$(as_3)_2]BPh_4$, has also shown the presence of three hydridic hydrogen atoms and a similar molecular geometry to the iron compound is suggested. Furthermore the strict geometrical similarity of the cobalt and arsenic atoms in this structure (Figure 3) to the iron and phosphorus atoms in the preceding structure suggests that in the cobalt compound there are also three bridging hydridic hydrogen atoms to complete a confacial-bioctahedral geometry. Also for this structure at this point of refinement (R = 8.2%) a ΔF Fourier synthesis was calculated. This map revealed three maxima with intensity of about 0.5 e/Å^3 in the expected positions. A ΔF Fourier, limited to the reflections having $(\sin\theta)/\lambda \leq 0.30$ Å^{-1}, confirmed the presence of these three peaks which then were considered hydrogen atoms. A least-squares refinement of these atoms resulted in a certain shift in their positions and furthermore yielded temperature factors rather high. However there was not any divergence during this refinement. Also in this case the positions obtained from the ΔF Fourier synthesis showed a more regular geometry and appeared more realistic. For this reason in the final structure factor calculation the three hydrogen atoms were introduced into the positions obtained from the ΔF Fourier and assigned an overall isotropic temperature factor, B, equal to 5 Å^2. The final R factor is 8.2%. Tables VI and VII give the final positional and thermal parameters of the atoms of the complex. Table VI also includes the refined parameters of the bridging hydrogen atoms.

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Registry No. $[Fe_2H_3(p_3)_2]PF_6\cdot1.5CH_2Cl_2$, 54003-33-7; $[Fe_2H_3(p_3)_2]BPh_4$, 41517-54-8; $[Co_2H_3(p_3)_2]BPh_4$, 54003-35-9; $[Co_2H_3(as_3)_2]BPh_4$, 54036-76-9; $[Co(p_3)(CO)_2]BPh_4$, 54003-37-1; $[Co(as_3)(CO)_2]BPh_4$, 54003-39-3.

Supplementary Material Available. Listings of structure factor amplitudes for $[Fe_2H_3(p_3)_2]PF_6\cdot1.5CH_2Cl_2$ and $[Co_2H_3(as_3)_2]BPh_4$ 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 the papers in this issue may be obtained from the Journals Department, 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 AIC405774.

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Crystal and Molecular Structure of Dichloronitrosylbis(triphenylphosphine)rhodium, $RhCl_2(NO)(P(C_6H_5)_3)_2$

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The structure of dichloronitrosylbis(triphenylphosphine)rhodium, $RhCl_2(NO)(P(C_6H_5)_3)_2$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the monoclinic space group $I2/c$ with four molecules in a unit cell of dimensions a = 22.019 (4) Å, b = 9.604 (2) Å, c = 15.854 (2) Å, β = 104.57 (1)°. Least-squares refinement of the structure converged to values of 0.0514 and 0.0569 for the unweighted and weighted discrepancy indices. The structure consists of discrete monomeric units. The molecular geometry is that of a distorted square pyramid with a bent nitrosyl in the apical position. A crystallographically imposed twofold axis passes through the molecule and requires a disorder of the nitrosyl ligand. In treating the disorder the N–O distance is constrained to be 1.15 Å. Other important distances are Rh–N = 1.912 (10) Å, Rh–Cl = 2.3439 (14) Å, and Rh–P = 2.3672 (13) Å. The Rh–N–O angle is 124.8 (16)° and the direction of the bend is such that the planes defined by Rh, N, O and P, Rh, P' form a dihedral angle of 10.3 (29)°.

Introduction

In the course of our studies[1] on the metal-catalyzed reduction of NO by CO it became clear that the isolation and identification of catalytically active intermediates would be exceedingly useful in elucidating the manner in which this reaction proceeds. With this aim in mind, we isolated a red-orange material via the addition of triphenylphosphine to the green catalytically active solution obtained when an ethanolic solution of $Rh(CO)_2Cl_2^-$ is exposed to an atmosphere of CO and NO for a period of several hours.[1]

The infrared spectrum of the material, both before and after recrystallization, showed bands at 1940 and 1630 cm^{-1} which strongly suggested that it was a triphenylphosphine-stabilized carbonyl–nitrosyl complex corresponding to one of the desired catalytic intermediates. An X-ray structural investigation was therefore carried out to identify unambiguously the nature of this material and to establish its detailed geometry. Only after we were well into the refinement stages of the complete structure determination, did it become clear that the material isolated from solution was not the hoped for carbonyl–nitrosyl species but rather dichloronitrosylbis(triphenylphosphine)-rhodium, $RhCl_2(NO)(P(C_6H_5)_3)_2$.

We report herein the structure determination of this complex because of (a) the continuing interest in metal–nitrosyl bonding including the development of predictive capabilities in molecular orbital treatments of these systems[2-5] and (b) the highly significant structural differences between $CoCl_2(NO)(PMePh_2)_2$[6] and $IrCl_2(NO)(PPh_3)_2$,[7] the former of which is a distorted trigonal bipyramid with an equatorial nitrosyl while the latter is a square pyramid with a bent apical nitrosyl. The complex $RhCl_2(NO)(PPh_3)_2$ is the third and missing member in this series of group 8 nitrosyl complexes of formula $MX_2(NO)L_2$.

Experimental Section

Synthesis of the $RhCl_2(NO)(P(C_6H_5)_3)_2$ Complex. As was noted above, the complex $RhCl_2(NO)(P(C_6H_5)_3)_2$ was prepared inadvertently through the addition of triphenylphosphine to the catalytically active solution formed when $RhCl_2(CO)_2^-$ in ethanol is placed under a CO–NO atmosphere.[1] In a typical experiment, 0.307 g (0.5 mmol) of $[As(C_6H_5)_4][RhCl_2(CO_2)]$ is placed in a 3-l. flask, dissolved in 50 ml of ethanol containing 2 ml of concentrated HCl and the system evacuated. Carbon monoxide and nitric oxide are then added in a 3:4 ratio to give a total system pressure of 620 Torr. The solution is stirred for several hours during which time it changes in color from yellow to green and the evolution of N_2O and CO_2 is observed.[1] Addition of 0.75 g of $P(C_6H_5)_3$ dissolved in ca. 10 ml of ethanol leads to immediate precipitation of an orange solid which was filtered, washed with ether, and vacuum-dried. The ir spectrum of this crude product shows bands at 1940 and 1630 cm^{-1} assigned to ν_{CO} and ν_{NO}, respectively, as well as a less intense carbonyl absorption at 1960 cm^{-1} readily assigned to $RhCl(CO)(P(C_6H_5)_3)_2$.[8]

The recrystallized material, which appeared homogeneous to visual inspection, also exhibited bands at 1940 and 1630 cm^{-1}. The absence of the carbonyl absorption at 1960 cm^{-1} indicated complete removal of $RhCl(CO)(P(C_6H_5)_3)_2$ upon recrystallization. Subsequent to the structural study, a sample of the recrystallized material was washed with methylene chloride, leading to a change in the relative intensities of the bands at 1940 and 1630 cm^{-1}, thus establishing that this material was in fact a mixture. This was confirmed by TLC methods using methylene chloride, which also showed definitively that the compound with ν_{CO} of 1940 cm^{-1} was not $RhCl(CO)(P(C_6H_5)_3)_2$. With the exception of the band at 1940 cm^{-1}, the ir spectrum of the recrystallized material is superimposable with that of an authentic sample of $RhCl_2(NO)(P(C_6H_5)_3)_2$ prepared as by Collman and coworkers.[9]

The sample was sent for analysis (to Micro-analysis, Inc., Wilmington, Del.), and simultaneously X-ray work was begun. By the time the analytical results were received 9 days later, the structural analysis described below was essentially complete. This report is thus another example of the utility of X-ray structure determination as a method for material characterization.

Anal. Calcd for $RhCl_2(NO)(P(C_6H_5)_3)_2$: C, 59.36; H, 4.15; Cl, 9.73; N, 1.92; O, 2.20. Found for mixture: C, 60.72; H, 4.51; Cl, 8.73; N, 1.99; O, 2.67.

Data Collection and Reduction. Small orange crystals of $RhCl_2(NO)(P(C_6H_5)_3)_2$ were obtained as above. On the basis of Weissenberg and precession photographs it was established that the crystals belong to the monoclinic system. The observed systematic absences of $h + k + l = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$ are consistent with the space groups $I2/c$ (C_{2h}^6) and Ic (C_s^4) which are nonstandard settings for $C2/c$ and Cc, respectively.[10] The lattice constants at 22° were determined from a least-squares refinement of the setting angles of 12 high-angle reflections ($(\sin \theta)/\lambda \geq 0.394$).[11] The reflections were carefully centered, using Mo $K\alpha_1$ radiation (λ 0.709261 Å), on a Picker FACS-1 diffractometer equipped with a graphite monochromator. The lattice constants are $a = 22.019$ (4) Å, $b = 9.604$ (2) Å, $c = 15.854$ (2) Å, and $\beta = 104.57$ (1)°. The density calculated for four molecules per unit cell is 1.49 g/cm^3, which agrees with an experimentally determined value of 1.48 (1) g/cm^3 using the flotation method.

The mosaicity of the crystal was examined by means of the narrow-source, open-counter ω-scan technique.[12] The full widths at half-maximum for typical strong reflections were 0.05–0.06°. The crystal dimensions were approximately 0.22 × 0.19 × 0.16 mm and the crystal was mounted with the b^* axis offset 6° from the ϕ axis of the diffractometer.

Intensities were measured by the θ–2θ scan technique. The takeoff angle for the X-ray tube was 1.5°. At this angle the intensity of a reflection was roughly 80% of its maximum as a function of takeoff angle. The scan was from 0.7° below the $K\alpha_1$ peak to 0.7° above the $K\alpha_2$ peak. The scan rate was 2°/min and backgrounds were counted for 10 sec at each end of the scan. Attenuator foils were automatically inserted when the intensity of the diffracted beam reached 10000 counts/sec. The pulse height analyzer was set for a 90% window centered on Mo $K\alpha$ radiation.

Data were collected in the range $3° \leq 2\theta \leq 55°$. The quadrant with $h \geq 0$, $k \geq 0$ was collected. Three standard reflections were monitored every 100 observations. The intensities of the standards varied by less than ±1% throughout the data collection. A total of 4080 reflections allowed by the centering condition were observed. The values of $\sigma^2(I)$ were estimated using the expression

$$\sigma^2(I) = q\{10\text{CT} + 12.75 + [(t_c/2t_b)^2(10(\text{BL} + \text{BH}) + 25.5)]\} + (pI)^2$$

where q is the attenuator factor, t_c is the scan time, t_b is the time spent counting background at each end of the scan, and CT, BL, and BH are the counts for the scan and the low and high backgrounds, respectively. The numerical factors arise from the fact that CT, BL, and BH are truncated values obtained from the Picker instrument rather than actual counts.[13] The intensity, I, is given by

$$I = q\{10\text{CT} + 4.5 - [(t_c/2t_b)(10(\text{BL} + \text{BH}) + 9)]\}$$

The term $(pI)^2$ is included in the expression for the variance to prevent the overweighting of strong reflections,[14] and the value of p was chosen as 0.03. Values of I and $\sigma^2(I)$ were converted to F^2 and $\sigma^2(F^2)$ by application of Lorentz and polarization corrections.

Of the 224 reflections systematically absent as a result of the c glide all had $F^2 < 3\sigma(F^2)$ and only five had $F^2 > 2\sigma(F^2)$. The absorption coefficient for Mo$K\bar{\alpha}$ radiation is 8.06 cm^{-1} and no correction for absorption was made. On the assumption that the correct space group is $I2/c$ equivalent reflections were averaged. The R factor for averaging was 1.5% for the 98 reflections observed twice. The final data set consisted of 3758 independent reflections of which 2598 had $F^2 \geq 3\sigma(F^2)$.

Solution and Refinement of the Structure. In the space group $I2/c$ the general eightfold positions are $(0, 0, 0; {}^1/_2, {}^1/_2, {}^1/_2) \pm (x, y, z; x, \bar{y}, {}^1/_2 + z)$. The position of the rhodium atom was determined from a three-dimensional Patterson map.[15] The metal atom position was consistent with its being on a twofold axis in space group $I2/c$ or at a general position in Ic. The Patterson map also provided indications for the location of the chlorine and phosphorus atoms. Refinement of the scale factor, metal positional coordinates, and an isotropic temperature factor resulted in residuals of $R_1 = 0.43$, $R_2 = 0.47$.[16] In this and all subsequent refinements the quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where the weights, w, were taken as $4F^2/\sigma^2(F^2)$. Only those reflections with $F^2 \geq 3\sigma(F^2)$ were included in the refinements. Scattering factors for neutral Rh, Cl, P, C, N, and O were those of Cromer and Mann.[17] The scattering factors for hydrogen were those of Stewart et al.[18] The effects of anomolous dispersion were included in the calculation of $|F_c|$; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer and Liberman.[19]

A difference Fourier phased by the Rh revealed the position of the chlorine and phosphorus atoms as well as those of several phenyl carbons. Two cycles of refinement followed by difference Fouriers revealed the remaining atoms of the structure. The phenyl rings were treated as rigid groups[20] with $d(\text{C–C}) = 1.392$ Å. Although the nitrosyl N atom appeared to be slightly off the twofold axis, it was

Table I. Positional, Thermal, and Group Parameters for $RhCl_2(NO)(P(C_6H_5)_3)_2$

Atom	x	y	z	β_{11}[a,b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	0	0.20942 (6)[c]	1/4	12.61 (13)	55.3 (7)	21.49 (25)	0	4.41 (13)	0
Cl	0.05405 (7)	0.15995 (16)	0.14366 (9)	18.5 (4)	120.2 (20)	39.2 (7)	0.7 (6)	8.5 (4)	−17.1 (9)
P	0.09455 (6)	0.18723 (13)	0.36026 (8)	13.3 (3)	63.0 (16)	22.4 (6)	−2.9 (5)	3.4 (3)	0.3 (7)
N	−0.0051 (14)[d]	0.4075 (10)	0.2381 (17)	37 (6)	72 (12)	48 (10)	8 (9)	19 (4)	24 (13)
O	0.0262 (5)[d]	0.4852 (10)	0.2848 (6)	33 (3)	85 (12)	67 (6)	−8 (5)	7 (3)	−12 (7)

Group	x_c[e]	y_c	z_c	δ	ϵ	η
NO	0.0262 (5)	0.4852 (10)	0.2848 (6)	2.412 (26)	2.63 (4)	0
Ph1	0.08797 (10)	0.29423 (26)	0.55006 (16)	0.1156 (25)	2.7773 (19)	1.5710 (25)
Ph2	0.21602 (11)	0.35721 (26)	0.33996 (16)	−2.147 (3)	−2.2191 (23)	−2.626 (4)
Ph3	0.12961 (12)	−0.13793 (28)	0.37145 (14)	1.7917 (22)	−2.7126 (25)	−3.1185 (25)

[a] The form of the anisotropic thermal 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] Values of the thermal parameters have been multiplied by 10^4. [c] Standard deviations of the least significant figures are given in parentheses. [d] Positional parameters derived from the group parameters for NO. [e] The parameters for refinement of a rigid group have been previously defined.[20]

initially constrained to the C_2 special position. Refinement of a model in which all atoms were treated isotropically resulted in $R_1 = 0.073$, $R_2 = 0.090$.

Since it was thought that the compound contained one Cl and one CO, a structure factor calculation was performed for a model with a 50% disorder at the Cl position. This calculation yielded values of 0.148 and 0.177 for R_1 and R_2. Furthermore, the model could not be refined.

A model which provided for anisotropic thermal motion of the nongroup atoms revealed nothing unusual in the shape of the chlorine ellipsoid; however, the nitrogen atom did show unusually large thermal motion normal to the twofold axis. The nitrosyl was then treated as a rigid group with an N–O distance of 1.15 Å. Both atoms were assigned an occupancy factor of 0.5 to account for the disorder about the twofold axis. No additional constraints were placed on the group, and both the nitrogen and oxygen atoms were refined anisotropically. Individual isotropic temperature factors were refined for each of the phenyl ring carbon atoms. In the final cycles of refinement, contributions from all of the phenyl ring hydrogen atoms, which had been located in a difference Fourier, were included based on $d(C-H) = 1.0$ Å and isotropic temperature factors which were 1 Å^2 greater than those of their respective carbon atoms. This model refined smoothly until near convergence, at which point slight oscillation in the nitrosyl thermal parameters occurred. The final values of R_1 and R_2 were 0.0514 and 0.0569, respectively. The final estimated standard deviation for an observation of unit weight[16] was 1.94. This function showed no dependence as a function of $|F_o|$ but increased for small values of $(\sin\theta)/\lambda$, possibly as a result of our model for the disorder not being completely adequate. The largest peak of a final difference Fourier was 0.52 e/Å^3 or 15% of the height of a typical carbon peak in this study.

The final positional, thermal, and group parameters are given in Table I. The derived carbon atom positions are presented in Table II. A listing of the observed and calculated structure factors is available.[21]

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

Atom	x	y	z	B, Å^2
C(11)	0.09068 (17)	0.24294 (35)	0.46897 (17)	2.57 (9)
C(12)	0.09542 (17)	0.15208 (26)	0.53874 (22)	3.22 (10)
C(13)	0.09272 (18)	0.20338 (36)	0.61983 (18)	3.87 (11)
C(14)	0.08527 (19)	0.34553 (39)	0.63116 (19)	3.99 (12)
C(15)	0.08053 (19)	0.43638 (27)	0.56139 (26)	4.93 (14)
C(16)	0.08323 (19)	0.38508 (32)	0.48029 (21)	4.51 (13)
C(21)	0.16352 (14)	0.28253 (36)	0.34774 (21)	2.64 (9)
C(22)	0.16114 (13)	0.36120 (38)	0.27324 (19)	2.89 (10)
C(23)	0.21364 (17)	0.43588 (37)	0.26545 (21)	3.51 (11)
C(24)	0.26852 (14)	0.43189 (42)	0.33218 (26)	4.40 (13)
C(25)	0.27091 (14)	0.35323 (47)	0.40668 (22)	5.17 (15)
C(26)	0.21841 (17)	0.27854 (41)	0.41447 (19)	4.31 (12)
C(31)	0.11592 (16)	0.00375 (29)	0.36851 (23)	2.48 (9)
C(32)	0.17296 (15)	−0.04208 (35)	0.35589 (24)	3.59 (11)
C(33)	0.18665 (14)	−0.18377 (39)	0.35883 (27)	4.52 (13)
C(34)	0.14331 (19)	−0.27962 (29)	0.37439 (27)	4.68 (13)
C(35)	0.08627 (17)	−0.23379 (36)	0.38701 (27)	4.99 (14)
C(36)	0.07257 (13)	−0.09210 (40)	0.38407 (25)	3.98 (12)

[a] C(*i*1) is attached to P; other carbon atoms are numbered in order so that C(*i*4) is para to C(*i*1).

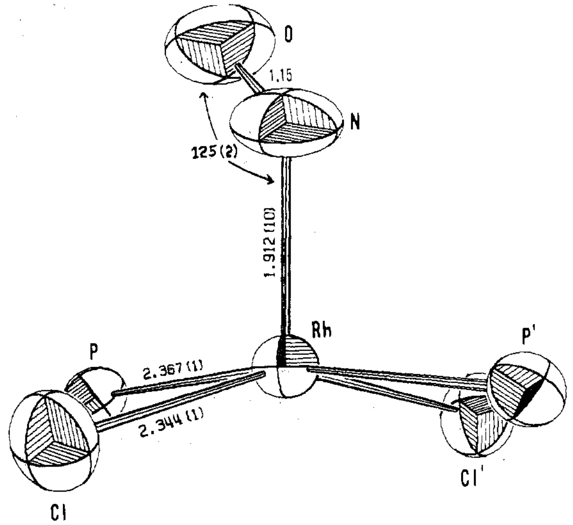

Figure 1. Inner coordination sphere of $RhCl_2(NO)(P(C_6H_5)_3)_2$. Thermal ellipsoids enclose 50% of the electron density.

Results and Description of the Structure

The title compound has been reported previously by several workers.[9,22,23] In 1962 Hieber et al.[22] isolated $RhCl_2(NO)(P(C_6H_5)_3)_2$ (in addition to $RhNO(P(C_6H_5)_3)_3$) by the addition of $P(C_6H_5)_3$ to solutions of $[RhCl(NO)_2]_x$, and the complex was later formed in an analogous manner by addition of triphenylphosphine to solutions obtained by reaction of $RhCl_3 \cdot xH_2O$ with NO.[23a] Collman and coworkers[9] have since reported the preparation of $RhCl_2(NO)(P(C_6H_5)_3)_2$ from $Rh(NO)(P(C_6H_5)_3)_3$ either by chlorination or by stoichiometric reaction with 2 equiv of dry HCl in benzene. Finally, Robinson and Uttley[23b] have developed a convenient single-step synthesis involving the successive addition of ethanolic $RhCl_3 \cdot xH_2O$ and *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide solutions to a boiling solution of triphenylphosphine in alcoholic solvent.

The structure of $RhCl_2(NO)(P(C_6H_5)_3)_2$ is isomorphous with that of the iridium analog $IrCl_2(NO)(P(C_6H_5)_3)_2$.[7] Our choice of the unit cell corresponds to an alternate setting of that chosen by Mingos and Ibers[7] (our choice of the *a* axis of the monoclinic cell corresponds to their *c*; positional parameters may be compared directly by interchanging *x* and *z*). The crystal structure consists of discrete monomeric molecules. The molecular packing is determined by the bulky phenyl groups and there are no unusual intermolecular contacts. Figures 1 and 2 show two different views of the inner coordination sphere of the molecule. The inner coordination sphere has a distorted square-pyramidal geometry. Selected distances and angles are presented in Table III. Root-mean-square amplitudes of vibration along the principal axes are given in Table IV.

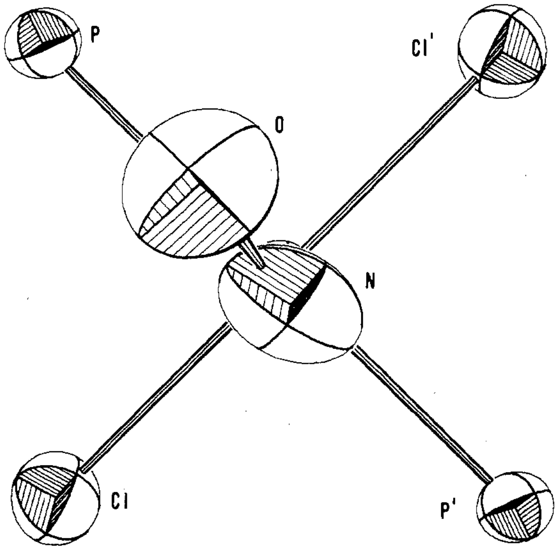

Figure 2. Inner coordination sphere of $RhCl_2(NO)(P(C_6H_5)_3)_2$ showing the direction of the Rh-N-O bend. Thermal ellipsoids enclose 50% of the electron density.

Table III. Selected Distances and Angles[a,b]

	Distance, Å		
Rh-Cl	2.3439 (14)	P-P'	4.715 (3)
Rh-P	2.3672 (13)	P-Cl	3.334 (2)
Rh-N	1.912 (10)	P-Cl'	3.267 (2)
Rh-O	2.737 (9)	Cl-Cl'	4.591 (3)
N-O	1.15[c]	P-C(11)	1.827 (3)
N-P	3.30 (2)	P-C(21)	1.826 (4)
N-P'	3.04 (2)	P-C(31)	1.820 (3)
N-Cl	3.25 (2)	P-C(av)[d]	1.824 (2)
N-Cl'	3.37 (2)		
	Angle, Deg		
N-Rh-P	100.5 (8)	Rh-N-O	124.8 (16)
N-Rh-P'	89.9 (8)	Rh-P-C(11)	115.41 (13)
N-Rh-Cl	99.1 (10)	Rh-P-C(21)	118.39 (11)
N-Rh-Cl'	104.2 (10)	Rh-P-C(31)	107.68 (11)
P-Rh-P'	169.67 (7)	C(11)-P-C(21)	101.14 (18)
P-Rh-Cl	90.09 (5)	C(11)-P-C(31)	106.75 (17)
P-Rh-Cl'	87.82 (5)	C(21)-P-C(31)	106.62 (17)
Cl-Rh-Cl'	156.61 (8)		

[a] Errors are estimated from the full variance-covariance except for values involving group atoms, in which case only the variances were used. [b] X and X' represent atoms related by the crystallographic twofold axis. [c] Value constrained in the refinement. [d] $\bar{x} = \Sigma(x_i)/n$; $\sigma(\bar{x}) = \{[\Sigma(x_i - \bar{x})^2]/n(n-1)\}^{1/2}$.

In the final model chosen the nitrogen is displaced from the twofold axis by 0.194 (25) Å. Attempted refinement of the nitrosyl N and O as independent atoms with anisotropic thermal parameters resulted in the expected shift of the nitrogen toward the twofold axis leading to a chemically unreasonable NO distance of 1.05 Å. Since there was no improvement in the discrepancy indices, the group model was retained.

Not only are the Ir and Rh compounds isomorphous, but we find the structural parameters for $RhCl_2(NO)(PPh_3)_2$ to be virtually identical with those of the Ir analog. In the iridium structure the metal–nitrogen distance and metal–nitrogen–oxygen angle are 1.94 (2) Å and 123.4 (20)°, respectively,[7] compared with the values of 1.912 (10) Å and 124.8 (16)° in the present study. The Co analog, however, is rather different from the other two members of the series. The inner coordination sphere of the Co compound may be best described as a distorted trigonal bipyramid with an essentially linear nitrosyl in an equatorial position.[6] The Co–N–O unit does, however, show significant deviation from linearity with a Co–N–O bond angle of 164.5 (5)° whereas the Co–N distance of 1.705 (5) Å is short (based on the internal standard provided by the metal–phosphorus distances) indicating that the strong metal–nitrosyl π interaction characteristic of the linear MNO group is intact. The Cl–Co–Cl angle is 108.4 (1)° and the two independent Cl–Co–N angles are 134.3 (2) and 117.3 (2)°.[6]

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

Atom	Min	Intermed	Max
Rh	0.1594 (9)	0.1608 (10)	0.1703 (9)
Cl	0.1867 (21)	0.2093 (20)	0.2554 (19)
P	0.1621 (21)	0.1657 (22)	0.1841 (20)
N	0.154 (34)	0.234 (32)	0.301 (19)
O	0.191 (15)	0.273 (12)	0.301 (17)

[a] Measured along the principal axes of the thermal ellipsoids.

In both the rhodium and the iridium compounds the nitrosyl ligand lies approximately in the P–metal–P' plane. This is clearly indicated in Figure 2. The dihedral angle formed by the Rh–N–O and P–Rh–P' planes is 10.3 (29)°. It has been proposed that the nitrosyl group bends in the direction of the strongest π-acceptor ligand coordinated in the basal plane,[7,24] and recent molecular orbital calculations tend to support this view.[5] In complexes of the type $M(NO)L_2L'_2$, the bending of the nitrosyl occurs in the L–M–L plane where L is the better π acceptor or poorer σ donor.[5] However, an interesting and contrasting feature of the $CoCl_2(NO)(PMePh_2)_2$ structure is that the slight bending of the nitrosyl group in that system appears to occur more in the $CoCl_2$ plane than in the CoP_2 plane (dihedral angles calculated: CoNO and $CoCl_2$, 25.4°; CoNO and CoP_2, 67.8°). It has been suggested recently that the two nitrosyl stretching frequencies found in the $CoCl_2(NO)L_2$ systems arise from different and interconvertible *orientations* of the nitrosyl group.[4]

In conclusion, this study shows that within the group 8 triad Co, Rh, Ir there is no gradual change in the structures of $MCl_2(NO)(PR_3)_2$. The cobalt member of the series is rather different from the other two compounds and to within experimental accuracy there are no detectable differences between the Rh and Ir structures.

Registry No. $RhCl_2(NO)(P(C_6H_5)_3)_2$, 40231-80-9.

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Supplementary Material Available. A listing of the observed and calculated structure factor 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 the papers in this issue may be obtained from the Journals Department, 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 AIC40769Z.

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Spectroscopic Properties and Crystal Structure Analysis of an Intermediate in the Reaction of Bis(oxalato)platinate(II) with Thiocyanate: Potassium Bis(oxalato)bis(thiocyanato)platinate(II) Tetrahydrate

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Potassium bis(oxalato)bis(thiocyanato)platinate(II) tetrahydrate, $K_4[Pt(C_2O_4)_2(SCN)_2]\cdot 4H_2O$, has been obtained as intermediate in the reaction of bis(oxalato)platinate(II) with potassium thiocyanate. Its structure has been determined from three-dimensional X-ray data collected by counter methods using the θ–2θ technique. The complex crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.04$ (1), $b = 7.14$ (1), $c = 6.66$ (1) Å; $\alpha = 108.6$ (1), $\beta = 90.3$ (1), $\gamma = 101.1$ (1)°. Observed and calculated densities are 2.40 and 2.38 g cm^{-3}, respectively, for mol wt 715.9 and $Z = 1$. The structure was solved by the standard heavy-atom technique and refined by least squares to a conventional R factor of 0.049. The unidentate character of the oxalate ion in this compound has been confirmed. Coordination around platinum is square planar and involves two thiocyanate groups and two oxalate ions (Pt–S = 2.329 (4) and Pt–O(1) = 2.015 (6) Å). Ir and NMR experiments prove that the tendency to be associated with the crystal is greater for H_2O than for D_2O.

Introduction

In a preceding paper[2] on the rate of the reaction between bis(oxalato)platinate(II) and thiocyanate, an intermediate product was isolated which contained two oxalate and two thiocyanate groups per atom of platinum. This was considered evidence that the first step of the substitution reaction involves oxalate groups which act as unidentate ligands. Such intermediates have been postulated many times in substitution reactions of oxalato complexes as well in racemization and exchange reactions.[3] However, as far as we know, no coordination compounds with unidentate oxalate had been previously isolated. We succeeded in recrystallizing the intermediate without decomposition and in obtaining crystals large enough for X-ray analysis. We proceeded therefore to a more accurate investigation of this compound.

Experimental Section

Preparation. A mixture of 0.02 *M* $K_2Pt(C_2O_4)_2$ and 0.1 *M* KSCN was allowed to react at 45° under spectrophotometric control. When the optical density reached a minimum, 3 volumes of cooled acetone were added and the mixture was quickly cooled to 0°. The precipitate was filtered, washed with acetone, and dissolved in the minimum amount of water at room temperature. By slow addition of acetone gold-yellow prismatic crystals suitable for a single-crystal X-ray analysis could be obtained in about 6 hr. The ir spectra in Nujol and Tripen (poly(chlorotrifluoroethylene) oil) were the same as with the original precipitate.[2]

X-Ray Data. The unit cell dimensions, determined from rotation and Weissenberg photographs and refined by an "on-line" single-crystal automated Siemens diffractometer, are as follows, for $K_4[Pt(C_2O_4)_2(SCN)_2]\cdot 4H_2O$, fw = 715.9: a 11.04 (1), $b = 7.14$ (1), $c = 6.66$ (1) Å; $\alpha = 108.6$ (1), $\beta = 90.3$ (1), $\gamma = 101.1$ (1)°; $V = 487.0$ Å^3; $d_{\text{measd}} = 2.40$ g cm^{-3} (by flotation); $Z = 1$; $d_{\text{calcd}} = 2.38$ g cm^{-3}, $F(000) = 340$; $\mu = 86.7$ cm^{-1} (Mo Kα); triclinic, space group $P\bar{1}$ (from structural analysis).

Three-dimensional intensity data were taken at room temperature from a prismatic crystal of length 0.21 mm and of cross section measuring 0.09 mm × 0.11 mm mounted with c along the ϕ axis of the Siemens diffractometer. Niobium-filtered Mo Kα radiation at a takeoff angle of 4° was employed. The pulse height discriminator was set to accept 90% of the Mo K$\bar{\alpha}$ peak. The moving counter–moving crystal scan technique was used with a drive speed related to the number of counts on the peak (lowest speed 2.5°/min).

The 120 reflection was remeasured after every 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensity of this reflection was observed during data collection. For intensities and background the "five-points technique"[4] was used. A total of 2600 independent reflections were measured and 2563 were used in the crystal analysis considering the reflections whose intensities were less than twice their standard deviations ($\sigma^2(I)$ = total counts + $(0.01 \times \text{intensity})^2$) as being unobserved.

The structure amplitudes were obtained after the usual Lorentz and polarization reduction and the absolute scale was established by successive comparison with the calculated values. No correction for absorption was applied ($\mu\bar{r} = 0.4$) and therefore the thermal coefficients given in Table I are influenced by this omission.

Solution and Refinement of the Structure. The structure was solved considering all the structure factors to be positive; this implied the assumption of the space group $P\bar{1}$ with the Pt atom at the origin. The Fourier map confirmed this assumption revealing all nonhydrogen atoms and the presence of four water molecules instead of the three suggested in the previous paper.[2]

The refinement was carried out by means of block-diagonal least squares, isotropically down to $R = 15.1\%$ and anisotropically down to $R = 5.0\%$ ($R = \sum||F_o| - |F_c||/\sum|F_o|$). The lack of corrections for absorption and anomalous scattering resulted in data which do not