CF_3CH=SF_4 and CF_3CHSF_5, probably as a result of HF formation due to a hydrocarbon impurity.

Crystal Growth. An X-ray capillary (0.2 mm) was attached to the trap and after evacuation to 10^{-4} torr CF_3C≡SF_3 was evaporated and condensed into the capillary by cooling with liquid nitrogen. In order to guarantee good control of crystal growth, the capillary was thoroughly cleaned with 2% HF and detergent in water. Then it was sealed under 1 atm of argon and transferred to the diffractometer in a stream of nitrogen at −160 °C.

Growing of suitable single crystals was performed on a four-circle diffractometer P2₁, which carries a specially designed low-temperature device.[24]

CF_3C≡SF_3 (I) The sample, which was partly solid at −126 °C, was annealed at this temperature for 15 h, yielding several monomer crystals with sizes below 1 mm. At −124 °C a few crystals remained suspended in liquid. Their sizes were increased by oscillating the temperature between −124 and −126 °C monitoring the diffraction intensity of a suitable reflection. A specimen of approximately 2 mm length oriented along [010] in the capillary axis was chosen for the data collection at −130 °C. The crystal nearly filled the diameter of the capillary but was still surrounded by some melt and slightly changed its position during the data collection. A further reduction of the temperature was not feasible as the scattering intensity of the polycrystalline eutectic was significant.

$CF_3(SF_3)C$=$C(CF_3)SF_3$ (II). After the completion of the data collection for I the sample was warmed, kept at −20 °C for approximately 5 min, and cooled to −133 °C again. During this cooling process the dimer which had formed first separated in supercooled droplets before crystallizing. At −80 °C approximately 50% of the sample consisted of solid II, besides solution. With the exception of a few crystals all the solid was dissolved again at −45 °C. The sizes of these crystals were slowly increased by carefully lowering the temperature in steps of 1° until a suitable needle-shaped crystal of approximately 2-mm length resulted, which again was oriented along [010] in the capillary axis. Data collection was performed at −122 °C.

Data Collection and Structure Solutions. Measurements were performed with Mo Kα radiation using a graphite monochromator. The lattice constants of I and II resulted from a least-squares refinement of the positions of 15 reflections measured at −130 and −122 °C, respectively, in the range $8° \leq 2\theta \leq 28°$. Scattering intensities were measured in the ω–2θ scan mode in the range $3° \leq 2\theta \leq 55°$, with a scan width

of 1° and equal times for scan and total background measurements. The scan rate varied between 1 and 29 deg/min. The data were corrected for absorption by using the semiempirical ϕ-scan technique. No further corrections except the usual polarization and Lorentz corrections were applied. The structures were solved by direct methods and refined by least-squares methods using the program system SHELXTL (version 3.0, 1981) on a Data General Eclipse computer. Final full-matrix least-squares refinements converged to the values of $R = \Sigma\Delta F/\Sigma F_o$ and $R_w = [\Sigma w(\Delta F)^2/wF_r^2]$ listed in Table III; the atomic parameters are summarized in Table IV (see paragraph at the end of the paper regarding supplementary material).

CF_3C≡SF_3 (I). Data were collected in the sector $0 \leq h \leq 8$, $0 \leq k \leq 9$, and $-7 \leq l \leq 7$ resulting in a total of 698 reflections out of which 608 had an intensity $I > 2\sigma(I)$. The only observed systematic absences were $0k0$ for $k = 2n + 1$, indicating $P2_1$ or $P2_1/m$, out of which the noncentrosymmetric space group had to be chosen. The atomic positions came out from an E-map and were refined to an isotropic value $R = 0.16$. Anisotropic refinement led to the final value $R = 0.05$.

$CF_3(SF_3)C$=$C(CF_3)SF_3$ (II). Diffraction data were collected within the range $0 \leq h \leq 16$, $0 \leq k \leq 7$, $-8 \leq l \leq 8$. Out of 1258 measured reflections 952 had intensities larger than $I = 2\sigma(I)$ and were used for solving the phase problem and for refinement. The observed systematic absenses were $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$ leading to the space group $P2_1/n$. All atomic positions came out from an E-map and least-squares refinement with isotropic temperature factors led to a reliability factor $R = 0.09$. The anisotropic refinement converged to $R = 0.045$.

Supplementary Material Available: Tables of structure factors, atomic positional parameters, and anisotropic thermal parameters (12 pages). Ordering information is given on any current masthead page.

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Comparative Study of Nucleophilic Addition to Free and Metal-Coordinated Carbocations

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Abstract: A kinetic study in acetone is prepared for phosphorus and nitrogen donor nucleophile addition to three carbocations: (*p*-(dimethylamino)triphenyl)methyl (**1**), pyronin (**2**), and (*p*-(dimethylamino)phenyl)tropylium (**3**). In the absence of steric effects, the Ritchie N_+ correlation is obeyed by the reactions; i.e., relative nucleophilic reactivity is electrophile independent. More significantly, the relative reactivities of phosphorus and nitrogen donors toward free carbocations are the same as that observed for addition to metal-coordinated cyclic π-hydrocarbons even though the latter reactions involve metal–carbon bond cleavage. Both types of reactions have similar transition states.

The addition of nucleophiles to free carbocations is a fundamental reaction in organic chemistry. Ritchie et al.[1] have shown that oxygen and nitrogen donor nucleophiles add to a wide range of stabilized carbocations according to eq 1, in which k is the second-order rate constant for the electrophile–nucleophile com-

bination, k_0 is the rate constant for a reference nucleophile, and N_+ is a parameter dependent only on the nucleophile and reaction conditions.

$$\log (k/k_0) = N_+ \qquad (1)$$

This relationship means that relative nucleophilic reactivity is electrophile independent. It follows that selectivity is constant and hence does not correlate with reactivity as would be required

(1) Ritchie, C. D.; Kubisty, C.; Ting, G. Y. *J. Am. Chem. Soc.* **1983,** *105,* 279 and references therein.

by the reactivity–selectivity principle. Although eq 1 holds for electrophiles spanning a wide reactivity range, it should be noted that extremely reactive carbocations, e.g., substituted 1-phenylethyl cations, can show large changes in selectivity as the reactivity of the cation increases.[2,3] The relationship in eq 1 is also claimed to hold for attack on esters and activated arenes, providing that the leaving group departure is not rate-determining.[4,5] However, other work questions the applicability of the N_+ scale to acyl compounds generally and acetyl chloride in particular.[6]

We have been interested for some time in the electrophilic reactivity of π-hydrocarbons coordinated to a transition-metal moiety, e.g., eq 2. Utilizing a wide range of coordinated cyclic

(2)
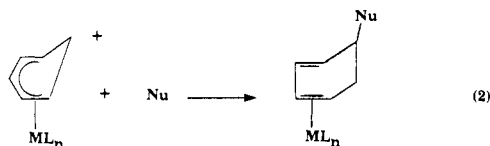
π-hydrocarbons (C_4H_4, C_6H_6, C_6H_7, C_7H_7, C_7H_8, C_7H_9, etc.) and metal fragments, we have shown[7] that eq 1 is followed with nitrogen and phosphorus donor nucleophiles. This is true even though the nucleophilic reactivities span a factor of 10^7 and the electrophilic reactivities a factor of 10^9. Nucleophilic addition to the π-hydrocarbon ring in (ring)ML_n^{m+} is obviously closely related to additions to free carbocations. The latter reactions involve simple electrophile–nucleophile combination, whereas the organometallic reactions also involve cleavage of a metal–carbon bond, i.e., are really S_N2 reactions in which the leaving group (ML_n) remains bonded to the periphery of the molecule.

Herein we report results that address two important aspects of the above reactions. Kinetic studies of phosphorus donor additions to the free carbocations 1–3 were done to determine if eq 1 can be extended to these nucleophiles. Thermodynamic studies

1   **2**   **3**
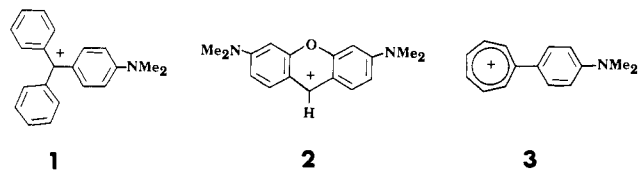
have been reported[8,9] for phosphine and phosphite additions to triarylmethyl cations, but no kinetic work has been published. Herein we show that such additions indeed obey eq 1. More significantly, we show that the relative reactivities of phosphorus and nitrogen donors toward unhindered carbocations are the same as that observed with organometallic electrophiles, even though the latter reactions are in reality substitutions in which a metal–carbon bond is broken.

Experimental Section

Acetonitrile was fractionally distilled from calcium hydride. Acetone, predried with molecular sieves, was freshly distilled and further dried for 1 h with 4-Å sieves prior to use. Liquid phosphorus nucleophiles were fractionally distilled from sodium at reduced pressure. $P(C_6H_5)_3$ was recrystallized from benzene and $P(C_2H_4CN)_3$ from water. Imidazole (HIm) and p-toluidine were sublimed, and N-methylimidazole (N-MeIm) was distilled from KOH at reduced pressure.

All synthetic procedures were carried out under an atmosphere of nitrogen or argon. The hexafluorophosphate salt of cation 1 was prepared essentially as described previously[10,11] by the reaction of phenylmagnesium bromide and p-(dimethylamino)benzophenone in diethyl ether to give the alcohol, which was converted to the cation salt by

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Table I. Reactivity Data for Carbocation Electrophiles in Acetone at 25 °C

electro-phile	nucleophile	k, M^{-1} s^{-1}	N_+^a	N_M^b
1	P(OBu)$_3$	4.2	0	0 (11)
1	PBu$_3$	5 600	3.1	3.8$_5$ (7)
1	HIm	230	1.7	2.1 (5)
1	4-MeC$_6$H$_4$NH$_2$	230	1.7	2.4 (3)
1	morpholine	1 400	2.5	4.2^c (3)
2	P(OBu)$_3$	6.8	0	0 (11)
2	PBu$_3$	70 000	4.0	3.8$_5$ (7)
2	HIm	1 140	2.2	2.1 (5)
2	morpholine	90 000^e	4.1	4.2^c (3)
3	P(OBu)$_3$	63	0	0 (11)
3	P(OBu)$_3$	75^d		
3	P(C$_2$H$_4$CN)$_3$	210	0.5	0.2 (6)
3	P(4-FC$_6$H$_4$)$_3$	1 300	1.3	1.3 (2)
3	P(C$_6$H$_5$)$_3$	6 000	2.0	2.1 (12)
3	P(4-MeC$_6$H$_4$)$_3$	20 000^e	2.5	2.6 (5)
3	PBu$_3$	600 000^e	4.0	3.8$_5$ (7)
3	HIm	6 800	2.0	2.1 (5)
3	N-MeIm	6 800	2.0	2.3 (2)
3	morpholine	1 300 000^e	4.3	4.2^c (3)

^{a} Computed from eq 1 with P(OBu)$_3$ as the reference nucleophile. ^{b} This is an average N_+ value calculated from data for a variety of organometallic electrophiles, the number of which is given in parentheses; see ref 7. ^{c} Estimated standard deviation in this value is ±0.3; for other N_M values the standard deviation is ±0.2 or less. ^{d} Acetonitrile solvent. ^{e} These values are approximate, although probably correct within a factor of 2.

treatment with trityl hexafluorophosphate. Cation 2 was purchased from Aldrich as the chloride and converted to the hexafluorophosphate salt by a procedure used to synthesize the tetrafluoroborate salt.[1] Cation 3 was synthesized by a published method[12] that involves the reaction of 7-methoxycycloheptatriene with N,N-dimethylaniline, followed by addition of trityl cation. The same product was more conveniently obtained by adding N,N-dimethylaniline to tropylium hexafluorophosphate in a 1:2 molar ratio in acetone or acetonitrile. The solution turned deep purple after 10–15 min at room temperature. The solvent was evaporated and washed with water and hexane and then vacuum dried. All of the carbocation salts were characterized by ^{1}H NMR and optical spectra.

Kinetic studies were done under nitrogen or argon. Experiments at 25 °C were done with a Dionex 110 stopped-flow instrument. Work at other temperatures utilized a homemade stopped-flow of the Canterbury design.[13] This instrument incorporates a Jarrell-Ash Mark X monochromator and a Neslab cooling equipment (RTE-8, DCR-4, and CC-80) and operates down to –50 °C. The wavelengths used to follow the reactions were 460, 540, and 569 nm for cations 1–3, respectively. Pseudo-first-order conditions were maintained by keeping the nucleophiles in at least tenfold excess over the cation concentration, which was 1–5 × 10^{-5} M.

Results and Discussion

Phosphorus and nitrogen donor nucleophiles react rapidly with carbocations 1–3. For these reactions the pseudo-first-order rate constants in acetone obey the equation $k_{obsd} = k[\text{nucleophile}]$. The second-order rate constants k are listed in Table I. All k values were calculated from k_{obsd} measured at three or more different nucleophile concentrations except for the reaction of 3 with PBu$_3$, P(4-MeC$_6$H$_4$)$_3$, and morpholine. The latter reactions are too rapid to allow significant variation of the nucleophile concentration. The color of carbocations 1–3 is bleached by the nucleophiles; the subsequent addition of excess tropylium or trityl hexafluorophosphate was found to regenerate the original color. This occurs because tropylium and trityl cations are stronger electrophiles than 1–3 and verifies that the reactions with 1–3 involve only simple electrophile–nucleophile combination.

For the reaction of 3 and P(C$_6$H$_5$)$_3$, activation parameters were determined from rate measurements in acetone at seven temperatures over the range +25 to –40 °C. An Eyring equation plot gave an excellent fit with the following results: $\Delta H^\ddagger = 6.3 \pm 0.15$ kcal mol^{-1} and $\Delta S^\ddagger = -19 \pm 1$ cal deg^{-1} mol^{-1}. The small $\Delta H^\ddagger$

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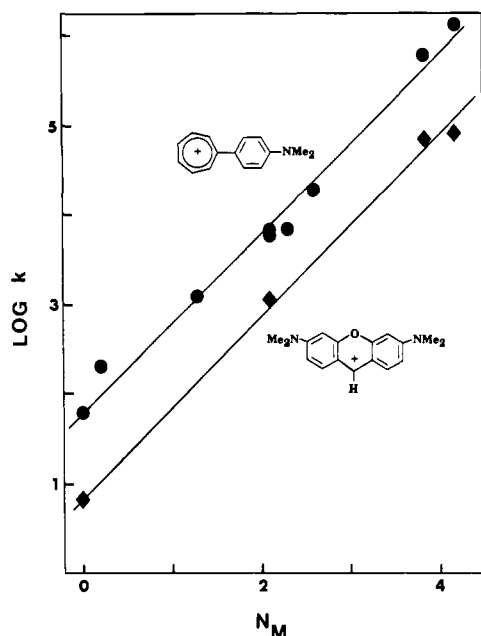(13) Designed and built by Dr. N. Rees, University College, Cardiff, U.K.

Figure 1. Plot of reactivity vs. N_M for carbocations **2** and **3** in acetone at 25 °C. The N_M values are taken from ref 7.

and negative $\Delta S^{\ddagger}$ are, of course, reasonable for a combination reaction. Significantly, for tertiary phosphine addition to organometallic electrophiles, $\Delta H^{\ddagger}$ is also small and $\Delta S^{\ddagger}$ is generally[7] ca. -20 cal deg^{-1} mol^{-1}.

The results in Table I show that the pyronin cation (**2**) and the (*p*-(dimethylamino)phenyl)tropylium cation (**3**) give very similar N_+ values and, therefore, conform to eq 1. However, the (*p*-(dimethylamino)triphenyl)methyl cation (**1**) is much less reactive toward PBu$_3$ and morpholine (relative to P(OBu)$_3$) than would be expected from the N_+ values for **2** and **3**. This could mean that relative nucleophilic reactivities are not really electrophile independent, although in this case the deviation is opposite to that expected from the reactivity–selectivity principle. However, a much more likely explanation is that the steric bulk of the nucleophile is important for reactions with **1** and that the greater size of PBu$_3$ and morpholine relative to P(OBu)$_3$ is responsible for the observed rate retardations. Indeed, there is compelling evidence[1,14] that the reactions of triarylmethyl cations involve significant steric effects and that these are largely absent with **2** and **3**. With this assumption, it can be concluded from our results that the relative reactivities (N_+) of phosphorus donors seem to be carbocation independent in the absence of steric effects. Hence, phosphorus donors join oxygen and nitrogen donors as nucleophiles that obey eq 1. Interestingly, this statement cannot be extended to sulfur donors, as judged from studies of alkylthiolate nucleophiles, which show substantial deviations from eq 1 in some cases.[15,16]

The data in Table I reveal a striking correlation between N_+ values for free carbocations **2** and **3** and N_+ values (relabeled N_M) for coordinated cyclic π-hydrocarbons. Thus, N_+ and N_M are nearly identical for a given nitrogen or phosphorus donor nucleophile. This is illustrated in Figure 1 which gives plots of log k vs. N_M for the reactions of **2** and **3**. The slopes are 0.98 ± 0.04 and 1.00 ± 0.04, respectively. This means that the relative nucleophilic reactivities of nitrogen and phosphorus donors are the same for organic and organometallic electrophiles. In other words, *nucleophilic attack on both free and complexed π-hydrocarbons follows a simple unified reactivity law* (eq 1). It follows, therefore, that eq 1 applies to a great variety of electrophilic molecules. The generality of this is further apparent from the observation[7] that the N_M parameters for (π-hydrocarbons)ML$_n$$^{m+}$ are independent of the nature of the metal, nonreacting ligands, and the π hydrocarbon. Whether or not eq 1 applies in such a general way to carbon donor nucleophiles is an important unanswered question.

The transition state for organometallic reactions such as eq 2 is believed[7] to be an early one, with the metal–carbon bond cleavage not making a major contribution to the activation energy. This probably accounts in part for the equality of N_+ and N_M, i.e., the transition states are similar for both types of reactions. Analogous activation parameters for P(C$_6$H$_5$)$_3$ addition to **3** and tertiary phosphine addition to (ring)ML$_n$$^{m+}$ also suggests similar transition states.

Nucleophilic addition to ferrocenyl-stabilized carbocations (FcCR$_2$$^+$) has been shown to follow the N_+ correlation.[14,17-19] Although these reactions involve organometallic substrates, the carbon atom attacked is at best weakly interacting with the metal.[20] Therefore, these reactions are best classified as simple combinations and not as substitutions with cleavage of a metal–carbon bond.

Conclusions

Phosphorus nucleophile addition to free carbocations obeys the Ritchie N_+ correlation. The relative reactivities of phosphorus and nitrogen donors towards free carbocations are identical with that observed for addition to metal-coordinated cyclic π-hydrocarbons, showing that both types of reactions have similar transition states and that the metal–carbon bond cleavage in the latter reaction does not markedly influence the dynamics. The Ritchie correlation probably applies to a great many organometallic electrophiles.

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