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Crystal and Molecular Structure of Dinitrosylbis(triphenylphosphine)rhodium Perchlorate, $[Rh(NO)_2(P(C_6H_5)_3)_2][ClO_4]$

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The structure of dinitrosylbis(triphenylphosphine)rhodium perchlorate, $[Rh(NO)_2(P(C_6H_5)_3)_2][ClO_4]$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the space group $C2/c$ of the monoclinic system with four molecules in a unit cell of dimensions $a = 17.134$ (4) Å, $b = 12.327$ (3) Å, $c = 17.166$ (4) Å, and $\beta = 108.17$ (2)°. The observed and calculated densities are 1.55 (3) and 1.52 g cm^{-3}, respectively. Least-squares refinement of the structure has led to a value of the conventional R index (on F) of 0.061 for the 4649 independent reflections having $F_o^2 > 3\sigma(F_o^2)$. The crystal structure consists of well-separated, discrete, monomeric ions. The coordination geometry around the rhodium atom is best described as intermediate between tetrahedral and square planar; N–Rh–N = 157.5 (3) and P–Rh–P = 115.88 (5)°. The Rh–N–O angle is 158.9 (4)°. The dihedral angle between the N–Rh–N and P–Rh–P planes is 86.0 (1)°. The structure is compared with those of other isoelectronic $M(NO)_2(PPh_3)_2$ complexes, and trends in structure and activity as catalysts for the reaction $2NO + CO \rightarrow N_2O + CO_2$ are correlated.

Introduction

Complexes of the form $M(NO)_2P_2$, in which M is Fe, Ru, Os, Co^+, Rh^+, or Ir^+ and P is a phosphine, are of both structural and catalytic interest. Details of the geometrical structures may provide information about the electronic structures of the complexes and the ability of NO to act as a Lewis acid (NO^-) or a Lewis base (NO^+) on coordination. Several structures of $M(NO)_2(PPh_3)_2(Ph{=}C_6H_5)$ complexes have been determined: M = Fe,[1] Ru,[2,3] Os,[4] Co^+,[5] and Ir^+.[6] Certain of these complexes have been found to be catalysts for the reaction[7-10,11]

$$2NO + CO \rightarrow CO_2 + N_2O \tag{1}$$

As the structure may reflect the electronic requirements of the metal center, we sought to determine the structure of $[Rh(NO)_2(PPh_3)_2][ClO_4]$ to complete the series of isoelectronic complexes and therefore to determine whether correlations could be made between structure and catalytic activity.

Experimental Section

The title compound was prepared from $Rh(NO)(PPh_3)_3$.[12] A sample of 2.15 g of $Rh(NO)(PPh_3)_3$ was dissolved in 100 ml of argon-saturated benzene. To 10 ml of cold methanol, 0.30 ml of *tert*-butyl nitrite and 0.25 ml of 70% $HClO_4$ were added. This solution was immediately added rapidly dropwise to the well-stirred $Rh(NO)(PPh_3)_3$ solution. The resulting solution was cooled to −20° overnight. The tiny black crystals were washed with ethanol; yield 76%; ν(NO) 1759, 1714 cm^{-1} (Nujol mull). Anal. Calcd for $C_{36}H_{30}ClN_2O_6P_2Rh$: C, 54.9; H, 3.9; N, 3.6. Found: C, 54.7; H, 3.5; N, 3.4.

Suitable crystals were grown by slowly diffusing ethanol into a concentrated solution of the complex in dichloromethane. A fragment with approximate dimensions 0.30 × 0.30 × 0.57 mm was cut from one of the deep purple needles. On the basis of optical goniometry, the principal faces were identified as belonging to the forms $\{\bar{1}11\}$ and $\{101\}$. One end of the crystal was jagged and was approximated by the faces (011), (110), and (100). On the basis of Weissenberg and precession photography using Cu Kα radiation, it was established that the crystal belongs to the monoclinic system. The observed extinctions $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$ suggested the space groups $C2/c$ or Cc. By analogy to $[Ir(NO)_2(PPh_3)_2][ClO_4]$,[6] the space group was assumed to be $C2/c$. The lattice constants at 23°, which were determined from a least-squares refinement of the setting angles of 16 strong reflections which had been centered on a Picker FACS-1 diffractometer using Mo Kα radiation (λ 0.709300 Å), are $a = 17.134$ (4) Å, $b = 12.327$ (3) Å, $c = 17.166$ (4) Å, and $\beta = 108.17$ (2)°. The density calculated for four formula weights per unit cell is 1.52 g cm^{-3} which agrees well with the value of 1.55 (3) g cm^{-3} measured by suspending the crystals in a mixture of bromoform and ethanol. With four formula weights per unit cell either a twofold axis or a center of symmetry is imposed on the ions in $C2/c$.

For data collection Mo Kα radiation was used. The intensities were measured by the θ–2θ technique at a takeoff angle of 2°. At this angle the intensity of a reflection was about 90% of the maximum value

Table I. Positional, Thermal, and Group Parameters for $[Rh(NO)_2(PPh_3)_2][ClO_4]$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	0	0.02667 (3)[b]	1/4	0.00281 (2)	0.00475 (3)	0.00301 (2)	0	0.00038 (1)	0
P	0.10008 (5)	0.12806 (8)	0.34825 (6)	0.00261 (3)	0.00504 (6)	0.00276 (3)	0.00000 (3)	0.00084 (3)	−0.00023 (3)
N	0.0568 (3)	−0.0021 (4)	0.1789 (3)	0.0038 (2)	0.0095 (3)	0.0042 (2)	0.0013 (2)	0.0008 (1)	−0.0018 (2)
O	0.0904 (3)	0.0136 (5)	0.1310 (3)	0.0061 (2)	0.0213 (6)	0.0060 (3)	0.0014 (3)	0.0032 (2)	−0.0022 (3)
Cl	1/2	0.1226 (2)	1/4	0.00508 (9)	0.0191 (3)	0.00336 (7)	0	0.00121 (6)	0
OP1	0.4465 (5)	0.189 (1)	0.1993 (6)	0.0119 (6)	0.072 (3)	0.0134 (6)	0.014 (1)	0.0034 (5)	0.008 (1)
OP2	0.4643 (9)	0.073 (1)	0.2961 (6)	0.044 (2)	0.037 (2)	0.0126 (6)	−0.027 (2)	0.0181 (9)	−0.0104 (8)

Group	x_c[c]	y_c	z_c	δ	ϵ	η
R1	0.2062 (1)	0.2831 (2)	0.2702 (1)	0.433 (2)	0.456 (2)	−2.385 (2)
R2	0.2287 (1)	−0.0262 (1)	0.4760 (1)	2.295 (2)	0.186 (2)	0.551 (2)
R3	0.0273 (1)	0.2712 (2)	0.4654 (1)	0.956 (2)	−0.703 (2)	1.810 (2)

[a] The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. [b] Standard deviations of the least significant figures are given in parentheses here and in subsequent tables. [c] x_c, y_c, z_c are fractional coordinates of the rigid group centers. The angles δ, ϵ, and η have been defined previously.[16]

as a function of takeoff angle. A receiving counter aperture 5 mm high and 2 mm wide was used and was positioned 35 cm from the crystal. Symmetric scans in 2θ were used, 0.9° on each side of the $K\alpha_1$ peak. Stationary-counter, stationary-crystal background counts of 10 sec were measured at the beginning and end of each scan. Attenuators were inserted automatically if the intensity of the diffracted beam exceeded about 7000 counts/sec.

The unique data set having $2\theta < 64°$ was gathered; the intensities of 6624 reflections were recorded. The intensities of six standard reflections, measured after every 100 reflections, remained essentially constant throughout data collection.

All data processing was carried out as previously described.[13] The value of p was selected as 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects. Of the 6624 reflections, 864 had intensities which were less than their standard deviations. The linear absorption coefficient, μ, for this compound using Mo $K\alpha$ radiation is 7.03 cm^{-1}. For the data crystal trial calculations showed that the transmission coefficients ranged from 0.820 to 0.841 and therefore no absorption correction was deemed necessary.

Solution and Refinement

Among inner reflections, 213 Friedel pairs were measured and upon comparison were found to deviate from their averages by 1.1%. This supports our assumption of the centrosymmetric space group $C2/c$. The positions of the metal and phosphorus atoms were assumed to be the same as those in $[Ir(NO)_2(PPh_3)_2][ClO_4]$. The position of the rhodium atom at 0, y, 1/4 requires that twofold symmetry be imposed on the cation. A least-squares refinement on F using 2104 inner data was computed[14] and the function $\sum w(|F_o| - |F_c|)^2$ was minimized, in which $w = 4F_o^2/\sigma^2(F_o^2)$ and $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. Values of the atomic scattering factors and anomalous terms were taken from the usual sources.[15] Only the positional parameters of the Rh and P were varied, and the refinement gave the agreement indices $R_1 = 0.66$ and $R_2 = 0.71$, where $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$.

Subsequent difference Fourier syntheses revealed the positions of all nonhydrogen atoms. The nonphenyl atoms were refined anisotropically; the phenyl rings were treated as rigid groups[16] and restricted to their known geometry ($6/mmm$ symmetry, d (C–C) = 1.390 Å). The variable parameters for the rings included the coordinates of the ring center and three orientation angles. Each ring carbon atom was assigned an individual isotropic thermal parameter. Four cycles of refinement gave $R_1 = 0.067$ and $R_2 = 0.102$. A difference Fourier map revealed the positions of all 15 unique hydrogen atoms, confirming our choice of space group. They were included in later structure factor calculations in calculated positions (d(C–H) = 0.95 Å) which were not refined. The perchlorate oxygen atoms were refined anisotropically, as no good model for their probable disorder could be found.

The final refinement, using the complete data set (4649 observed unique reflections for which $F_o^2 > 3\sigma(F_o^2)$), resulted in $R_1 = 0.061$ and $R_2 = 0.090$. Agreement of $|F_o|$ and $|F_c|$ is poorest for relatively weak, low-angle reflections. Presumably our model of the perchlorate anion is not completely satisfactory. The highest peak in a final difference Fourier map was 0.61 e Å^{-3}, near an oxygen atom of the perchlorate anion. The error of an observation of unit weight is 2.94 electrons.

The positional, thermal, and group parameters derived from the last cycle of least-squares refinement are given in Table I, along with the standard deviations estimated from the inverse matrix. The positional parameters of the ring carbon atoms which may be derived from the data in Table I are presented in Table II together with thermal parameters as obtained from the last cycle of refinement. The final values of $10|F_o|$ and $10|F_c|$ in electrons are given in Table III;[17] only the 4649 reflections which were used in the refinements are listed in this table. Among those 1622 unique reflections omitted from the refinements because $F_o^2 < 3\sigma(F_o^2)$, $|F_o^2 - F_c^2|$ was greater than $3\sigma(F_o^2)$ for 31 of them and was greater than $5\sigma(F_o^2)$ for 4 of them. Table IV presents the root-mean-square amplitudes of vibration.

Table II. Derived Parameters for Ring Carbon Atoms[a]

Atom	x	y	z	B, Å^2
C1R1	0.1604 (2)	0.2174 (2)	0.3106 (2)	3.19 (6)
C2R1	0.2112 (2)	0.1702 (2)	0.2659 (2)	4.33 (8)
C3R1	0.2571 (2)	0.2360 (3)	0.2299 (2)	4.98 (9)
C4R1	0.2519 (2)	0.3488 (2)	0.2343 (2)	5.6 (1)
C5R1	0.2011 (2)	0.3960 (2)	0.2746 (2)	6.0 (1)
C6R1	0.1553 (2)	0.3302 (2)	0.3105 (2)	4.54 (8)
C1R2	0.1740 (1)	0.0388 (2)	0.4171 (2)	3.32 (6)
C2R2	0.2560 (2)	0.0702 (2)	0.4505 (2)	4.15 (7)
C3R2	0.3107 (1)	0.0051 (2)	0.5095 (2)	5.2 (1)
C4R2	0.2833 (2)	−0.0912 (2)	0.5349 (2)	5.04 (9)
C5R2	0.2013 (2)	−0.1226 (2)	0.5016 (2)	5.2 (1)
C6R2	0.1466 (1)	−0.0576 (2)	0.4426 (2)	4.36 (8)
C1R3	0.0597 (2)	0.2082 (2)	0.4152 (1)	3.21 (6)
C2R3	0.0899 (2)	0.1965 (2)	0.5003 (2)	4.16 (8)
C3R3	0.0575 (2)	0.2595 (3)	0.5506 (1)	5.10 (9)
C4R3	−0.0050 (2)	0.3341 (2)	0.5157 (2)	5.11 (9)
C5R3	−0.0352 (2)	0.3459 (2)	0.4306 (2)	5.1 (1)
C6R3	−0.0028 (2)	0.2828 (2)	0.3803 (1)	4.33 (8)

[a] C1 is attached to P; other C atoms are numbered in succession so that C4 is para to C1.

Table IV. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Intermed	Max
Rh	0.1833 (6)	0.1912 (6)	0.2228 (6)
P	0.187 (1)	0.189 (1)	0.202 (1)
N	0.202 (3)	0.223 (5)	0.308 (5)
O	0.214 (5)	0.309 (5)	0.416 (6)
Cl	0.212 (2)	0.264 (2)	0.383 (2)
OP1	0.332 (9)	0.430 (10)	0.776 (16)
OP2	0.272 (8)	0.356 (9)	0.870 (18)

Description of the Structure and Discussion

The crystal structure consists of discrete monomeric ions, nearly identical with the iridium analogue,[6] with the cation and anion on twofold axes of symmetry. The inner coordination geometry of the cation is shown in Figure 1, and a view of the asymmetric unit, in Figure 2.

A selection of distances and angles is given in Table V. The structure is severely distorted from the ideal tetrahedral geometry and is best described as intermediate between tetrahedral and square planar. Crystal packing is naturally dominated by the bulky triphenylphosphine groups, leaving

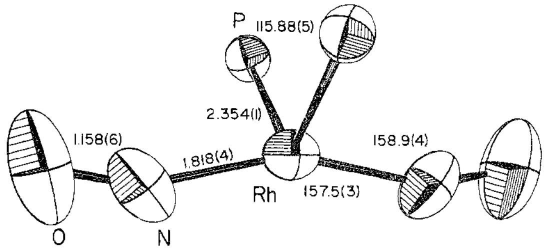

Figure 1. A perspective view of the coordination geometry about the rhodium atom. The view is approximately along the *x* axis. The shapes of the atoms in this and the following drawing represent 50% probability contours of thermal motion.

Table V. Selected Distances and Angles[a]

	Cation Intramolecular Dist, Å		
Rh-P	2.355 (1)	P-C1R2	1.811 (2)
Rh-N	1.818 (4)	P-C1R3	1.809 (3)
Rh-O	2.928 (4)	Rh-H(H6R3)	3.55
P-N	3.199 (4)	Rh-H(H6R2)	3.13
P-N′	3.040 (4)	N-H(H2R1)	2.87
N-N′	3.566 (9)	N-H(H6R2)′	2.74
N-O	1.158 (6)	O-H(H2R1)	2.73
P-P′	3.991 (2)	O-H(H6R2)′	3.17
P-C1R1	1.809 (3)		
	Intermolecular Dist, Å		
N-H(H4R1)	3.09	O-H(H2R3)	2.93
	Anion Dist, Å		
Cl-OP1	1.33 (1)	Cl-OP2	1.30 (1)
	Cation Angle, Deg		
P-Rh-P′	115.88 (5)	Rh-P-C1R1	114.6 (1)
P-Rh-N	99.3 (1)	Rh-P-C1R2	110.5 (1)
P-Rh-N′	92.6 (1)	Rh-P-C1R3	114.0 (1)
Rh-N-O	158.9 (4)	C1R1-P-C1R2	105.1 (1)
N-Rh-N′	157.5 (3)	C1R1-P-C1R3	107.5 (1)
P-Rh-O	95.9 (1)	C1R2-P-C1R3	104.2 (1)
P-Rh-O′	87.4 (1)		
Dihedral Angle between P-Rh-P′ and N-Rh-N′			86.0 (1)°
	Anion Angle, Deg		
OP1-Cl-OP2	109.3 (9)	Op1-Cl-OP2′	104.6 (6)
OP1-Cl-OP1′	104.1 (13)	OP2-Cl-OP2′	123.4 (12)

[a] X and X′ represent atoms related by the twofold axis.

the Rh atom fairly accessible. The nonbonded contacts near the rhodium atom are not particularly short, suggesting little tendency to fill a vacant coordination site.

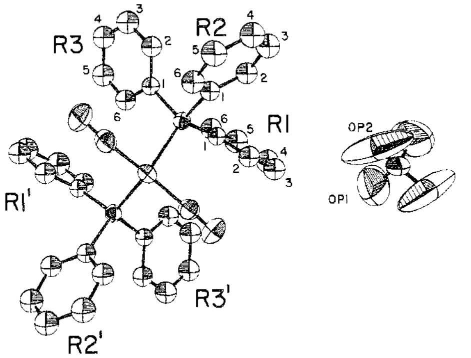

Figure 2. A perspective view of the asymmetric unit. The view is approximately along the *y* axis.

Interesting and fruitful comparisons can be made between this structure and that of the analogous Ir complex.[6] The M–N and M–P bonds are longer in the Rh complex: 1.818 (4) and 2.354 (1) Å vs. 1.771 (12) and 2.339 (3) Å for M = Ir. The N–M–N angles are 157.5 (3) and 154.2 (7)°, respectively, for Rh and Ir. The nitrosyl groups are less linear in the Rh complex (M–N–O = 158.9 (4)°, vs. 163.5 (10)° for the Ir analog). Nonbonded intramolecular contacts near the metal are generally larger in the Rh complex: Rh–H6R2 = 3.13 and Ir–H6R2 = 3.08 Å, N–H2R1(Rh) = 2.87 and N–H2R1(Ir) = 2.80 Å, N–H6R2′(Rh) = 2.74 and N–H6R2′(Ir) = 2.61 Å, O–H2R1(Rh) = 2.73 and O–H2R1(Ir) = 2.67 Å, O–H6R2′(Rh) = 3.16 and O–H6R2′(Ir) = 3.02 Å. Intermolecular contacts follow the same pattern: N–H4R1(Rh) = 3.09 and N–H4R1(Ir) = 3.04 Å, O–H2R3(Rh) = 2.93 and O–H2R3(Ir) = 2.79 Å. Since the two crystal structures are nearly identical and the packing must be dominated by the triphenylphosphine groups, we attribute these differences around the metal centers to the electronic differences between Rh and Ir. The greater bending of the nitrosyl groups and the longer M–N bonds in the rhodium complex indicate a greater amount of NO^- character. The larger N–M–N angle supports this picture. These facts, plus the larger distortion from tetrahedral geometry and the longer nonbonded contacts show that in this environment a rhodium atom shows less tendency to accept electrons (or a greater tendency to donate electrons to ligands) than does an iridium atom. This differs from the usual (and intuitive) picture in which an iridium atom should be more electron rich. The M–P distances are consistent with this usual picture. Though the errors associated with the nitrosyl parameters in these two structures are relatively large and the differences in structural parameters are on the order of a few standard deviations, we believe that these differences are real because of the chemical behavior of these two complexes.

Table VI presents selected structural parameters for the several isoelectronic $M(NO)_2(PPh_3)_2$ complexes whose structures have been determined. The trend in M–N–O angles is approximately Rh < Ir < Co < Ru, Os < Fe; the opposite ordering is observed for the N–M–N angles. The relative activity of these complexes as catalysts for reaction 1 is Rh

Table VI. Selected Structural Parameters of $M(NO)_2(PPh_3)_2$ Complexes

M	M–P, Å	M–N, Å	N–O, Å	P–M–P, deg	N–M–N, deg	M–N–O, deg	ν(NO), cm^{-1}
Fe[a,b]	2.267 (2)	1.650 (7)	1.190 (10)	111.9 (1)	123.8 (4)	178.2 (7)	1723 1679 (CCl_4)
Ru[c]	2.337 (2) 2.353 (2)	1.762 (6) 1.776 (6)	1.190 (7) 1.194 (7)	103.85 (6)	139.2 (3)	177.7 (6) 170.6 (5)	1665 1615 (Nujol)
Ru[d]	2.332 (9) 2.346 (9)	1.748 (20) 1.688 (20)	1.215 (18) 1.229 (18)	105.5 (2)	139.9 (8)	174.7 (17) 168.0 (16)	
Os[e]	2.324 (2) 2.340 (2)	1.771 (6) 1.776 (7)	1.195 (8) 1.211 (7)	103.51 (6)	139.1 (3)	178.7 (7) 174.0 (6)	1645 1597
Co^+ [f]	2.282 (5) 2.273 (5)	1.663 (5) 1.664 (5)	1.157 (5) 1.156 (5)	106.7	132.4	170.9 171.2	1836 1784 (Nujol)
Rh^+ [a,g]	2.354 (1)	1.818 (4)	1.158 (6)	115.88 (5)	157.5 (3)	158.9 (4)	1759 1714 (Nujol)
Ir^+ [a,h]	2.339 (3)	1.771 (12)	1.213 (13)	116.3 (2)	154.2 (7)	163.5 (10)	1760 1715 (Nujol)

[a] Crystallographically imposed twofold symmetry. [b] Reference 1. [c] Reference 2. The crystal contains half a benzene molecule of solvation per formula unit. [d] Reference 3. [e] Reference 4. [f] Reference 5. [g] This work. [h] Reference 6.

> Ir > Co > Ru, Os.[9] These observations, together with the M–N bond distances and other facts mentioned above, indicate that the most active catalysts are those metals which have the greatest tendency to back-donate electrons to the ligands. This electron transfer would tend to make the presumed five-coordinate catalytic intermediates[9,10] more reactive and could provide the driving force for the coupling of the nitrosyl groups, thus increasing catalytic activity. Back-donation into NO π^* orbitals should also make the oxygen transfer in reaction 1 more facile.

We believe that the structural differences observed in this series of complexes primarily result from the different electronic requirements of the metals, as the packing forces around the metal atoms should be very similar. The structural trends are consistent with the observed catalytic behavior and may provide some help in elucidating a mechanism for the catalysis of reaction 1 by systems containing these complexes.

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Registry No. $[Rh(NO)_2(P(C_6H_5)_3)_2][ClO_4]$, 47841-81-6; $Rh(NO)(PPh_3)_3$, 21558-94-1.

Supplementary Material Available. Table III, the structure amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC504584-12-75.

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A Fumaronitrile Complex of Rhodium(I). Structure of Iodo(fumaronitrile)(triphenyl phosphite)bis(*p*-methoxyphenyl isocyanide)rhodium(I), $RhI(\textit{trans}\text{-}H(NC)C{=}C(CN)H)(P(OC_6H_5)_3)(p\text{-}CH_3OC_6H_4NC)_2$

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The solid-state structure of the title complex which exhibits dynamic solution behavior has been determined from three-dimensional X-ray data collected by counter techniques. The material crystallizes in space group C_{2h}^5-$P2_1/c$ of the monoclinic system with four molecules of the complex in the unit cell. Crystal data are a = 15.252 (7) Å, b = 11.454 (6) Å, c = 21.933 (11) Å, β = 103.62 (2)°, and V = 3723.7 Å^3. The observed and calculated (Z = 4) densities are 1.57 (2) and 1.577 g/cm^3, respectively. The structure, including the H atoms of the fumaronitrile ligand, has been refined (on F) by a full-matrix least-squares procedure to a conventional agreement index of 0.040 for 4357 observations having $F_o^2 > 3\sigma(F_o^2)$. The structural results reveal trigonal-bipyramidal coordination about the Rh atom with trans-axial isocyanide ligands (C–Rh–C = 177.7 (2)°) situated at 1.964 Å (average) from the metal. The equatorial plane contains an iodo, a triphenyl phosphite, and a symmetrically π-bonded fumaronitrile ligand. The olefinic carbon atoms lie almost exactly in the plane defined by Rh, I, and P (average deviation 0.05 Å) and are equidistant from the metal: Rh–C = 2.139 Å (average). The distance from the Rh atom to the midpoint of the olefinic bond (Ct) is 2.013 Å. There is considerable angular distortion in the equatorial plane: I–Rh–P = 102.37 (5)°, I–Rh–Ct = 118.9 (2)°, and P–Rh–Ct = 138.7 (2)°. The distortions within the olefin are about as expected: the olefinic C–C distance is 1.444 (10) Å and the substituents are bent back and away from the metal center by 28° (average). Other distances of interest are Rh–P = 2.265 (2) Å and Rh–I = 2.739 (2) Å. The implications of the solid-state structure on the interpretation of the dynamic solution behavior of this and related complexes are discussed.

Introduction

Solid-state structures of isolable transition metal–olefin complexes are useful models for the interaction of the olefinic bond with transition metals in homogenously catalytic reactions. Spectroscopic studies of the various dynamical processes that certain of such complexes undergo in solution provide valuable insight into the possibly facile and important rearrangements that occur during such reactions. Generally these isolable complexes contain olefins substituted with various electron-withdrawing groups, such as halogen or cyanide. As a result the determination by X-ray diffraction of the metrical details of the metal–olefin interaction is facilitated. In addition the activated olefinic systems are of intrinsic interest because they occasionally mimic the catalytically induced hydrogenation of simple olefins.[1]

Over the past decade a large number of accurate transition metal–olefin structures have been reported. In particular, those of d^8 metals in complexes containing monodentate ligands have