(5) Å, respectively, some 0.08 Å shorter and 0.03 Å longer than those we find in $Co(CO)_3NO$. These differences are the consequence of the replacement of a relatively poor π acceptor ($SbPh_3$) with a good one (CO), followed by more effective competition for the available π-bonding electrons by a still better π acceptor (NO). We note that for $Co(SbPh_3)(CO)_2NO$ the sum of the bond orders of the bonds to cobalt, calculated as described in the preceding article,[16] is 7.87, in reasonably good agreement with the value 7.33 calculated for $Co(CO)_3NO$, as is also the value 6.95 calculated for $Co(PPh_3)_2(SO_2)(NO)$.[15] The total amount of π bonding from cobalt to its ligands in d^{10} complexes thus tends to be constant.

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Registry No. $Co(CO)_3NO$, 14096-82-3.

Supplementary Material Available: Tables of intensity data from each plate and averages from each camera distance (5 pages). Ordering information is given on any current masthead page.

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Dichlorotrifluorophosphorane (PCl_2F_3): Molecular Structure by Gas-Phase Electron Diffraction and Quadratic Force Field

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The molecular structure of gaseous PCl_2F_3 has been determined at a nozzle temperature of 22–24 °C. The chlorine atoms are found to be in equatorial sites, as predicted from other types of experiments. The values of some of the distance and angle parameters and some of the more important root-mean-square amplitudes of vibration are $r_g(P–F_e) = 1.546\ (9)$ Å, $r_g(P–F_a) = 1.593\ (4)$ Å, $r_g(P–Cl) = 2.004\ (2)$ Å, $\angle_\alpha(F_a–P–F_e) = 89.3\ (3)°$, $\angle_\alpha(Cl–P–Cl) = 122.0\ (5)°$, $l(P–F_e) = 0.052\ (8)$ Å, $l(P–F_a) = 0.047\ (3)$ Å, and $l(P–Cl) = 0.050\ (2)$ Å, where parenthesized quantities are estimated 2σ. Although the fluorine atoms are known to exchange at the temperature of our experiment, presumably by a Berry type mechanism that would generate isomers with chlorine atoms in axial positions, the diffraction data give no reliable indication of the presence of such isomers; neither, however, can small amounts be ruled out. Details of the structure are discussed.

Introduction

Pentacoordinated molecules having more than one type of ligand may exist in several stereoisomeric forms. In many of these molecules with fluorine atoms in both equatorial and axial sites—examples are $PF_3(NH_2)_2$, $PClF_4$, and PCl_2F_3, as well as PF_5 itself—the fluorine atoms are known to exchange. A possible mechanism for such exchange is the well-known Berry inversion,[2] which, in the case of PF_5, may be visualized as an increase of one of the equatorial angles from 120 to 180° accompanied by a simultaneous movement of the (former) axial fluorines into the gap. The detailed dynamics of the process are not well understood, but it appears[3] that the motion must be characterized in the classical sense as "flipping" rather than "flowing".

An interesting subject for study of inversion dynamics is the molecule PCl_2F_3. The distances involving the chlorine atoms are longer and are of greater weight than those involving fluorines at corresponding sites, so that identification of possible isomers from electron-diffraction measurements should be straightforward. In turn, both the kinds of isomers and the mixture composition are connected to the mechanism of the exchange process.

An early electron diffraction investigation of PCl_2F_3 by the "visual" method has been reported,[4] from which it was deduced that the chlorine atoms were located in the axial positions of a trigonal bipyramid. However, later NMR,[5,6] NQR,[6] infrared,[7,8] and Raman[7a] evidence points strongly to a molecule with equatorially sited chlorine atoms as the principal isomer. The electron-diffraction investigation reported here was undertaken to explore the questions of isomeric composition as well as to measure the values of the principal structural parameters.

Experimental Section

The sample of PCl_2F_3 was prepared as follows. To a 1-L Pyrex round-bottom bulb were added PF_3 (10 mmol) and anhydrous Cl_2 (9.5 mmol) at −196 °C. The reaction mixture was allowed to warm slowly and to remain at 25 °C for 1 h. The mixture was purified by a trap-to-trap distillation where the pure PCl_2F_3 was retained at −95 °C after having passed through a trap at −78 °C. The entire system had been carefully dried before any operation began. The purity of the compound was confirmed by infrared[7,8] and ^{19}F and ^{31}P NMR[6] spectroscopy. The spectra agreed with those in the literature.

The diffraction experiments were carried out in the Oregon State apparatus with the nozzle tip at 22–24 °C. Because PCl_2F_3 is readily hydrolyzed, the nozzle was first heated for 2 h at 200 °C under vacuum and then seasoned by a stream of sample to remove adsorbed water vapor. Conditions of the experiments were an r^3 sector, electron wavelengths of 0.054 95–0.054 99 Å (calibrated against CO_2 in separate experiments: $r_a(C{=}O) = 1.1646$ Å, $r_a(O{\cdot}O) = 2.3244$ Å), camera distances of 746.9 and 300.9 mm, exposure times of 70–189 s, 8 × 10 in. Kodak projector slide plates (medium), and development in Kodak D-19 developer diluted 1:1 for 10 min. Scattered intensity data were obtained in the usual way[9,10] from three plates made at each camera distance. Computer-generated backgrounds were subtracted,[11] and the result was multiplied by s ($s = 4\pi\lambda^{-1} \sin \theta$; 2θ is the scattering angle) to give useful molecular intensity data in the form[9] $sI_m(s)$ over the ranges $2.00 < s < 13.00$ Å^{-1} and $6.00 < s < 31.75$ Å^{-1} from the longer and shorter camera distances, respectively. Curves of the intensity data are shown in Figure 1. The data are available as supplementary material.

Radial Distribution. Figure 2 shows the final radial distribution of distances in PCl_2F_3 calculated in the usual way[9] from the modified mo-

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(1) (a) Oregon State University. (b) University of Idaho.

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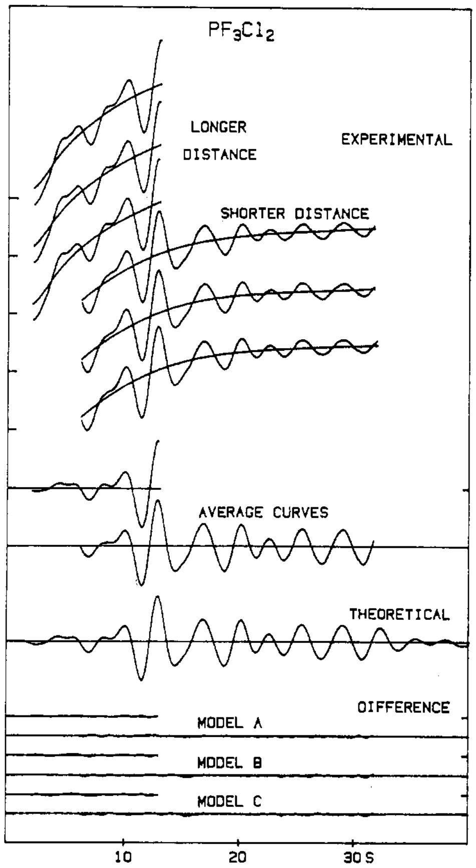

Figure 1. Intensity curves. Experimental total intensity curves, $s^4I_t(s)$, from individual plates are shown superimposed on the final calculated backgrounds. The average curves, $sI_m(s)$, are from the total intensities minus backgrounds times s. The theoretical curve corresponds to model A of Table II. The difference curves are experimental minus theoretical.

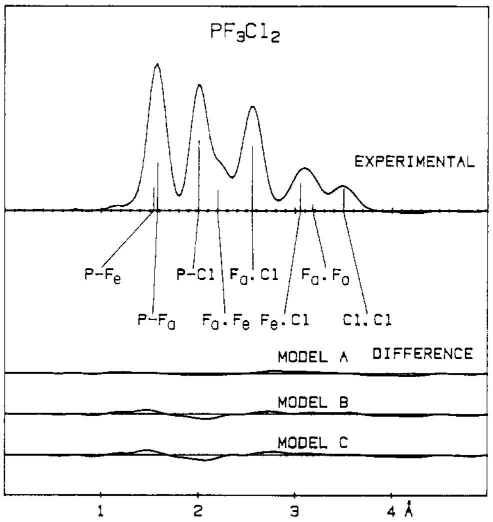

Figure 2. Radial distribution curves. The bars indicate the interatomic distances for model A; their lengths are proportional to the weights of the terms. The convergence factor B had the value 0.0025 Å^2.

lecular intensity $I'(s) = sI_m(s)Z_{\mathrm{Cl}}A_{\mathrm{P}}^{-1}A_{\mathrm{Cl}}^{-1}\exp(-0.0024s^2)$, where $A = s^2|F|$ and F is the complex electron-scattering amplitude.[12] Data in the unobserved region $s < 2.00$ Å^{-1} were taken from the theoretical intensity curve corresponding to the final model. As expected, the peaks of the radial distribution curve indicated that at least the principal isomer of gaseous PCl_2F_3 has the chlorine atoms in equatorial sites (Figure 3).

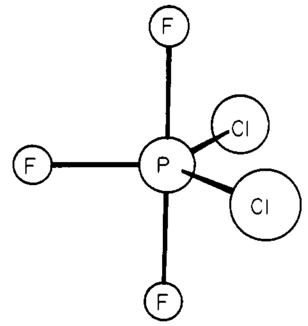

Figure 3. Diagram of the molecule.

Table I. Symmetry Force Constants and Calculated Wavenumbers for PF_3Cl_2[a]

a_1	F_{11}	P–F$_e$	5.900	0.7	0.5	0.3	1.0	925
	F_{22}	P–Cl		3.110	0.3	−0.1	−0.4	650
	F_{33}	P–F$_a$			4.782	0.0	−0.1	562
	F_{44}	α_e				0.465	−0.4	407
	F_{55}	α_a					2.859	124
a_2	F_{66}	α_a	1.684					363
b_1	F_{77}	P–Cl	2.706	0.15	1.0			667
	F_{88}	α_e		0.305	−0.4			429
	F_{99}	α_a			2.446			124
b_2	F_{1010}	P–F$_a$	4.627	0.6	0.9			895
	F_{1111}	α_a		1.834	0.1			490
	F_{1212}	α_a			1.745			337

[a] Units are aJ/Å^2 for stretching and aJ/rad^2 for bending constants. Units for interaction constants are commensurate. Wavenumbers (last column) are in cm^{-1}.

Quadratic Force Field. It was thought best to base the structure refinement on r_α type distances, which required calculation of corrections for the effects of vibrational averging. A quadratic force field for PCl_2F_3 consistent with the vibrational spectra[7] was available,[7b] but the later infrared work[8] had suggested some frequency and assignment changes that would affect the C_{2v} symmetrized force constants for the a_1, b_1, and b_2 blocks. However, our normal-coordinate analysis based on these suggestions led to C_{2v} symmetrized constants somewhat out of line with those for PF_5 and PCl_5 recalculated to the same symmetry.[13] It was found that force constants for PCl_2F_3 consistent with those for the other molecules required a reassignment of the 562-cm^{-1} band to a_1 (a combination of P–Cl stretch and axial and equatorial bends), the 429-cm^{-1} band to b_1 (a combination of P–Cl stretch and axial bend), and the 337-cm^{-1} band to b_2 (PCl_2 wag). This force field is shown in Table I; it reproduces the observed frequencies to within ±0.1 cm^{-1}. The symmetry coordinates were the same as those used for SOF_4 with $\zeta = 0.0$ and $\kappa = 1.0$, but the labels b_1 and b_2 are interchanged here to correspond with the earlier designations.[7b,8]

Structure Refinement. The structure of a PCl_2F_3 molecule of C_{2v} symmetry is defined by five parameters. These were taken to be $\langle r_\alpha(\mathrm{P{-}F})\rangle = [2r_\alpha(\mathrm{P{-}F_a}) + r_\alpha(\mathrm{P{-}F_e})]/3$, $\Delta r_\alpha = r_\alpha(\mathrm{P{-}F_a}) - r_\alpha(\mathrm{P{-}F_e})$, $r_\alpha(\mathrm{P{-}Cl})$, $\angle_\alpha(\mathrm{F_a{-}P{-}F_e})$, and $\angle_\alpha(\mathrm{Cl{-}P{-}Cl})$. The force field of Table I was used to calculate values for centrifugal distortion (δr) and the perpendicular amplitude corrections (K). These quantities, together with the experimental mean-square amplitudes of vibration (l), were used to convert the r_α distances specifyng the structure to average distance r_g and to r_a distances appropriate for the scattered-intensity formula. These distance conversions are given by $r_a = r_\alpha + \delta r + K - l^2/r_\alpha = r_g - l^2/r_\alpha$.

With use of the average intensity curves (Figure 1), refinement of the C_{2v} model converged rapidly to the results listed in Table II as model C. Since the agreement of the calculated and experimental curves (Figures 1 and 2) was excellent, it was clear that the amounts of other isomers, if present at all, must be small. In this circumstances our task was to set a likely upper limit for the amount of such isomers, and accordingly model C was modified to include allowance, through composition parameters, for molecules with one or two chlorine atoms in axial positions. Since the structures of these two isomers are not known, we used the bond lengths in PF_5,[14] PCl_5,[15] and our model C to deduce hypothetical struc-

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[12] The elastic amplitudes and phases were from: Schafer, L.; Yates, A. C.; Bonham, R. A. *J. Chem. Phys.* **1971**, *55*, 3055. The fluorine amplitudes were recalculated. Inelastic amplitudes used in the background removal were from: Cromer, D. T.; Mann, J. B. *J. Chem. Phys.* **1967**, *47*, 1892; Cromer, D. T. *Ibid.* **1969**, *50*, 4857.

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Table II. Refinement Results[a,b]

	model A[c]					model B		model C	
param	r_α, $\angle_\alpha$	r_g[d]	r_a[d]	l	l(calcd)[e]	r_α, $\angle_\alpha$	l	r_α, $\angle_\alpha$	l
$\langle r(P–F)\rangle$[f]	1.574 (2)					1.572 (2)		1.572 (2)	
$\Delta r(P–F)$[f]	0.052 (13)					0.061 (14)		0.062 (11)	
$r(P–Cl)$	2.001 (2)					2.001 (2)		2.002 (2)	
$\angle(F_a–P–F_e)$	89.3 (3)					89.8 (3)		89.8 (2)	
$\angle(Cl–P–Cl)$	122.2 (5)					121.5 (6)		121.6 (6)	
$P–F_e$	1.539 (9)	1.546	1.545	0.052 (8)	0.042	1.531 (10)	0.047 (8)	1.527 (8)	0.042 (7)
$P–F_a$	1.591 (4)	1.593	1.592	0.047 (3)	0.043	1.592 (5)	0.047 (5)	1.593 (4)	0.045 (5)
P–Cl	2.001 (2)	2.004	2.003	0.050 (2)	0.051	2.001 (2)	0.051 (3)	2.002 (2)	0.052 (2)
$F_a·F_e$	2.201 (4)	2.209	2.207	0.063 (5)	0.061	2.205 (5)	0.065 (6)	2.203 (4)	0.062 (4)
$F_a·Cl$	2.563 (3)	2.567	2.565	0.073 (3)	0.066	2.559 (3)	0.074 (3))	2.561 (3)	0.074 (3)
$F_e·Cl$	3.059 (7)	3.063	3.060	0.101 (8)	0.122	3.057 (8)	0.100 (9)	3.053 (7)	0.100 (9)
Cl·Cl	3.500 (9)	3.502	3.499	0.106 (8)	0.106	3.492 (11)	0.106 (9)	3.496 (11)	0.109 (9)
$F_a·F_a$	3.181 (9)	3.183	3.182	0.062 (11)	0.055	3.184 (9)	0.059 (13)	3.187 (8)	0.058 (12)
$\chi(PF_3(Cl_e)_2)$[g]	0.926 (42)					0.944 (52)		[1.000]	
$\chi(PF_3Cl_aCl_e)$[g]	0.019 (44)					0.056 (52)			
$\chi(PF_3O·2HCl)$[g]	0.054 (17)								
R[h]	0.030					0.039		0.040	

[a] Distances (r) and amplitudes (l) in angstroms; angles ($\angle$) in degrees. Uncertainties are estimated 2σ. [b] The first five parameters were used to define the geometry. [c] Preferred model; see text. [d] Uncertainties estimated to be the same as for r_α. [e] Calculated from force field of Table I. [f] See text for definitions. [g] Mole fractions. [h] $R = [\sum_i w_i \Delta_i^2 / \sum_i w_i (s_i I_i(\text{obsd}))^2]^{1/2}$ where $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$.

Table III. Correlation Matrix (×100) for Model A[a]

		σ[b]	r_1	r_2	r_3	r_4	r_5	$\angle_6$	$\angle_7$	χ_8	χ_9	l_{10}	l_{11}	l_{12}	l_{13}	l_{14}	l_{15}	l_{16}	l_{17}
1	$\langle r(P–F)\rangle$	0.045	100	−33	45	−4	−17	25	−31	29	42	1	46	−12	9	−12	6	−18	18
2	$\Delta(P–F)$	0.46		100	−99	96	40	−35	79	−50	−20	−83	−70	42	−32	25	−64	35	−62
3	$r(P–F_e)$	0.33			100	−91	−41	37	−79	51	25	79	73	−41	32	−25	61	−36	61
4	$r(P–F_a)$	0.15				100	38	−29	74	−44	−8	−88	−60	41	−31	22	−65	32	−60
5	$r(P–Cl)$	0.042					100	4	36	−71	3	−52	−13	58	−70	28	−14	30	−12
1	$\angle(Cl–P–Cl)$	17.3						100	−46	−12	34	17	27	3	−12	<1	32	7	20
7	$\angle(F_a–P–F_e)$	9.6							100	−25	−52	−65	−40	41	−16	27	−47	19	−47
8	$\chi(PF_3Cl_aCl_e)$	1.5								100	9	65	22	−72	63	−42	16	−46	18
9	$\chi(PF_3O·2HCl)$	0.60									100	17	−12	−22	−20	−25	4	<1	8
10	$l(P–F_e)$	0.26										100	36	−56	41	−30	53	−36	47
11	$l(P–F_a)$	0.093											100	2	16	10	51	−23	52
12	$l(P–Cl)$	0.050												100	−50	57	−8	34	−9
13	$l(F_a·F_e)$	0.14													100	−20	13	−29	12
14	$l(F_a·Cl)$	0.052														100	−2	22	−6
15	$l(F_e·Cl)$	0.23															100	−25	65
16	$l(Cl·Cl)$	0.23																100	−25
17	$l(F_a·F_a)$	0.38																	100

[a] For definitions of parameters see text. [b] Standard deviations (×100) from least squares. Distances (r) and amplitudes (l) in angstroms; angles in degrees.

tures for them adequate for our purpose. The parameters for the hypothetical structures were $r(P–F_e) = 1.54$ Å, $r(P–F_a) = 1.59$ Å, $r(P–Cl_e) = 2.00$ Å, $r(P–Cl_a) = 2.12$ Å, equatorial angles of 120°, and axial–equatorial angles of 90°. Refinements of PCl_2F_3 in which one or the other or both of these isomers were included as mixture components led to an only marginally better fit than that given by model C. The results from one of these refinements, that which included the more likely of the two isomers, $PCl_aCl_eF_3$, are found in Table II as model **B**. As a final refinement we designed a model that included provision for the isomer $PCl_aCl_eF_3$ and for the impurities PF_3O and HCl, products of the ready reaction of PCl_2F_3 with OH groups. Even though considerable care had been taken to eliminate moisture from the reaction vessels and the nozzle system of the diffraction apparatus, the knowledge that small amounts of PF_3O could affect our conclusions about the isomeric composition of PCl_2F_3 seemed to require a test. The parameters for this model included, besides those for the C_{2v} form of PCl_2F_3, the mole fraction of $PCl_aCl_eF_3$ (assumed structure as in model B) and the mole fraction of $PF_3O·2HCl$ (structure of PF_3O from the literature,[16] $r_a(HCl) = 1.250$ Å). The results are listed as model A in Table II.

Choice of Best Model. As is seen from the goodness-of-fit factor R, model A provides significantly better agreement with experiment than do models B and C; it follows from the remarks of the previous section that model A is also significantly better than the other models tested. Accordingly, we select model A as the best representation of our overall results. The intensity curve for this model as well as intensity differences for the other models of Table II is shown in Figure 1. The radial distribution curve differences are shown in Figure 2. Table III is a correlation matrix for the parameters of model A.

Discussion

Although the methods of structure analysis used by the early workers in gas electron diffraction were primitive by today's standards, their results nearly always agree to within their estimated uncertainties with those obtained from modern work. It is surprising, therefore, that Brockway and Beach (BB)[4] reached the wrong conclusion about the location of the chlorine atoms in PCl_2F_3. BB's theoretical intensity curves for their D_{3h} models and models with two equatorial chlorines are quite different, and they remark that the latter are in pronounced disagreement with the appearance of their diffraction photographs. On the other hand, the curve for BB's preferred D_{3h} model is completely different from our experimental intensity curve even after taking account of the curves' different mathematical forms. We have found that the differences between BB's preferred curves and ours cannot be due to PF_3O as an impurity in BB's sample. From the simple nature of BB's diffraction pattern, one may speculate that their sample was largely PF_3 and Cl_2.

So far as the structure of $P(Cl_e)_2F_3$ is concerned, all models tested give nearly the same answer. This may be seen by comparison of the results for models A and C; the differences seen here are the largest encountered and are only marginally significant. The P–Cl bond in PCl_2F_3 is shorter than the equatorial bonds in PCl_5 (2.023 Å,[15a] 2.020 Å[15b]). The $P–F_e$ bond in PCl_2F_3 is about equal to its counterparts and the $P–F_a$ bond is longer than

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its counterpart in PF_5[14] ($r(P-F_a) = 1.577$ Å, $r(P-F_e) = 1.534$ Å). At the same time the sum of the bond orders of the phosphorus bonds, estimated from Pauling's empirical bond order-bond length formula using the Schomaker-Stevenson radii with correction for electronegativity difference,[17] decreases from 7.2 (PF_5) through 6.1 (PCl_2F_3) to 4.6 (PCl_5). The decrease in bond order may be attributed to a parallel decreasing participation of phosphorus 3d orbitals in the bonding from that atom: as the fluorine atoms in PF_5 are replaced by the less electronegative chlorines, the positive charge on phosphorus decreases, the 3p-3d energy gap increases, and the bonding contribution of the 3d orbitals becomes smaller. One may suppose that, in the limit of no 3d participation, the equatorial bonds are sp^2 hybrids and the axial bonds are three-center bonds involving the last phosphorus p orbital. The more rapid increase in the axial compared to the equatorial bond lengths as fluorine atoms are replaced, for example in the series $PF_5 \rightarrow PCl_2F_3 \rightarrow PCl_5$, is consistent with this picture.

It is by now well established, especially from NMR experiments,[5,6] that the equatorial and axial fluorine atoms in pentavalent phosphorus compounds undergo rapid exchange at ordinary temperatures. It has also been shown[18] that the mechanism for the exchange is almost certainly the Berry inversion.[2] Since the Berry mechanism leads to at least one chlorine atom in an axial site in the case of PCl_2F_3, it was hoped that our measurements would provide direct structural evidence for the consequences of Berry inversion. Unfortunately, the results in Table II indicate that we have no proof of the presence of $PCl_aCl_eF_3$ in our sample: the allowance for possible PF_3O (model A compared to model B) leads to significantly better agreement than does allowance for $PCl_aCl_eF_3$ (model B compared to model C). Similar remarks could, of course, be made about the isomer $P(Cl_a)_2F_3$. Nevertheless, if one regards the value 0.056 as an upper limit for the mole fraction of $PCl_aCl_eF_3$ (model B), one may make a crude estimate of the lower limit for the free energy difference of the two isomers. The result for $\Delta G° = G°(PCl_aCl_eF_3) - G°(P(Cl_e)_2F_3)$ calculated from the mole ratio 0.056/0.94 is about 1.7 kcal/mol at room temperature and is consistent with the value 7.2 ± 0.5 kcal/mol estimated[5a] for the activation energy of the interconversion.

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Registry No. PCl_2F_3, 13454-99-4.

Supplementary Material Available: Tables of total scattered intensities, calculated backgrounds, and average molecular intensities from two camera distances (9 pages). Ordering information is given on any current masthead page.

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Axial-Equatorial Isomerism in the Complexes $M(CO)_4(L)$ (M = Fe, Ru, Os; L = Group 15[†] Ligand). Crystal Structures of ax-$Ru(CO)_4(AsPh_3)$, ax-$Ru(CO)_4(SbMe_3)$, and eq-$Os(CO)_4(SbPh_3)$

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The compounds $M(CO)_4(L)$ (M = Fe, Ru, Os; L = EPh_3, E = P, As, Sb; L = PMe_3, $P(OCH_2)_3CMe$. M = Ru, Os; L = $SbMe_3$) have been synthesized from L and $M(CO)_5$. The crystal structures of ax-$Ru(CO)_4(AsPh_3)$, ax-$Ru(CO)_4(SbMe_3)$, and eq-$Os(CO)_4(SbPh_3)$ have been determined by X-ray crystallography. ax-$Ru(CO)_4(AsPh_3)$: space group $P\bar{1}$; $a = 10.605$ (3), $b = 11.068$ (4), $c = 9.979$ (3) Å; $\alpha = 113.57$ (3), $\beta = 93.14$ (3), $\gamma = 91.47$ (3)°; $Z = 2$; $R_1 = 0.020$, $R_2 = 0.021$ (1650 observed reflections); $AsPh_3$ in an axial position of the trigonal-bipyramidal coordination sphere, Ru-As = 2.461 (1) Å. ax-$Ru(CO)_4(SbMe_3)$: space group $R3$, $a = 10.378$ (1), $c = 9.632$ (1) Å; $Z = 3$; $R_1 = 0.023$, $R_2 = 0.030$ (523 observed reflections); $SbMe_3$ axial, Ru-Sb = 2.619 (1) Å. eq-$Os(CO)_4(SbPh_3)$: space group $P\bar{1}$; $a = 11.123$ (2), $b = 11.284$ (4), $c = 12.714$ (4) Å; $\alpha = 129.29$ (2), $\beta = 102.35$ (2), $\gamma = 102.45$ (2)°; $Z = 2$; $R_1 = 0.019$, $R_2 = 0.021$ (3115 observed reflections); $SbPh_3$ equatorial, Os-Sb = 2.612 (2) Å. Infrared spectroscopy revealed that in solution many of the complexes exhibited axial-equatorial isomerism. The tendency to give the less common equatorial isomer was Ru > Os >> Fe, Sb > As > P, Ph > Me, and $P(OCH_2)_3CMe$ > PMe_3, PPh_3. The order for the group 15 element was rationalized in terms of the σ-donor ability of the element: in agreement with theoretical predictions, weaker donors prefer the equatorial site. The π-bonding ability of the ligands may also be important in determining the other trends. Carbon-13 NMR spectra, which revealed the isomers were in rapid equilibrium in solution, were also recorded.

Introduction

The site preference of ligands in trigonal-bipyramidal complexes has been the subject of considerable theoretical and experimental interest.[1-9] For most compounds of the type $M(CO)_4(L)$ (M = Fe, Ru; L = group 15 ligand), spectroscopic and crystallographic evidence shows that the non-carbonyl ligand adopts an axial site in the coordination sphere of the metal.[5,10-14] This site preference has usually been rationalized in terms of the π-acceptor properties of the ligands: the better π-acceptor ligand, CO, has a greater preference for the equatorial position.[15] This assumption has

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[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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