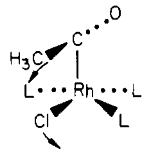


11

significantly closer to the vacant site than expected for ideal square-pyramidal geometry may account in part for the rapidity of the migration; i.e., the structure of the acetyl complex may be close to that of the transition state for methyl migration even though this would require concerted reorientation of the substituents on phosphorus. Another important contributor to the fast methyl migration may be the positive charge on the complex. On the basis of calculations on model systems, it has been suggested[43] that a strong π-acceptor ligand such as NO placed opposite either CH_3 or CO will lower the activation energy for methyl migration from metal to carbonyl carbon whereas a strong σ donor such as a tertiary phosphine will have the reverse effect. In the present case, the effect of the phosphine ligands may be outweighed by that of the positive charge, which reduces π bonding to the CO group of **10** and to the acetyl group of **9** relative to that in uncharged complexes and thus destabilizes the ground states relative to the transition state for methyl migration.

Acknowledgment. We thank Dr. Paul Tucker for helpful discussions.

Registry No. **1**, 75183-84-5; **2**, 75183-85-6; **3**, 75183-86-7; **4**, 22605-70-5; **5**, 22605-71-6; **6**, 75183-87-8; **7**, 75198-20-8; **8**, 75198-22-0; **9**, 75198-24-2; **10**, 75183-89-0; $[IrCl(C_8H_{14})_2]_3$, 12246-51-4; $[RhCl(C_2H_4)_2]_2$, 12081-16-2; CH_3COCl, 75-36-5; $CH_3CH_2CH_2COCl$, 141-75-3; $CH(CH_3)_2COCl$, 79-30-1; CH_3CH_2COCl, 79-03-8.

Supplementary Material Available: Listings of data collection details (Table III), atomic coordinates and isotropic thermal parameters, bond distances and angles, and structure factor amplitudes (20 pages). Ordering information is given on any curent masthead page.

---

[43] Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224–7236.

Contribution from the Research School of Chemistry,
The Australian National University, Canberra, A.C.T., 2600, Australia

Formation and X-ray Structure of the Dinuclear Tri-μ-chloro Acetylrhodium(III) Complex $[Rh_2Cl_3(COCH_3)_2(PMe_2Ph)_4]PF_6{\cdot}0.5C_2H_4Cl_2$

M. A. BENNETT,* J. C. JEFFERY, and G. B. ROBERTSON

Received March 26, 1980

Reaction of $RhCl_2(COR)L_3$ ($L = PMe_2Ph$; $R = CH_3$, C_2H_5) with NH_4PF_6 in the presence of air gives dinuclear tri-μ-chloro acylrhodium(III) complexes $[Rh_2Cl_3(COR)_2L_4]PF_6$. The acetyl complex has also been made by treating $[RhCl(C_2H_4)_2]_2$ (1 mol) successively with dimethylphenylphosphine (4 mol), acetyl chloride, and NH_4PF_6. Crystals of $[Rh_2Cl_3(COCH_3)_2L_4]PF_6{\cdot}0.5C_2H_4Cl_2$ obtained from dichloromethane/methanol are monoclinic, of space group $P2_1/c$, with $a = 11.174$ (2) Å, $b = 19.340$ (4) Å, $c = 21.931$ (4) Å, $\beta = 106.33$ (1)°, and $Z = 4$. The structure was solved by direct methods using MULTAN and refined by block-diagonal least-squares analysis to a conventional R factor of 0.037 (6104 reflections). The cation has a confacial bioctahedral structure, each rhodium atom being octahedrally coordinated by an acetyl group, two phosphine ligands, and three bridging chlorine atoms. One of the chlorine atoms (Cl(2)) is trans to a phosphine ligand on each rhodium atom; the other two (Cl(1), Cl(3)) are trans to an acetyl group on one rhodium atom and a phosphine ligand on the other. The Rh–Cl distances trans to L show considerable variation, those involving Cl(2) (Rh(1)–Cl(2) = 2.485 (1) Å, Rh(2)–Cl(2) = 2.462 (2) Å) being significantly longer than those involving Cl(1) or Cl(3) (Rh(1)–Cl(1) = 2.431 (2) Å, Rh(2)–Cl(3) = 2.446 (1) Å). All of these are significantly shorter than the Rh–Cl distances trans to acetyl (Rh(1)–Cl(3) = 2.624 (1) Å, Rh(2)–Cl(1) = 2.612 (1) Å), indicating the high trans influence of the acetyl group relative to that of dimethylphenylphosphine. Other important distances are Rh–C(acyl) = 2.002 (4) Å, C(acyl)–O = 1.202 (7) Å (average) and Rh–Rh = 3.3284 (6) Å, the last of these being incompatible with significant metal–metal interaction. An unexpected feature is the presence in the unit cell of two molecules of the anti conformer of 1,2-dichloroethane, the source of which is unknown.

Introduction

In the preceding paper[1] we showed that the complex $RhCl_2(COCH_3)L_3$ ($L = PMe_2Ph$),[2] formed by oxidative addition of acetyl chloride to $RhClL_3$,[1,3] loses chloride ion on treatment with NH_4PF_6. The product isolated in the absence of air, $[RhCl(COCH_3)L_3]PF_6$, has an essentially square-pyramidal structure with an apical acetyl group in the solid state, but in solution this species is in equilibrium with a six-coordinate methylrhodium(III) salt $[RhCl(CH_3)(CO)L_3]PF_6$. Solutions of this equilibrium mixture smell strongly of dimethylphenylphosphine, and unless air is rigorously excluded, it is difficult to obtain a pure product having reproducible NMR spectra. We report here a single-crystal X-ray structural characterization of a compound formed when $[RhCl(COCH_3)L_3]PF_6$ is exposed to air.

Experimental Section

Measurement, analytical, and general procedures have been described.[4] The complexes $[RhCl(C_2H_4)_2]_2$[5] and $RhCl_2(COR)L_3$[1,3] ($R = CH_3$, C_2H_5) were prepared by literature methods.

Preparations. (i) $[Rh_2Cl_3(COR)_2L_4]PF_6$ (1) ($R = CH_3$, C_2H_5) from $RhCl_2(COR)L_3$. To a solution of $RhCl_2(COCH_3)L_3$ (0.3 g, 0.48 mmol) in dichloromethane (10 mL) and acetone (10 mL) was added ammonium hexafluorophosphate (0.09 g, 0.55 mmol) dissolved in the

---

[1] Bennett, M. A.; Jeffery, J. C.; Robertson, G. B. *Inorg. Chem.*, preceding paper in this issue.

[2] This abbreviation will be used throughout this paper. Other abbreviations: Et, ethyl; *n*-Bu, *n*-butyl; mnt = maleonitriledithiolate.

[3] Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 597–602.

[4] Bennett, M. A.; Jeffery, J. C. *Inorg. Chem.* **1980**, *19*, 3763.

[5] Cramer, R. *Inorg. Synth.* **1974**, *15*, 14–18.

0020-1669/81/1320-0330$01.00/0 © 1981 American Chemical Society

minimum volume of methanol. After the mixture had been stirred for 24 h in the presence of air, solvents were evaporated under reduced pressure and the residue was extracted with three 5-mL portions of dichloromethane. The filtered extracts were evaporated to give a yellow oil which crystallized on addition of ca. 1 mL of methanol. Approximately 2 mL of hexane was added to complete crystallization. The pale yellow crystals were filtered off and dried in vacuo. The yield was 0.16 g (60%): IR (Nujol) 1650 s, 1680 sh cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.60 (approx d, J = 11 Hz, PMe_2Ph), 2.74 (s, $COCH_3$), ca. 7.4 (m, $PMe_2$$Ph$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ_p +17.64 (br dd, J_{Rh-P} = 153 Hz) (R = CH_3). Anal. Calcd for $C_{36}H_{50}Cl_3F_6O_2P_5Rh_2$: C, 39.4; H, 4.6; Cl, 9.7; P, 14.15. Found: C, 39.1; H, 5.1; Cl, 9.2; P, 13.75.

A sample of **1** which had crystallized over 3 weeks from dichloromethane/methanol, from which the crystal used for X-ray study was taken, showed a sharp singlet at δ 3.74 assignable to 0.5 mol of 1,2-dichloroethane/mol of dimer. The presence of this "impurity" solvent was first established by the X-ray work (see below), but its origin has not been clarified.

Similarly prepared from $RhCl_2(COC_2H_5)L_3$ in 57% yield was $[Rh_2Cl_3(COC_2H_5)_2L_4]PF_6$: IR (Nujol) 1670 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.54 (approx d, J = 11 Hz, PMe_2Ph), 0.97 (t, $COCH_2$$CH_3$, $J_{CH_2-CH_3}$ = 8 Hz), 2.2 (m, CO$CH_2$$CH_3$), ca. 7.4 (m, $PMe_2$$Ph$). Anal. Calcd for $C_{38}H_{54}Cl_3F_6O_2P_5Rh_2$: C, 40.6; H, 4.8; Cl, 9.5; P, 13.8. Found: C, 41.5; H, 5.6; Cl, 9.25; H, 14.7.

(ii) $[Rh_2Cl_3(COCH_3)_2L_4]PF_6$ from $[RhCl(C_2H_4)_2]_2$. Dimethylphenylphosphine (0.57 g, 4.1 mmol) was added by syringe to a solution of $[RhCl(C_2H_4)_2]_2$ (0.4 g, 1.0 mmol) in benzene (15 mL). The orange-red solution was stirred for 10 min and was then treated with acetyl chloride (0.2 mL) from a syringe. The resulting orange solution was stirred for 20 min, during which time a canary yellow precipitate formed. The volume of solution was reduced to about 10 mL under reduced pressure, and hexane (20 mL) was added to complete precipitation of the yellow solid, which was filtered off and dried in vacuo (yield about 0.9 g). A 0.3-g sample of this complex dissolved in dichloromethane (10 mL) and acetone (10 mL) was treated with a solution of ammonium hexafluorophosphate (0.2 g) in methanol. After 1 h of stirring the solution was worked up as under (i). The yield of $[Rh_2Cl_3(COCH_3)_2L_4]PF_6$ was 0.26 g (88%).

Collection and Reduction of X-ray Intensity Data. The complex $[Rh_2Cl_3(COCH_3)_2L_4]PF_6$ was slowly recrystallized by covering a saturated solution of the complex in dichloromethane with methanol and allowing the solvent layers to diffuse together over a period of 3 weeks. The Laue group and approximate cell dimensions of the resulting yellow crystals were obtained from preliminary Weissenberg and precession photographs. Systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ uniquely define the monoclinic space group as $P2_1/c$ (C_{2h}^5, No. 14)

Crystal Data[6] for $[Rh_2Cl_3(COCH_3)_2(P(CH_3)_2C_6H_5)_4]PF_6 \cdot 0.5C_2H_4Cl_2$: fw = 1145.3, monoclinic, space group $P2_1/c$, a = 11.174 (2) Å, b = 19.340 (4) Å, c = 21.931 (4) Å, β = 106.33 (1)°, V_{calcd} = 4548.2 Å^3, ρ_{calcd} = 1.67 g cm^{-3}, ρ_{obsd} = 1.69 (1) g cm^{-3}, Z = 4, μ(Mo Kα) = 11.73 cm^{-1}, t = 20.5 ± 1 °C. Crystal dimensions, quoted as the perpendicular distance between the faces (hkl): (010 to $0\bar{1}0$), 0.1 mm; (012 to $0\bar{1}\bar{2}$), 0.28 mm; ($01\bar{2}$ to $0\bar{1}2$), 0.28 mm; (100 to $\bar{1}00$), 0.23 mm.

Reflection data were collected on a Picker FACS-I fully automatic four-circle diffractometer with the crystallographic a axis and the instrumental ϕ axis approximately coincident. Accurate unit cell dimensions and crystal orientation matrix, together with their estimated standard errors, were obtained from the least-squares analysis[7] of the 2θ, ω, χ, and Φ values of 12 carefully centered high-angle reflections (χ = 0.709 26 Å).

Full details of the experimental conditions and data collection methods used are in Table I (supplementary material). During data collection the intensities of three "standard" reflections showed a smooth isotropic decrease of ca. 9% (assumed to be 2θ-independent), and the intensity data were corrected accordingly.

Reflection intensities were reduced to values of $|F_o|$, and each reflection was assigned an estimated standard deviation $[\sigma(F_o)]$.[8] Reflection data were sorted, equivalent reflections were averaged, and reflections with $I/\sigma(I) < 3$ were discarded. The statistical R factor (R_s)[8] for the 6104 reflections of the terminal data set was 0.023.

Solution and Refinement of the Structure. The structure was solved by direct methods using MULTAN and was refined by block-diagonal least-squares analysis. Anisotropic thermal parameters were specified for all nonhydrogen atoms. The atomic scattering factors and the anomalous scattering factors for the nonhydrogen atoms were taken from ref 9. The data were corrected for absorption by the literature method.[10] The phenyl hydrogen atoms were included in the scattering model as fixed contributions (C–H = 0.95 Å,[11] $B_H = 1.1B_C$). The hydrogen atom coordinates and temperature factors were recalculated prior to each cycle of refinement. Neither methyl nor solvent hydrogen atoms were located or included in the scattering model.

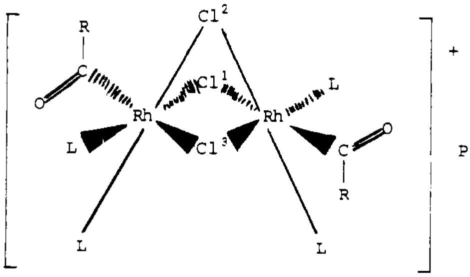
The fluorine atoms of the PF_6 anion were readily located but, as is often the case, have comparatively high temperature factors. Surprisingly, the unit cell also contains two molecules of 1,2-dichloroethane of unknown origin. These lie with the midpoints of their C–C bonds on the inversion centers at ($^1/_2$, $^1/_2$, 0) and ($^1/_2$, 0, $^1/_2$) and are therefore constrained to adopt an anti conformation with trans chlorine atoms. Although the temperature factors of the chlorine and carbon atoms are rather high, the individual atoms were clearly defined in the Fourier map of this region and these peaks could not be related to components of disordered dichloromethane molecules.

Refinement converged with a final conventional R factor of 0.037[8] (R_w = 0.050). No individual parameter shift was greater than 0.1 of the corresponding esd. A final difference Fourier synthesis showed no residual peaks greater than ca. 0.7 e/Å^3, the largest peaks being in the vicinity of the PF_6^- anion and 1,2-dichloroethane solvent molecules. The standard deviation of an observation of unit weight, defined as $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ (where m is the number of observations, 6104, and n is the number of parameters varied, 505), is 1.61.

Final atomic positional parameters, together with their estimated standard deviations, are listed in Table V. Tables of structure factors, anisotropic thermal parameters, and phenyl hydrogen atom parameters, are available as supplementary material (Tables II and III). The computer and programs used for calculations (including ORTEP for the drawings) are as described previously.[1]

Results

Reaction of $RhCl_2(COCH_3)L_3$ with NH_4PF_6 in the presence of air for 24 h gives the yellow PF_6 salt of a tri-μ-chloro-dirhodium cation, $[Rh_2Cl_3(COCH_3)_2L_4]PF_6$ (**1**), in 60–70% yield, as shown by X-ray crystallography. The same complex can be obtained in higher yield from $[RhCl(C_2H_4)_2]_2$ by successive treatment with PMe_2Ph (4 mol/mol of dimer), acetyl chloride, and NH_4PF_6. ^{1}H NMR spectra indicate that freshly recrystallized samples of the complex contain variable amounts of solvent (CH_2Cl_2, CH_3OH, and traces of hexane) which are not completely removed in vacuo. For this reason, analytical data on $[Rh_2Cl_3(COCH_3)_2L_4]PF_6$ and on the similarly prepared propionyl complex **2** are not in entirely satisfactory agreement with the formulation; agreement with the alternative (expected) formulation $[Rh_2Cl_2(COR)_2L_4](PF_6)_2$



1, R = CH_3, L = PMe_2Ph
2, R = C_2H_5, L = PMe_2Ph

---

(6) Estimated standard deviations are in parentheses.

(7) The programs contained in the Picker Corp. FACS-I disk operating system were used for all phases of diffractometer control and data collection.

(8) The formulas used for data reduction are as given in ref 1.

(9) "International Tables for X-Ray Crystallograpy"; Kynoch Press: Birmingham, England, 1974; Vol. 4: (a) pp 99–101; (b) pp 149–150.

(10) De Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014–1018.

(11) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213–1214.

Table V. Refined Atomic Positional and Thermal Parameters for $[Rh_2Cl_3(COCH_3)_2(PMe_2Ph)_4]PF_6 \cdot 0.5C_2H_4Cl_2$

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Rh(1)	0.02967 (4)	0.79389 (2)	0.70650 (2)	C(116)	−0.3371 (5)	0.7981 (3)	0.6434 (3)
Rh(2)	0.12917 (4)	0.65945 (2)	0.63946 (2)	C(121)	0.1026 (5)	0.9514 (3)	0.6540 (3)
P(11)	−0.13497 (13)	0.78142 (7)	0.74940 (6)	C(122)	0.1304 (6)	0.9582 (3)	0.5963 (3)
P(12)	−0.02827 (13)	0.89806 (7)	0.66025 (6)	C(123)	0.2262 (7)	1.0027 (4)	0.5916 (4)
P(21)	0.11104 (13)	0.64838 (7)	0.53381 (6)	C(124)	0.2952 (7)	1.0379 (4)	0.6442 (4)
P(22)	0.32933 (12)	0.62160 (7)	0.68441 (6)	C(125)	0.2719 (7)	1.0296 (4)	0.7010 (4)
Cl(1)	0.18946 (12)	0.79027 (6)	0.65084 (6)	C(126)	0.1752 (6)	0.9869 (3)	0.7059 (3)
Cl(2)	0.11677 (12)	0.67957 (7)	0.74835 (5)	C(211)	0.1189 (5)	0.7307 (3)	0.4948 (2)
Cl(3)	−0.07720 (11)	0.71329 (6)	0.61035 (5)	C(212)	0.2261 (6)	0.7512 (4)	0.4816 (3)
O(1)	0.0927 (4)	0.8901 (2)	0.8109 (2)	C(213)	0.2305 (8)	0.8132 (4)	0.4505 (4)
O(2)	0.1260 (4)	0.5132 (2)	0.6235 (2)	C(214)	0.1266 (8)	0.8532 (4)	0.4315 (3)
C(11)	0.1315 (5)	0.8448 (3)	0.7835 (2)	C(215)	0.0168 (7)	0.8345 (3)	0.4448 (3)
C(12)	0.2672 (6)	0.8235 (4)	0.8081 (3)	C(216)	0.0142 (6)	0.7722 (3)	0.4768 (3)
C(13)	−0.1735 (6)	0.6907 (3)	0.7558 (3)	C(221)	0.4259 (5)	0.5820 (3)	0.6395 (3)
C(14)	−0.1106 (7)	0.8142 (4)	0.8306 (3)	C(222)	0.5035 (6)	0.6221 (3)	0.6155 (3)
C(15)	−0.1127 (6)	0.9575 (3)	0.6975 (3)	C(223)	0.5828 (7)	0.5925 (5)	0.5843 (4)
C(16)	−0.1274 (6)	0.8893 (3)	0.5788 (3)	C(224)	0.5829 (8)	0.5221 (5)	0.5784 (4)
C(21)	0.0702 (5)	0.5617 (3)	0.6353 (2)	C(225)	0.5057 (7)	0.4814 (4)	0.6000 (4)
C(22)	−0.0564 (6)	0.5512 (3)	0.6478 (3)	C(226)	0.4250 (6)	0.5099 (3)	0.6309 (3)
C(23)	0.2148 (6)	0.5905 (3)	0.5062 (3)	P	0.39970 (16)	0.25662 (11)	0.07711 (8)
C(24)	−0.0413 (5)	0.6122 (3)	0.4924 (2)	F(1)	0.2998 (5)	0.2042 (4)	0.0467 (4)
C(25)	0.3368 (6)	0.5582 (3)	0.7475 (3)	F(2)	0.3094 (7)	0.2906 (3)	0.1116 (4)
C(26)	0.4283 (5)	0.6919 (3)	0.7257 (3)	F(3)	0.5018 (6)	0.3099 (4)	0.1112 (3)
C(111)	−0.2868 (5)	0.8157 (3)	0.7058 (3)	F(4)	0.4944 (6)	0.2207 (4)	0.0485 (3)
C(112)	−0.3583 (6)	0.8554 (3)	0.7352 (3)	F(5)	0.3596 (9)	0.3090 (5)	0.0238 (4)
C(113)	−0.4771 (6)	0.8764 (4)	0.7001 (4)	F(6)	0.4461 (6)	0.2093 (3)	0.1355 (3)
C(114)	−0.5247 (6)	0.8593 (4)	0.6389 (4)	Cl	0.6209 (3)	0.4781 (2)	0.0892 (1)
	−0.4557 (6)	0.8199 (4)	0.6094 (3)	C	0.5206 (14)	0.4652 (6)	0.0158 (6)

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh(1)	0.00456 (3)	0.00139 (1)	0.00127 (1)	0.00010 (2)	0.00075 (1)	−0.00010 (1)
Rh(2)	0.00431 (3)	0.00126 (1)	0.00120 (1)	0.00020 (2)	0.00058 (1)	0.00001 (1)
P(11)	0.00627 (13)	0.00212 (4)	0.00155 (3)	0.00000 (6)	0.00148 (5)	0.00000 (3)
P(12)	0.00604 (13)	0.00153 (4)	0.00178 (3)	0.00023 (6)	0.00124 (5)	0.00004 (3)
P(21)	0.00614 (13)	0.00187 (4)	0.00128 (3)	0.00051 (6)	0.00069 (5)	−0.00015 (3)
P(22)	0.00483 (12)	0.00172 (4)	0.00163 (3)	0.00054 (6)	0.00060 (5)	0.00019 (3)
Cl(1)	0.00544 (11)	0.00166 (3)	0.00198 (3)	−0.00011 (5)	0.00145 (5)	−0.00005 (3)
Cl(2)	0.00656 (12)	0.00201 (4)	0.00129 (3)	0.00049 (5)	0.00081 (5)	0.00015 (2)
Cl(3)	0.00475 (11)	0.00179 (3)	0.00148 (3)	0.00026 (5)	0.00046 (4)	−0.00011 (2)
O(1)	0.0103 (5)	0.0029 (1)	0.0025 (1)	0.0000 (2)	0.0006 (2)	−0.0012 (1)
O(2)	0.0101 (5)	0.0016 (1)	0.0039 (1)	0.0002 (2)	0.0020 (2)	−0.0004 (1)
C(11)	0.0075 (6)	0.0020 (2)	0.0018 (1)	−0.0002 (3)	0.0006 (2)	−0.0004 (1)
C(12)	0.0071 (6)	0.0042 (3)	0.0033 (2)	0.0012 (3)	−0.0007 (3)	−0.0016 (2)
C(13)	0.0089 (7)	0.0020 (2)	0.0039 (2)	0.0001 (3)	0.0025 (3)	0.0009 (2)
C(14)	0.0128 (8)	0.0050 (3)	0.0014 (1)	−0.0009 (4)	0.0023 (3)	−0.0005 (2)
C(15)	0.0090 (6)	0.0018 (2)	0.0029 (2)	0.0007 (3)	0.0024 (3)	−0.0002 (1)
C(16)	0.0084 (6)	0.0028 (2)	0.0018 (1)	0.0004 (3)	0.0004 (2)	0.0004 (1)
C(21)	0.0061 (5)	0.0017 (1)	0.0015 (1)	−0.0001 (2)	0.0002 (2)	−0.0001 (1)
C(22)	0.0073 (6)	0.0019 (2)	0.0041 (2)	−0.0012 (3)	0.0021 (3)	0.0005 (2)
C(23)	0.0113 (8)	0.0037 (2)	0.0020 (1)	0.0030 (3)	0.0015 (3)	−0.0006 (1)
C(24)	0.0079 (6)	0.0025 (2)	0.0018 (1)	−0.0009 (3)	0.0002 (2)	−0.0003 (1)
C(25)	0.0092 (7)	0.0034 (2)	0.0027 (2)	0.0016 (3)	0.0014 (3)	0.0016 (2)
C(26)	0.0054 (5)	0.0027 (2)	0.0029 (2)	−0.0002 (3)	−0.0001 (3)	−0.0011 (1)
C(111)	0.0052 (5)	0.0019 (1)	0.0025 (1)	−0.0001 (2)	0.0018 (2)	0.0001 (1)
C(112)	0.0101 (7)	0.0022 (2)	0.0037 (2)	−0.0004 (3)	0.0036 (3)	−0.0003 (2)
C(113)	0.0083 (7)	0.0027 (2)	0.0064 (3)	0.0012 (3)	0.0053 (4)	0.0003 (2)
C(114)	0.0070 (6)	0.0036 (2)	0.0047 (3)	0.0007 (3)	0.0017 (3)	0.0016 (2)
C(115)	0.0065 (6)	0.0041 (2)	0.0031 (2)	0.0002 (3)	0.0011 (3)	0.0010 (2)
C(116)	0.0061 (5)	0.0029 (2)	0.0022 (1)	0.0001 (3)	0.0015 (2)	0.0003 (1)
C(121)	0.0081 (6)	0.0013 (1)	0.0027 (2)	0.0004 (2)	0.0021 (3)	0.0001 (1)
C(122)	0.0088 (7)	0.0030 (2)	0.0032 (2)	0.0003 (3)	0.0023 (3)	0.0009 (2)
C(123)	0.0095 (8)	0.0050 (3)	0.0050 (3)	0.0008 (4)	0.0034 (4)	0.0025 (2)
C(124)	0.0100 (8)	0.0026 (2)	0.0064 (3)	−0.0005 (3)	0.0038 (4)	0.0014 (2)
C(125)	0.0094 (7)	0.0028 (2)	0.0056 (3)	−0.0015 (3)	0.0027 (4)	−0.0004 (2)
C(126)	0.0099 (7)	0.0025 (2)	0.0039 (2)	−0.0014 (3)	0.0029 (3)	−0.0008 (2)
C(211)	0.0073 (5)	0.0022 (2)	0.0011 (1)	−0.0002 (2)	0.0009 (2)	0.0000 (1)
C(212)	0.0092 (7)	0.0039 (2)	0.0032 (2)	0.0005 (4)	0.0022 (3)	0.0009 (2)
C(213)	0.0145 (10)	0.0044 (3)	0.0051 (3)	−0.0006 (4)	0.0050 (5)	0.0019 (2)
C(214)	0.0161 (10)	0.0037 (2)	0.0033 (2)	−0.0005 (4)	0.0035 (4)	0.0014 (2)
C(215)	0.0141 (9)	0.0024 (2)	0.0022 (2)	0.0015 (3)	0.0014 (3)	0.0004 (1)
C(216)	0.0087 (6)	0.0025 (2)	0.0018 (1)	0.0005 (3)	0.0016 (2)	0.0002 (1)
C(221)	0.0056 (5)	0.0025 (2)	0.0021 (1)	0.0009 (3)	0.0006 (2)	0.0001 (1)
C(222)	0.0084 (7)	0.0033 (2)	0.0029 (2)	−0.0005 (3)	0.0023 (3)	−0.0006 (2)
C(223)	0.0100 (8)	0.0073 (4)	0.0039 (2)	−0.0014 (5)	0.0035 (4)	−0.0015 (3)
C(224)	0.0112 (9)	0.0070 (4)	0.0047 (3)	0.0017 (5)	0.0033 (4)	−0.0023 (3)
C(225)	0.0132 (9)	0.0044 (3)	0.0042 (2)	0.0041 (4)	0.0002 (4)	−0.0017 (2)

Table V (*Continued*)

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(226)	0.0107 (7)	0.0023 (2)	0.0030 (2)	0.0020 (3)	0.0010 (3)	−0.0001 (1)
P	0.00643 (15)	0.00462 (7)	0.00233 (4)	−0.00033 (9)	0.00099 (7)	0.00024 (4)
F(1)	0.0135 (7)	0.0106 (4)	0.0118 (4)	−0.0054 (4)	0.0000 (4)	−0.0053 (3)
F(2)	0.0266 (10)	0.0068 (3)	0.0118 (4)	0.0005 (4)	0.0135 (6)	−0.0013 (2)
F(3)	0.0193 (8)	0.0092 (3)	0.0078 (3)	−0.0063 (4)	0.0043 (4)	−0.0026 (2)
F(4)	0.0211 (9)	0.0097 (3)	0.0087 (3)	−0.0009 (4)	0.0084 (4)	−0.0030 (3)
F(5)	0.0407 (16)	0.0144 (5)	0.0072 (3)	0.0038 (8)	0.0021 (6)	0.0072 (3)
F(6)	0.0240 (10)	0.0089 (3)	0.0061 (2)	0.0029 (4)	0.0023 (4)	0.0030 (2)
Cl	0.0239 (4)	0.0066 (1)	0.0048 (1)	0.0000 (2)	0.0002 (2)	−0.0002 (1)
C	0.0307 (22)	0.0060 (5)	0.0075 (5)	0.0011 (9)	0.0025 (9)	0.0014 (4)

($R = CH_3, C_2H_5$) is even less satisfactory. The presence of acyl groups is confirmed by IR and ^1H NMR spectroscopy; e.g., the acetyl complex shows a split $\nu(C{=}O)$ band in the 1650–1700-cm^{-1} region of the IR spectrum and a singlet methyl resonance at δ 2.74 in the ^1H NMR spectrum. At room temperature the P–CH_3 resonance appears as an approximate doublet with a separation of 11 Hz, but under high resolution the higher field component resembles an asymmetric triplet. The entire spectrum shows some broadening at −85 °C, the P–CH_3 signal at this temperature now resembling an asymmetric triplet. On ^{31}P decoupling at ambient temperature, the P–CH_3 signal simplifies to two singlets separated by about 6 Hz, the lower field singlet being the more intense. The $^{31}P\{^1H\}$ NMR spectrum at 32 °C consists of a broad, asymmetric doublet of doublets, the larger separation clearly arising from $^{103}Rh-^{31}P$ coupling ($J = 153$ Hz). Since the idealized structure of **1** has C_2 symmetry, the phosphorus atoms on each rhodium atom would be inequivalent and there should be four inequivalent methyl groups. Thus the $^{31}P\{^1H\}$ NMR spectrum would be expected to consist of an AB quartet with $J_{AB} \approx 20$ Hz,[12,13] doubled by coupling with ^{103}Rh. The observed magnitude of J_{RhP} is consistent with the arrangement of L trans to Cl in octahedral rhodium(III) complexes,[12,13] but the broadness and asymmetry of the spectrum remain unexplained. We cannot rule out the possibility that isomers of **1** are present in solution. The P–CH_3 $^1H\{^{31}P\}$ NMR spectrum presumably arises from fortuitous overlap of resonances.

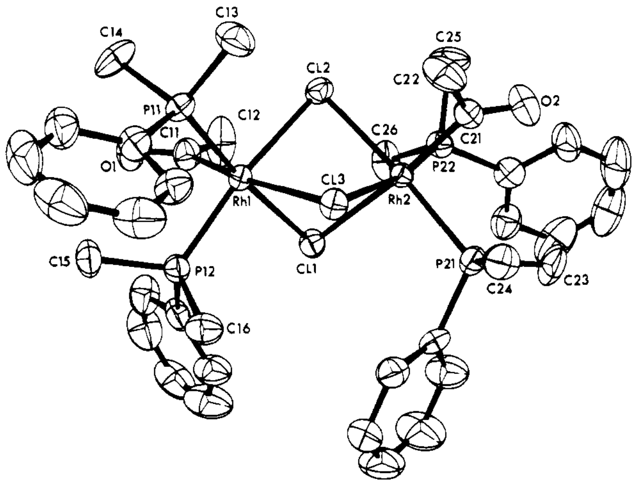


Figure 1. Overall stereochemistry of the $[Rh_2Cl_3(COCH_3)_2(PMe_2Ph)_4]^+$ cation, together with the atom numbering scheme. Phenyl hydrogen atom nomenclature follows that of the parent carbon atoms.

Description of the Structure

The crystal structure comprises discrete moieties $[Rh_2Cl_3(COCH_3)_2L_4]^+$, PF_6^-, and $C_2H_4Cl_2$, separated by normal van der Waals contacts. A perspective view of the cation $[Rh_2Cl_3(COCH_3)_2L_4]^+$ (**1**) is shown in Figure 1. Principal bond lengths and angles together with their estimated standard deviations in parentheses are listed in Table VI. Bond distances and interbond angles for the phenyl rings are available as supplementary material (Table IV).

The cation has a distorted confacial bioctahedral geometry with the two rhodium atoms sharing a triangular face of three bridging chlorine atoms. A similar geometry is observed in the complexes $[Ru_2Cl_3(PEt_2Ph)_6]Cl$,[14] $Rh_2Cl_6(P\text{-}n\text{-}Bu_3)_3$,[15] and $[Me_3PhN]_3Rh_2Cl_9$,[16] and the Rh–Rh distance in **1** (3.3284 (6) Å) is comparable with the values found in the two rhodium complexes quoted (3.187 (4) and 3.121 (5) Å, respectively). These distances are considerably longer than those normally associated with two-electron Rh–Rh bonds (2.617 (3)–2.841 (1) Å)[17] and probably indicate a repulsive rather than an attractive Rh–Rh interaction. The Rh–Cl–Rh angles in **1** differ somewhat among themselves (82.52 (4), 84.57 (4), and 81.99 (3)°) but are close to those observed in $Rh_2Cl_6(P\text{-}n\text{-}Bu_3)_3$ (82°)[15] and in $[Rh_2Cl_9]^{3-}$ (81.3 (3)°, average).[16] The M–Cl–M angles in related complexes having metal–metal bonds are much more acute, e.g., $[W_2Cl_9]^{3-}$ (58°)[18] and $[Mo_2Cl_9]^{3-}$ (64.5°).[19] As observed also in $[Rh_2Cl_9]^{3-}$,[16] the opening out of the Rh–Cl(bridge)–Rh angle in **1** from the "ideal" confacial bioctahedral value of 70.5° is matched by a reduction of approximately 9° in the average Cl(bridge)–Rh–Cl(bridge) angle from the ideal value of 90°. Related angular distortions from ideal octahedral geometry are found for the remaining interligand angles at each rhodium atom.

The average Rh–C(acyl) distance (2.002 (4) Å) is in the middle of the range for rhodium(III)–acyl complexes, e.g., $[RhCl(COCH_3)(PMe_2Ph)_3]PF_6$ (1.971 (5) Å),[1] $RhCl_2(COPh)(Ph_2PCH_2CH_2CH_2PPh_2)$ (1.991 (3) Å),[20] $Rh(COCH_2CH_2CH_3)(PEt_3)_2(mnt)$ (2.001 (7) Å),[21] $[Ph_4As][RhI(COC_2H_5)(PPh_3)(mnt)]$ (2.006 (14) Å),[22] and $[Me_3PhN]_2[Rh_2I_6(COCH_3)_2(CO)_2]$ (2.062 (23) Å).[23] The acetyl groups are oriented so that the acyl oxygen atoms are as far away as possible from the bridging chlorine atoms.

The Rh–Cl distances trans to L show considerable variation, those involving Cl(2), which is trans to a phosphine ligand on each rhodium atom, being significantly longer than those involving Cl(1) or Cl(3), which are trans to an acetyl group on

---

(12) Grim, S. O.; Ference, R. A. *Inorg. Chim. Acta* **1970**, *4*, 277–282.

(13) Mann, B. E.; Masters, C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1972**, 704–708.

(14) Raspin, K. A. *J. Chem. Soc. A* **1969**, 461–473.

(15) Muir, J. A.; Baretty, R.; Muir, M. M. *Acta Crystallogr., Sect. B* **1976**, *B32*, 315–317.

(16) Cotton, F. A.; Ucko, D. A. *Inorg. Chim. Acta* **1972**, *6*, 161–172.

(17) Cowie, M.; Mague, J. T.; Sanger, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 3628–3629 and references quoted therein.

(18) Watson, W. H., Jr.; Waser, J. *Acta Crystallogr.* **1958**, *11*, 689–692.

(19) Saillant, R.; Jackson, R. B.; Streib, W. E.; Folting, K.; Wentworth, R. A. D. *Inorg. Chem.* **1971**, *10*, 1453–1457.

(20) McGuiggan, M. J.; Pignolet, L. H. *Cryst. Struct. Commun.* **1979**, *8*, 709–714.

(21) Cheng, Chien-Hong; Hendriksen, D. E.; Eisenberg, R. *J. Organomet. Chem.* **1977**, *142*, C65–C68.

(22) Cheng, Chien-Hong; Spivak, B. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1977**, *99*, 3003–3011.

(23) Adamson, G. W.; Daly, J. J.; Forster, D. *J. Organomet. Chem.* **1974**, *71*, C17–C19.

Table VI. Principal Bond Distances (Å) and Interbond Angles (Deg) for $[Rh_2Cl_3(COCH_3)_2(PMe_2Ph)_4]PF_6 \cdot 0.5C_2H_4Cl_2$

(a) Bond Distances

atoms	$m = 1$	$m = 2$
Rh(*m*)-C(*m*1)	2.010 (5)	1.995 (5)
Rh(*m*)-P(*m*1)	2.302 (2)	2.278 (1)
Rh(*m*)-P(*m*2)	2.267 (1)	2.296 (1)
Rh(*m*)-Cl(1)	2.431 (2)	2.612 (1)
Rh(*m*)-Cl(2)	2.485 (1)	2.462 (1)
Rh(*m*)-Cl(3)	2.624 (1)	2.446 (1)
C(*m*1)-C(*m*2)	1.517 (9)	1.528 (9)
C(*m*1)-O(*m*)	1.210 (7)	1.195 (7)
P(*m*1)-C(*m*3)	1.821 (6)	1.832 (7)
P(*m*1)-C(*m*4)	1.838 (6)	1.828 (6)
P(*m*2)-C(*m*5)	1.820 (7)	1.833 (7)
P(*m*2)-C(*m*6)	1.825 (5)	1.824 (6)
P(*m*1)-C(*m*11)	1.822 (5)	1.826 (5)
P(*m*2)-C(*m*21)	1.826 (6)	1.822 (6)
Rh(1)-Rh(2)	3.3284 (6)	

(b) Bond Angles

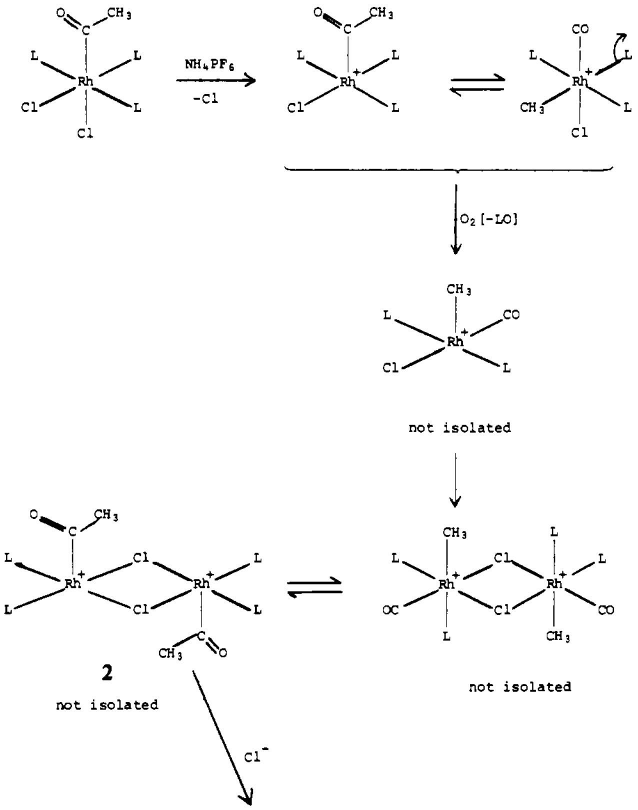
atoms	$m = 1$	$m = 2$
C(*m*1)-Rh(*m*)-P(*m*1)	92.1 (2)	86.0 (2)
P(*m*1)-Rh(*m*)-P(*m*2)	96.63 (5)	101.78 (5)
P(*m*2)-Rh(*m*)-C(*m*1)	87.9 (2)	89.3 (2)
Cl(1)-Rh(*m*)-P(*m*1)	170.51 (5)	97.76 (5)
Cl(1)-Rh(*m*)-P(*m*2)	87.62 (5)	94.23 (4)
Cl(1)-Rh(*m*)-C(*m*1)	96.6 (2)	174.2 (2)
Cl(2)-Rh(*m*)-P(*m*1)	91.77 (5)	171.20 (5)
Cl(2)-Rh(*m*)-P(*m*2)	171.49 (6)	87.00 (5)
Cl(2)-Rh(*m*)-C(*m*1)	93.2 (2)	95.0 (2)
Cl(3)-Rh(*m*)-P(*m*1)	91.76 (5)	88.10 (5)
Cl(3)-Rh(*m*)-P(*m*2)	99.22 (4)	168.84 (5)
Cl(3)-Rh(*m*)-C(*m*1)	171.5 (2)	96.7 (2)
Cl(1)-Rh(*m*)-Cl(2)	83.87 (5)	80.65 (4)
Cl(2)-Rh(*m*)-Cl(3)	79.09 (4)	83.09 (4)
Cl(3)-Rh(*m*)-Cl(1)	79.16 (4)	79.13 (4)
Rh(*m*)-P(*m*1)-C(*m*3)	111.5 (3)	120.6 (2)
Rh(*m*)-P(*m*1)-C(*m*4)	116.3 (2)	110.2 (2)
Rh(*m*)-P(*m*1)-C(*m*11)	118.7 (2)	113.1 (2)
C(*m*3)-P(*m*1)-C(*m*4)	103.3 (3)	100.9 (3)
C(*m*4)-P(*m*1)-C(*m*11)	104.2 (3)	105.3 (2)
C(*m*11)-P(*m*1)-C(*m*3)	100.7 (3)	105.1 (3)
Rh(*m*)-P(*m*2)-C(*m*5)	118.6 (2)	111.7 (2)
Rh(*m*)-P(*m*2)-C(*m*6)	112.0 (2)	110.9 (2)
Rh(*m*)-P(*m*2)-C(*m*21)	113.7 (2)	123.7 (2)
C(*m*5)-P(*m*2)-C(*m*6)	104.4 (3)	103.3 (3)
C(*m*6)-P(*m*2)-C(*m*21)	104.9 (3)	102.4 (3)
C(*m*21)-P(*m*2)-C(*m*5)	101.8 (3)	102.6 (3)
Rh(*m*)-C(*m*1)-O(*m*)	125.1 (4)	124.6 (5)
Rh(*m*)-C(*m*1)-C(*m*2)	116.0 (4)	115.3 (4)
C(*m*2)-C(*m*1)-O(*m*)	118.8 (5)	120.0 (5)
Rh(1)-Cl(1)-Rh(2)	82.52 (4)	
Rh(1)-Cl(2)-Rh(2)	84.57 (4)	
Rh(1)-Cl(3)-Rh(2)	81.99 (3)	

(c) Distances (Å) and Angles (Deg) for the PF_6^- Anion and the $C_2H_4Cl_2$ Solvent Molecule

average[a] P-F	1.541 (9)	C-Cl	1.70 (1)
average[a] F-P-F (cis)	90.6 (7)	C-C	1.53 (3)
average[a] F-P-F (trans)	175.8 (9)	C-C-Cl	110 (1)

[a] Quoted standard errors are sampling estimates $[\Sigma\Delta^2/n(n-1)]^{1/2}$.

Scheme I



1, R = CH_3; L = PMe_2Ph

one rhodium atom and a phosphine ligand on the other [Rh(1)–Cl(2) = 2.485 (1) Å, Rh(2)–Cl(2) = 2.462 (2) Å; Rh(1)–Cl(1) = 2.431 (2) Å, Rh(2)–Cl(3) = 2.446 (1) Å]. All these distances are significantly shorter than those trans to acetyl [Rh(1)–Cl(3) = 2.624 (1) Å, Rh(2)–Cl(1) = 2.612 (1) Å] as expected on the basis of the relative trans influences of acyl groups and tertiary phosphines.[24] A similar effect is observed in $[Rh_2I_6(COCH_3)_2(CO)_2]^{2-}$, where the Rh–I-(bridging) distance trans to acetyl (3.001 (2) Å) is markedly greater than that trans to a terminal Rh–I bond (2.679 (2) Å).[23]

The Rh–P distances and C–P–C angles are comparable with values found in related structures, e.g., $Rh_2Cl_6(P\text{-}n\text{-}Bu_3)_3$.[15] The Rh–P–C angles range from 110.2 to 123.7°, the smallest angles being associated with substituents directed toward the bridging chlorine atoms, thus presumably minimizing nonbonded contacts within the structure; cf. $[RhCl(COCH_3)(PMe_2Ph)_3]PF_6$.[1]

The unit cell contains two solvent molecules which are shown unambiguously to be 1,2-dichloroethane rather than the expected dichloromethane. They are constrained by crystal symmetry to have C_i symmetry and thus adopt the anti configuration, which has been shown by electron diffraction to be the conformer favored at lower temperatures in the gas phase.[25] The geometric parameters found in our study (C–Cl = 1.70 (1) Å, C–C = 1.53 (2) Å, C–C–Cl = 110 (1)°) are in reasonably good agreement with the more precise electron diffraction data (C–Cl = 1.788 (2) Å, C–C = 1.510 (6) Å, C–C–Cl = 109.2 (3)°).[25] The rather short C–Cl distance in the X-ray structure is almost certainly an artifact caused by our inability to analyze correctly and allow for the effects of the anisotropic thermal motion of the chlorine atoms. The presence of 0.5 mol of 1,2-dichloroethane/mol of dimer in the sample from which the crystal was taken was confirmed by ^1H NMR spectroscopy (see Experimental Section), but we do not know whether it was an adventitious impurity in the particular sample of dichloromethane used or whether it was formed by reaction of the complex with dichloromethane over the 3 weeks during which the crystals were grown. In either case it is remarkable that the small amount of 1,2-dichloroethane present was incorporated in preference to dichloromethane.

---

(24) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335–422.

(25) Kveseth, K. *Acta Chem. Scand., Ser. A* **1975**, *A28*, 482–490; **1975**, *29*, 307–311.

Discussion

It seems likely that when a solution containing the equilibrium mixture $[RhCl(COCH_3)L_3]^+ \rightleftarrows [RhCl(CH_3)(CO)L_3]^+$ is exposed to air, the dimethylphenylphosphine ligand trans to methyl dissociates and is oxidized irreversibly (Scheme I). The five-coordinate cation $[RhCl(CH_3)(CO)L_2]^+$ so formed might reasonably be expected to dimerize to give a dicationic di-μ-chloro complex containing six-coordinate rhodium(III), and this in turn could undergo methyl migration to give a dinuclear acetyl complex **2** containing five-coordinate rhodium(III). The observed tri-μ-chloro complex **1** presumably is formed by addition of Cl^- to **2**, the chloride ion probably being derived either from that eliminated on reaction of $RhCl_2(COCH_3)L_3$ with NH_4PF_6 or from the dichloromethane solvent. The latter source is a possibility in view of the unexpected finding of 1,2-dichloroethane in crystals of **1** (R = CH_3) grown from dichloromethane/methanol. Although we have not been able to isolate the di-μ-chloro complex **2**, Clark and Reimer[26] have reported the formation of the analogous di-μ-bromo complex $[Rh_2Br_2(COCH_3)_2L_4](PF_6)_2$ by treatment of 1 mol of $RhBr_2(CH_3)(CO)L_2$ with 1 mol of $AgPF_6$. However, the reported IR (C=O) and ^1H NMR data are sufficiently similar to those for our tri-μ-chloro complex as to suggest that the compound may in fact be the corresponding tri-μ-bromo complex, formed by the reaction

$$2RhBr_2(CH_3)(CO)L_3 + AgPF_6 \rightarrow [Rh_2Br_3(COCH_3)_2L_4]PF_6 + AgBr$$

Acknowledgment. We thank Dr P. A. Tucker for helpful discussion.

Registry No. $1\cdot0.5C_2H_4Cl_2$, 75149-77-8; **2**, 75149-79-0; $RhCl_2(COCH_3)L_3$, 22605-70-5; $RhCl_2(COC_2H_5)L_3$, 22605-71-6; $[RhCl(C_2H_4)_2]_2$, 12081-16-2; acetyl chloride, 75-36-5.

Supplementary Material Available: Listings of details of data collection (Table I), calculated phenyl hydrogen atom coordinates and isotropic thermal parameters (Table II), structure factor amplitudes (Table III), and bond distances and interbond angles of the phenyl rings (Table IV) (23 pages). Ordering information is given on any current masthead page.

---

(26) Clark, H. C.; Reimer, K. J. *Inorg. Chem.* **1975**, *14*, 2133–2139.

Contribution from the Institute for Materials Research, McMaster University, Hamilton, Ontario, L8S 4M1, Canada, and the Institute for Inorganic Chemistry, Technical University of Munich, 8046 Garching, Federal Republic of Germany

Crystal Structures of Two Crystalline Forms of Chloro-*cis*-diammine(1-methylcytosine-N^3)platinum(II) Nitrate, $[PtCl(NH_3)_2(C_5H_7N_3O)](NO_3)$, and Their ^1H NMR, IR, and Raman Spectra

BERNHARD LIPPERT,[1a] COLIN JAMES LYNE LOCK,*[1b] and ROBERT ANTHONY SPERANZINI[1b]

Received December 28, 1979

Chloro-*cis*-diammine(1-methylcytosine-N^3)platinum(II) nitrate, $[PtCl(NH_3)_2(C_5H_7N_3O)](NO_3)$, can be obtained in two monoclinic crystal forms: $P2_1/c$, a = 8.143 (2) Å, b = 6.899 (1) Å, c = 21.434 (3) Å, β = 91.27 (2)°, Z = 4; $C2/c$, a = 13.155 (6) Å, b = 9.754 (5) Å, c = 19.097 (7) Å, β = 99.70 (3)°, Z = 8. Data were collected for both crystals with use of Mo Kα radiation and a Syntex P2_1 diffractometer. The crystal structures were determined by standard methods; that of the $P2_1/c$ crystal was refined to R_1 = 0.035 and R_2 = 0.040 on the basis of 3018 reflections and that of the $C2/c$ crystal to R_1 = 0.047 and R_2 = 0.064 on the basis of 1700 reflections. The cation, in both crystals, has a normal structure and bond lengths (Pt–N(ammonia) = 2.04 (1)–2.053 (8) Å; Pt–N(3) = 2.026 (6), 2.06 (1) Å; Pt–Cl = 2.299 (2), 2.300 (2) Å). Both crystals contain a unit composed of two cations and two nitrate ions, both cations being hydrogen bonded to the same oxygen atom of a nitrate group through a proton on 4-NH_2 of the cytosine ring. Thus both nitrate ions can be considered as bridging the two cations. The principal difference in the crystal packing is that in the $P2_1/c$ structure this two cation–two anion unit is essentially planar, whereas in the $C2/c$ structure it is bent about the nitrate–nitrate axis. ^1H NMR spectra of the two compounds in D_2O reveal a fast exchange of the C(5) proton of the 1-methylcytosine ligand with deuterium ion upon heating. The corresponding C(5) deuterated 1-methylcytosine complexes have been isolated and studied by infrared spectroscopy.

Introduction

cis-Dichlorodiammineplatinum(II) is a useful anticancer agent[2–4] and is used in the treatment of testicular cancer.[4,5] The drug's mode of action has been postulated to involve cross-linking of the two strands of DNA, thus interfering with replication, and there is experimental evidence that, in vivo, the ability of *cis*-dichlorodiammineplatinum(II) to cross-link DNA is very much greater than that of *trans*-dichlorodiammineplatinum(II), which has no anticancer activity.[6]

We have been studying the interaction of *cis*-dichlorodiammineplatinum(II) with various DNA bases in order to investigate the stereochemistry of the interactions, and we routinely use X-ray crystallography to characterize the products. It has been shown that, in vitro, the platinum complex interacts preferentially with the guanine- plus cytosine-rich areas of DNA,[7] and we have obtained and examined a crystalline product of the type $[Pt(NH_3)_2(9\text{-ethylguanine})(1\text{-methylcytosine})](ClO_4)_2$.[8] In order to make these mixed complexes, it is necessary to make products in which one chlorine ion of *cis*-$PtCl_2(NH_3)_2$ has been replaced by a DNA base. Few, if any, of these complexes had been adequately characterized although products in which one chloride ion of K_2PtCl_4 had been replaced by a DNA base have been described.[9,10] In addition, complexes with one base attached

---

(1) (a) Technical University of Munich. (b) McMaster University.

(2) (a) Rosenberg, B. *Platinum Met. Rev.* **1971**, *15*, 42. (b) Cleare, M. J.; Hoeschele, J. D. *Ibid.* **1973**, *17*, 2. (c) Cleare, M. J. *Coord. Chem. Rev.* **1974**, *12*, 349.

(3) Roberts, J. J.; Thomson, A. J. *Prog. Nucleic Acid Res. Mol. Biol.* **1979**, *22*, 71.

(4) Cf. conference papers in *Biochimie*.

(5) Einhorn, L. H.; Furnas, B. *J. Clin. Hematol. Oncol.* **1977**, *7*, 662.

(6) Roberts, J. J.; Pascoe, J. M. *Nature (London)* **1972**, *235*, 282.

(7) Stone, P. J.; Kelman, A. D.; Sinex, F. M. *Nature (London)* **1974**, *251*, 736.

(8) Lippert, B.; Lock, C. J. L.; Speranzini, R. A., unpublished work.

(9) Terzis, A.; Hadjiliadis, N.; Rivest, R.; Theophanides, T. *Inorg. Chim. Acta* **1975**, *12*, L5.

(10) Kong, P. C.; Rochon, F. D. *J. Chem. Soc., Chem. Commun.* **1975**, 599.

0020-1669/81/1320-0335$01.00/0