0.1928 (3)	0.3866 (5)	0.0110 (3)	4.27 (9)		
C(15)	0.1600 (2)	0.2821 (4)	0.0060 (3)	4.01 (9)		
C(16)	0.1114 (2)	0.2548 (3)	0.0692 (3)	3.20 (7)		
C(21)	0.0000	0.5065 (5)	0.2500	2.70 (9)		
C(22)	0.0258 (2)	0.5646 (4)	0.3289 (3)	3.71 (8)		
C(23)	0.0252 (3)	0.6825 (4)	0.3272 (4)	4.44 (9)		
C(24)	0.0000	0.7398 (6)	0.2500	4.65 (14)		
C(31)	0.1733 (2)	0.2161 (3)	0.3387 (3)	2.92 (7)		
C(32)	0.1989 (3)	0.3181 (4)	0.3762 (4)	4.39 (9)		
C(33)	0.2620 (3)	0.3603 (5)	0.3505 (4)	5.23 (11)		
C(34)	0.3008 (3)	0.3019 (5)	0.2900 (4)	4.96 (10)		
C(35)	0.2766 (3)	0.2024 (4)	0.2515 (4)	4.47 (9)		
C(36)	0.2122 (3)	0.1602 (3)	0.2745 (3)	3.88 (9)		
B. Anisotropic Thermal Parameters ^c						
atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	142 (1)	299 (3)	307 (3)	0	51 (1)	0
Cl	235 (3)	412 (7)	493 (6)	49 (3)	94 (3)	-57 (5)
P	169 (3)	480 (8)	326 (5)	19 (3)	25 (3)	40 (5)
C(1)	16 (1)	38 (2)	30 (2)	-3 (1)	3 (1)	1 (2)
C(2)	20 (2)	34 (3)	34 (3)	0	4 (2)	0

^a Estimated standard deviations of the least significant figures are given in parentheses. ^b Overall isotropic B's equivalent to the anisotropic β 's listed above. ^c Anisotropic temperature factors ($\beta_{ij} \times 10^5$ for Rh, Cl, P and $\beta_{ij} \times 10^4$ for C(1), C(2)) are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

of an oxidative addition reaction involving the $\text{M}(\text{CO})\text{Cl}(\text{PR})_2$, $\text{M} = \text{Rh}$ or Ir , complexes where CO is lost under such mild conditions. There are reports where various other ligands

Table III. Interatomic Distances and Angles

A. Bond Distances, Å			
Rh-Cl	2.472 (1)	P-C3	1.816 (5)
Rh-P	2.354 (1)	P-C4	1.830 (5)
Rh-C(1)	2.000 (4)	P-C(31)	1.815 (4)
C(1)-C(2)	1.404 (5)	C(21)-C(22)	1.388 (5)
C(1)-C(11)	1.459 (5)	C(22)-C(23)	1.402 (7)
C(2)-C(21)	1.506 (8)	C(23)-C(24)	1.362 (7)
		C-C (av)	1.385 (4)
C(11)-C(12)	1.407 (6)	C(31)-C(32)	1.403 (6)
C(12)-C(13)	1.390 (6)	C(32)-C(33)	1.383 (8)
C(13)-C(14)	1.372 (7)	C(33)-C(34)	1.371 (8)
C(14)-C(15)	1.393 (7)	C(34)-C(35)	1.373 (8)
C(15)-C(16)	1.382 (6)	C(35)-C(36)	1.395 (7)
C(16)-C(11)	1.392 (6)	C(36)-C(31)	1.393 (6)
C-C (av)	1.389 (3)	C-C (av)	1.389 (3)
B. Bond Angles, Deg			
Cl-Rh-P	88.93 (3)	Rh-P-C(3)	115.7 (2)
Cl-Rh-C(1)	103.19 (11)	Rh-P-C(4)	113.0 (2)
Cl-Rh-C(1')	168.35 (11)	Rh-P-C(31)	115.5 (1)
Cl-Rh-P'	88.54 (3)	C(3)-P-C(4)	102.7 (2)
Cl-Rh-Cl'	88.38 (5)	C(3)-P-C(31)	104.8 (2)
P-Rh-C(1)	90.31 (11)	C(4)-P-C(31)	103.6 (2)
P-Rh-C(1')	92.67 (11)	Rh-C(1)-C(11)	135.4 (3)
P-Rh-P'	176.47 (5)	Rh-C(1)-C(2)	97.2 (3)
C(1)-Rh-C(1')	65.28 (21)	C(2)-C(1)-C(11)	127.3 (3)
C(1)-C(2)-C(21)	129.8 (2)	C(1)-C(2)-C(11)	100.3 (5)
C(1)-C(11)-C(12)	120.8 (3)	C(22)-C(21)-C(22)	120.4 (5)
C(1)-C(11)-C(16)	120.5 (3)	C(21)-C(22)-C(23)	118.8 (4)
C(2)-C(21)-C(22)	119.8 (3)	C(22)-C(23)-C(24)	121.1 (5)
P-C(31)-C(32)	122.3 (3)	C(23)-C(24)-C(23)'	119.9 (7)
P-C(31)-C(36)	119.2 (3)	C-C-C (av)	119.9 (2)
C(11)-C(12)-C(13)	119.7 (4)	C(31)-C(32)-C(33)	120.1 (5)
C(12)-C(13)-C(14)	120.8 (4)	C(32)-C(33)-C(34)	120.5 (5)
C(13)-C(14)-C(15)	119.9 (4)	C(33)-C(34)-C(35)	120.6 (5)
C(14)-C(15)-C(16)	119.9 (4)	C(34)-C(35)-C(36)	119.7 (5)
C(15)-C(16)-C(11)	120.9 (4)	C(35)-C(36)-C(31)	120.5 (4)
C(16)-C(11)-C(12)	118.7 (4)	C(36)-C(31)-C(32)	118.5 (4)
C-C-C (av)	120.0 (2)	C-C-C (av)	119.9 (2)

have been lost but under more drastic reaction conditions.¹³ Figure 2 displays the packing of the four $\text{RhCl}_2(\text{PMe}_2\text{Ph})_2(\text{C}_3\text{Ph}_3)$ molecular units into the centrosymmetric

Table IV. Equations of Weighted Least-Squares Planes and Distances of Atoms (Å) from These Planes

A. Plane through Rh, C(1), C(2), and C(1)'

$$0.6625X + 0.0000Y + 0.7490Z + 2.5195 = 0$$

C11	0.051	Cl	-0.074
C21	0.000	Cl'	0.074

B. Plane through Rh, Cl, Cl', C(1), C(2), and C(1)'

$$0.6932X + 0.0000Y + 0.7207Z + 2.4106 = 0$$

Rh	0.000	C2	0.000
Cl	-0.002	C11	0.156
Cl	0.045	C21	0.000

C. Plane through C(11), C(12), C(13), C(14), C(15), and C(16);
i.e., Ring 1

$$0.6795X - 0.3872Y + 0.6232Z + 0.8383 = 0$$

C11	-0.012	C15	-0.002
C12	0.004	C16	0.013
C13	0.010	Cl	-0.071
C14	-0.014		

D. Plane through C(21), C(22), C(23), and C(24);
i.e., Ring 2

$$-0.9378X + 0.0000Y + 0.3473Z + 1.4702 = 0$$

C21	0.0000	C24	0.0000
C22	0.0005	C2	0.0000
C23	-0.0006		

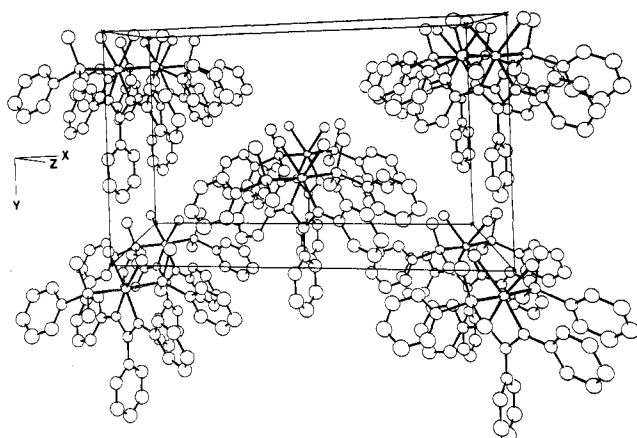
E. Plane through C(31), C(32), C(33), C(34), C(35), and C(36);
i.e., Ring 3

$$0.4169X - 0.5010Y + 0.7584Z + 3.6275 = 0$$

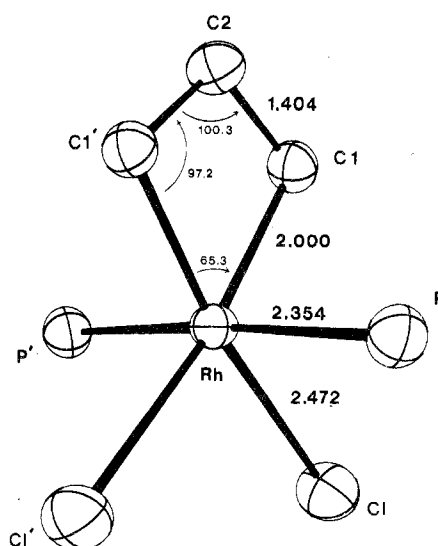
C31	0.011	C34	0.011
C32	0.000	C35	0.008
C33	-0.014	C36	-0.015

F. Dihedral Angles between Planes (deg)

A,B	2.4	A,D	68.2
A,C	23.5	B,D	66.6
B,C	23.1	C,D	65.9

**Figure 2.** The packing diagram of the $C2/c$ unit cell containing four $\text{RhCl}_2(\text{PMe}_2\text{Ph})_2(\text{C}_3\text{Ph}_3)$ molecular units.

$C2/c$ unit cell. Normal van der Waals contact distances are observed, and no unusual intermolecular interactions are noted. As a consequence of the crystal symmetry, each $\text{RhCl}_2(\text{PMe}_2\text{Ph})_2(\text{C}_3\text{Ph}_3)$ molecule is required to possess twofold symmetry. The inner coordination sphere of the Rh(III) is shown in Figure 3; the rhodium atom sits in a pseudooctahedral environment of two chloro ligands, two phosphines, and a chelating C_3Ph_3 moiety. The dimethylphenylphosphine groups are disposed trans to each other (twofold related) as is normally observed in oxidative addition adducts of metal bis(phosphine) complexes. The phosphine ligand is well-behaved with approximately tetrahedral coordination around phosphorus, equivalent P-C(methyl, phenyl) bonds of 1.82 (1) Å, and a regular phenyl group with average C-C bond distances and C-C-C bond angles of 1.39 (1) Å and 119.9 (2)°, respectively.

**Figure 3.** Inner coordination sphere of the rhodium(III) atom showing some key bond distances and angles. The RhC_3 unit is rigorously planar.

The Rh-P bond length which measures 2.354 (1) Å is consistent with the observation¹⁵ that Rh-P bonds generally fall in the range 2.31–2.40 Å regardless of phosphine substitution or metal oxidation state.

The Rh-Cl bond of 2.472 (1) Å is lengthened by approximately 0.15 Å over the idealized distance one calculates on the basis of the sum of the covalent radii (2.32 Å). This lengthening is attributable to the strong trans influence exerted by the carbon atom of the chelating C_3Ph_3 group and is a well-documented observation.^{16–18} Examples of $\text{Rh}^{\text{III}}\text{-Cl}$ complexes in which this effect is most obvious include $\text{RhCl}_2(\text{py})_2[\text{CH}_2\text{C}_6\text{H}_4\text{P}(\text{tolyl})_2]$ ¹⁷ where Rh-Cl distances measure 2.339 (4) Å when trans to pyridine and 2.531 (4) Å when trans to $\sigma\text{-C}$ and $[\text{RhCl}(\text{pyMe})_2(\text{CH}_2\text{-C}_7\text{H}_{13}\text{O})(\mu_2\text{-Cl})]_2$ ¹⁸ where the Rh-($\mu_2\text{-Cl}$) bond (2.632 Å) trans to $\sigma\text{-C}$ measures 0.267 Å longer than the one trans to chlorine (2.365 Å). Also noteworthy here are the Rh-Cl bond lengths in the structurally similar $\text{RhCl}(\text{H}_2\text{O})(\text{AsMe}_3)_2\text{C}_4(\text{CF}_3)_4$ ¹⁹ (2.448 (5) Å) and $\text{RhCl}(\text{H}_2\text{O})(\text{PMe}_2\text{Ph})_2(\text{C}_4\text{O}_2\text{Cl}_2)$ ²⁰ (2.502 (2) Å) complexes and in the electronically equivalent $[\text{Ir}(\text{CO})\text{Cl}(\text{PMe}_3)_2(\text{C}_3\text{Ph}_3)]^+$ cation^{2a,b} (2.472 (5) Å) where all chlorine atoms are trans to the strong influence of a chelating carbon ligand.

The greatest deviation from a regular octahedral geometry around the rhodium atom occurs as a consequence of the small bite of the C_3Ph_3^+ chelate; the C(1)-Rh-C(1)' angle measures an acute 65.3 (2)° and can be compared to the 77–82° angles observed in larger five-membered MC_4 metallocycles.²¹ A comparison of this C-M-C angle as well as some other selected parameters for the electronically equivalent $\text{RhCl}_2(\text{PMe}_2\text{Ph})_2(\text{C}_3\text{Ph}_3)$ and $[\text{Ir}(\text{CO})\text{Cl}(\text{PMe}_3)_2(\text{C}_3\text{Ph}_3)]^+$ ^{2a,b} complexes is presented in Table V. It can be seen from these data that both MC_3Ph_3 metallocyclic units are essentially identical. The RhC_3 unit is required by symmetry to be planar, and the corresponding IrC_3 unit, although subject to no symmetry constraints, is also planar within experimental limits. The exocyclic C-C(Ph) bonds average 1.475 Å (1.49 Å for the Ir complex) as expected for a single bond between two sp^2 -hybridized carbon atoms. The rather substantial twist angles of the phenyl groups noted in Table V undoubtedly preclude any charge delocalization onto these rings. Comparison of these exocyclic C-C(Ph) bonds with the metallocyclic C-C bonds which measure 1.40 Å (1.39 Å for the Ir complex) indicate that a substantial degree of electron delocalization and multiple bonding is operational in the C_3

Table V. Comparison of Selected Bond Distances (Å) and Angles (deg) for $[\text{Ir}(\text{CO})\text{Cl}(\text{PMe}_3)_2(\text{C}_3\text{Ph}_3)]^+$ ^a and $\text{RhCl}_2(\text{PMe}_2\text{Ph})_2(\text{C}_3\text{Ph}_3)$

	Ir ^{b,c}	Rh ^{b,c}
Distances		
M-C(1)	1.99 (2), 2.10 (2)	2.000 (4)
C(1)-C(2)	1.36 (2)	1.404 (5)
C(2)-C(3)	1.41 (2)	1.404 (5)
C(1)-C(11)	1.49 (2)	1.459 (5)
C(2)-C(22)	1.52 (2)	1.506 (8)
C(3)-C(33)	1.47 (2)	1.459 (5)
M-P	2.360 (5), 2.369 (5)	2.354 (1)
M-Cl	2.472 (5)	2.472 (1)
C(1)···C(3)	2.15 (2)	2.156 (6)
M···C(2)	2.61 (2)	2.582 (5)
Angles		
C(1)-M-C(3)	63.5 (3)	65.3 (2)
M-C(1)-C(2)	95.5 (10)	97.2 (3)
C(1)-C(2)-C(3)	102.0 (13)	100.3 (5)
C(2)-C(3)-M	99.0 (10)	97.2 (3)
Angles of Tilt of Phenyl Group ^d (deg)		
C(11)···C(16)	8.5	2.1
C(21)···C(26)	-2.2	0.0
C(31)···C(36)	-3.9	-2.1
Angles of Twist of Phenyl Group ^d (deg)		
C(11)···C(16)	18.1	23.4
C(21)···C(26)	60.6	68.2
C(31)···C(36)	33.5	23.4

^a Reference 2b. ^b Pauling²³ lists the octahedral covalent radii of both Ir(III) and Rh(III) as 1.32 Å. ^c In the metallocycle labeling used in this table C(3) is equivalent to C(1)' and C(33) to C(11)' in the Rh structure, and C(1), C(2), and C(3) are equivalent to C(10), C(20), and C(30) in the Ir analogue. ^d The tilt and twist angles have been defined in ref 2b.

fragment of the metallocycle. The transannular C(1)···C(1)' distance of 2.156 (6) Å is too long to propose a strong σ - or π -bonding interaction but is too short to suggest no interaction at all since the van der Waals contact distance is substantially longer (3.40 Å).²³ Calculations reported by Weaver^{2b} of carbon p_π - p_π overlap integrals using STO-6G type orbitals for various allyl and propenyl systems suggest that a significant amount of π -orbital overlap is possible in the IrC_3 ring of the $[\text{Ir}(\text{CO})\text{Cl}(\text{PMe}_3)_2(\text{C}_3\text{Ph}_3)]^+$ cation (approximately 20% of that which exists in the cyclic cation). Since calculations of the p_σ - p_σ overlap integrals demonstrate a significant overlap of the p_σ orbitals as well ($\sigma > \pi$), it is impossible a priori to attribute the transannular C···C interaction in these two MC_3 rings to either a σ - or π -bonding component.

The question of the extent to which the electron delocalization includes the metal atom is a complex one based upon the radius assigned to the central Rh(III) atom. We believe that the Rh-C distance, at 2.000 (4) Å, is indicative of a minor degree of d_π - p_π delocalization on the basis of a 0.05–0.10 Å shortening of the Rh-C bond. The radius of Rh(III) has been estimated by several authors to be in the range 1.32–1.34 Å.^{17,23} If one adds to this the accepted $\text{C}(\text{sp}^2)$ single-bond radius of 0.74 Å, the result suggests that a normal $\text{Rh}^{\text{III}}\text{-C}(\text{sp}^2)$ bond should be approximately 2.07 ± 0.01 Å. A comparison of the 2.000 (4) Å bond length observed in the $\text{RhCl}_2(\text{PMe}_2\text{Ph})_2(\text{C}_3\text{Ph}_3)$ complex with other complexes containing similar linkages (Table VI) shows that with two exceptions these bonds are in a relatively narrow range between 1.96 and 2.00 Å. It has been noted³¹ that ligand electronegativity is capable of altering the radius of the metal center, but such effects are believed to be secondary here. The above data can be interpreted in two ways: viz., that the estimated $\text{Rh}^{\text{III}}\text{-C}(\text{sp}^2)$ bond distance is approximately 0.10 Å too long or that, in fact, a degree of π -bonding (of approximately the same magnitude) exists in all the complexes in Table VI and is the

Table VI. Representative $\text{Rh}^{\text{III}}\text{-C}(\text{sp}^2)$ Bond Distances (Å)

compound	bond length	ref
$\text{RhCl}_3(\text{PEt}_3)_2(\text{CHNMe}_2)$	1.961 (11)	15a
$\text{Rh}(\text{O}_2\text{CMe})(\text{C}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_5)_2$	1.982 (9)	16b
	2.000 (9)	
$\text{RhCl}(\text{PhCONCS})_2(\text{PPh}_3)_2$	1.930 (6)	16c
$\text{RhCl}(\text{H}_2\text{O})(\text{AsMe}_3)_2\text{C}_4(\text{CF}_3)_4$	1.998 (16)	19
	2.047 (16)	
$\text{RhCl}(\text{H}_2\text{O})(\text{PMe}_2\text{Ph})_2(\text{C}_4\text{O}_2\text{Cl}_2)$	1.970 (2)	20
	1.973 (2)	
$\text{RhCl}(\text{EtOCONCS})_3(\text{PPh}_3)_2$	1.930 (11)	24
$\text{RhI}_3(\text{CO})(\text{CPhNMeCPhNMe})$	1.968 (13)	25
$\text{Rh}_2\text{Cl}_2(\text{CO})_2(\text{C}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_5)_2$	1.980 (17)	26
	1.988 (16)	
$\text{RhCl}(\text{SbPh}_3)_2\text{C}_4(\text{CF}_3)_4$	2.000 (10)	27
	1.964 (11)	
$\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{C}_4(\text{C}_6\text{F}_5)_4$	2.060 (12)	28
	2.067 (11)	
$\text{RhCl}(\text{PPh}_3)_2(\text{C}_{12}\text{H}_4\text{O}_2)(\text{PPh}_3)_2$	2.006 ^a	29
	2.002	
$\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2[\text{C}_2(\text{CO}_2\text{Me})_2(\text{CS}_2\text{Me})]^+$	1.99 ^a	30
$\text{RhCl}_2(\text{PMe}_2\text{Ph})_2(\text{C}_3\text{Ph}_3)$	2.000 (4)	this work

^a No estimated standard deviations reported.

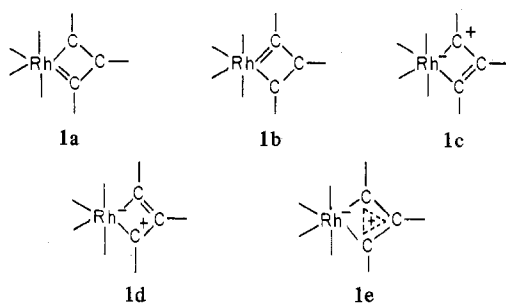
Table VII. Representative $\text{Rh}^{\text{III}}\text{-C}(\text{sp}^3)$ Bond Distances (Å)

compound	bond length	ref
$\text{RhCl}_2(\text{py})_2\text{P}(\text{o-C}_6\text{H}_4\text{CH}_3)_2(\text{o-C}_6\text{H}_4\text{CH}_3)$	2.083 (16)	17
$[\text{RhCl}_2(\text{C}_8\text{H}_5\text{O})(4\text{-Me}(\text{py}))_2]_2$	2.07 (3)	18
$\text{Rh}(\text{acac})(\text{py})_2(\text{C}_6\text{H}_8)$	2.042 (10)	32
	2.045 (10)	
$\text{Rh}_2(\text{acac})_2(\text{PPh}_3)_2(\text{C}_6\text{H}_8)$	2.085 (10)	32
	2.078 (10)	
$[\text{RhCl}(\text{C}_7\text{H}_8)(\text{C}_4\text{F}_6)]_4$	2.081 (36)	33
$\text{Rh}(\text{acac})(\text{C}_8\text{H}_{12})(\text{C}_4\text{F}_6)(\text{H}_2\text{O})$	2.05 (2)	34
$[\text{RhCl}_2(\text{C}_8\text{H}_{11}\text{O})]_2$	2.04 (2)	35
	2.07 (2)	
$[\text{Rh}(\text{C}_2\text{H}_5)(\text{NH}_3)_5]^{2+}$	2.048 (16)	36
$\text{RhI}_2\text{Me}(\text{PPh}_3)_2$	2.081 (9)	37
$\text{Rh}_2\text{I}_2(\text{SMe}_2)_3\text{Me}_4$	2.08 ^a	38

^a No estimated standard deviations reported.

normal situation when metals are bonded to sp^2 -hybridized carbon. The former interpretation suggests that the sum of the radii of Rh(III) and $\text{C}(\text{sp}^2)$ is approximately 0.10 Å too large. We believe the latter to be the case because comparable $\text{Rh}^{\text{III}}\text{-X}$ distances for other ligands, especially $\text{Cl}^{15a,16}$ and $\text{C}(\text{sp}^3)$,^{17,18,32–38} generate a much more consistent set of bond distances when the radius of Rh(III) is assumed to be 1.33 ± 0.02 Å. For example, the $\text{Rh}^{\text{III}}\text{-C}(\text{sp}^3)$ bond distances listed in Table VII average 2.07 ± 0.02 Å and, after subtraction of the covalent radius of sp^3 -hybridized carbon (0.77 Å), predict a Rh(III) radius of 1.30 ± 0.02 Å. In support of the π -bonding argument, Mague and co-workers^{19,39} have carried out molecular orbital calculations on the $\text{RhCl}(\text{SbPh}_3)_2\text{C}_4(\text{CF}_3)_4$ and $\text{RhCl}(\text{H}_2\text{O})(\text{AsMe}_3)_2\text{C}_4(\text{CF}_3)_4$ complexes which suggest a significant π component to the Rh-C linkage. The above discussion based on an accumulation of X-ray data on similar types of Rh(III) complexes demonstrates that there is a 0.05–0.10 Å decrease in the Rh-C bond length which can be attributed to (d-p) π electron delocalization, the extent of which must be small.

The bonding within the metallocyclic unit is quite complex and can only be treated adequately by sophisticated molecular orbital techniques. In a simplified valence-bond description of the MC_3 unit, a resonance hybrid which includes five possible canonical forms (**1a-e**) must be used. Forms **1a,b** account for the d_π - p_π electron delocalization (minor) whereas forms **1c,d** account for the localized C_3 p_π - p_π delocalization (major). Form **1e** attempts to describe the trans-annular $\text{C}(1)\cdots\text{C}(1)'$ interaction.



Subsequent chemistry on the $C_3Ph_3^+PF_6^-$ salt has shown that the CO elimination is not a base-induced (Cl^-) CO elimination reaction. Moreover the loss is common to all $Rh(CO)Cl(PR_3)_2$ compounds which react (the PPh_3 complex does not react) and therefore is not an electronic effect peculiar to the PMe_2Ph complex, although a qualitative variation of the rate with the phosphine basicity (size) was noted. The blue-green oils which are isolated are believed to be the five-coordinate cations $[RhCl(PR_3)_2(C_3Ph_3)]^+$. Such differences in reactivity of the rhodium and iridium analogues of the Vaska complex must be metal centered. $Rh(III)$ complexes have a greater tendency to display pentacoordination than $Ir(III)$ does. The last step of the $C_3Ph_3^+Cl^-$ reaction is believed to be the reaction of the coordinating chloride counterion with the $[RhCl(PMe_2Ph)_2(C_3Ph_3)]^+$ cation to generate the observed octahedral $RhCl_2(PMe_2Ph)_2(C_3Ph_3)$ product.

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Registry No. $RhCl_2(PMe_2Ph)_2(C_3Ph_3)$, 65849-05-0; $RhCl_2(PPh_2Me)_2(C_3Ph_7)$, 68782-41-2; $RhCl_2(PMe_3)_2(C_3Ph_3)$, 68782-42-3; $Rh(CO)Cl(PMe_2Ph)_2$, 36713-96-9; $Rh(CO)Cl(PPh_2Me)_2$, 52611-29-7; $Rh(CO)Cl(PMe_3)_2$, 36713-95-8; $C_3Ph_3^+Cl^-$, 58090-78-1; $C_3Ph_3^+PF_6^-$, 42134-08-7.

Supplementary Material Available: A table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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