$k_2[H^+]^2$. Contributions from the $[H^+]$-dependent terms are small however (k_{obsd} is 125 M^{-1} s^{-1} at $[H^+] = 0.1$ M and 350 M^{-1} s^{-1} at $[H^+] = 3.0$ M). The rate constant $k_0 = 120$ M^{-1} s^{-1} at 25 °C is to be compared with values in Table V.

Registry No. TiO^{2+}, 12192-25-5; NCS^-, 1111-68-8; HF, 7664-39-3; $H_4P_2O_7$, 2466-09-3.

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The Relative Basicity of 4-Cyclohexylphosphorin and Aryl Phosphines from Hydrogen Bonding Studies

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The 1:1 equilibrium constants (K_1) have been determined in carbon disulfide by an infrared technique for the association of *p*-trifluromethylphenol with various para-substituted triphenylphosphines, 4-cyclohexylphosphorin, and 4-*tert*-butylpyridine. The relative Lewis basicities established from the equilibria studies on the phosphines are: tri-*p*-methoxyphenylphosphine ≫ 4-cyclohexylphosphorin > tri-*p*-methylphenylphosphine ≈ tri-*p*-chlorophenylphosphine > triphenylphosphine. 4-Cyclohexylphosphorin has a K_1 which is 36 times smaller than the similarly substituted nitrogen analogue, 4-*tert*-butylpyridine.

Introduction

It has long been recognized that phosphine, the phosphorus analogue of ammonia, and its alkyl and aryl derivatives represent an important class of bases with widely varying basicities. The pK_a of phosphine in aqueous solution has been estimated to be −14 from kinetic measurements[1] whereas the pK_a of diethylphenylphosphine is reported to be 6.25 in water.[2] An even larger value (9.7) is estimated for tricyclohexylphosphine.[3] In the gas phase the proton affinity of phosphine is less then that of ammonia, but trimethylphosphine has a larger proton affinity than trimethylamine.[4] This is contrasted with the conclusion of Henderson and Streuli[2] that in aqueous solution "a phosphine with a given number of alkyl substituents is a weaker base than an amine of the same $\Sigma\sigma^*$ value". In studies involving Lewis acids amines are more basic than phosphines in reactions with $AlMe_3$, $GaMe_3$, BMe_3, and BF_3 but the reverse is found for BH_3.[5] The large variation in basicity for aryl and alkyl phosphines has also been observed in the tendency of these ligands to form metal complexes with unusual stabilities and properties.[6] Recently, the kinetic reactivity of iridium phosphine complexes ($Ir(CO)ClL_2$, L = tertiary aryl phosphine) toward oxidative addition of methyl iodide was observed to change dramatically upon substitution at the para position of the phenyl ring.[7]

The phosphorus analogue of pyridine, phosphorin, has recently been synthesized[8] and the physical and chemical properties of this compound and its substituted derivatives are under investigation in several laboratories. The 2,4,6-triphenyl- and tri-*tert*-butyl-substituted phosphorins form stable π complexes when reacted with chromium hexacarbonyl.[9a] Nainan and Sears observed that 4-cyclohexylphosphorin forms stable complexes with other transition metals; in the reaction of 4-cyclohexylphosphorin[4] and chromium hexacarbonyl they find that this ligand exhibits bidentate character.[9b] Theoretical calculations employing[10] the CNDO/2 method indicate that phosphorin should have an aqueous pK_a of −10, but to date all attempts at producing the phosphorium cation have failed. This is, in part, due to the facile oxidation of phosphorin by $HClO_4$ and H_2SO_4. It has also been reported (unpublished data) that[11] "Addition of trifluoroacetic acid to cyclohexane solutions of various λ^3-phosphorins fail to produce any change in the UV spectra". Several efforts in our laboratories to measure the Gibbs free energy of formation of the 4-cyclohexylphosphorin cation have also failed to produce an unambiguous value for the quantity due to oxidation and side reactions. Consequently, it seems unlikely that a simple determination of the basicity of phosphorin will be forthcoming in the near future.

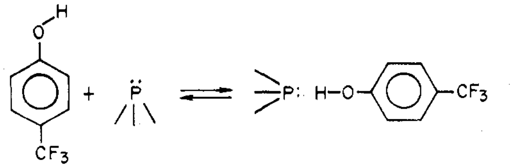
Hydrogen bonding studies have been shown to be a convenient means of determining the relative basicity of a related series of compounds.[12,13] For example, in the substituted pyridine series it has been shown that the hydrogen bonding basicities correlate with the aqueous pK_a values[14] and the gas phase proton affinities.[15] In view of the experimental diffi-

Table I. Equilibrium Constant Data for the *p*-Trifluoromethylphenol 1:1 Complexes with Aryl Phosphines, 4-Cyclohexylphosphorin, and 4-*tert*-Butylpyridine in Carbon Disulfide

	C^0_{ph}, M	C^0_B, M	A_{ph}	A_{mix}	A_B	K_1	Av K_1
Ph_3P	8.201×10^{-3}	3.817×10^{-2}	0.529	0.500	0.010	2.1	2.3
	8.201×10^{-3}	6.299×10^{-2}	0.529	0.474	0.014	2.4	
	4.578×10^{-3}	6.119×10^{-2}	0.288	0.263	0.013	2.5	
$(p\text{-}CH_3C_6H_4)_3P$	1.030×10^{-2}	2.032×10^{-2}	0.683	0.633	0.003	4.3	4.0
	1.030×10^{-2}	6.098×10^{-2}	0.683	0.566	0.009	3.8	
	1.030×10^{-2}	1.178×10^{-1}	0.683	0.497	0.018	3.7	
$(p\text{-}CH_3OC_6H_4)_3P$	9.755×10^{-3}	1.154×10^{-2}	0.624	0.492	0.006	30.2	32.8
	9.755×10^{-3}	2.141×10^{-2}	0.624	0.396	0.012	35.4	
$(p\text{-}ClC_6H_4)_3P$	7.414×10^{-3}	2.174×10^{-2}	0.516	0.484	0.004	3.5	3.6
	7.414×10^{-3}	3.569×10^{-2}	0.516	0.465	0.007	3.6	
	7.414×10^{-3}	6.535×10^{-2}	0.516	0.430	0.013	3.7	
$c\text{-}C_6H_{11}(p\text{-}PC_6H_4)P$	8.201×10^{-3}	4.107×10^{-2}	0.519	0.394	0.028	10.8	11.1
	8.201×10^{-3}	5.213×10^{-2}	0.519	0.369	0.036	11.4	
$tert\text{-}C_4H_9(p\text{-}NC_6H_4)N$	6.886×10^{-3}	3.083×10^{-3}	0.451	0.317	0.000	408	396
	6.886×10^{-3}	6.166×10^{-3}	0.451	0.222	0.000	386	
	6.886×10^{-3}	9.249×10^{-3}	0.451	0.157	0.000	393	

culties encountered in the attempts at the direct evaluation of the basicity by protonation procedures and the theoretical interest in an experimental comparison of the basicity of phosphorin to other phosphorus compounds, it seems appropriate to determine the basicity of phosphorin relative to some aryl phosphines.

Hydrogen bonding studies have been employed to establish the relative basicity of carbonyl compounds where pK_a values are very low[12,13] and this technique seemed particularly suitable for accomplishing the above objective. Consequently, an infrared technique was chosen to determine the equilibrium constant for the formation of the hydrogen bonded complex with *p*-trifluoromethylphenol (pK_a = 8.68)[16] according to eq 1.



(1)

p-Trifluoromethylphenol was chosen as the acid in these studies because it (1) has a pK_a which is much lower than that of phenol or *p*-fluorophenol often used in hydrogen bonding studies, (2) is highly soluble in organic solvent, and (3) is readily purified by vacuum sublimation to exclude moisture from the sample.

Initially, the studies were undertaken in carbon tetrachloride solution, but reaction of the phosphines with the solvent to produce the triphenylphosphine dichloromethylene ylide[17] produced a pronounced time dependence in the spectral measurement. Except for tri-*p*-chlorophenylphosphine, the time dependence severely limited the accuracy of the derived equilibrium constants. Estimates for the equilibrium constant (K_1) for reaction 1 were obtained for several aryl phosphines,[18] but the alkyl phosphines instantaneously formed white precipitates when added to carbon tetrachloride. Several other chlorinated solvents and benzene were tried but a solvent was not found where both aryl and alkyl phosphines could be studied with the same acid. Although the alkyl phosphines reacted instantaneously with carbon disulfide to give red-colored precipitates,[19] the triaryl phosphines were stable for extended periods of time in this solvent. Thus, the equilibrium constants for eq 1 were determined in carbon disulfide for a series of triaryl phosphines and 4-cyclohexylphosphorin to provide the relative basicities of these compounds. For comparison purposes, 4-*tert*-butylpyridine was also included in the study.

Experimental Section

All spectra were recorded with a Beckman IR-12 spectrometer using a 5 mm variable path length cell. The temperature of the cell was regulated at 25 ± 1 °C by circulating water through a jacket attached to the cell. The temperature of the cell was monitored by means of a copper–constantan thermocouple in contact with a window of the cell.

Fisher reagent grade carbon disulfide was dried over freshly activated (600 °C) Linde 4A molecular sieves. *p*-Trifluoromethylphenol (Aldrich, 98%) was vacuum sublimed.

Eastman white label triphenylphosphine was recrystalized once from methanol and dried under vacuum for 8 h. 4-*tert*-Butylpyridine (Aldrich 99%) was used without further purification. 4-Cyclohexylphosphorin was prepared following the procedure of Märkl[20] and purified by passing through a silica gel column. Tri-*p*-chloro-, tri-*p*-methyl-, and tri-*p*-methoxyphenylphosphines were synthesized by reaction of PCl_3 with the appropriate Grignard reagent.

While the reaction of triaryl phosphine with carbon disulfide to form the analogous aryl phosphine addition product has not been reported in the literature and no evidence for such a reaction was observed in this study, the following method was employed to minimize the possible interference from any slow reaction. The appropriate amounts of base were weighed directly in a 10-mL volumetric flask and then mixed with a *p*-trifluoromethylphenol solution of known molarity. Therefore, the waiting time (from mixing to measurement) was minimized and was kept the same for each sample solution. All sample preparations and the cell manipulations were carried out in a drybox which was constantly flushed with high-purity nitrogen.

The equilibrium concentration of *p*-trifluoromethylphenol in the carbon disulfide solutions containing the bases was obtained by monitoring the absorbance of the band centered at 3583 cm^{-1} assigned to the OH stretching frequency of monomeric *p*-trifluoromethylphenol. At concentrations below 1.1×10^{-2} M the apparent extinction coefficient at 3583 cm^{-1} was independent of concentration indicating that the monomer is the predominant species in these solutions. Since the path length of the cell could not be directly determined and the actual extinction coefficient is not needed in the equilibrium calculations, the path length was routinely held fixed during a particular set of experiments. Small variations (less than 9%) were observed in the apparent extinction coefficient from one run to another.

The equilibrium constants, K_1, were calculated for a 1:1 model using the observed equilibrium concentration of free *p*-trifluoromethylphenol calculated from the peak absorbance at 3583 cm^{-1}. The band attributed to the hydrogen bonded OH stretching frequency was at least 300 cm^{-1} below the free OH band in all cases and did not overlap the free OH band. For the very weak bases the maximum could not be located due to the broad nature of the band. In the worse case, triphenylphosphine, the band was virtually undetectable due to the broad nature of the band and the overall absorption of the base in this region (Figure 1). However, this band does not appear to overlap the free OH peak, since the slight increase found between 3500 and 3400 cm^{-1} (Figure 1) is present in the spectrum of the pure base (~0.015 absorbance units; see Table I). All the bases studied have

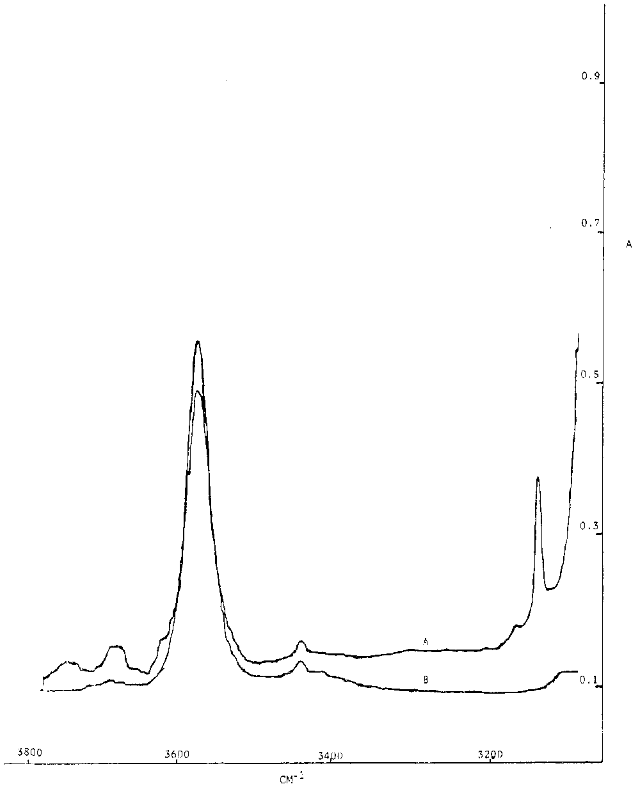


Figure 1. The actual spectrometer recording of the spectrum in the 3600-cm^{-1} region is presented in absorbance units for a CS_2 solution of 5.772 × 10^{-3} M *p*-trifluromethylphenol (A). In the spectrum labeled (B) triphenylphosphine has been added to solution (A) such that the concentration is 6.299 × 10^{-3} M.

a small absorbance in this region; therefore, a correction to the absorbance at 3583 cm^{-1} was made due to the base. In each experimental determination, the absorbances of three solutions were used to obtain the concentration of the monomeric *p*-trifluoromethylphenol at equilibrium. These included the absorbance (A_{ph}) for *p*-trifluoromethylphenol at concentration C^0_{ph}, the absorbance of the mixture (A_{mix}) containing the base (C^0_B), and the absorbance of the base (C^0_B) at 3583 cm^{-1} (A_B). The concentration of the *p*-trifluoromethylphenol at equilibrium in the presence of the base was taken to be $C_{ph} = (A_{mix} - A_B)(C^0_{ph}/A_{ph})$.

Results and Conclusions

The concentrations and absorbance data employed in the calculation of the hydrogen bonding equilibrium constants for each compound are listed in Table I. The average K_1 values are uncertain by at least 10% due to the uncertainty in the absorbance measurement and the influence of small concentrations of water in the carbon disulfide solutions. The duplicate and triplicate runs for all the compounds studied are within 10% of the average K_1 value.

Attempts were made to determine the position of the maximum absorption for the hydrogen bonded OH stretching frequency. However, due to the small K_1 values and the overlap with the aromatic CH region of the acid the maxima of the broad and weak hydrogen bonded OH bands could not be reliably located.

From the K_1 values listed in Table I, the relative basicities are 4-*tert*-butylpyridine >>> tri-*p*-methoxyphenylphosphine ≫ 4-cyclohexylphosphorin > tri-*p*-methylphenylphosphine ≈ tri-*p*-chlorophenylphosphine > triphenylphosphine. The *p*-methyl- and *p*-methoxytriphenylphosphines have relative basicities which are in the same order as the σ^+ values of the Taft equation ($\sigma^+ = -0.256$ for methyl and $\sigma^+ = -0.648$ for methoxy).[21] The tri-*p*-chlorophenylphosphine has a K_1 almost twice that of triphenylphosphine which is not consistent with the expectation that para substitution on the phenyl ring by an electron-withdrawing chlorine atom should decrease the electron density at the phosphorus atom. This observation is, however, in agreement with the results of Goetz and Sidhu[22] who found that in 80% by volume ethanol–water quite surprisingly tri-*p*-chlorophenylphosphine (pK_a = 2.86) is more basic than either *p*-chlorophenyldiphenylphosphine (pK_a = 2.18) or triphenylphosphine (pK_a = 2.30) but only slightly less basic than tri-*p*-methoxyphenylphosphine (pK_a = 3.15). Since the same relative order of basicity is obtained in the hydrogen bonding studies as in the pK_a determinations it is unlikely that the anomalous pK_a value for tri-*p*-chlorophenylphosphine is due to solvation effects in the equilibria.

4-Cyclohexylphosphorin is now seen to be more basic than triphenylphosphine whose pK_a is 2.30. This is quite surprising since it has been reported that efforts to protonate phosphorin have been unsuccessful.[11] The reason for the more basic character of 4-cyclohexylphosphorin relative to triphenylphosphine is not immediately apparent but could be due to (1) the delocalization of the developing charge at phosphorus in the complex via increased resonance or (2) an unusual transmission of the substituent effect through the π system. An alternate possibility is that the hydrogen bonding is to the π system rather than the σ or n electrons primarily centered on the phosphorus atom. Molecular orbital calculations have shown that the HOMO in phosphorin is a π orbital with electron density distributed over the entire ring, whereas in pyridine the HOMO is an n orbital primarily on the nitrogen.[23] Previous hydrogen bonding studies have suggested that the K_1 values correlate with the HOMO energy values,[12] which suggests that phosphorin could act as a π base in these studies. However, a definite hydrogen bonded OH peak was found for phosphorin at ~3160 cm^{-1}, which is a much larger shift than is usually found for π bases.[13]

The much larger basicity of 4-*tert*-butylpyridine which was chosen as a close analogue of 4-cyclohexylphosphorin (the inductive effects of a *tert*-butyl, $\sigma^+ = -0.26$, and cyclohexyl should be similar since for methyl $\sigma^+ = 0.256$)[21] provides additional evidence that nitrogen bases are stronger than the corresponding phosphorus analogues. Oehling and Schweig[10] have attributed this to the much weaker bond strength of the P–H bond than that of the N–H bond.[24] It is also very probable that the pyridine ring system is more able to stabilize the positive charge via delocalization than the phosphorin ring system.

Registry No. *p*-Trifluoromethylphenol, 402-45-9; Ph_3P, 603-35-0; $(p\text{-}CH_3C_6H_4)_3P$, 1038-95-5; $(p\text{-}CH_3OC_6H_4)_3P$, 855-38-9; $(p\text{-}ClC_6H_4)_3P$, 1159-54-2; $c\text{-}C_6H_{11}(p\text{-}PC_6H_4)$, 51470-98-5; $tert\text{-}C_4H_9\text{-}(p\text{-}NC_6H_4)$, 3978-81-2.

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Phosphoranes. 5. Chemistry and Stereochemistry of Tetraalkylphosphoranes, $CH_3(CF_3)_3PX$, with One Methyl Group and Monofunctional [F, Cl, OCH_3, SCH_3, $N(CH_3)_2$] Substituents[1]

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Methylation of $(CF_3)_3PF_2$ with tetramethyltin or $(CF_3)_3PX_2$ (X = F, Cl) with tetramethyllead gave the tetraalkylphosphoranes, $CH_3(CF_3)_3PX$, which, according to the NMR spectra, are best formulated as five-coordinate phosphoranes rather than isomeric phosphonium salts. NMR (^{19}F, ^{31}P, and ^{13}C) spectroscopic studies at low temperatures consistently indicate that the halogen, F or Cl, occupies an axial position in an assumed trigonal-bipyramidal structure and that the methyl group resides in the trigonal plane giving a ground-state structure with one axial and two equatorial CF_3 groups. Metathetical substitution of the halogen with groups Y (Y = OCH_3, SCH_3, $N(CH_3)_2$) using $(CH_3)_3SiY$ reagents or $(CH_3)_2NH$ gives the derivative phosphoranes $CH_3(CF_3)_3PY$ which, according to NMR (^{19}F, ^{31}P) spectroscopic studies at appropriate temperatures, have ground-state structures in which Y and CH_3 reside in the equatorial plane of the trigonal bipyramid placing one CF_3 group in an equatorial position and two CF_3 groups in axial positions. In general CF_3 environments are averaged by an exchange process with barriers, as indicated by coalescence temperatures, decreasing in the order $N(CH_3)_2 > SCH_3 > OCH_3 >> F > Cl$. The different CF_3 environments in $CH_3(CF_3)_3PN(CH_3)_2$ are observed at normal room temperatures. Other mass, ^1H NMR, and infrared spectroscopic data are reported as well as the hydrolytic behavior of the phosphoranes.

Introduction

While many derivatives of five-coordinate phosphorus are known, there are few examples in which more than three carbon atoms are bound to phosphorus and, of these, alkyl substituents are very rare.[2] In contrast, fully alkylated three- and four-coordinate phosphorus derivatives are well-known.[3] As part of a study of the substitutional chemistry and dynamic stereochemistry of five-coordinate phosphorus we have now prepared and studied a series of tetraalkylphosphoranes[4] containing one CH_3 group, three CF_3 groups, and one of the monofunctional substituents F,[5] Cl,[5] OCH_3,[5] SCH_3, or $N(CH_3)_2$.

Although the usual methylation reagents[6] (CH_3Li, CH_3MgX, and $Hg(CH_3)_2$) have been employed on occasion to methylate phosphines,[7,8] widespread application of these reagents to produce methylphosphoranes has not been undertaken. One potential source of difficulty is the reactivity of the methylation reagent as exemplified by the formation of the ylide $(CH_3)_3PCH_2$ with $LiCH_3$.[9] Another constraint of particular importance to the chemistry of (fluoroalkyl)phosphorus derivatives is the possibility of halogen abstraction by the electropositive metal atom of the alkylating reagent. This latter potential difficulty can be avoided by the use of tetramethyltin and tetramethyllead wherein the metal possesses a reasonably high electronegativity. Tetramethyllead, which is a more reactive methylating agent than the tin compound as a result of the weaker Pb–C bond, has not been extensively used as a methylation agent although it has been shown to be an effective reagent in the case of boron.[10] Both of these reagents are effective but relatively mild methylation reagents which are volatile and easily handled by standard vacuum techniques. Furthermore, the reactions with these reagents are assisted by the involatility and insolubility of the trimethyltin or the lead halide by-product formed in the reaction.

Tetramethyltin has previously been used to prepare methylated fluoro- and (trifluoromethyl)phosphoranes such as CH_3PF_4,[11] $CF_3(CH_3)PF_3$,[12] $(CF_3)_2CH_3PF_2$,[12] and related derivatives of these compounds, but tetramethyllead has not been previously used to methylate pentacoordinate phosphorus. Until the present study,[5] reported in detail herein, no pentacoordinate (trifluoromethyl)phosphorane containing more than three P–C bonds had been reported.

Results and Discussion

Tetramethyltin was found to be without effect on $(CF_3)_3PCl_2$. In parallel with the previous use of this reagent to prepare CH_3PF_4,[11] $CH_3(CF_3)PF_3$,[12] and $(CH_3)(CF_3)_2PF_2$,[12] however, tetramethyltin converted tris(trifluoromethyl)difluorophosphorane, $(CF_3)_3PF_2$, to methyltris(trifluoromethyl)fluorophosphorane, $CH_3(CF_3)_3PF$, in 82% yield according to eq 1. Equimolar proportions of tetramethyllead

$$(CF_3)_3PF_2 + (CH_3)_4Sn \rightarrow CH_3(CF_3)_3PF + (CH_3)_3SnF \qquad (1)$$

(80% in toluene) and the dichlorophosphorane gave, after several days at room temperature, $CH_3(CF_3)_3PCl$ in 69% yield (eq 2), and, under the same conditions, $CH_3(CF_3)_3PF$ was

$$(CF_3)_3PCl_2 + (CH_3)_4Pb \rightarrow CH_3(CF_3)_3PCl + (CH_3)_3PbCl \qquad (2)$$

obtained from $(CF_3)_3PF_2$ and a stoichiometric quantity of tetramethyllead. In addition $CH_3(CF_3)_3PCl$ was readily converted to $CH_3(CF_3)_3PF$ in good yield by reaction with SbF_3 at room temperature.

Reaction of the tetraalkylhalogenophosphoranes with trimethylmethoxysilane or -methylthiosilane[13] gave the corresponding methoxy- or methylthiophosphorane in quantitative yield:

$$\begin{aligned} &CH_3(CF_3)_3PX + (CH_3)_3SiE(CH_3) \rightarrow CH_3(CF_3)_3PE(CH_3) + \\ &\quad (CH_3)_3SiX \qquad (3) \\ &\qquad [E = O;\ X = F, Cl;\ E = S, X = F] \end{aligned}$$

The oxygen derivative formed readily from either the chloro- or the fluorophosphorane. The sulfur derivative was obtained only from the fluorophosphorane and only after several hours of reaction at room temperature. In general, the methoxy derivatives of (trifluoromethyl)phosphoranes appear to be more