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Isolation, X-ray Structures, and Electronic Spectra of Reactive Intermediates in Friedel–Crafts Acylations[†]

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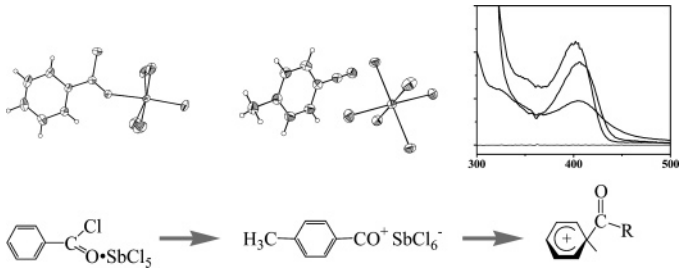

Reactive intermediates in the Friedel–Crafts acylation of aromatic donors are scrutinized upon their successful isolation and X-ray crystallography at very low temperatures. Detailed analyses of the X-ray parameters for the [1:1] complexes of different aliphatic and aromatic-acid chlorides with the Lewis acids antimony pentafluoride and pentachloride, gallium trichloride, titanium and zirconium tetrachlorides provide unexpected insight into the activation mechanism for the formation of the critical acylium carbocations. Likewise, the X-ray-structure examinations of aliphatic and aromatic acylium electrophiles also isolated as crystalline salts point to the origins of their electrophilic reactivity. Although the Wheland intermediates (as acylium adducts to arene donors) could not be isolated in crystalline form owing to their exceedingly short lifetimes, transient (UV–vis) spectra of benzenium adducts of acylium carbocations with hexamethylbenzene can be measured and directly related to Wheland intermediates with other cationic electrophiles that have been structurally established via X-ray studies.

Introduction

The commonly used Lewis acid induced or Friedel–Crafts acylation of various aromatic substrates with carboxylic-acid halides is one prototypical (textbook) example of a wide variety of electrophilic aromatic-substitution processes.[1] As such, mechanistic studies have generally focused on three principal stages of reaction involving: (I) activation of acyl halide by Lewis acid, (II) heterolysis of the acyl–halogen bond to generate the reactive acylium electrophile, and (III) electrophilic attack on arene donors via cationic σ-adducts.[2] The identification of such reactive intermediates has largely relied on transient spectroscopy, especially NMR and IR techniques as elegantly employed by Olah and co-workers in their pioneering studies.[3–5]

We now explore some of the limits to which the ultimate structural tool of X-ray crystallography can be employed in the experimental study of these reactive intermediates insofar as the definitive bond (length/angle) parameters that are well provided by X-ray structures can shed additional insight onto their reactivity.[6,7] It is important to recognize, however, that the requisite isolation of metastable species in crystalline form poses a difficult experimental problem since those

[†] This paper is dedicated to George Olah and was presented (in part) at the Loker Hydrocarbon Institute celebrating "125 Years of Friedel–Crafts Chemistry".

(1) See, e.g.: (a) McMurry, J. *Organic Chemistry*; Brooks/Cole: Monterey, CA, 1984; p 529 ff. (b) Solomons, T. W. G. *Organic Chemistry*, 6th ed.; Wiley: New York, 1996; p 664 ff. (c) Wade, L. J., Jr. *Organic Chemistry*; Prentice Hall: Upper Saddle River, NJ, 1999; p 757 ff. (d) Streitwieser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 2nd ed.; Macmillan: New York, 1981; p 690 ff.

(2) (a) Taylor, R. *Electrophilic Aromatic Substitution*; Wiley: New York, 1990. (b) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; p 501 ff.

(3) Olah, G. A. *Friedel–Crafts Chemistry*; Wiley: New York, 1973.

(4) Olah, G. A., Ed. *Friedel–Crafts and Related Reactions*; Interscience: New York, 1964; Vol. III.

(5) For the latest overview, see: Olah, G. A.; Molnar, A. *Hydrocarbon Chemistry*, 2nd ed.; Wiley-Interscience: Hoboken, NJ, 2003.

(6) Insofar as X-ray structural parameters reflect molecular electron-density distributions.[7]

(7) See, e.g.: Koritsanszky, T. S.; Coppens, P. *Chem. Rev.* **2001**, *101*, 1583.

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Published on Web 04/12/2005

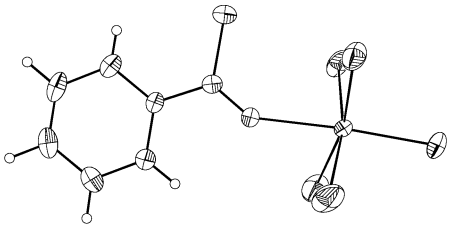


FIGURE 1. Molecular (ORTEP) structure of the [1:1] complex of benzoyl chloride with antimony pentachloride.

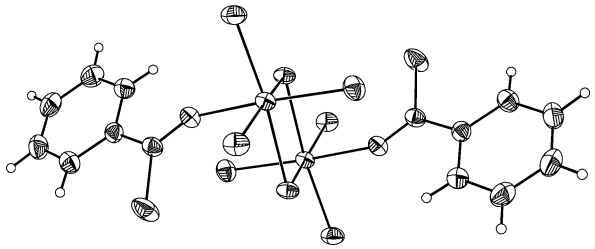


FIGURE 2. Molecular structure of the [2:2] adduct of benzoyl chloride with titanium tetrachloride.

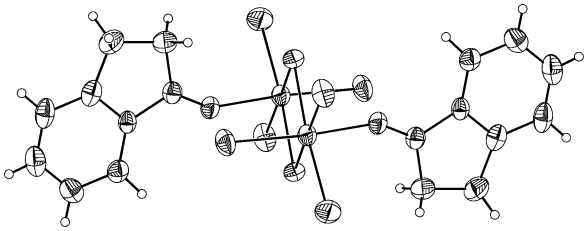


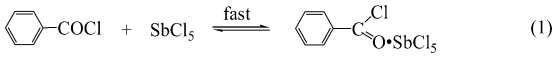
FIGURE 3. Molecular structure of the intramolecular Friedel–Crafts product (hydrindone) as the dimeric titanium–tetrachloride complex.

which are successfully crystallized from solution are not necessarily the principal intermediates.[8] With this caveat in mind, our aim in this study is to ascertain how the twin tools provided by (a) X-ray crystallography of isolable species and (b) the time-resolved electronic spectroscopy of other intermediates with lifetimes (τ) $<10^{-8}$ s can be exploited to provide new insight into the mechanism of electrophilic aromatic acylation. Experimentally, we employ low-temperature crystallization and X-ray crystallography at −150 °C in conjunction with UV–vis spectroscopy to identify species too labile to isolate in crystalline form.[9]

Results

To mimic reaction conditions found to be favorable to Friedel–Crafts acylations, we initially examined the direct interaction of both aliphatic and aromatic-acid chlorides in dichloromethane solution with the pure metal chlorides: $SbCl_5$ and $GaCl_3$ as well as $TiCl_4$ and $ZrCl_4$, to represent Lewis acids of moderate and limited reactivity, respectively.

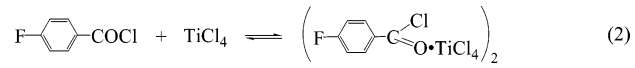
I. Isolation and X-ray Structures of Lewis Acid Complexes with Acyl Halides. A rigorously dry dichloromethane solution of freshly purified benzoyl chloride was cooled to −10 °C and the CH_2Cl_2 solution of antimony pentachloride was slowly added with stirring under a dry argon atmosphere. The colorless precipitate was collected, washed with cold dichloromethane, and recrystallized by the slow cooling of a solution of the complex that was presaturated at 30–40 °C. A single crystal was isolated at low temperature and X-ray crystallography was carried out at −150 °C to a uniform precision of 0.3–0.5 pm (esd). The ORTEP diagram in Figure 1 shows the [1:1] adduct of C_6H_5COCl and $SbCl_5$ that is σ-bonded through the carbonyl oxygen,[10] i.e.,



(1)

A slightly varied procedure was successfully used for the fluoro analogue by slowly adding a CH_2Cl_2 solution of p-FC_6H_4COCl to a $SbCl_5$ solution held at −40 °C. After a short induction period, colorless crystals of the [1:1] adduct were collected, washed with cold CH_2Cl_2, and dried in vacuo. The carbonyl stretching band at ν_{CO} = 1561 cm^{-1} for this crystal was essentially the same as that of the benzoyl analogue (vide supra) to confirm that O-complexation had occurred in the manner shown in Figure 1. The slightly deactivated p-fluorobenzoyl chloride also afforded the colorless [1:1] adduct of gallium trichloride that was isostructural with the benzoyl–chloride complex of $SbCl_5$, as established by the bonding parameters in Table 1.

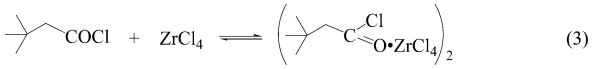
The weaker Lewis acid, $TiCl_4$, afforded a series of [2:2] adducts with p-fluorobenzoyl chloride, the parent benzoyl chloride, and with the slightly activated p-toluoyl chloride, in which the Lewis acid exists as a dimeric unit with each titanium center directly bonded to the carbonyl oxygen (Figure 2), e.g.,



(2)

in the manner found with $SbCl_5$ and $GaCl_3$, as listed in Table 1.

A similar dimeric Lewis acid unit was also found as the [2:2] complex of zirconium tetrachloride with the aliphatic-acid chloride, *tert*-butylacetyl chloride.



(3)

Interestingly, the direct interaction of the aliphatic hydrocinnamyl chloride with both titanium and zirconium chloride at −60 °C for several days yielded crystals of only the intramolecular Friedel–Crafts product as hydrindone complexed with the Lewis acid in the [2:2] complex shown in Figure 3.

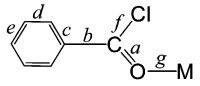
II. Isolation and X-ray Structures of Acylium Carbocations. Freshly purified p-methylbenzoyl chlo-

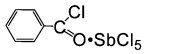
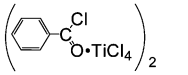
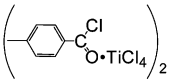
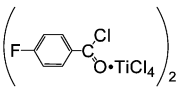
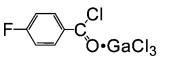
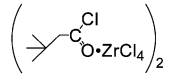
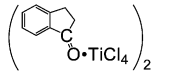
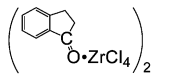
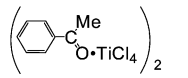
(8) When a number of reactive intermediates are extant in solution, especially under equilibrium control, those which are isolated in crystal form generally depend on their solvation energy, crystal-lattice energy, molecular symmetry, etc., and not necessarily on their abundance (importance).

(9) Rathore, R.; Kochi, J. K. *Adv. Phys. Org. Chem.* **2000**, *33*, 193.

(10) For previous X-ray studies of analogous structures, mostly carried out at higher (room) temperature and lower precision, see: (a) Chevrier, B.; Le Carpentier, J.-H.; Weiss, R. *Acta Crystallogr.* **1972**, *B28*, 2659, 2667. (b) Rasmussen, S. E.; Broch, N. C. *Acta Chem. Scand.* **1966**, *20*, 1351. (c) Le Carpentier, J.-H.; Weiss, R. *Acta Crystallogr.* **1972**, *B28*, 1437, 1442. (d) Chevrier, B.; Le Carpentier, J.-H.; Weiss, R. *J. Am. Chem. Soc.* **1972**, *94*, 5718. (e) Baroni, T. E.; Kolesnichenko, V.; Seib, L.; Heppert, J. A.; Liable-Sands, L. M.; Yap, G. P. A.; Rheingold, A. E. *Polyhedron* **1998**, *17*, 759.

TABLE 1. X-ray Structural Parameters of Lewis acid Adducts to Aliphatic and Aromatic-Acid Chlorides[a]



Adduct	*a*	*b*	*c*	*d*	*e*	*f*	*g*
	1.226(3)	1.461(3)	1.394(3) 1.399(3)	1.383(4) 1.400(4)	1.373(5) 1.386(5)	1.713(2)	2.270(2)
	1.218(2)	1.459(3)	1.396(3) 1.396(3)	1.386(3) 1.384(3)	1.378(3) 1.378(3)	1.724(2)	2.111(1)
	1.216(2)	1.450(2)	1.400(2) 1.403(2)	1.377(2) 1.383(2)	1.391(2) 1.397(2)	1.734(1)	2.114(1)
	1.219(1)	1.453(2)	1.400(1) 1.401(1)	1.380(2) 1.386(2)	1.376(2) 1.384(2)	1.729(1)	2.128(1)
	1.231(2)	1.446(2)	1.396(2) 1.398(2)	1.382(3) 1.375(3)	1.371(3) 1.374(3)	1.719(2)	1.965(1)
	1.211(2)	1.478(2)	—	—	—	1.721(2)	2.207(1)
	1.243(4)	1.452(5)	1.387(4) 1.397(5)	1.372(5) 1.380(5)	1.394(6) 1.354(7)	—	2.026(2)
	1.253(5)	1.441(7)	1.400(7) 1.375(7)	1.376(7) 1.369(9)	1.374(9) 1.386(9)	—	2.090(3)
	1.239(2)	1.467(3)	1.384(3) 1.399(3)	1.389(3) 1.376(3)	1.371(4) 1.382(4)	—	1.998(1)

[a] Diffraction data collected at −150 °C and esd's in parentheses.

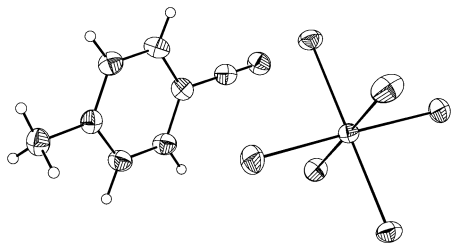
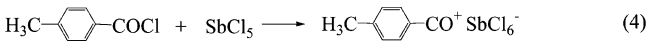


FIGURE 4. ORTEP diagram of *p*-methylbenzoyl carbocation ion paired with hexachloroantimonate.

ride was treated directly with antimony pentachloride in dichloromethane by essentially the same procedure as described above for the parent benzoyl chloride (see Experimental Section for details). However, X-ray crystallographic analysis of the colorless crystals at −150 °C led to the ORTEP diagram in Figure 4 that depicts the [1:1] salt comprised of the *p*-methylbenzoyl cation and the coordinatively saturated hexachloroantimonate counteranion,[11] i.e.,



(4)

Indeed, such an acylium salt represents the free carbocation as the separated ion pair owing to the wide interionic separation of 3.29 Å (C···ClSbCl$_5$).

Furthermore, the trimethyl analogue, mesitoyl chloride, also reacted directly with antimony pentachloride under similar low-temperature conditions to yield the acylium salt, 2,4,6-trimethylphenyloxocarbonium hexachloroantimonate, as structurally established by X-ray crystallography (Table S1 in the Supporting Information). In contrast to benzoyl chloride, no crystals of the corresponding Lewis acid complexes (vide supra) were found when either *p*-toluoyl or mesitoyl chloride was treated with antimony pentachloride under the same conditions.

The clear-cut distinction between the formation of the Lewis acid complex versus the acylium salt, i.e.,

(5)

was also observed when acid fluorides were treated with antimony pentafluoride in dichloromethane solution. Thus benzoyl fluoride and SbF_5 yielded the acylium salt $PhCO^+SbF_6^-$ that was readily identified by the diagnostic carbonyl stretching band at ν_{CO} = 2225 cm^{-1} in the IR spectrum. Even the aliphatic derivative acetyl fluoride

(11) Davlieva, M. G.; Lindeman, S. V.; Neretin, I. S.; Kochi, J. K. *New J. Chem.* **2004**, *28*, 1568.

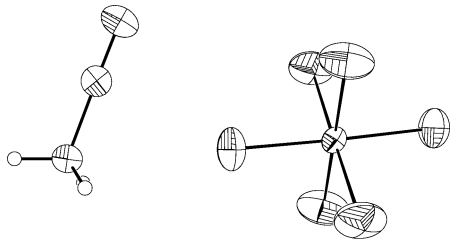


FIGURE 5. Acylium salt $CH_3CO^+SbF_6^-$ derived from acetyl fluoride and antimony pentafluoride in dichloromethane.

afforded only the acetylium salt $CH_3CO^+SbF_6^-$ upon direct treatment with antimony pentafluoride in dichloromethane solution as shown by the ORTEP diagram in Figure 5.

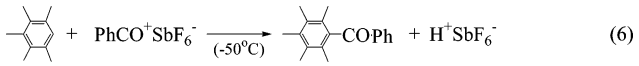
Gallium trichloride is also an effective Lewis acid for the direct production of acylium salts from aliphatic acid chlorides, as shown by the conversion of acetyl chloride and propionyl chloride to the corresponding acylium salts, $RCO^+GaCl_4^-$ (R = methyl and ethyl), as judged both by X-ray crystallographic analysis[11−13] and diagnostic carbonyl stretching bands at ν_{CO} = 2284 and 2282 cm^{-1}, respectively.[14] By way of contrast, however, the aromatic-acid chloride *p*-fluorobenzoyl chloride mainly afforded only crystals of the Lewis acid adduct that is O-bonded to $GaCl_3$ with ν_{CO} = 1549 cm^{-1}.

Titanium and zirconium tetrachlorides as the weakest Lewis acids examined in this study did not afford acylium salts when treated directly with either aromatic or aliphatic-acid chlorides, and only Lewis acid complexes were isolated (Table 1, entries 2−4). Despite the fact that the treatment of hydrocinnamoyl chloride directly with titanium chloride afforded the Friedel−Crafts product even at −40 °C, no acylium salts could be detected—and hydrindone was merely isolated as the crystalline dimeric titanium and zirconium tetrachloride complexes (Table 1, entries 7 and 8). [The structure of the related acetophenone complex is also included in Table 1 (entry 9) for comparison.]

III. Spontaneous Interaction of Acylium Salts with Aromatic Donors. Controlled exposure of electron-rich arenes to the cationic electrophile was carried out by prior dissolution of the pure acylium salt into dichloromethane (or nitromethane mixture) at low temperature, followed by the careful introduction of the donor. [The high reactivity of the acylium electrophile as a "free" cation was ensured by the use of the poorly coordinating counteranions SbF_6^- and $SbCl_6^-$ for these studies.] The colorless solutions were examined in two ways: first with respect to the aromatic-substitution product and then by UV−vis analysis of reactive intermediates, as follows.

A. Friedel−Crafts and other aromatic products were identified by letting the homogeneous solution stand for short periods and then diluting the mixture with benzene and quenching with water. After washing, the organic extract was directly analyzed for comparison with the Friedel−Crafts acylation product,[15] as well as scrutiny for any other important (side) product.

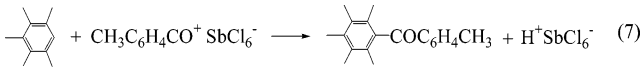
The behavior of three prototypical arenes—durene (DUR), pentamethylbenzene (PMB), and hexamethylbenzene (HMB)—was first examined with a series of aromatic and aliphatic acylium derivatives as the hexafluoroantimonate salts; and the facile conversion of durene and pentamethylbenzene to the corresponding Friedel−Crafts ketones (Table S2) was found to occur with each of these acylium salts under very mild reaction conditions,[16] e.g.,



(6)

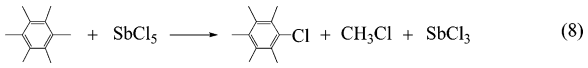
and the recovered methylarene constituted the remainder of the material balance, except for small but significant amount of the transalkylated hexamethylbenzene that was observed with the aliphatic acetylium and *tert*-butylacetylium hexafluoroantimonates. The fully substituted hexamethylbenzene was recovered intact, with no other aromatic product being detected; and the isosteric chloropentamethylbenzene was similarly recovered quantitatively. It is thus noteworthy that bromopentamethylbenzene yielded significant amounts of the transalkylated hexamethylbenzene (24%) as well as 1,2-dibromotetramethylbenzene (12%) in addition to recovered bromopentamethylbenzene.

Similar treatment of methylarene donors was then carried out with some of the same acylium salts, but as the hexachloroantimonate analogues, e.g.,



(7)

Indeed, the same trends in Friedel−Crafts reactivity were observed, but with the exception that significant amounts of chlorinated byproducts were identified in the form arising from both side chain and nuclear substitution (Table S3). Since such electrophilic chlorinations are known to derive via the pure Lewis acid,[17] e.g.,



(8)

we infer that the formation of the acylium salt in eq 4 is

(12) For X-ray diffraction studies at room temperature, see: (a) Boer, F. P. *J. Am. Chem. Soc.* **1968**, *90*, 6706. (b) Le Carpentier, J. M.; Weiss, R. *Acta Crystallogr.* **1972**, *B28*, 1421, 1430. (c) Chevrier, B.; Le Carpentier, J. M.; Weiss, R. *Acta Crystallogr.* **1972**, *B28*, 2673. (d) Chevrier, B.; Le Carpentier, J. M.; Weiss, R. *J. Am. Chem. Soc.* **1972**, *94*, 5718.

(13) Hurlburt, P. K.; Rack, J. J.; Luck, J. S.; Dec, S. F.; Webb, J. D.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1994**, *116*, 10003.

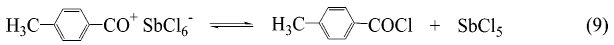
(14) (a) Olah, G. A.; Kuhn, S. J.; Tolgyesi, W. S.; Baker, E. B. *J. Am. Chem. Soc.* **1962**, *84*, 2733. (b) Olah, G. A.; Tolgyesi, W. S.; Kuhn, S. J.; Moffat, M. E.; Bastien, I. J.; Baker, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 1328. See also: Davlieva, M. G. et al. in ref 11.

(15) For earlier conversions of acylium salts directly into Friedel−Crafts ketones, see: (a) Olah, G. A.; Kuhn, S. J.; Flood, S. H.; Hardie, B. A. *J. Am. Chem. Soc.* **1964**, *86*, 2203. (b) Olah, G. A.; Lukas, J.; Lukas, E. *J. Am. Chem. Soc.* **1969**, *91*, 5319. (c) Olah, G. A.; Lin, H. C.; Germain, A. *Synthesis* **1974**, *12*, 895. See also Olah et al. in ref 14.

(16) (a) We were limited in our mechanistic objectives (vide infra) to these difficult (low-temperature) experimental problems, so it is important to emphasize the caveat that the GC-MS analyses in Table S2 (and Table S3) were not required to be highly reproducible. The semiquantitative results are thus primarily intended to convey the relative trends in arene conversions to Friedel−Crafts ketones, as well as arene recovery and byproduct formation under low-temperature conditions. (b) For the synthetic utility of acylium salts, see the extensive studies of Olah et al. cited in ref 15.

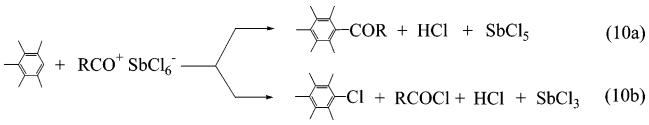
(17) (a) Kovacic, P.; Sparks, A. K. *J. Am. Chem. Soc.* **1960**, *82*, 5740. (b) Kovacic, P. In *Friedel−Crafts and Related Reactions*; Olah, G. A., Ed.; Interscience: New York, 1965; Vol. IV. (c) Rathore, R.; Loyd, S. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1994**, *116*, 8414. (d) Rathore, R.; Hecht, J.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 13278.

reversible, i.e.,



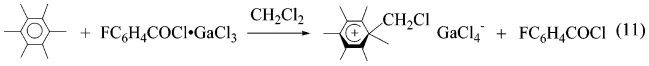
(9)

especially when in contact with those arene donors with no readily replaceable aromatic hydrogens. Indeed, the reduced antimony trichloride that was formed in the chlorination (eq 8) was isolated from the mixture and characterized (X-ray) in crystalline form as the π-arene complex.[18] Otherwise, PMB and DUR afforded respectable amounts of Friedel–Crafts acylation product when exposed to the same acylium hexachloroantimonate salts. Moreover, the presence of significant amounts of both nuclear and side chain chlorination products indicated that electrophilic aromatic chlorination and acylation were more or less competitive, i.e.,



(10a) (10b)

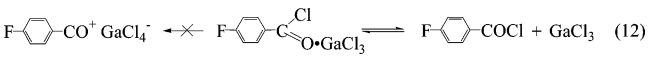
To evaluate the reactivity of gallium trichloride as a weak Lewis acid, the [1:1] complex with *p*-FC_6H_4COCl (see Table 1, entry 5) was treated directly with hexamethylbenzene. After the dark red solution was allowed to stand for 10 days at −70 °C, it deposited only yellow crystals of the Friedel–Crafts (alkylation) salt derived from the solvent, i.e.,



(11)

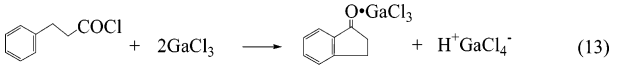
and the benzenium structure of this σ-adduct was verified by X-ray crystallography (Figure 6) together with its characteristic UV–vis absorption ($\lambda_{max} = 400$ nm, $\epsilon = 6.7 \times 10^3$ M^{-1} cm^{-1}).

Thus the full recovery of FC_6H_4COCl pointed to the efficient reversion of the [1:1] complex to free gallium trichloride (but not to the acylium salt), i.e.,



(12)

which was independently confirmed by the isolation of the same benzenium salt from treatment of hexamethylbenzene in dichloromethane solution with pure gallium trichloride. Moreover, the analogous reversion of the acylium salt is also indicated by the isolation of the same crystalline salt (Figure 6) when hexamethylbenzene was treated with the aliphatic *tert*-butylacetyl tetrachlorogallate at −70 °C for 12 days. Although no evidence of Friedel–Crafts acylation could be detected, it is noteworthy that the treatment of the aliphatic hydrocinnamoyl chloride with gallium trichloride at −70 °C for 2 days led to colorless crystals of the cyclized hydrindone complex, i.e.,



(13)

the structure of which was established by X-ray crystallography (Table 1).

B. Transient (UV–Vis) spectra of acylium electrophiles were measured in the presence of hexamethylbenzene, pentamethylbenzene, or durene under precisely the same conditions employed in the product studies (vide supra), with the exception that the systems were never allowed to rise above the lowest practicable temperature of −70 °C.

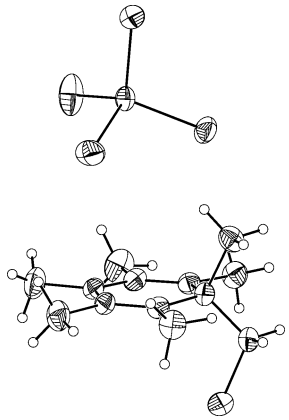


FIGURE 6. Benzenium structure of the product of Friedel–Crafts alkylation of hexamethylbenzene with $FC_6H_4COCl \cdot GaCl_3$ in dichloromethane.

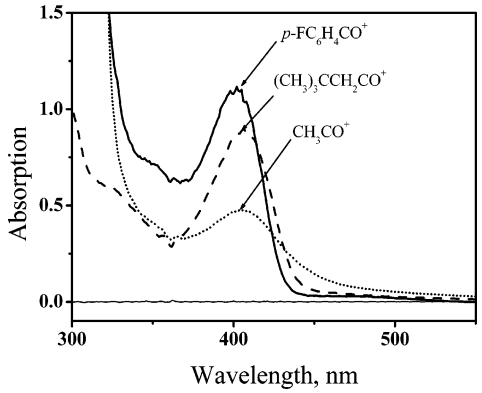


FIGURE 7. UV–vis absorption spectra observed at −70 °C upon the addition of hexamethylbenzene to CH_2Cl_2 solutions of acylium hexafluoroantimonates (as indicated).

Dichloromethane solutions of pure acylium hexafluoroantimonates are colorless and show no significant absorption in the 350 to 800-nm spectral region. However, upon the addition of hexamethylbenzene under rigorously anhydrous conditions, the CH_2Cl_2 solutions turned yellow and pronounced new bands were observed with $\lambda_{max} \approx 400$ nm (Figure 7).

The results in Table 2 show that the new absorptions were essentially invariant with acylium structure, independent of whether aliphatic (R = CH_3, $(CH_3)_3CCH_2$) or aromatic (4-CH_3, 2,4,6-$(CH_3)_3$, 4-F, or 2,6-F_2) derivatives were employed. The same insensitivity of λ_{max} was observed with changes in solvent polarity (CH_3COCl, $PrNO_2$) and counteranion ($SbCl_6^-$). It is noteworthy that no changes in the absorption spectra of acylium cations were observed upon the addition of the sterically hindered hexaethylbenzene (HEB).[19,20] Similarly, only very weak (indeterminate) bands were detected when either

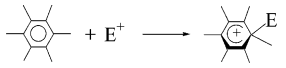
(18) (a) Hubig, S. M.; Lindeman, S. V.; Kochi, J. K. Electronic submission to the Cambridge Structural Database, 2000, CCDC 138873. (b) Schmidbaur, H.; Nowak, R.; Schier, A.; Wallis, J. M.; Huber, B.; Mueller, G. *Chem. Ber.* **1987**, *120*, 1829.

TABLE 2. Transient UV−Vis Spectra Attendant upon the Addition of Various Acylium Cations to Different Aromatic Donors in Dichloromethane Solution

acylium	absorption, λ_{max} (nm) HMB	HEB	PMB
CH_3CO^+	405[a]	no band	no band
	405[b]		
	405[c]		
	400[d]		
$(CH_3)_3CCH_2CO^+$	397		no band
4-$FC_6H_4CO^+$	400	no band	*e*
2,4,6-$(CH_3)_3C_6H_2CO^+$	404	no band	no band
4-$CH_3C_6H_4CO^+$	400		
2,6-$F_2C_6H_3CO^+$	395		

[a] In dichloromethane at −70 °C, with acylium carbocations taken as hexafluoroantimonate salts, unless otherwise noted. [b] In AcCl solution. [c] In $PrNO_2$ solution. [d] $CH_3CO^+SbCl_6^-$ salt. [e] Very weak band appeared at ∼410 nm.

pentamethylbenzene or durene was added under the same (low-temperature) conditions.[21] Such a spectral behavior accompanying the exposure of different acyl cations to hexamethylbenzene is strongly reminiscent of the formation of σ-adducts as benzenium cations with other cationic electrophiles such as $E^+ = H^+$, CH_3^+, NO_2^+, and Br^+ summarized recently,[22] i.e.,



(14)

Although this characteristic absorption band experiences a noticeable red shift with strong electrophiles such as $E^+ = NO_2^+$ and Br^+, it will be rather invariant among the HMB adducts of the family of carbon-centered cations such as $E^+ = CH_3^+$, $ClCH_2^+$, $CH_3C^+{=}O$, and $PhC^+{=}O$, which are unlikely to exert appreciably different perturbations of the cyclohexadienyl chromophore (especially at its nodal position) owing to their essential carbocationic character.[23]

Discussion

The successful isolation of reactive intermediates in crystalline form for X-ray analysis must be reconciled with the mechanism of the prototypical electrophilic substitution of aromatic donors. As such, let us discuss how the availability of (static) X-ray structures coupled with transient (UV−vis) spectral analysis can be used to elucidate the three critical stages (I−III described above in the Introduction) for Friedel−Crafts acylation.

Stage I: Activation of Acid Chlorides by Lewis Acids. The preferential and facile coordination at the carbonyl−oxygen center of acid chlorides by all of the different Lewis acids, including antimony pentachloride, gallium trichloride, titanium, and zirconium tetrachlorides used in this study, is established by the consistent set of X-ray structures presented in Figures 1−3 and Table 1, independent of whether monomeric or dimeric Lewis acid moieties are involved.

The mechanism of the Lewis acid effect on acid chloride can be gleaned from the scrutiny of the small structural changes that is allowed by the X-ray structural parameters in Table 1 obtained at low (−150 °C) temperatures.[24a] Thus upon Lewis acid coordination, all the acid chlorides suffer significant elongation of the C=O bond from 1.18 to 1.22 Å (av) and shortening of the C−Cl bond from 1.80 to 1.72 Å, together with a slight contraction of the C−C bond to the aliphatic or aromatic group.[24b] Such trends when evaluated on the basis of Pauling's bond-length/bond-order relationship[25] indicate the increased electron deficiency that is induced at the carbonyl center by the Lewis acid coordination is compensated by π-electron donation from chlorine, resulting in the *strengthening* of the C−Cl bond (as well as increased conjugation of the alkyl/aryl group). This important step leading to the extensive electron polarization of the acid chloride must either be separate from or lie prior to the activation of the C−Cl bond. However, the singular absence of any crystallographic evidence for the formation of structures involving Lewis acid coordination to the chlorine center indicates that the concentration of such an isomeric adduct is not likely to be mechanistically significant, and thus relegated to a weak intermediate or a transition-state structure. This dilemma can be circumvented if the predominant acyl−chloride complex undergoes a facile *intramolecular* (direct) chlorine transfer to the complexed Lewis acid moiety, e.g.,

(15)

Indeed, this concerted rearrangement is consistent with the competition between the formation of acylium cation and the [1:1] complex in eq 5, as shown by its sensitivity to the acid−chloride structure. For example, the minor replacement of benzoyl chloride with the slightly more electron-rich methyl-substituted analogue is sufficient to lead from the isolation of the crystalline [1:1] complex of

(19) (a) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073. (b) Hunter, G.; Iverson, D. J.; Mislow, K.; Blount, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 5942. (c) Hunter, G.; Weakley, T. J. R.; Mislow, K.; Wong, M. G. *J. Chem. Soc., Dalton Trans.* **1986**, 577.

(20) Rathore, R.; Lindeman, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 9393.

(21) (a) The corresponding arenium cations with $E^+ = H^+$ also have similar absorptions in this region but are generally blue-shifted by about 5−10 nm. (b) Mamatyuk, V. I.; Rezvukhin, A. I.; Detsina, A. V.; Buraev, V. I.; Isaev, I. S.; Koptyug, V. A. *Zh. Org. Khim.* **1973**, *9*, 2429. (c) Koptyug, V. A. *Top. Curr. Chem.* **1984**, *122*, 1.

(22) Hubig, S. M.; Kochi, J. K. *J. Org. Chem.* **2000**, *65*, 6807.

(23) (a) The relative acceptor properties of the carbocations can be judged by differences in their reduction potentials.[23d] See: (b) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132. (c) Lund, T.; Wayner, D. D. M.; Jonsson, M.; Larsen, A. G.; Daasbjerg, K. *J. Am. Chem. Soc.* **2001**, *123*, 12590 and references therein. (d) See: Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley-Interscience: New York, 1969.

(24) (a) The precision/accuracy of the earlier X-ray diffraction data collected at room temperature[10,12] was limited to 1−1.5 pm (largely owing to thermal motion) in contrast to 0.3−0.5 pm from our low-temperature data.[11] (b) The bond lengths for C=O and C−Cl of 1.181 and 1.804 Å that were determined in hydrocinnamoyl chloride at −150 °C generally fall in the range (1.16−1.21 and 1.75−1.83 Å) of those in other acid chlorides typically reported by: Leser, J.; Rabinovich, D. *Acta Crystallogr.* **1978**, *B34*, 2253, 2257, 2260, 2264. Fukushima, S.; Ito, Y.; Hosomi, H.; Ohba, S. *Acta Crystallogr.* **1998**, *B54*, 895. Sandor, R. B.; Foxman, B. M. *Tetrahedron* **2000**, *56*, 6805.

(25) (a) Pauling, L. *Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; p 239. (b) According to Pauling, the bond order (n) is related to the bond distance r_i by the following relationship: $n_i = \exp[2.303(r_1 - r_i)/K]$, where r_1 is the single-bond distance, r_i is the observed distance, and K is an empirical constant. For the carbonyl bond, $r_1 = 1.43$ Å and $K = 0.75$. For the bond to alkyl, $r_1 = 1.48$ Å and K = 0.50, which includes the correction for the change in covalent radius with hybridization.

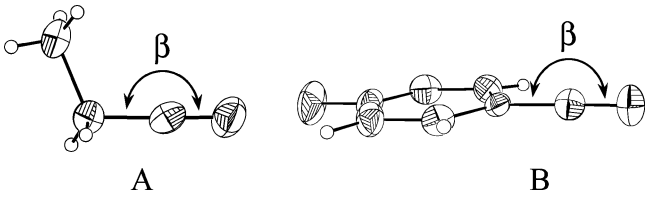
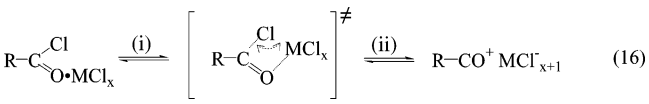


FIGURE 8. ORTEP diagrams of (A) propionyl and (B) *p*-fluorobenzoyl cations showing linear bindings of CO with $\beta \approx 180°$.

benzoyl chloride in eq 1 as opposed to the isolation of the acylium salt of the toluoylium cation in eq 4, when antimony pentachloride is simply added to the dichloromethane solution of benzoyl chloride and *p*-toluoyl chloride, respectively, under otherwise identical reaction conditions.

The conceptual interchangeability between the Lewis acid complex and the acylium salt (eq 15) demands that (i) the formation of the acylium salt involving the unimolecular rearrangement of the [1:1] complex and then (ii) the sequestration of the acylium cation via the *microscopic-reverse* process involving chlorine transfer from the $SbCl_6^-$ counterion proceed via the same transition state, i.e.,



(16)

Otherwise, crystallographic studies would provide no further insight into the mechanism of the Lewis acid activation of the acyl chloride.[26]

Stage II: Structure/Reactivity of Acylium Electrophiles. Aliphatic and aromatic acyl cations (RCO^+ and $ArCO^+$) independently synthesized from the corresponding carboxylic-acid halides and Lewis acids (or an alternative procedure with silver (I) salts[3]) can be structurally characterized as free carbocations by isolating them as crystalline salts with low-nucleophilic counteranions such as SbF_6^-, $SbCl_6^-$, or $GaCl_4^-$. X-ray analyses at low temperatures (−150 °C) afford crystallographic parameters sufficient to detect subtle changes in acyl structures.[11,24] Thus the series of aliphatic [with R = CH_3, CH_3CH_2, and $(CH_3)_2CH$] and X-substituted benzoyl [with X = 4-CH_3, 2,4,6-$(CH_3)_3$, 4-CH_3O, and 4-F] structures are characterized by carbonyl groups that are linearly bonded[12] (Figure 8) and show significant triple-bond character as follows from C−O bond lengths of $r_{CO} \sim 1.10$Å (av)[27] and enhanced carbonyl stretching frequences of ∼2300 cm^{-1} (av).[11]

Furthermore, the adjacent single bonds attached to the carbonyl groups in both aromatic and aliphatic acyl cations are also shortened to $r_{C\alpha} \sim 1.37$ and 1.42 Å, respectively. Such bond-length variations reflect increased electron donation from the aliphatic and aromatic moieties to compensate for the electron-deficient (carbocationic) center with sp^1-hybridized linear configuration for the C_α−C−O angle close to $\beta = 180°$. Indeed, aromatic acyl cations show $\pi-\pi$ conjugation between the carbocationic center and the attached benzenoid ring, which increases progressively with aryl donicity so that the shortening of the single (conjugated) C−C bond of $r_{C\alpha}$ down to 1.37 Å matches the corresponding elongation of the carbonyl triple bond with r_{CO} of up to 1.125 Å [and tracks the decreasing IR stretching frequency (ν_{CO})]. Quantitative analysis of the bond-length changes with the aid of the Pauling bond-length/bond-order relationship[25] leads to the conclusion that the total bond order at the carbonyl-carbon site is rather invariant with substituents in the aromatic ring.[11] Such an unexpected result predicts the intrinsic electrophilic reactivities of benzoyl cations to be largely unaffected by nuclear substituents.

By contrast, structural analysis of aliphatic acyl cations indicates that $\sigma-\pi$ hyperconjugation in the acetyl cation[28] can contribute only about 60% and results in the rather short value of $r_{C\alpha} \sim 1.42$ Å for this bond type. The effectiveness of $\sigma-\pi$ hyperconjugation is reduced in the isobutyryl (R = isopropyl) cation owing to the availability of only a single C_α−H bond. Significantly, the bond-length changes are insufficient to complete the bond-order requirement at the carbonyl-carbon in the isobutyryl cation, resulting in its significant electron deficiency. As such, the electrophilic reactivities of the aliphatic acyl cations are expected to increase in the following order: R = CH_3 < CH_3CH_2 < $(CH_3)_2CH$.

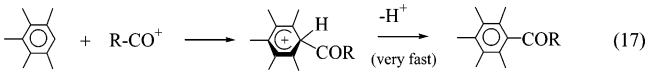
Stage III: Electrophilic Addition of Acyl Cations onto Aromatic Donors. Product studies establish the facile interaction between electron-rich arene donors and acyl cations under rather mild conditions to effect Friedel−Crafts acylation (Tables S2 and S3) at rather low temperatures. However, it is the competitive side reactions that provide information as to the reactive intermediates involved. Thus the transalkylation products hexamethylbenzene from pentamethylbenzene and the trans-chlorination products chloropentamethylbenzene and α-chlorohexamethylbenzene from both hexamethylbenzene and pentamethylbenzene as well as chloropentaethylbenzene from pentaethylbenzene and α-chlorodurene from durene suggest that benzenium adducts are involved as Wheland intermediates (consider, for example, eq 11). Moreover, the transient (UV−vis) spectra of the benzenium adducts of acyl cations observed in Figure 7 confirm the presence of such electrophilic adducts when hexamethylbenzene is the arene donor. Likewise, the absence of such absorption bands when either pentamethylbenzene or durene are exposed to acyl cations under the same conditions (Table 2, columns 3 and 4) is consistent with rapid proton loss from the Wheland intermediate,[29] e.g.,

(26) (a) It should be noted, however, that Friedel−Crafts acylation is often carried out in the presence of excess Lewis acid;[3,5] and further activation of the acylium cation by "superelectrophilic solvation" as described by Olah and co-workers[26b] is possible, particularly with regard to solvation of the oxygen nonbonded electron pairs to induce acylium bending (vide infra). Unfortunately, the X-ray results do not address this possibility. (b) Olah, G. A.; Klumpp, D. A. *Acc. Chem. Res.* **2004**, *37*, 211. Olah, G. A.; Laali, K. A.; Wang, Q.; Prakash, G. K. S. *Onium Ions*; Wiley: New York, 1998.

(27) Relative to the bond length of 1.07 Å estimated for a C≡O triple bond as described by Davlieva et al. in ref 11 (footnote 18).

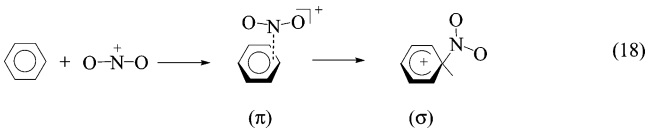
(28) Originally proposed by Boer[12a] but based on an erroneously short value of $r_{CO} = 1.385 \pm 0.016$ Å. Our redetermination[11] confirms that this bond is still exceedingly short (1.419 ± 0.004 Å) as compared to the standard C(sp^3)−C(sp) bond length of 1.47 Å (Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1)

(29) Olah, G. A. *Acc. Chem. Res.* **1971**, *4*, 240.



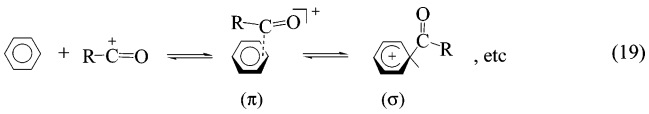
(17)

Our failure to obtain the X-ray structures of any Wheland intermediates under the reaction conditions of Friedel–Crafts acylation indicates their lifetimes are too short to isolate in crystalline form relative to the free acyl cation and even such electron-rich and polyalkylated arene donors as hexamethylbenzene. However, if this electrophilic addition/reversion process is considered in the context of the acylium structures illustrated in Figure 8, the direct addition of the linear structure requires its simultaneous bending in order to achieve the structure of the acyl adduct in the benzenium state. As such, the reorganization energy required for the simultaneous bending of $\Delta\beta \approx 60°$ will exact a sizable penalty on the activation barrier. Indeed, we faced a similar mechanistic conundrum in the very rapid addition of the nitronium (NO_2^+) cation during electrophilic aromatic nitration involving an analogous bending from linear to highly bent (NO_2) structures.[30] In this case, theoretical (molecular-orbital) studies predicted the existence of a contiguous pair of π/σ structures, i.e.,



(18)

in which the bending penalty is separated from the activation barrier for conversion to the σ-adduct (Wheland intermediate).[31,32] Due cognizance of the same reorganization problem in Friedel–Crafts acylation then leads to a similar 2-step process, i.e.,



(19)

Preliminary DFT calculations support π-acyl/arene structures as a stationary point along the potential-energy surface but require more extensive validation.[33] And from a more related structural perspective, the X-ray structures of π-arene complexes with planar carbocations are established;[34,35] and they have been directly related to a wide variety of π-arene complexes held together by Mulliken charge-transfer forces.[9,22]

Summary and Conclusions

Isolation and X-ray crystallography of some of the important reactive intermediates provide insight into the three critical stages in Friedel–Crafts acylation of arene donors. First, the spontaneous association of the acid chloride and Lewis acid occurs at the oxygen center of the carbonyl moiety, and analysis of the X-ray parameters of the [1:1] complex shows the elongation of the carbonyl bond accompanied by the tightening of the (single) bond to chlorine. Although the latter may seem to represent passivation of the acyl chloride, facile (concerted) rearrangement of the Lewis acid complex by the *intramolecular* delivery of chlorine leads directly to the critical acylium electrophile, as depicted in eq 16. Second, its isolation and X-ray crystallography establish the linear binding of the cationic carbonyl ($-C^+{=}O$) center to both alkyl (R) and aryl (Ar) groups. Detailed analyses of the X-ray parameters point to the electrophilic reactivity of such linear aliphatic acylium carbocations that increases in the order $R = CH_3 < CH_3CH_2 < (CH_3)_2CH$, whereas it is predicted to be relatively insensitive to substituent changes in Ar. Third, the enhanced electrophilic reactivity of both aliphatic and aromatic acylium carbocations is confirmed by Friedel–Crafts acylations of methylarenes that occur readily even at very low temperatures. Although the short-lived Wheland intermediates could not be isolated in crystalline form despite these drastic conditions, transient electronic (UV–vis) spectra of cationic acyl adducts can be observed with the strong hexamethylbenzene donor, and structurally related to other benzenium adducts established in previous studies.[35]

Experimental Section

Materials. Acetyl chloride, acetyl fluoride, propionyl chloride, *tert*-butylacetyl chloride, benzoyl chloride, *p*-toluoyl chloride, *p*-anisoyl chloride, *p*-fluorobenzoyl chloride, hydrocinnamoyl chloride, 2,4,6-mesitoyl chloride, and pentamethylbenzoyl chloride were prepared from the corresponding carboxylic acids by treatment with oxalyl chloride; the Lewis acids were used as received: $SbCl_5$, SbF_5, $GaCl_3$, $TiCl_4$, and $ZrCl_4$. Solvents were purified according to published procedures.[36] Hexamethylbenzene was additionally sublimed, but pentamethylbenzene and durene were used without additional purification. Chloropentamethylbenzene was prepared as described by Aitken et al.[37]

Syntheses of [1:1] Crystalline Addition Complexes. All the Lewis acid adducts were extremely moisture sensitive, and necessitated the synthetic preparations and physical measurement to be carried out with the rigorous exclusion of air and water. Schlenk flasks and an inert atmosphere glovebox with purified argon and high-vacuum techniques were routinely employed. In every case, the acyl halides were freshly distilled prior to use. Dichloromethane and hexane were additionally passed through an activated molecular sieves column prior to use. **Benzoyl chloride:antimony pentachloride complexes:** Freshly distilled benzoyl chloride (1.4 g, 10 mmol) was dissolved in 10 mL of dry CH_2Cl_2 under an argon atmosphere, and the solution was cooled to −10 °C. Under careful stirring, a solution of 2.99 g of $SbCl_5$ (10 mmol) in 10 mL of dry dichloromethane was added. After 15 min of continued stirring, the white, crystalline precipitate was collected, washed with cold CH_2Cl_2, and dried under vacuum. Single crystals suitable for X-ray analysis were obtained by slow cooling of the dry CH_2Cl_2 solution initially saturated at 40 °C. ***p*-Fluorobenzoyl chloride:antimony pentachloride complexes:** Antimony

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(33) (a) Gwaltney, S. R. Unpublished results. (b) The incursion of such a cationic π-complex (or benzonium ion) was proposed as a precursor step in the general mechanism of electrophilic aromatic substitution by Olah[29] following Mulliken's theoretical classification of intermolecular interactions. (c) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 600. Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811.
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(37) Aitken, R. R.; Badger, G. M.; Cook, J. W. *J. Chem. Soc.* **1950**, 331.

pentachloride (1.2 g, 4 mmol) was dissolved in 15 mL of dry dichloromethane under an argon atmosphere, and the solution was cooled to −40 °C. Into the stirred solution was introduced *p*-fluorobenzoyl chloride (0.58 g, 4 mmol) in 5 mL of dichloromethane. After 15 min of continued stirring, the white crystalline precipitate was collected, washed with cold CH_2Cl_2, and dried in vacuo. **Aromatic acid-halide (benzoyl-, *p*-fluorobenzoyl chloride):titanium(IV) chloride complexes:** Titanium(IV) chloride (1.89 g, 10 mmol) was dissolved in 10 mL of dry CH_2Cl_2 under an argon atmosphere. Under careful stirring, 5 mL of dichloromethane solution containing 1.4 g (1.44 g, 10 mmol) of freshly distilled benzoyl (*p*-fluorobenzoyl) chloride were introduced. After 15 min of continued stirring the solution was covered with a layer of *n*-hexane (15 mL), and after 3−5 days standing at −40 °C colorless crystals suitable for X-ray analyses were collected from the trap wall near the phase borderline. **Hydrocinnamoyl chloride:titanium(IV) chloride complex:** Titanium(IV) chloride (1.89 g, 10 mmol) was dissolved in 10 mL of dry CH_2Cl_2 under an argon atmosphere. Under careful stirring, 5 mL of dichloromethane solution containing 1.68 g (10 mmol) of hydrocinnamoyl chloride was added. Stirring was continued for 15 min. Crystals suitable for X-ray study were obtained by slow evaporation of the dichloromethane solution (12 h) under an argon atmosphere. ***tert*-Butylacetyl chloride:zirconium(IV) chloride complex:** Zirconium(IV) chloride (2.33 g, 10 mmol) was suspended in 5 mL of dry dichloromethane under an argon atmosphere. Under careful stirring, a solution of 1.34 g (10 mmol) of *tert*-butylacetyl chloride in 10 mL of dry dichloromethane was added. A yellow suspension was obtained, which turned to a dark yellow clear solution after 30 min of continued stirring. Single crystals suitable for X-ray analysis were obtained by slow evaporation under an argon atmosphere over a period of 6 h. **Hydrocinnamoyl chloride:zirconium(IV) chloride complex:** Zirconium(IV) chloride (2.33 g, 10 mmol) was suspended in 5 mL of dry dichloromethane under an argon atmosphere. Under careful stirring, a solution of 1.68 g (10 mmol) of hydrocinnamoyl chloride in 10 mL of dry dichloromethane was added. After 30 min of continued stirring a yellow suspension was obtained. The solution was covered with a layer of dry *n*-hexane (15 mL) and allowed to stand at −70 °C. Well-formed crystals of the complex were collected at the solvent interface after 12 days. ***p*-Fluorobenzoyl chloride:trichlorogallate complex:** *p*-Fluorobenzoyl chloride (1.44 g, 10 mmol) was dissolved in 10 mL of dry CH_2Cl_2 under an argon atmosphere. Under careful stirring, 5 mL of dichloromethane solution containing 1.76 g (10 mmol) of $GaCl_3$ was added. Stirring was continued for 15 min. Crystals suitable for X-ray study were obtained by slow evaporation of the dichloromethane solution (2 h) under an argon atmosphere.

Reaction of Acylium Salts with Aromatic Compounds. The reactions were carried out in dry dichloromethane solution in which the aromatic donors and the acylium salts are both soluble at the low temperatures used. The appropriate acylium salt (0.05 mmol) in 1 mL of dry dichloromethane solution was cooled and added with stirring into 0.05 mmol of the aromatic donor. After continuous stirring, the solvent was removed, and 2 mL of benzene was added. The resulting mixture was washed with water, and the organic phase was separated, dried over $MgSO_4$, and analyzed by GC/MS techniques (Tables S2 and S3, Supporting Information).

Electronic (UV−Vis) Spectra of Acylium Adducts to Aromatic Donors. A spectroscopic study were carried out on a HP 8453 diode-array or Cary 5 spectrophotometer in a Dewar equipped with quartz lens, and the temperature was adjusted with an ethanol−liquid nitrogen bath. Measurements were carried out in the quartz (0.1 to 1.0 cm path length) spectroscopic cells fitted with a sidearm and equipped with a Teflon valve with Viton O-rings. The sample of the acylium salt (typically 3−5 mg, as the crystalline salt with hexafluoroantimonate or hexachloroantimonate anion) was placed into a spectroscopic cell and the sample of aromatic donor (e.g., hexamethylbenzene, typically 10 mg) was placed in the sidearm. Dichloromethane (3−4 mL) was added to dissolve the acylium salt within the cell. [All these operations were carried out under argon atmosphere in the glovebox to avoid any contact of acylium salt with air or moisture and carefully dried solvent was used.] The tightly closed cell was transferred from the glovebox and placed in Dewar cooled to −70 °C, and absorption spectrum was measured. After measurement of the spectrum of pure acyl cation, the solution was transferred to the sidearm of a UV−vis cell to dissolve aromatic donor (at low temperature), and then back to the cell, and the spectrum of the solution containing both acylium cation and aromatic donor was measured immediately. Then the solution were warmed and cooled back to −70 to −80 °C, and spectra were measured at room temperature and low-temperature again. The solutions of the pure oxocarbonium cations are colorless and do not show any noticeable absorption bands in the 350−800 nm range of electronic spectra. However, these solutions turned yellow upon addition of the hexamethylbenzene and an absorption band appeared at $\lambda_{max} \approx 400$ nm (see Figure 7).

X-ray Crystallography. The diffraction data for the crystalline compounds were collected at −150 °C on a diffractometer with a CCD detector using Mo *K*α radiation ($\lambda = 0.71073$ Å). In all cases, a semiempirical (SADABS) absorption correction was applied.[38] The structures were solved by direct methods and refined by a full-matrix least-squares procedure with the SHELXTL suite of programs.[39] The structural data on the compounds listed in Table 1 are on deposit (as CCDC 261514-261523) and can be obtained from the Cambridge Crystallographic Data Center, U.K.

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Supporting Information Available: X-ray structural parameters of aliphatic and aromatic acylium salts (Table S1); product analysis from Friedel−Crafts acylation carried out with acylium hexafluoroantimonates (Table S2); product analysis from Friedel−Crafts acylation carried out with acylium hexachloroantimonates (Table S3) and typical examples 1−4. This material is available free of charge via the Internet at http://pubs.acs.org.

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(39) G. M. Sheldrick, *SHELXTL*, v. 6.12, Program Library for Structure Solution and Molecular Graphics; Bruker Analytical X-ray Systems: Madison, WI, 2000.