than that of the uncomplexed dianion **8** or the anionic aluminum or gallium complexes by 82 and 12 cm^{-1}, respectively, which is consistent with the coordination of the triacylmetalate ligands to the group 4A metal ions.[4]

The proton NMR spectra are of poor quality owing to the solution instability and slight impurity of these compounds. The methyl substituent resonances of the triacetylhafnium and -zirconium complexes, **16** and **19**, appear at δ 2.46 and 2.42, respectively, in acetone-d_6 solution. These resonances appear ca. 16 Hz downfield from the methyl resonance of the uncomplexed dianion **8** which is consistent with complexation to the hafnium and zirconium ions.

Compounds **17** and **18** should exhibit geometrical isomerism; however, the poor quality of the spectra prevents this analysis. The peak width at half-height for the methyl substituent resonances of **17** and **18** are 16 and 12 Hz, respectively. Since the average separation of these resonances due to isomerization in the unsymmetrically substituted aluminum and gallium complexes, **11**, **12**, **14**, and **15**, is only 4 Hz, the observation of isomerism in **17** and **18** is not expected.

The aluminum compounds **20** and **21** are bis-chelate triacylmetalate complexes where the two metalla ligands are connected via a six- or seven-methylene bridge, respectively. These compounds are prepared with slightly more dilute solutions to favor the formation of a monomeric complex. Molecular models revealed that such complexes would exist only as the gauche isomer, and they would be, presumably, more stable in solution due to an imposed "chelate effect". Only the aluminum complexes were prepared, however, due to the inability to purify these compounds adequately. The complexes are very soluble in methylene chloride or THF, but they do not crystallize from solution.

The diacyl complexes **6** and **7** readily form the expected tetraacyl dianion (2067 (w), 1947 (br, vs), 1917 (sh, s), 1577 (m) cm^{-1}) and hexaacyl tetraanion (1952 (s), 1863 (vs), 1539 (m) cm^{-1}) when being treated with the stoichiometric amounts of methyllithium in THF solution. The aluminum complexes show the expected IR shifts (1989 (s), 1890 (vs), 1485 (m) cm^{-1}) due to complexation, and the proton NMR resonances of the methyl substituents appear as two singlets for the gauche isomer only at the expected frequencies (average values are δ 2.53 and 2.56). Because of the high solubility of these compounds and the observation of only the gauche isomer, these complexes are assumed to be either monomeric or dimeric in solution rather than a long-chain polymer. Further work with these bridged ligands is not planned.

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Registry No. **3**, 23319-44-0; **4**, 59831-00-4; **5**, 65312-81-4; **6**, 69439-94-7; **7**, 69439-95-8; **9**, 65337-55-5; **10**, 65274-13-7; **11**, gauche, 69493-70-5; **11**, anti, 69515-84-0; **12**, gauche, 69515-86-2; **12**, anti, 69493-81-8; **13**, 69493-72-7; **14**, gauche, 69515-60-2; **14**, anti, 69493-65-8; **15**, gauche, 69493-74-9; **15**, anti, 69576-01-8; **16**, 65319-76-8; **17**, 69454-62-2; **18**, 69439-98-1; **19**, 69439-99-2; **20**, gauche, 69508-46-9; **21**, gauche, 69493-67-0; $(PPN)_2[fac\text{-}(OC)_3Re(CH_3CO)_3]$, 69439-97-0; $NaRe(CO)_5$, 33634-75-2; suberyl dichloride, 10027-07-3; azelayl dichloride, 123-98-8; $AlCl_3$, 7446-70-0; $GaCl_3$, 13450-90-3.

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Phosphoranes. 9. Barrier to Exchange in $CF_3(CH_3)PF_3$. Comparison to Related Molecules Including $CF_3(CH_3)PCl_3$

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At reduced temperatures the directly bound F atoms in $CF_3(CH_3)PF_3$ are resolved into axial (two) and equatorial (one) environments. The barrier to fluorine permutation has been determined ($\Delta G^{\ddagger}_{298}$ = 8.8 kcal) from temperature-dependent ^{31}P (^{1}H-decoupled) and ^{19}F (CF_3 region) NMR spectroscopies. Comparing this barrier to those in similar trifluorophosphoranes with monodentate substituents suggests that the barrier to F permutation in $(CF_3)_2PF_3$ is very low (1–3 kcal), accounting the long-established inability to observe distinct F environments in this compound by NMR techniques. The behavior of $CF_3(CH_3)PCl_3$ which, in contrast to $CF_3(CH_3)PF_3$, exhibits pronounced temperature dependence of $^2J_{PF}$ and ϕ_{CF_3} suggests that the exchange process in the chloride is different from that of the fluoride. Spectroscopic characterization of $CF_3(CH_3)PF_3$, $CF_3(CH_3)PCl_3$, and the anion $CF_3(CH_3)PO_2^-$, formed by hydrolysis of both halides, is reported.

Introduction

Barriers to fluorine permutational exchange for a variety of trifluorophosphoranes with monodentate substituents[1-4] range from 6 to 20 kcal. The observed equivalence of F atoms in $(CF_3)_2PF_3$ even at very low temperatures has been interpreted in terms of D_{3h} molecular symmetry with two freely rotating axial CF_3 groups, a structure which violates the "electronegativity" rule.[5] NMR (^{19}F and ^{13}C)[6,7] data suggest that the appropriate ground-state structure of $(CF_3)_2PF_3$ has essentially C_{2v} symmetry with two CF_3 groups in the equatorial plane. We report herein the barrier for fluorine exchange in the related trifluorophosphorane $CF_3(CH_3)PF_3$ which, when compared to previously reported barriers for X_2PF_3 molecules, provides an insight to the behavior of $(CF_3)_2PF_3$.

Results and Discussion

^{19}F NMR spectra of the directly bound fluorine atoms of $CF_3(CH_3)PF_3$, illustrated in Figure 1, show typical fast-exchange behavior at ~300 K resolving to distinct fluorine environments (in a 2:1 intensity ratio) at 163 K. The pattern

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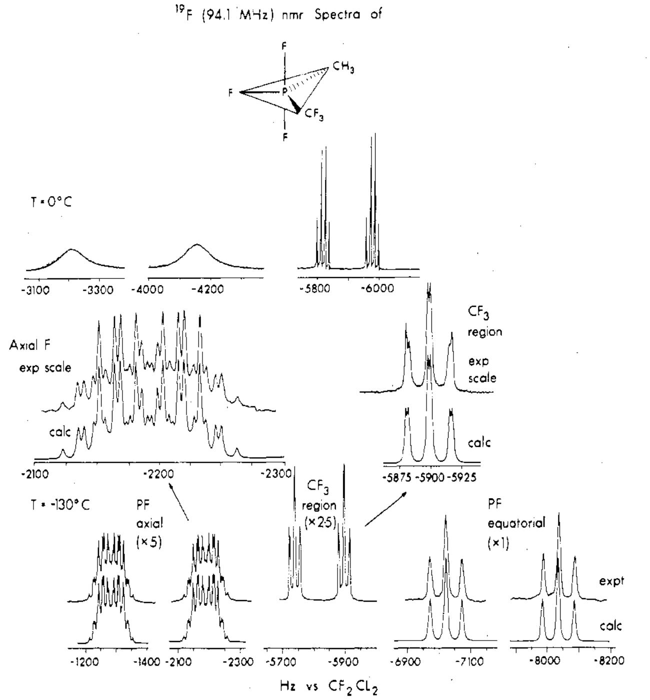

Figure 1. Temperature dependence of the ^{19}F NMR spectrum of $CF_3(CH_3)PF_3$ (CW at 94.1 MHz) compared with spectra calculated by using the parameters given in Table I. The scale gives the offset frequency shift in hertz vs. CCl_2F_2 negative values indicating resonance to high field of the standard.

Table I. NMR Parameters for $CF_3(CH_3)PX_3$

	$CH_3(CF_3)PCl_3$		$CH_3(CF_3)PF_3$	
	+30 °C	−80 °C	0 °C	−100 °C
		Chemical Shifts		
τ^a	6.96^b		8.30^c	$8.1^{c,d}$
$\phi_F{}^e$			46.2	$25.9,^f\ 86.5^g$
$\phi_{CF_3}{}^e$	74.1	76.7	69.6	69.0
$\delta_{^{13}CH}{}^h$	~46	41.6	16.0	~16
$\delta_{^{13}CF}$	125.0^l	124.9	123	123
$\delta_{^{31}P}{}^i$	148.4	151.7^m	124.2	120
		Coupling Constants (Hz)		
$^1J_{PF}$			955	$909,^f\ 1026^g$
$^1J_{PC(F)}$	184.2	140.6	332.0	333.9^m
$^1J_{PC(H)}$	85.0	76.2	152.0	151.4^m
$^2J_{PF}$	114.6	90.5	156	157.5
$^2J_{PH}$	12.4		17.5	18.0
$^3J_{FH}$	0.7^j		8.4	9.0^d
$^3J_{FF}$			12.0	17.0, 2.2
$^2J_{FF}$				50.80^k

[a] Vs. $(CH_3)_4Si$, $\tau = 10.0$. [b] In a solution of $CFCl_3/CF_2Cl_2$. [c] Sextet: two exactly overlapping quartets due to average of $^2J_{PH}$ and $^3J_{FH}$. [d] At −80 °C. [e] Vs. CCl_3F; positive values indicate resonance to high field of standard. [f] Axial fluorine. [g] Equatorial fluorine. [h] In a solution of 1:1 $EtCl/CD_2Cl_2$. [i] Vs. P_4O_6.[26] Positive values indicate resonance to high field of standard. [j] Quartet. [k] $^2J_{F_{ax}-F_{eq}}$ from equatorial F region of low-temperature limiting NMR spectra: a doublet of very broad triplets. [l] At −20 °C, in $CF_2Cl_2/CFCl_3/CD_2Cl_2$. [m] At −90 °C in a solution of 1:1 $EtCl/CD_2Cl_2$.

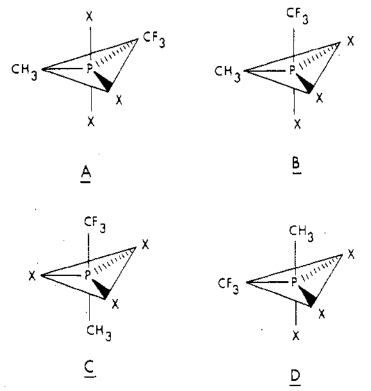

Figure 2. Possible trigonal-bipyramidal isomers of $CF_3(CH_3)PX_3$ molecules (X = F, Cl).

Table II. Portion of the Infrared Spectra of $CF_3(CH_3)PX_3$[a]

$CF_3(CH_3)PF_3$	$CF_3(CH_3)PCl_3$	
	1380 s	$\delta_{asym}(CH_3)$
1325 w	1325 w	
1216 s	1245 m	$\nu(CF_3)$
1153 s	1190 s	
961 s		$\nu(PF)$
873 m		
828 s		
733 m	740 m	$\delta_{asym}(CF_3)$
	580 m	$\nu_{asym}(P-Cl)$
	540 m	$\nu_{sym}(P-Cl)$
512 m		
466 w	488 m	$\nu(PCF_3)$

[a] Gas-phase spectra at +25 °C unless otherwise noted. All values are in cm^{-1}. Abbreviations and symbols are s = strong, m = medium, w = weak, v = very, sh = shoulder, ν = stretch, δ = deformation, sym = symmetric, and asym = asymmetric.

is consistent with one axial and two equatorial fluorine substituents in a trigonal bipyramid. The absence of significant variation in the CF_3 chemical shift throughout this temperature range suggests that the CF_3 group remains in a fixed skeletal position. While we cannot absolutely exclude the possibilities that different CF_3 skeletal positions are characterized by nearly identical NMR parameters or that any permutational exchange affecting the CF_3 group is fast at all temperatures, related studies on similar molecules[7,8] suggest that these possibilities are unlikely.

The ^{19}F spectrum of the CF_3 group also reflects the permutational behavior of the directly bound F atoms. At low temperatures the spectrum is a double doublet of triplets due to the existence of two distinct $^3J_{FCPF}$ values arising respectively from the two axial and the single equatorial F atoms. Both this spectrum and that of the directly bound F atoms are consistent with that expected for the trigonal-bipyramidal ground state A (Figure 2). At elevated temperatures the CF_3 region spectrum is transformed to a doublet of quartets indicating equivalence of the directly bound fluorine atoms at the fast-exchange limit.

The ^{31}P spectrum, a doublet of triplets of quartets at 153 K and a quartet of quartets at 300 K (Figure 3), is compatible with the ^{19}F spectra and the ground-state assignment. Temperature studies of the $^{13}C\{\sim^{19}F\}$ spectrum show that $^1J_{PC}$ is temperature independent and that its magnitude is compatible with an equatorial CF_3 group.[7] For reasons outlined earlier[7,8] we favor the trigonal-bipyramidal structure A (Figure 2) analogous to those found for the gaseous $(CH_3)_nPF_{5-n}$ molecules[9] as the ground (solution state) structure of $CF_3(CH_3)PF_3$, but it must be recognized that the spectral data are also consistent with any of three square-pyramidal alternatives having apical CF_3, CH_3, or F substituents. All NMR parameters are listed in Table I.

The three strong infrared bands (Table II) in the PF region of $CF_3(CH_3)PF_3$ are also consistent with A based on comparisons with infrared data for methylfluorophosphoranes[10,11] and CF_3PF_4,[12] and hence we will consider A to be the most probable ground-state structure of $CF_3(CH_3)PF_3$.

Line-shape analyses[13] of the $^{31}P\{\sim^1H\}$ and the ^{19}F (CF_3 region) spectra yield similar values for the barrier to the rearrangement process. The kinetic magnetization transfer (**K**) matrix (Table III) was constructed assuming an observable

Table III. K Matrix for Axial–Equatorial F Exchange in $CH_3(CF_3)PF_3$[a]

	e|aa					
e|aa	$\alpha\|\alpha\alpha$	$\alpha\|\alpha\beta$	$\beta\|\alpha\alpha$	$\alpha\|\beta\beta$	$\beta\|\alpha\beta$	$\beta\|\beta\beta$
$\alpha\|\alpha\alpha$	0	0	0	0	0	0
$\alpha\|\alpha\beta$	0	−0.5	0.5	0	0	0
$\beta\|\alpha\alpha$	0	1.0	−1.0	0	0	0
$\alpha\|\beta\beta$	0	0	0	−1.0	1.0	0
$\beta\|\alpha\beta$	0	0	0	0.5	−0.5	0
$\beta\|\beta\beta$	0	0	0	0	0	0

[a] One of four 6 × 6 submatrices for the ^{31}P spectrum. The spectrum consists of a quartet due to coupling of the CF_3 group with phosphorus. Complete reproduction of the $^{31}P\{\sim{}^1H\}$ spectrum with all couplings requires that the above matrix be repeated four times with line spacings given by $^2J_{PF}$.

process[14] which corresponds to the permutational mode[15] M_4 (aae) for the fluorine atoms which is equivalent to a series of aeae cyclic Berry[16] (BPR) or equivalent turnstile (TR)[17] processes. One BPR process in itself is not sufficient to exchange the F environments in A since the result of a single BPR is to transform A into distinguishable isomers B, C, or D which must subsequently undergo a second BPR to return to the ground state. A matrix constructed assuming a bond-breaking process did not fit the observed spectra. Analysis of several samples with different sample concentrations indicated that the rate data were concentration independent.

The resultant temperature–rate data yielded activation barriers from the Arrhenius and Eyring equations[18] which we ascribe to the essential overall permutational processes in this molecule. The thermodynamic parameters are given in Table IV. Comparisons of this barrier with those of related molecules are best based on values of $\Delta G_{298}^{\ddagger}$ which are more reliable[19] than E_a values.[20]

The barrier for $CF_3(CH_3)PF_3$ permutational exchange, 8.8 kcal, is similar to that observed for tetrafluorophosphoranes and lies in the midpoint of the range encompassed by X_2PF_3 systems. Comparing the series $(CH_3)_2PF_3$ (17.8 kcal),[1] $CF_3(CH_3)PF_3$, and $(CF_3)_2PF_3$, we may extrapolate the difference between the first two to predict a barrier of approximately zero for the permutational exchange in the third. Similar extrapolation within the series H_2PF_3 (10.2 kcal),[3] $CF_3(H)PF_3$ (6.3 kcal)[3] yields a predicted barrier of ~2.4 kcal for $(CF_3)_2PF_3$. While it is speculative to assume equal changes of barrier with successive replacement of substituent, the reinforcement of two series suggests that a plausible explanation for the failure[5,7] to observe distinct environments for the fluorine atoms in $(CF_3)_2PF_3$ is a low barrier, ranging from 1 to 3 kcal, which is unobservable by available NMR techniques and not the existence of a D_{3h} ground-state structure.

No consistent trend of barrier values is apparent. The minimum barrier in $F_3P(NH_2)_2$ (12.3 kcal),[21] a molecule which is static to F permutation at 300 K, contrasts with that of $(CF_3)_3P(N(CH_3)_2)_2$ (15 kcal),[22] in which CF_3 groups are interchanging at 300 K, and suggests that replacement of F by CF_3 decreases the barrier to pseudorotation. The apparent barrier of $(CF_3)_3P(CH_3)_2$ (static up to 353 K)[23d] compared to that of $F_3P(CH_3)_2$ (17.8 kcal)[1] suggests the opposite. The effect of CF_3 substitution on the permutational barriers in phosphoranes is not clear.

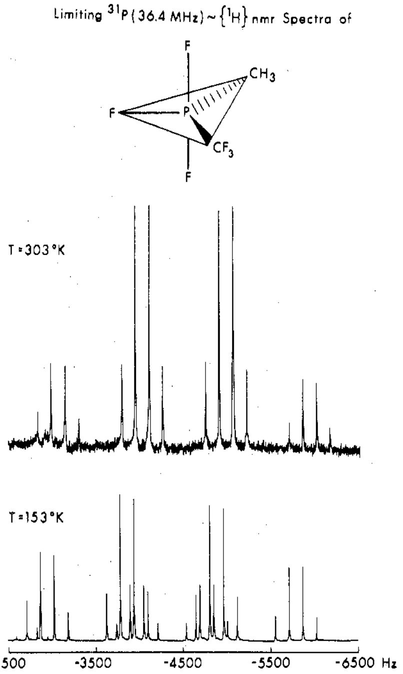

Figure 3. Normal-temperature and limiting ^{31}P (36.4 MHz) proton-decoupled Fourier transform spectrum of $CF_3(CH_3)PF_3$. The scale gives the offset frequency shift in hertz relative to P_4O_6 measured with the heteronuclear lock system of the Bruker HFX 90. Negative values indicate resonance to high field of standard.

NMR Spectral Behavior of $CF_3(CH_3)PCl_3$

In contrast to $CF_3(CH_3)PF_3$ the analogous NMR parameters of $CF_3(CH_3)PCl_3$ [especially $^2J_{PF}$, $^1J_{PC(F)}$, $\sigma(^{31}P)$, and $\sigma(^{13}C(H))$] are markedly temperature dependent (Figure 4). Attempts to resolve structurally meaningful features in the spectra have been unsuccessful so far because of the limitations imposed by solubility in the appropriate solvents. The most pronounced changes are in $^2J_{PF}$ and $^1J_{PC(F)}$ which decrease with decreasing temperature. The direct coupling to the methyl carbon $^1J_{PC(H)}$ also decreases, but less markedly. One can associate these changes with an exchange process which, if a true intramolecular process, suggests that the proportion of isomers is changing with temperature. In this case the three most likely trigonal-bipyramidal isomers are A, B, or C (X = Cl, Figure 2) because available structural evidence suggests that CH_3 groups do not occupy axial sites in the presence of halogens.[9] If we presume that five-coordinate geometry is preserved and that our previous association of coupling constant with the substitutional site in the five-coordinate phosphorus molecule is valid,[6–8,23] then the trends indicate that the proportion of the isomer with equatorial CF_3 is decreasing with decreasing temperature suggesting that A (X = Cl) is not the most stable (i.e., ground state) structure. This contrasts with our earlier suggestion that Cl occupies the axial site in preference to CF_3.[6] Although a four-coordinate phosphonium intermediate cannot be excluded, the shift of the ^{31}P chemical shift to high field with decreasing temperature indicates that phosphonium ions (with typically lower field shifts than

Table IV. Activation Parameters for $CF_3(CH_3)PF_3$[a]

$10^{-10}A$, s^{-1}	E_a, kcal	$\Delta S^{\ddagger}$, eu	$\Delta H^{\ddagger}$, kcal	$\Delta G_T^{\ddagger}$, kcal	(T),[b] K	$\Delta G_{298}^{\ddagger}$, kcal	remarks
129 (±129)	7.7 ± 0.3	−4 ± 2	7.4 ± 0.3	8.0 ± 0.4	(159)	8.5 ± 0.7	CF_3
4.6 (±3.1)	6.5 ± 0.2	−10.7 ± 1.3	6.2 ± 0.2	8.1 ± 0.3	(178)	9.4 ± 0.4	^{31}P
57 (±19)	7.4 ± 0.1	−5.6 ± 0.6	7.1 ± 0.1	8.0 ± 0.1	(171)	8.8 ± 0.2	combined

[a] Error limits are those obtained from statistical analysis and do not include systematic errors. [b] T is the average temperature of the data analyzed to obtain $\Delta G_T^{\ddagger}$ and is *not* the coalescence temperature.

Table V. NMR Parameters for $CF_3(CH_3)PO_2^-$

chemical shifts		coupling constants, Hz	
τ_H^a	8.51	$^2J_{PF}$	95.5
ϕ^b	76.7 $(CF_3)^d$	$^2J_{PH}$	15.9
$\sigma_{^{31}P}^c$	87.5	$^4J_{FH}$	0.80

[a] Vs. $(CH_3)_4Si$, $\tau = 10.0$. [b] Vs. CCl_3F; positive values indicate resonance to high field. [c] Vs. P_4O_6.[26] Positive values indicate resonance to high field. [d] Also observed were singlets at ϕ_F 128.0 and ϕ_F 149.5 for F^- and BF_4^- in solution.

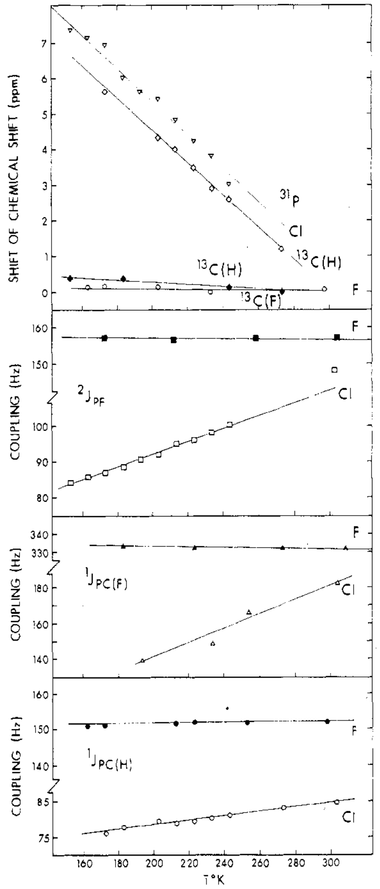

Figure 4. Variations of the NMR parameters of $CF_3(CH_3)PCl_3$ with temperature compared with the temperature behavior of the corresponding parameters for $CF_3(CH_3)PF_3$.

five-coordinate phosphorus) cannot be of increasing importance at the lower temperatures.

It is premature to reach a final conclusion on this preliminary evidence. It is however clear that the behavior of the chloride is different from that of the fluoride perhaps because the mechanism of the exchange process is different for the two cases. Dissociative processes may play a greater role in the exchange of chlorophosphoranes and further study is warranted.

Experimental Section

All reactions were done in sealed tubes, and standard vacuum techniques were used throughout for the manipulation of volatile compounds. CF_3PCl_4[24] and CF_3PF_4[25] were prepared according to published methods. $(CH_3)_4Pb$ (as a 70% solution in toluene) was used as obtained from Alfa Inorganics. Antimony trifluoride was sublimed twice under vacuum before use to remove oxide and water impurities which lead to formation of phosphine oxide impurities.

Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer using a 9-cm gas cell fitted with KBr windows. Mass spectra were recorded with an AEI MS-9 spectrometer operating at an ionizing voltage of 70 eV. Proton and ^{19}F NMR spectra were recorded on solutions of the compound (approximately 10%) in CCl_3F with a small amount of $(CH_3)_4Si$ (in CCl_3F, capillary) reference at 100.1 and 94.2 MHz with a Varian HA 100 instrument in the continuous wave mode. ^{31}P NMR spectra were recorded at 36.4 MHz with a Bruker HFX 90 spectrometer in the pulsed Fourier-transform mode with a Nicolet 1085 computer. Samples were prepared in 5-mm o.d. tubes in CCl_3F solvent including CD_2Cl_2 for heteronuclear reference lock signal.

Fluorine chemical shifts were measured relative to internal CCl_3F solvent; proton shifts are relative to external (capillary) $(CH_3)_4Si$ (as a 5% solution in CCl_3F). Phosphorus-31 shifts were measured with respect to the heteronuclear ^2D lock signal and converted to the P_4O_6[26] scale by means of the appropriate conversion factor which in the case of ^2D (CD_2Cl_2) is 6100 Hz to low field of P_4O_6.

Both instruments were equipped with the Bruker temperature controller which provided temperature accuracy of ±1 °C in the probe according to direct calibration. Direct measurement established that no detectable thermal gradients (>0.1 °C) existed in the sample tube.

Preparation of $CF_3(CH_3)PCl_3$ from CF_3PCl_4 and $(CH_3)_4Pb$. *Caution.* On two occasions this reaction mixture has exploded violently after approximately $^1/_2$ h at room temperature. Increased scale is not recommended and precautions appropriate to a potentially explosive reaction should always be used.

In a typical reaction CF_3PCl_4[24] (5.74 g, 23.9 mmol) was condensed into a 75-cm^3 reaction vessel containing $(CH_3)_4Pb$ (~9 g, 70% solution in toluene) which was then sealed under vacuum. After several days' reaction with agitation at room temperature a considerable quantity of an insoluble white solid formed. Separation of the volatile materials under vacuum gave $CF_3(CH_3)PCl_3$ (1.50 g, 6.8 mmol, ~30%) which was collected at −16 °C. The usual impurity $CF_3(CH_3)_2PCl_2$ was removed by a trap at −8 °C. Toluene and unreacted CF_3PCl_4 were also recovered in the more volatile fractions.

Alkaline hydrolysis of $CF_3(CH_3)PCl_3$ (0.130 g, 0.59 mmol) gave CF_3H (0.040 g, 0.58 mmol) leaving $CH_3PO_3^{2-}$ ion (identified by NMR)[27] in solution. Neutral hydrolysis yielded no CF_3H, and the $CF_3(CH_3)PO_2^-$ ion was observed in solution.

Preparation of $CF_3(CH_3)PF_3$. (A) Fluorination of $CF_3(CH_3)PCl_3$. Combining $CF_3(CH_3)PCl_3$ (0.75 g, 3.40 mmol) and freshly sublimed SbF_3 (~1.5 g) in a sealed tube for several days at room temperature gave $CF_3(CH_3)PF_3$ in nearly quantitative yield, and this was collected at −96 °C. Unreacted $CH_3(CF_3)PCl_3$ was removed with a −45 °C trap.

(B) Methylation of CF_3PF_4 with Tetramethyltin.[28] Combining CF_3PF_4[25] (0.81 g, 4.61 mmol) and $(CH_3)_4Sn$ (0.57 g, 3.2 mmol) in a sealed reaction vessel under vacuum gave, after several days' reaction at room temperature with agitation, a quantity of insoluble white solid. The volatile products were separated under vacuum from the solid, and an additional quantity of CF_3PF_4 (0.141 g, 0.8 mmol) was added to the reaction vessel and the reaction allowed to proceed. Separation of the volatile products yielded $CF_3(CH_3)PF_3$ free of $(CH_3)_4Sn$. Product yields of 17–78% were obtained. The compound hydrolyzed in neutral medium forming $CF_3(CH_3)PO_2^-$; this ion resisted further hydrolysis in alkali of moderate strength (10%). Saturated concentrated alkali yielded CF_3H (0.0148 g, 0.21 mmol) from $CF_3(CH_3)PF_3$ (0.0386 g, 0.22 mmol), leaving the $CH_3PO_3^{2-}$ ion[27] in solution.

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Registry No. $CF_3(CH_3)PCl_3$, 69517-30-2; $CF_3(CH_3)PF_3$, 69517-31-3; $CF_3(CH_3)PO_2^-$, 69517-32-4; CF_3PCl_4, 1066-48-4; CF_3PF_4, 1184-81-2; $(CH_3)_4Pb$, 75-74-1; $(CH_3)_4Sn$, 594-27-4.

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An Efficient Synthesis of Substituted Uranocenes

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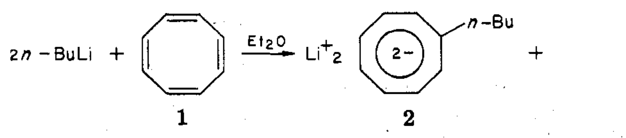
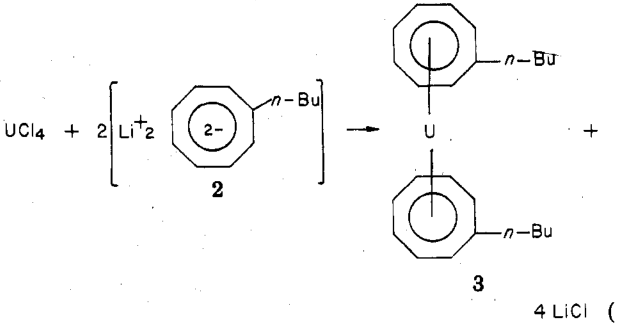
Dilithium *n*-butylcyclooctatetraenide is prepared by reaction of 2 equiv of *n*-butyllithium with 1 equiv of cyclooctatetraene in diethyl ether at 25 °C. Treatment of this solution with 0.5 equiv of UCl_4 dissolved in tetrahydrofuran followed by Soxhlet extraction with hexane resulted in a 50% yield of 1,1′-di-*n*-butyluranocene based on cyclooctatetraene. Treatment of 1,1′-di-*n*-butyluranocene with nitrobenzene resulted in a 51% yield of azobenzene based on cyclooctatetraene.

Grant and Streitwieser[1] have recently reported the reaction of uranocenes with aromatic and aliphatic nitro compounds to form azo compounds in good yield. They found the use of substituted uranocenes more convenient than uranocene itself due to the low solubility of the parent compound. The synthetic potential of substituted uranocenes is largely unexplored due, at least in part, to the time required for their preparation. This requires the preparation and isolation of the substituted cyclooctatetraene, reduction to the dianion, and addition of UCl_4 yielding the substituted uranocene. Currently, there are two methods for preparation of alkyl- or aryl-substituted cyclooctatetraenes. The procedure of Cope et al.[2] involves the addition of organolithium reagents to cyclooctatetraene, **1**, followed by refluxing and hydrolysis, to give a mixture of substituted cyclooctatetraenes and substituted cyclooctatrienes in low yield. Alternately, substituted cyclooctatetraenes may be prepared in high yield from bromocyclooctatetraene and lithium dialkylcuprate reagents.[3a,b] In this note we wish to report a simple, efficient method for the preparation of monosubstituted uranocenes.

Elsewhere we[4] have reported the preparation of the lithium alkyl- or aryl-substituted cyclooctatetraenide dianion from the reaction of **1** with organolithium reagents in diethyl ether. Treatment of **1** with 2 equiv of *n*-butyllithium in diethyl ether at 25 °C results in nearly quantitative formation of the lithium *n*-butylcyclooctatetraenide anion **2** within 1 h according to eq 1. Addition of 0.5 equiv of UCl_4 in tetrahydrofuran to this red solution containing **2** gave a 50% yield of 1,1′-di-*n*-butyluranocene, **3** (based on **1**), after removal of solvent and subsequent Soxhlet extraction with hexane. We have prepared other substituted uranocenes with this procedure by use of the appropriate alkyl- or aryllithium reagents in eq 1. We have found that eq 1 does not hold for lithium alkoxides or lithium dialkylamides.

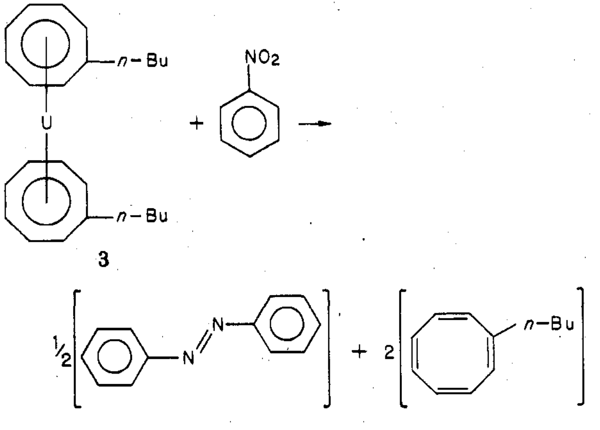


(1)



(2)

Taking advantage of this synthetic procedure, we prepared azobenzene by adding 1 equiv of nitrobenzene to the solution containing **3** according to eq 3. **3** was used without prior isolation. The reaction was instantaneous, yielding a brown



(3)