^{183}W, have a positive magnetogyric ratio. Since in Figure 3a the ^{31}P spins are not excited and the ^{183}W high-frequency cross-peak correlates with the low-frequency ^{1}H peak, it follows that sign J(W,P) $\neq$ sign J(H,P). By the same argumentation Figure 3b yields: sign J(W,H) $\neq$ sign J(P,H). Since ^1J(W,P) can be assumed to be positive,[7] the signs of the residual couplings can be fixed.

The $\delta(^{183}W)$ value for the Cp-bridged complex **1** is similar to that observed earlier for $CpW(CO)_3H$.[7] Also the ^{183}W shift of **2** fits well to what has been obtained for $[CpW(CO)_3]_2$.[7] In view of the large ^{183}W scale, in such binuclear tungsten complexes $\delta(^{183}W)$ does not seem to depend significantly upon the type of the substituent (CO, H, PMe_2) that bridges the two tungsten atoms. The ^{183}W parameters of **3** support the assumption that there is a heteroallylic PW^2P moiety.[22] In such a system the phosphorous atoms have partial double bond character that is reflected by (compared to **2**) smaller $J(W^1,P)$ and higher $J(W^2,P)$ values. The relatively unchanged shift for W^1 and the substantial deshielding of W^2 indicate that relevant contributions to the bonding in the heteroallylic system results from interactions of its terminal atoms with W^1.

Conclusion

From our findings we conclude that in practice the sensitivity gain of the reverse two-dimensional NMR technique over the INEPT observation scheme is quite dramatic for low-γ spin-$^1/_2$ nuclei like ^{183}W. In particular since on-resonance conditions for the ^{183}W nucleus to be measured hardly can be met if $\delta(^{183}W)$ is unknown, the advantage of the ^{1}H- and ^{31}P-detected multiple-quantum ^{183}W spectroscopy becomes evident. Furthermore this technique can also give the relative signs of scalar spin–spin couplings. Even when the scalar coupling of the insensitive low-γ nucleus to a sensitive nucleus like ^{1}H or ^{31}P is small, we feel that the reverse two-dimensional recording technique is the method of choice.

Registry No. **1**, 106468-74-0; **2**, 109390-34-3; **3**, 109390-35-4.

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Syntheses and Structural Characteristics of New Highly Fluorinated Di-*tert*-butyl-1,3,2,4-diazadiphosphetidines

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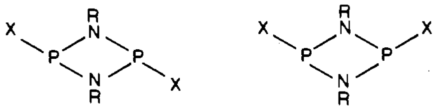
A series of lithium salts of polyfluorinated alcohols were reacted with *cis*-1,3-di-*tert*-butyl-2,4-dichloro-1,3,2,4-diazadiphosphetidine (II) to form the polyfluoroalkoxy derivatives. The acyclic derivatives, i.e., R_fO = CF_3CH_2O, $CF_3CF_2CH_2O$, or $CF_3CF_2CF_2CH_2O$, gave the trans isomer as the major and stable product. The trans isomer also was the sole product with hexamethyldisilazane. However, when R_fO = C_6F_5O or $(CF_3)_2CHO$, the cis isomer was more stable. Silver trifluoroacetate reacted with compound II resulting in the trans isomer as the major product that on standing at 25 °C underwent Arbuzov rearrangement. Reaction with lithiated polyfluorinated diols, $LiOCH_2(CF_2)_{2,3}CH_2OLi$, produced the polyfluorobis(alkoxy-bridged) diazaphosphetidine compounds.

Introduction

Syntheses and structural properties of 1,3,2,4-diazadiphosphetidines, I (R = aryl or alkyl; X = Cl), and their derivatives continue to attract considerable interest among synthetic chemists.[2–6] Although the first such compound, where R = C_6H_5 and X = Cl, was synthesized in 1894,[7] it was not until 1969 that a 1,3,2,4-diazadiphosphetidine (R = t-C_4H_9; X = Cl) was fully characterized.[8] Considerable structural data have been gathered for compound I, especially where R = t-C_4H_9 or C_6H_5 and X = OR or NR′R″ (R = R′ and R″ = alkyl), to learn about the geometry at P(III).[2,9,10] There appears to be a direct correlation between the ^{31}P chemical shift and the geometric isomer present; i.e., the typical chemical shift for the *trans* isomer is on average 80–90 ppm downfield from the cis isomer of I.[2]



trans cis

I

Advantage has been taken of the labile character of the phosphorus–chlorine bond to introduce alkoxy and dialkylamino substituents by straightforward metathetical reactions with retention of the four-membered heterocyclic ring.[2,9–11] When R = t-C_4H_9 and X = alkoxy or amino, the cis isomers are thermodynamically more stable and the trans isomers that are formed in smaller yield are readily converted to the cis isomers either in solution at 25 °C or upon extended heating. The ^{31}P NMR resonances for the cis isomers are found at higher field. Of particular relevance to our study of 1,3,2,4-diazadiphosphetidines with fluorinated substituents was the report that *only* the cis isomer was obtained when I (R = t-C_4H_9; X = Cl) was reacted with CF_3CH_2OH in the presence of triethylamine to form the first such compound with fluorine-containing substituents at P(III) (I: R = t-C_4H_9; X = CF_3CH_2O).[10,11]

In an attempt to learn more about the effects of introducing nonsterically demanding, as well as bulky, strongly electron-withdrawing, substituents at phosphorus(III) on the formation, stability, and relative amounts of cis and trans isomers, we report the results obtained when metathetical reactions were carried out

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(1) (a) University of Idaho. (b) Washington State University.
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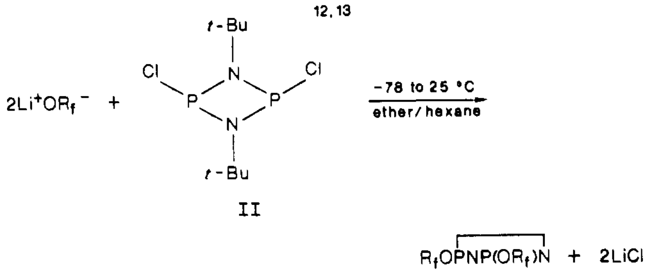
between II and (i) acyclic *n*-polyfluoroalkoxides, (ii) branched polyfluoroalkoxide and perfluoroaryloxide; (iii) polyfluorodialkoxides, (iv) trifluoroacetate, and (v) hexamethyldisilazane.

Results and Discussion

Compound II used throughout this study was the *cis*-1,3-di-*tert*-butyl-2,4-dichloro-1,3,2,4-diazadiphosphetidine (R = t-C_4H_9; X = Cl). It was prepared from trichlorophosphine and *tert*-butylamine based on the literature method.[12]

(i) Reactions of II with Cyclic and Acyclic Polyfluoroalkoxides. The lithium salt of each of the *n*-polyfluoroalcohols was preformed by reacting *n*-butyllithium with the respective alcohol prior to adding an ether solution of II slowly at −78 °C.

$$R_fOH + n\text{-}C_4H_9Li \xrightarrow[\text{ether/hexane}]{-78\text{ to }25\text{ °C}} Li^+OR_f^- + n\text{-}C_4H_{10}$$



t-Bu = $C(CH_3)_3$; R_f = CF_3CH_2 (III), $CF_3CF_2CH_2$ (IV), $CF_3CF_2CF_2CH_2$ (V), C_6F_5 (VI), $(CF_3)_2CH$ (VII)

With the exception of the lithium salt of pentafluorophenol, which was not stable above −40 °C, all of the lithium salts were formed by warming the reactants slowly to and holding the mixture at 25 °C for ~1 h. However, all reactions were carried out at −78 °C.

The presence and relative amounts of cis and trans isomers were established by the positions of the ^{31}P NMR chemical shifts and the relative areas of the resonance peaks observed. In some cases, the correlation of the ^{31}P NMR chemical shift with the cis or trans isomer was verified by an X-ray structure determination as described below. Earlier[10] in a series of alkoxy derivatives of II, where III is one example, the product was almost entirely the high-field isomer (cis) with a resonance in the ^{31}P NMR spectrum at δ 143.3. No isolable amount of a compound whose resonance was observed at δ 223.0 (trans) was obtained. The cis isomer was the stable one. In our present work, we find that the trans isomer (low field) was obtained in more than an 8-fold excess relative to the cis isomer (high field) for not only the CF_3CH_2O derivative but also derivatives that contain $CF_3CF_2CH_2O$ (IV) or $CF_3CF_2CF_2CH_2O$ (V). The ^{31}P NMR chemical shifts for the isomers of compounds III, IV, and V are essentially constant at δ 223 (trans) and at δ 144 (cis) with the ratio of trans/cis > 8.

The cases where the trans isomers were obtained as the major products occurred when lithiated *n*-polyfluoroalkoxides were reacted with II. However, we were able to reproduce the results of earlier workers,[10] i.e., formation of the cis isomer as the stable species when triethylamine was used as the base in the reaction of the polyfluoroalkyl alcohols with II. Interestingly, in our reactions, the trans isomers appear to be the thermodynamically stable ones since no change in isomer distribution occurred either when the compound was allowed to stand for a long time at 25 °C or when the compound was heated at 60 °C for 12 h. These results that at first seem rather puzzling can be rationalized by the fact that when triethylamine was utilized, triethylammonium chloride was a reaction product that could acid catalyze the isomerization of the trans isomer to the cis isomer. When the lithiated alcohol was used, the LiCl formed in the reaction did not play a similar catalytic role; thus, the trans isomer is both the kinetic and thermodynamic favored isomer.

Table I. ^{31}P NMR Chemical Shifts for Derivatives of II Where X = Branched Polyfluoroalkoxide or Other Bulky Group

	chem shift, ppm		
X	trans (low field)	cis (high field)	cis:trans ratio
C_6F_5O, VI	252	162.6	all cis
$(CF_3)_2CHO$, VII		157.4	all cis
$(CH_3)_2N^a$	184.7	95.0	10:1
$C_4H_8N^b$	165.1	76.7	
$Mo[\eta^5\text{-}C_5(CH_3)_5](CO)_2^c$	224.6		all trans
$C_5H_{10}N^b$	182.3	91.9	all cis
$C_2H_5O^d$	209.7	131	10:1
Cl, II		207.7	all cis

[a] Reference 9 (on standing at room temperature for 2 days). [b] Reference 11. [c] Reference 4. [d] Reference 10. (The amount of cis isomer increased relative to the trans isomer after 24 h heating at 120 °C)

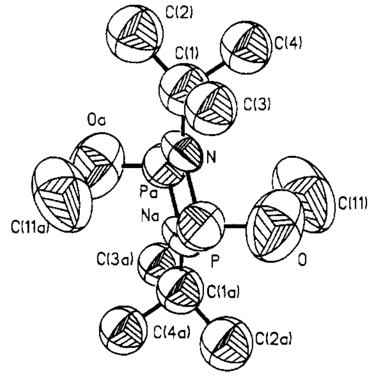


Figure 1. ORTEP view of *trans*-V showing the atom numbering scheme. Bond lengths and angles for core atoms [distances (Å); angles (deg)]: P(1)–N = 1.712 (12), P(1)–O = 1.615 (21), P(1)–P(1a) = 2.569 (12), O–C(11) = 1.476 (39), N–C(1) = 1.490 (19); ∠N–P(1)–N(a) = 79.5 (5), ∠O–P(1)–N = 104.2 (7), ∠P(1)–N–P(1a) = 100.5 (5), ∠C(11)–O–P(1) = 113.9 (19), ∠P(1)–N–C(1) = 125.7 (11), ∠P(1a)–N–C(1) = 133.8 (11).

When the lithium salts of hexafluoro-2-propanol and pentafluorophenol were reacted with II, cis isomers were formed in larger amounts than trans isomers. Upon standing or recrystallization, all of the trans isomer was converted to the cis isomer. In Table I are given the ^{31}P NMR chemical shifts for these compounds and for others from the literature.

With the exception of the ^{31}P NMR chemical shifts for II, the analogous shifts for III–VII are invariably shifted to much lower fields than other examples in the literature as shown in Table I. The trans isomer of VII was not observed in the ^{31}P NMR spectra and, thus, not isolated. This shift to lower field is to be expected since the fluorinated ligands would tend to deshield the phosphorus nuclei. The ^{31}P chemical shift for the cis isomer of VI is at relatively low field at δ 162.6, but this can be safely assigned to the cis isomer on the basis of an X-ray crystal structure determination.[14] The trans isomer of VI is formed in very small amounts and is converted rapidly on standing at 25 °C to the thermodynamically more stable cis form.

An X-ray crystal structure determination would confirm conclusively the existence of the trans isomer of the *n*-polyfluoroalkoxy-substituted diazodiphosphetidines. The crystals obtained thus far were badly twinned and showed great disorder in the portion of the *n*-polyfluoroalkoxy chain. The exact positions of the members of the alkoxy chains have not been determined. However, in Figure 1 is shown the ORTEP view of the ring portion of V. The trans isomer is definitely confirmed. The experimental details are as described earlier.[14,15]

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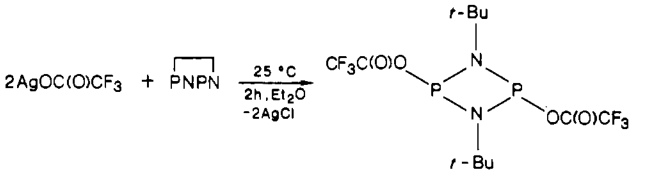
(13) For simplicity, compound **II**, *cis*-1,3-di-*tert*-butyl-2,4-dichlorodiazadiphosphetidine will be denoted as $\overline{\text{PNPN}}$ whereever applicable.

(14) Kamil, W. A.; Bond, M. R.; Shreeve, J. M. *Inorg. Chem.* **1987**, *26*, 2015.

We were less successful in synthesizing perfluoroalkoxy derivatives of II, particularly in our efforts to take advantage of the positive nature of the chlorine in perfluoroalkyl hypochlorites, e.g., in CF_3OCl which could have oxidized the chlorine bonded to phosphorus and formed a CF_3O-P bond. Unfortunately, after a variety of attempts, analysis of the products by ^1H, ^{31}P and ^{19}F NMR spectra showed only cleavage of the ring. Furthermore, we found it impossible to add chlorine to the ring phosphorus atoms in III either via chlorine itself or by using phosgene. On the basis of the ^{31}P NMR spectrum of the products from the phosgene reaction with III at -40 °C, the trans isomer had been converted to the cis isomer. The ^{31}P chemical shift had changed from δ 223 to 143. Carbonyl fluoride was not useful as a fluorinating reagent. This is surprising since trans isomers with nonpuckered rings and, thus, better eclipsing of nitrogen–phosphorus lone pairs, should render the phosphorus atoms more nucleophilic.[2] However, oxidation of phosphorus(III) bonded to three electronegative groups should be more difficult since the electron pair on P(III) is less reactive even though the geometry at phosphorus is pyramidal.

(ii) Reactions of II with Silver Trifluoroacetate, Lithium Hexamethyldisilazane, and Other Nucleophiles. In anhydrous diethyl ether, $AgOC(O)CF_0$ underwent metathesis with II to form VIII with concomitant precipitation of AgCl. The reaction was complete in ~2 h to form a product (45% yield) that was only marginally stable at 25 °C. The AgCl was removed by filtration. The trans isomer was the major product. Its ^{31}P NMR chemical shift was at δ 179.1 while the cis isomer had a ^{31}P resonance at δ 161.6. The decomposition products resulted from an Arbuzov rearrangement of the trifluoroacetate substituents. The $^{31}P\{H\}$ NMR showed a gradual increase in intensity of the peak at δ 3.88, and correspondingly the ^{19}F NMR spectra also showed another peak at ϕ -76.2. The IR spectra showed a new C=O stretching band at 1724 cm^{-1} ($CF_3C(O)-$) in addition to the one at 1777 cm^{-1} ($CF_3C(O)O-$) of higher intensity. Very strong IR bands in the 1300–1100-cm^{-1} region indicate the presence of $>P=O$ as well as CF_3 stretching vibrations.

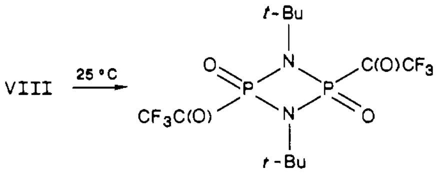


VIII

Table II. Summary of Stable Isomers Formed as a Function of Substituent on Nitrogen and on Phosphorus in II

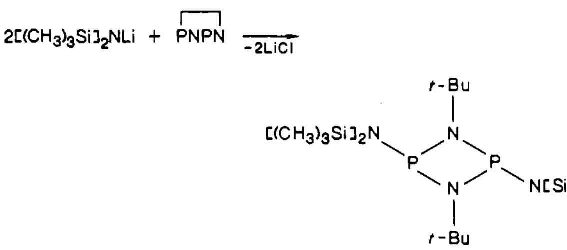
R	X	stable isomer
a	$CF_3C(O)O$	trans:cis = 7:1
a	$[(CH_3)_3Si]_2N$	trans
a	$OCH_2(CF_2)_{2,3}CH_2O$	cis
a[b]	C_5H_5N	cis
a[c]	$(CH_3)_3C$	trans
a[d]	$(CH_3)_3SiNCH_3$	cis
C_6H_5[e]	$(C_6H_5)_2N$	trans
$(CH_3)_3Si$[f]	$[(CH_3)_3Si]_2N$	trans
C_6H_5[g]	$(C_2H_5)_2N$	trans

[a] R = *tert*-butyl. [b] Reference 17. [c] Reference 18. [d] Reference 11. [e] Reference 3. [f] Reference 19. [g] Reference 9.



IX

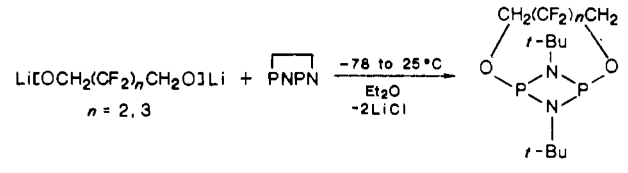
Since we had observed in this work that rather small changes in nucleophile character would cause the different isomer to be stable, e.g., compare CF_3CH_2O (trans) with $(CF_3)_2CHO$ (cis), we compared the reaction products obtained with $[(CH_3)_3Si]_2N^-$ and $[(CH_3)_3Si]N^-CH_3$ (cis).[11] The lithium salt of hexamethyldisilazane with II gave the trans isomer of X as the major product. The compound obtained in 30% yield was easily recrystallized from ether or pentane. Its ^{31}P NMR spectrum had only a single resonance at δ 211.9. Thus, in this case the bulkier ligand gives rise to a trans isomer in contrast to the stable cis isomers of C_6F_5O or $(CF_3)_2CH$.



X

Metathetical reactions of other nucleophiles, such as $Hg(CF_3)_2$, CF_3SH, and $CF_3C\equiv CH$, with II either did not proceed at all or else resulted in decomposition of the heterocyclic ring. The reactions of the latter two compounds were particularly vigorous either in the presence of $(C_2H_5)_3N$ or as their lithium salts, which precluded employment of these routes to the desired compounds.

(iii) Reactions of II with Polyfluorinated Diols. The reactions with lithiated polyfluorinated diols $HOCH_2(CF_2)_nCH_2OH$ (n = 2,3) proceeded smoothly to give bridged compounds under conditions analogous to those for the polyfluoroalkoxides described above.



XI

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(15) Crystal data: $C_{16}H_{22}N_2O_2P_2$ (V) is triclinic, space group $P\bar{1}$, with a = 6.169 (2) Å, b = 9.928 (4) Å, c = 11.164 (4) Å, α = 75.49 (3)°, β = 89.56 (3)°, γ = 80.89 (3)°, and Z = 1. X-ray diffraction data were collected on a Nicolet R3m/E diffractometer by using Mo Kα radiation with a graphite monochromator. Rotation photographs showed the crystal to be slightly twinned while peak scans showed broad, asymmetric peaks. Data collection proceeded on this crystal in spite of the poor crystal quality since it was one of the best crystals found (many others were badly twinned to the point of being polycrystalline). Data were collected out to 45° in 2θ with a total of 1906 reflections collected. Two check reflections, $(1\bar{3}\bar{3})$ and $(2\bar{2}\bar{1})$, were monitored every 93 reflections, and a crystal decay correction based on a curve fitted to the intensities of these reflections was applied to the data set. Lp corrections were also applied to the data; however, absorption corrections were not made. A total of 23 peaks were rejected from the data set because of background imbalance (the background imbalance rejection criteria had been increased to 2.5 times their default values to prevent rejection of too many peaks), and 15 peaks were rejected because of asymmetric peak shapes. The structure was solved by direct methods and refined by using the SHELXTL package of programs provided by Nicolet. Equivalent reflections were averaged together to give 1687 unique reflections (R_{merge} = 0.0181) with 934 reflections having $|F| > 3.0\sigma(F)$. Intensity statistics gave a strong indication that the crystal was centrosymmetric, so the structure was solved in space group $P\bar{1}$ with only one molecule per unit cell. The phosphorus, nitrogen, and oxygen atoms were found on the initial E map. Subsequent least-squares and electron density difference map refinement revealed that most of the atoms outside the core of the molecule were disordered. Atom positions were included in the refinement for many of these atoms; however, their bond lengths and angles are unreliable and are not reported. It was also found that the phosphorus atom was disordered, the refined site occupation factor showing one position to be occupied 90% of the time. The final refinement gave R = 0.2125, R_w = 0.2932 (w = $(\sigma^2(F) + gF^2)^{-1}$, g = 0.016), and goodness of fit = 2.028. Because of the extreme disorder and the poor quality of the data, the crystal structure refinement remains in an unfinished state. In spite of this fact, it is possible to draw several important conclusions. Since the molecule lies on a center of inversion, it is clear that it must contain the trans isomer and that the central P_2N_2 ring must be planar. Within this ring, the P–N distances are 1.712 (12) Å while the N–P–N and P–N–P angles are 79.5 (5) and 100.5 (5)°. The angles between the ring and substituents are O–P–N = 104.2 (7)° and P–N–C = 125.7 (11) and 133.8 (11)°.

The products obtained were slightly yellow, viscous, involatile liquids. Attempts to recrystallize them from pentane or ether were not successful. Both compounds ($n = 2, 3$) were characterized via elemental analysis, mass spectral analysis (M^+), and ^{1}H, ^{19}F, and ^{31}P NMR spectra. Interestingly, the ^{31}P NMR chemical shift at δ 220 (s) is well outside the range reported earlier for the high-field (cis) isomers including other bridged or caged compounds.[16] The ^{19}F chemical shifts did not change from those of the diols themselves, and the ^{31}P NMR shifts are essentially identical for both $n = 2$ and 3. This is not too surprising even though in nonfluorinated but shorter diol-bridged ($O(CH_2)_nO$; $n = 2, 3$) bridged diazadiphosphetidine systems,[10] a difference of ~40 ppm in the ^{31}P NMR chemical shift was observed in changing from $n = 2$ to $n = 3$. The polyfluorinated bridges contain six and seven atoms, respectively, while the nonfluorinated ones have five and six members.

In Table II, structural information for the new 1,3,2,4-diazadiphosphetidines, VIII, X, and XI, plus data for other similar systems is summarized. The correlation of the ^{31}P NMR chemical shifts with the geometric isomers is well established. For the 1,3-di-tert-butyl-2,4-diazaphosphetidines, the cis isomers give ^{31}P NMR chemical shifts at higher field than the trans isomers. In the case of large, more sterically demanding substituents at P(III) in II, it would be expected that the formation of the trans isomer would help to alleviate destablizing steric interactions. However, in our study and in those of others, this does not hold, e.g., in both the hexafluoroisopropanol, VII, and pentafluorophenol, VI, cases, the major thermodynamically stable product is the cis isomer. The cis pentafluorophenoxy rings orient themselves to relieve the steric strain, and also the $\overline{\text{PNPN}}$ skeleton is essentially planar having been changed markedly from the conformation of II.[14] In addition, the ^{31}P NMR chemical shift of VI is at a much lower value than that previously reported for nonbridged cis isomers.

Experimental Section

Materials. 1,3-Di-*tert*-butyl-2,4-dichlorodiazadiphosphetidine, $[ClPNC(CH_3)_3]_2$, was prepared as described in the literature.[12] CF_3CH_2OH, $CF_3CF_2CF_2CH_2OH$, C_6F_5OH, $(CF_3)_2CHOH$, $[(Me)_3Si]_2NH$, and $CF_3C(O)OAg$ were obtained from Aldrich, and $CF_3CF_2CH_2OH$ was obtained from Fairfield Chemical Co. The diols, $HOCH_2(CF_2)_nCH_2OH$ [$n = 2, 3$], were supplied by 3M.

General Procedure. Gases and volatile liquids were handled in a conventional Pyrex glass vacuum system equipped with Heise-Bourdon tube and Televac thermocouple gauges. All inert-atmosphere manipulations were carried out in a N_2-flushed drybox and with Schlenk-type glassware.[20] Infrared spectra were recorded with a Perkin-Elmer 599B or 1710 FT-IR spectrometer on liquid films between two KBr plates or as KBr pellets. ^{19}F, ^{1}H, and ^{31}P NMR spectra were obtained on a JEOL FX90Q spectrometer by using $CFCl_3$, $Si(CH_3)_4$, and 85% H_3PO_4 as internal standards, respectively. The chemical shifts downfield from these references have positive values. ^{19}F, ^{1}H, and ^{31}P NMR spectra were obtained at operating frequencies of 84.26, 90.0, and 36.20 MHz, respectively. All mass spectra were taken with a VG 7070HS mass spectrometer. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

Reaction of 1,3-Di-*tert*-butyl-2,4-dichlorodiazadiphosphetidine (II) with LiOR$_f$. The alcohol, dissolved in 75 mL of anhydrous diethyl ether, was lithiated by slowly adding to it a stoichiometric amount of 1.6 M *n*-butyllithium in hexane at −78 °C. The resulting slurry was warmed slowly to 25 °C over a 2 h period, with the exception of the pentafluorophenol derivative [$R_fOLi = C_6F_5O^-Li^+$], and stirring was continued for the next 30 min. It was then returned to −78 °C and a stoichiometric amount of the cyclodiphosphazane II in ether was added slowly. The solution was allowed to warm to 25 °C, and stirring was continued for another 1 h after the white precipitate was observed. The slurry was filtered with a Schlenk apparatus, and the solvent was evaporated slowly from the filtrate. The resulting solid formed (in most of the series) can then be recrystallized from anhydrous diethyl ether, hexane, or pentane. All procedures were carried out under a constant nitrogen flow.

(1) [CF$_3$CH$_2$OPN-*t*-Bu]$_2$ (III) is an involatile yellowish liquid. The ^{31}P{H} NMR spectrum shows singlets at δ 223.0 and 143.3 in a relative area ratio of 9:1. For the isolated low-field isomer, the ^{1}H NMR had a quartet centered at δ 3.26 for CH_2 ($J_{H-F} = 8.60$ Hz) and a CH_3 peak at δ 1.03, and the ^{19}F NMR spectrum had a peak at ϕ −72.6 (dt) ($J_{P-F} = 1.71$ Hz). In other trials, the low-field peak predominates repeatedly. On standing, no conversion to the high-field isomer was observed. No other spectroscopic data were obtained since the NMR data agreed with the results previously reported.[10]

(2) [CF$_3$CF$_2$CH$_2$OPN-*t*-Bu]$_2$ (IV) exists as colorless crystals (mp 39 °C; 75% yield) after recrystallization from pentane or hexane that turn slightly dark brown on standing. The ^{31}P{H} NMR spectrum had singlets at δ 222.8 and 144.4 with a ratio of 9:1. After IV was allowed to stand at 25 °C for 3 weeks, only the low-field isomer was observed. The sample dissolved in $CDCl_3$ in a 5-mm NMR tube was heated for 24 h at 60 °C and did not show any indication of conversion to the high-field isomer. In the ^{19}F NMR spectrum peaks were observed at ϕ −83.05 s (CF_3) and −123.3 t (CF_2) ($J = 13.4$ Hz). The ^{u}H NMR spectrum showed a triplet at δ 4.24 (CH_2) with $J_{CF_2-CH_2} = 13.68$ Hz and a peak at δ 1.20 (CH_3). The CI mass spectrum at 3.2 V had a molecular ion (M + 1) at *m/e* 503 (14.4%). Other fragments observed were at *m/e* 487 ($M^+ - CH_3$) 33.0%, 430 ($M^+ - C_5H_{12}$) 15%, 370 ($M^+ - CHCF_2CF_3$) 5.2%, 353 ($M^+ - OCH_2CF_2CF_3$) 29.1%, 236 ($M^+ - C_6H_4F_{10}$) 100%, 122 ($N_2O_2P_2^+$) 8.6%, 69 (CF_3^+) 12%, and 57 ($C_4H_9^+$) 78%.

Anal. Calcd for $C_{14}H_{22}F_{10}O_2P_2N_2$: P, 12.35; N, 5.58; F, 37.85. Found: P, 11.98; N, 5.58; F, 36.80.

(3) [CF$_3$CF$^1{}_2$CF$^2{}_2$CH$_2$OPN-*t*-Bu]$_2$ (V) is a white crystalline solid (mp 52 °C; yield 50%) that was obtained after recrystallization from anhydrous ether. The ^{31}P{H} NMR spectrum had singlets at δ 223.2 and 144.3 (ratio 8:1). The ^{19}F NMR spectrum had peaks at ϕ −80.9 (CF_3) ($J_{CF_3-CF_2} = 9.76$); −120.0 mult ($CF_2{}^1$), and −127 br, s ($CF_2{}^2$). The ^{1}H NMR spectrum had a resonance at δ 4.5 mult (CH_2) and 1.23 (CH_3). The CI mass spectrum at 9.7 V had a molecular ion ($M + 1$) at *m/e*, 603, 17%. Other fragments observed were *m/e* 587 ($M^+ - CH_3$) 30.4%, 530 ($M^+ - C_5H_{12}$) 12.7%, 403 ($M^+ - CF_3CF_2CF_2CH_2O$) 39.2%, 286 [$CF_3CF_2CF_2CH_2OPNC(CH_3)_2{}^+$] 100%, 125 ($CF_2CH_2OPN^+$) 14.7%, 122 ($N_2O_2P_2{}^+$) 9.2%, 102 [$PNC(CH_3)_3{}^+$] 12.5%, and 57 [$C(CH_3)_3{}^+$] 52.1%.

Anal. Calcd for $C_{16}H_{22}F_{14}O_2P_2N_2$: P, 10.30; F, 44.19; N, 4.65. Found: P, 10.12; F, 43.90; N, 4.32.

(4) [C$_6$F$_5$OPN-*t*-Bu]$_2$ (VI). The lithium salt was formed as described in the beginning of this section. However, the solution was only warmed to −40 °C due to the instability of the lithium salt, and then it was returned to −78 °C. Compound II was added. Colorless crystals were obtained after recrystallization from pentane and diethyl ether (mp) 78 °C; 70% yield). The ^{31}P{H} NMR spectrum had peaks at δ 252 (very small) and 162.6 (mult). The ^{19}F NMR spectrum had peaks at ϕ −152.5, −163.37, and −163.6. The CI mass spectrum at 5.2 V had a molecular ion (M + 1) at *m/e* 571, 1.3%. Other fragments observed were 514 ($M^+ - C_4H_8{}^+$) 1.4%, 387 ($M^+ - OC_6F_5$) 100%, 330 ($M^+ - OC_6F_5 - C_4H_9$) 10.4%, 274 ($M^+ - OC_6F_5 - C_8H_{17}$) 14.8%, 102 ($PNC_4H_9{}^+$) 18.1%, and 57 ($C_4H_9{}^+$) 23.6%.

Anal. Calcd for $C_{20}H_{18}F_{10}O_2N_2P_2$: P, 10.88; F, 33.33; C, 42.11. Found: P, 10.52; F, 33.00; C, 42.09.

(5) [(CF$_3$)$_2$CHOPN-*t*-Bu]$_2$ (VII). As in the case of pentafluorophenoxide, the lithium salt was held below −40 °C. A white solid was obtained after several washings with anhydrous ether and pentane (mp 80 °C; 40% yield). The ^{31}P{H} NMR spectrum had a singlet at δ 157. The ^{19}F NMR spectrum had peaks at ϕ −76.74 d ($J_{CF_3-H} = 6.5$ Hz). The CI mass spectrum at 8.2 V had a molecular ion (M + 1) at *m/e* 539, 5%. Other fragments observed were at *m/e* 523 ($M^+ - CH_3$) 53%, 467 ($M^+ - CF_3H_2$) 23%, 371 [$M^+ - (CF_3)_2HCO$] 45.8%, 254 [$(CF_3)_2HCOPNC(CH_3)_2{}^+$] 100%, 102 ($PNC_4H_9{}^+$) 8.2%, and 57 ($C_4H_9{}^+$) 58.9%.

Anal. Calcd for $C_{14}H_{20}F_{12}O_2P_2N_2$: P, 11.52; C, 31.23; H, 3.72. Found: P, 10.98; C, 31.02; H, 3.92.

(6) [CF$_3$C(O)OPN-*t*-Bu]$_2$ (VIII). Silver trifluoroacetate in 50 mL anhydrous diethyl ether was added slowly to a stoichiometric amount of II in 30 mL of anhydrous diethyl ether. A white precipitate formed immediately. The reaction was stirred at 25 °C for another 1 h after which the precipitate was separated by using a Schlenk apparatus. The solvent was slowly evaporated to leave a slightly brown sticky liquid (45% yield). The ^{31}P{H} NMR spectrum had peaks at δ 179.1 and 161.7 with the former peak as the major one. The ratio of the peak areas for the low-field to the high-field resonances is 6:1. The ^{19}F NMR spectrum had a single peak at ϕ −76.8. The compound decomposed slowly on standing, turning dark brown after 12 h under inert conditions. The CI mass spectrum at 4.2 V gave a very weak molecular ion at *m/e* 430 (1%). Other fragments observed were at *m/e* 229 ($CF_3CO_2PN_2C_4H_9{}^+$) 1.5%,

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204 ($M^+ - C_4F_6O_4$) 1%, 127 ($NPOC_5H_6^+$) 5.4%, 113 ($CF_3CO_2^+$) 35.4%, 99 ($NPC_4H_6^+$) 12.8%, 69 (CF_3^+) 37.7%, and 57 ($C_4H_9^+$) 100%.

Anal. Calcd for $C_{12}H_{18}F_6P_2N_2O_4$: P, 14.41; C, 33.49; H, 4.19. Found: P, 13.51; C, 33.08; H, 4.34.

(7) [$(Me_3Si)_2NPN$-*t*-Bu]$_2$ (X). The lithium salt of $(Me_3Si)_2NH$ was preformed in a manner similar to that described for the polyfluorinated alcohols. The large clear crystals were recrystallized by using diethyl ether (30% yield) in which it is only slightly soluble. Deuteriated acetone was used as the solvent for NMR. The $^{31}P\{H\}$ NMR spectrum had a peak at δ 211.8. The CI mass spectrum at 6.0 V gave an intense molecular ion (M + 1) of *m/e* 525 (50%). Other major fragments observed at *m/e* 467 ($M^+ - C_4H_9$) 8.8%, 451 ($M^+ - SiC_3H_9$) 5%, 364 ($M^+ - NSi_2C_6H_{18}$) 83%, 204 ($PN_2Si_2C_6H_{17}^+$) 12.2%, 191 ($PNSi_2C_6H_{18}^+$) 24.5%, and 73 ($SiC_3H_9^+$) 52%.

Anal. Calcd for $C_{20}H_{54}Si_4P_2N_4$: P, 11.83; C, 45.80; H, 10.31. Found: P, 11.20; C, 44.95; H, 10.10.

(8) [*t*-BuNPOCH$_2$(CF$_2$)$_n$CH$_2$OPN-*t*-Bu] (XI) (*n* = 2, 3). The lithium salt of each diol was preformed in a manner similar to the other polyfluorinated alcohols. After addition of *n*-BuLi at −78 °C, the solution was allowed to warm to 25 °C to ensure completion in the reaction. II was introduced slowly at −78 °C and the mixture was warmed slowly to 25 °C.

(a) For *n* = 2. After the precipitate was removed by filtration, the solvent was evaporated from the filtrate and a slightly brown sticky substance was obtained. The $^{31}P\{H\}$ NMR spectrum consisted of a peak at δ 221.5, and the ^{19}F NMR spectrum had a resonance at φ −121.4 mult. In the ^1H NMR spectrum a multiplet was centered at δ 4.41. The CI mass spectrum at 3.1 V gave a molecular ion (M + 1) at *m/e* 365 (14.9%). Other fragments observed were at *m/e* 349 ($M^+ - CH_3$) 4.7%, 307 ($M^+ - C_4H_9$) 6%, 292 ($M^+ - C_5H_{12}$) 7.1%, 277 ($M^+ - PC_4H_8$) 69.5%, 220 ($M^+ - OC_9H_{20}$) 31.7%, 204 ($N_2P_2C_8H_{18}^+$) 22.3%, 160 ($C_4H_4F_4O_2^+$) 14.3%, and 57 ($C_4H_9^+$) 100%.

Anal. Calcd for $C_{12}H_{22}F_4P_2N_2O_2$: C, 39.56; H, 6.04; N, 7.69. Found: C, 38.86; H, 6.01; N, 6.98.

(b) For *n* = 3. As for the *n* = 2 compound, upon evaporation of the solvent from the filtrate, a sticky light brown liquid was obtained. The $^{31}P\{H\}$ NMR spectrum consisted of a peak at δ 222.3, and in the ^{19}F NMR spectrum peaks at φ −119.9 and −126.0 were observed. The FAB mass spectrum at 10 V had molecular ions (M + 1, M + 2) at *m/e* 415, 9.1%, and 416, 14.2%, respectively. Other fragments found were at *m/e* 357 ($M^+ - C_4H_9$) 3%, 300 ($M^+ - C_8H_{18}$) 1%, 241 ($C_5H_4F_6O_2P^+$) 2.5%, 210 ($C_5H_4F_6O_2^+$) 8.9%, 204 ($M^+ - C_5H_4F_6O_2$) 2.3%, 182 ($C_6H_{11}F_2NOP^+$) 13.2%, 106 ($P_2N_2O^+$) 2.8%, 75 (PN_2O^+) 100%, and 57 ($C_4H_9^+$) 95%.

Anal. Calcd for $C_{13}H_{22}F_6P_2O_2N_2$: C, 37.68; H, 5.31; N, 6.76. Found: C, 37.77; H, 5.34; N, 5.92.

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Kinetics and Products of the Complexation of $(H_2O)_5CrCH_2CN^{2+}$ by Carboxylic Acids

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The kinetics and products of the reaction of $(H_2O)_5CrCH_2CN^{2+}$ with glycine, *N,N,N*-trimethylglycine, chloroacetate, trifluoroacetate, oxalate, and monomethyl oxalate have been studied. The systems show an initial reaction on the stopped-flow time scale that gives the mono-ligand product. For oxalate and methyl oxalate, subsequent reactions produce *cis*-$(C_2O_4)_2Cr(OH_2)_2^-$ as the dominant product in a more complex reaction sequence. Hydrolysis of the methyl ester is greatly accelerated by complexation.

Introduction

The anation reactions of pentaaquachromium(III) alkyl complexes are unusually rapid compared to substitution on most chromium(III) complexes.[1-6] The lability is attributed to the trans-labilizing influence of the alkyl group.

In this study the reaction of $(H_2O)_5CrCH_2CN^{2+}$ with several carboxylate ligands has been examined. The results provide information on the products, equilibrium constants, and kinetics for the general reaction

$$(H_2O)_5CrCH_2CN^{2+} + O_2CR^{n-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (H_2O)_4(RCO_2)CrCH_2CN^{2-n} + H_2O \quad (1)$$

Variations of k_1 and K_1 ($=k_1/k_{-1}$) with the nature and basicity of the carboxylate reactant have been determined.

The observations with oxalate and monomethyl oxalate show several reactions subsequent to (1). The products and kinetics of these processes have been studied and explained by isomerization and substitution reactions analogous to those proposed recently for hypophosphite.[6]

Results and Discussion

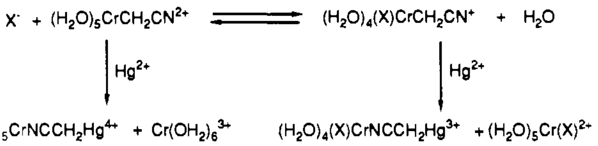
The details of the individual systems will be discussed in subsequent sections. However some of the common features will be noted here to avoid repetition. When a potential carboxylate ligand RCO_2^- and $(H_2O)_5CrCH_2CN^{2+}$ are mixed in dilute aqueous acid, there is an initial rapid reaction that is complete in at most a few minutes at normal reagent concentrations. This reaction causes a general increase in absorbance in the regions of the maxima of $(H_2O)_5CrCH_2CN^{2+}$ (525 and 408 nm).

In the case of oxalate and methyl oxalate, there are further slower changes that occur on the tens of minutes to hours time scale. There are at least two kinetically separable slower processes. These produce larger absorbance changes than the first stage.

Finally, there are much slower changes requiring many hours or days which are associated with loss of the alkyl group. These processes have not been studied in detail here, but have been reported for the acetate system.[7]

Because the reaction products are so labile it is generally necessary to remove the $-CH_2CN$ group by reaction with Hg(II) before separation by chromatography. The results of the Hg(II) reaction are described in Scheme I. The product distribution from $(H_2O)_5CrCH_2CN^{2+}$ + Hg^{2+} has been shown to be 52%

Scheme I



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