

Figure 1. Structure of the low-field ESR "line" produced by splitting by H_6 in pentacarboxyhydroxycyclohexadienyl radical: A, 0.1 M KOH; B, 0.1 M KOH + 0.1 M Na_2SO_4 ; C, 0.1 M KOH + 0.5 M Na_2SO_4 . In A additional splitting by the OH proton is observed showing that the rate of exchange with water is slow with respect to the frequency of the hyperfine interaction ($<10^7$ rad s^{-1}). The increased rate of exchange upon addition of sodium sulfate is directly demonstrated by the coalescence of this doublet into a single broad line in B, which is then narrowed in C. Line widths in A, B, and C are, respectively, 0.25, 0.44, and 0.20 G and are considerably greater than the limiting width of 0.11 G observed at both higher and lower base concentrations. The slight upfield shifts in the line centers in B and C correspond to decreases in a_{H_6} by 0.06 and 0.16 G and reflect increases in the equilibrium constant by factors of 3 and 9, respectively.

were produced by electron beam irradiation of N_2O -saturated basic solutions of carboxylated benzenes directly in the ESR cavity.¹¹ The radicals of interest resulted from OH addition. Sodium sulfate was used to increase ionic strength. At high base concentrations the ESR hyperfine constants represent the weighted average of the acidic and basic forms of the radical so that meaningful measurements can be made readily even if the radical represents only a minor component in the system. Hydroxycyclohexadienyl radicals are particularly suitable for probing basicity functions since their pK_a values are in the region above 13, and the proton hyperfine constant at C_6 is sensitive to the relative concentrations of the acidic and basic forms.⁶

The radicals chosen here to illustrate the effect of ionic strength were the OH adducts to 5-nitroisophthalic and benzenepentacarboxylic acids. In the latter case the effects on line shape at pH 13, illustrated in Figure 1, show dramatically that k_f increases with ionic strength. In the absence of sodium sulfate, splitting by the OH proton is still observed, showing that exchange with water is slow. Upon addition of 0.1 M sulfate the lines coalesce into a single broad line (width 0.44 G) which then narrows at higher sulfate concentrations. From the line widths pseudo-first-order rate constants of 0.4, 1.1, and 3.0×10^7 s^{-1} are estimated. Simultaneously there are slight decreases in a_{H_6} (27.94, 27.88, and 27.76 G). Since a_{H_6} drops by ~ 2 G on ionization,⁶ these small differences correspond to increases in K by factors of ~ 3 and 9. Thus k_f appears to be independent of ionic strength and is of the magnitude 3×10^9 s^{-1} . At 1 M KOH a_{H_6} decreases by 0.32 G on addition of 1 M sulfate, corresponding to an increase in K by only an additional factor of 2, about $1/2$ that expected from extrapolation of the above trend. The effect clearly approaches saturation so that an appropriate basicity scale will

largely parallel H_6 at high base concentrations.

Because its pK_a is lower (~ 13.5), the effect of increasing ionic strength on the OH adduct to 5-nitroisophthalic acid is considerably more pronounced. At pH 13 a_{H_6} decreases by 0.33 and 0.71 G upon addition of 0.1 and 0.5 M sulfate. When reflected on the base concentration dependence,⁶ these decreases correspond to increases in K by factors of 1.4 and 1.8, respectively. While the effect of increasing ionic strength is substantial, it is considerably less than the factors of 4 and 80 expected from the low-concentration limiting law and slightly less than the factors of 1.5 and 2.1 suggested by extension of Yagil's arguments to doubly charged ions.

Major questions are apparent about the manner of treating equilibria involving charged ions in strongly basic media. Yagil's H_2 -scale, in referencing measurements to zero ionic strength, is artificial in the sense that this scale does not correctly represent OH^- activity. On the basis of the above observations, we recommend that discussions be in terms of pH (H_6 at high base concentrations) and that appropriate considerations be given to ionic strength effects. The present observations agree with Yagil's treatment in indicating that for ionic strengths (μ) less than 2 the correction term can be approximated as $n_{-}\mu^{1/2}/(1 + A\mu^{1/2})$, with n_{-} the ionic charge in the acidic form and A taken as 2.0. Above 2 M KOH this correction is somewhat less than the difference between Yagil's experimental H_2 - and H_6 -scales. On what basis then does one compare acid-base equilibria measured at different ionic strength and for ions of different charge? If comparison is made after correction to zero ionic strength then the electrostatic energy will be important, but one is not usually interested in this aspect. It would appear better to make comparisons at high ionic strength where the effects of charge are minimized. In practical terms measurements made at base concentrations above 1 M will largely satisfy this criterion. In any event the basis on which the comparison is made should be stated clearly. Much more detail is, of course, needed, and it is clear that ESR measurements of the type reported here can give further insight. We are currently extending these investigations.

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Preparation and Spectral Characterization of Some Cyclic Acyl-1,1-diazenes

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Aminonitrenes or 1,1-diazenes, unlike the corresponding 1,2-diazene derivatives, are typically thermally unstable intermediates often used as in situ precursors of α,ω -biradicals.¹ Only recently Dervan and co-workers have succeeded in the preparation and spectral characterization of a number of persistent 1,1-diazenes,² which while stable enough for characterization in dilute solution rapidly decomposed below 0 °C. In spite of numerous synthetic and mechanistic studies presumably involving 1,1-diazenes as intermediates, very little experimental information is available on the effect of substituents on their thermal stability.^{1,2} We now report the first spectral characterization of a number of sterically

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(8) Kirino, Y. *J. Phys. Chem.* **1975**, *79*, 1296.

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(10) Taniguchi, H.; Kirino, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3625.

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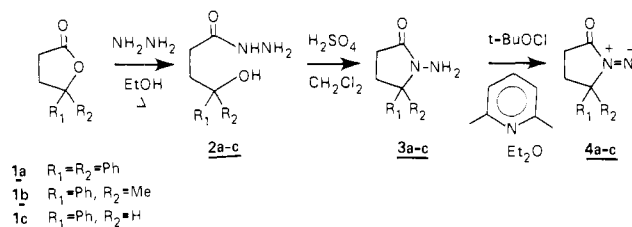
(1) (a) Lemal, D. M. "Nitrenes"; Lwowski, W., Ed.; Interscience: New York, 1970; Chapter 10. (b) Ioffe, B. V.; Kuznetsov, M. H. *Russ. Chem. Rev. (Engl. Transl.)* **1972**, *41*, 131 and references cited within.

(2) (a) Hinsberg, W. D., III; Schultz, P. G.; Dervan, P. B. *J. Am. Chem. Soc.* **1982**, *104*, 766. (b) McIntyre, D. K.; Dervan, P. B. *Ibid.* **1982**, *104*, 6466 and references cited therein.

(3) Satisfactory elemental and/or high-resolution mass spectroscopic analyses have been received for all new compounds.

hindered cyclic acyl-1,1-diazenes and describe their remarkable thermal stability.

The treatment of the substituted γ -butyrolactones **1a-c** with 100% hydrazine hydrate in refluxing ethanol resulted in the expected hydroxy hydrazides **2a-c**. When the hydrazides were dissolved in concentrated sulfuric acid, the solutions became yellow-brown in color and new products were isolated. The spectral data^{3,4} of the isolated products **3a-c** (50–65%), particularly



the presence of a strong carbonyl absorption in the infrared at $\sim 1690\text{ cm}^{-1}$ and the appearance of a broad two-proton resonance δ 3.8–4.8 (NH_2) in the NMR, strongly suggested that cyclization had occurred on the amide nitrogen to produce five-membered amino pyrrolidinones rather than the alternative hexahydropyridazin-3-ones. This structural assignment was confirmed for **3a** by unambiguous synthesis. In this case, the lithium salt of 5,5-diphenylpyrrolidinone⁵ was aminated in THF with (2,4-dinitrophenyl)hydroxylamine⁷ to yield an oily product with the same chromatographic and spectral properties as **3a**. The success of the electrophilic cyclization reaction was restricted to derivatives of **2** where R_1 and/or R_2 were aromatic substituents. When R_1 and R_2 were both alkyl or cycloalkyl, the solutions in sulfuric acid remained colorless and the corresponding lactone was isolated.

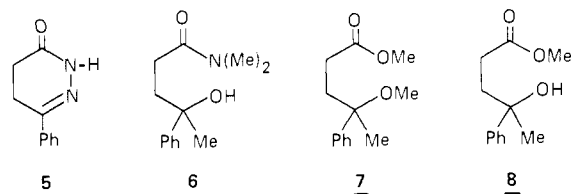
Oxidation of **3a-c** with *tert*-butyl hypochlorite–triethylamine in ether led to the development of a persistent purple color. Solutions resulting from the oxidation of **3a** and **3b** in this fashion remained colored for days at room temperature, while those derived from **3c** decolorized rapidly over a period of hours (*vide infra*). All attempts to purify the solutions by low-temperature chromatography (silica gel or deactivated alumina) resulted in rapid decoloration. More distressing was the variable stability of the colored solutions. This irreproducibility was eliminated by the substitution of the sterically hindered base 2,6-lutidine for triethylamine. The diazenes **4a** and **4b** prepared by this procedure were extremely stable in solution at room temperature, but **4c** still disappeared rapidly. In the latter case, the product was not phenylcyclobutanone as expected but was instead 6-phenyl-2,3,4,5-tetrahydropyridazin-3-one (**5**) (75%), which apparently arises via a 1,1-diazeno-hydrazone type rearrangement of the intermediate **4c**.¹

The spectral properties of **4a** and **4b** are, as expected, quite similar and are described for **4b**. The red-purple color of the diazene **4b** results from a broad featureless maximum of low intensity (ϵ 85–95)⁷ centered at 520 nm. No significant spectral shift is observed in a variety of solvents (ether, toluene, THF, Me_2SO). The infrared spectrum of **4b** shows a high-frequency absorption in the carbonyl region at 1755 cm^{-1} . It is interesting that the position of the carbonyl band shifts from 1705 cm^{-1} in the starting material to 1755 cm^{-1} for the diazene. No other strong absorptions were observed in the region from 1550 to 1800 cm^{-1} . This 50-cm^{-1} spectral shift confirms the strongly

electrophilic nature of the nitrene nitrogen, which apparently results in the withdrawal of electron density from the adjacent amide linkage. The ^1H NMR spectrum of **4b** in $\text{Et}_2\text{O-d}_{10}$ showed a broad 5 H singlet at δ 7.29 (aromatic), a four proton multiplet at 2.21–2.7 (ring methylenes), and a sharp singlet at 1.8 (methyl). The spectrum was quite similar in shape and position to that of **3b** except that all resonances appeared at slightly lower fields.

Preliminary studies on the reactivity of the diazene **4b** were conducted *in situ* by monitoring the disappearance of the visible absorption at 520 nm. In this regard, **4b** was unaffected by the presence of such trapping reagents as cyclohexene, dihydroxyran, or methyl acrylate, and no definitive adduct could be isolated.

In contrast, however, **4b** is quite sensitive to nucleophiles. For example, solutions of **4b** are instantly decolorized by the addition of 1° and 2° amines. In this regard, the addition of dry dimethylamine led to the isolation of the hydroxy amide **6** (50%)^{3,8} together with some of the original lactone **1b** (20%). The addition of methanol to ethereal solutions of **4b** resulted in a slower decoloration, which was greatly accelerated by the presence of excess oxidizing reagent. The ester **7** (50%)³ and the ubiquitous



lactone **1b** were isolated under these conditions. In 5% aqueous methanol, **7** was not observed and an inseparable mixture of the hydroxy ester **8** and the lactone **1b** (50%) as well as a fragmentation product acetophenone (25%) resulted. Although the resulting product mixtures are somewhat complex, it seems obvious from the isolation of acyclic derivatives such as **6–8**, as major products, that the acyldiazeno **4b** is susceptible to facile nucleophilic attack at the carbonyl group. This unusual reactivity is consistent with the increased electron deficiency at the carbonyl group caused by the demands of the electrophilic nitrene.

In spite of their sensitivity toward external nucleophilic reagents, the acylnitrenes were quite stable in dilute solution. For example, samples of **4b** prepared by oxidation in ether remained colored upon standing for over a month at room temperature. Although diethyl ether was the best solvent for the oxidative generation of the diazenes, once formed they could be transferred to higher boiling solvents for kinetic studies.⁹ The diazenes **4a** and **4b**, which possess no α hydrogens, decomposed in a unimolecular fashion ($E_a = 24.5\text{ kcal mol}^{-1}$, $\log A = 14.6$, and $E_a = 29.1\text{ kcal mol}^{-1}$, $\log A = 14.9$, respectively) at elevated temperatures to yield mainly 2,2-diphenyl- and 2-methyl-2-phenylcyclobutanone. Also detected in the respective pyrolysates were small quantities of either benzophenone or acetophenone and the lactones **1a** or **1b**. The mass balance of volatile products in each case was $>90\%$. It is remarkable that in spite of the aromatic substitution at the tertiary site of bond breaking, the activation energy for **4b** is still $>29\text{ kcal mol}^{-1}$. While the substitution of a second phenyl substituent on the same site (**4a**) does result in a significant decrease in the activation energy for decomposition (5.5 kcal mol^{-1}), this highly substituted material is considerably more stable than even the most persistent alkyl-1,1-diazene.² It is obvious that the acyl substituent exerts an unexpected and strong stabilizing influence on the 1,1-diazeno moiety, which suggests that suitably sterically hindered

(4) **3a** oil: ^1H NMR δ (CDCl_3) 2.55 (m, 4 H), 3.8 (br s, 2 H), 7.22 (m, 10 H); IR (CDCl_3) 3320, (NH_2), 1690 cm^{-1} (CO). **3b**: mp $85\text{--}87^\circ\text{C}$; ^1H NMR δ (CDCl_3) 1.65 (s, 3 H), 1.89–2.55 (m, 4 H), 4.7 (br s, 2 H), 7.0–7.43 (m, 5 H); IR (CDCl_3) 3320, 1680 cm^{-1} . **3c**: mp $68\text{--}70^\circ\text{C}$; ^1H NMR δ (CDCl_3) 1.52–2.00 (m, 1 H), 2.12–2.62 (m, 3 H), 3.92 (br s, 2 H), 4.45–4.80 (m, 1 H), 7.0–7.5 (m, 5 H); IR (neat) 3320, 3200, 1685 cm^{-1} .

(5) Miller, R. D.; Göllitz, P. *J. Org. Chem.* **1981**, *46*, 1616. The lithium salt was generated by treatment of the lactam with 1 equiv of butyl lithium in THF at -78°C .

(6) Tamura, Y.; Minamikawa, J.; Sumuoto, K.; Fujii, S.; Ikeda, M. *J. Org. Chem.* **1973**, *38*, 1239.

(7) This calculated extinction coefficient is based on 100% conversion to the diazene and is therefore an approximate value.

(8) The origin of the second oxygen in **6** is mechanistically interesting. One highly speculative suggestion is that it arises by an intramolecular cyclization involving the original carbonyl group and the tertiary site followed by hydrolysis of the resulting iminum lactone upon workup. Mechanistic studies are proceeding.

(9) Samples for kinetic study were prepared by oxidation in ether and filtration followed by stirring for 1 h over powdered sodium thiosulfate in order to destroy any excess oxidizing reagent. The purity of the sample was monitored by IR (1755 cm^{-1}). At this point, the desired quantity of a higher boiling solvent was added and the ether removed on the rotary evaporatory at 25°C .

diacyl derivatives could be even more stable.

Registry No. 1a, 7746-94-3; 1b, 21303-80-0; 1c, 1008-76-0; 2a, 88730-03-4; 2b, 88730-04-5; 2c, 51800-35-2; 3a, 88730-05-6; 3b, 88730-06-7; 3c, 88730-07-8; 4a, 88730-08-9; 4b, 88730-09-0; 5, 1011-46-7; 6, 88730-10-3; 7, 88730-11-4; 8, 88730-12-5.

Protonation of Organometallic Hydrides with Fluorochemical Acids[†]

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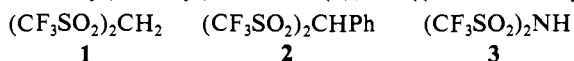
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We wish to report some results of a comprehensive investigation of bis((perfluoroalkyl)sulfonyl)alkanes and -amines and of perfluoroalkanesulfonic acids which presage a substantial scope and diversity for the chemistry of these materials. This is exemplified here by their reactions with organometallic hydrides. Protonation is, in principle, one of the most elementary reactions of such hydrides and is a key step in numerous catalytic and synthetic processes. Idealized protonation proceeds in two steps: proton transfer then, in some cases, reductive elimination of dihydrogen. If, however, a nucleophilic solvent or counterion is present, either of the cationic products, M^+ or MH_2^+ , may be captured and neutralized or coordinated. Described in this work is the protonation of a wide variety of transition-metal hydrides under conditions in which noncoordinated M^+ or MH_2^+ salts may be easily isolated in highly soluble forms.

For this purpose, the novel fluorochemical acids bis((trifluoromethyl)sulfonyl)methane (**1**); bis((trifluoromethyl)-



sulfonyl)phenylmethane (**2**),¹ and bis((trifluoromethyl)sulfonyl)amine (**3**) were employed. These acids possess a combination of properties that make them virtually unique in the context of their organometallic chemistry. All are volatile, crystalline solids; **1** and **2** are not hygroscopic and may be easily handled in air. They are strong nonoxidizing acids ($\text{p}K_a$ of **1** was estimated to be about -1 in water). All are soluble in apolar, nondonor solvents such as dichloromethane or toluene, and, finally, their conjugate bases are essentially noncoordinating. The reactions described below were effected by combining equimolar amounts of **1-3** with a suspension of the metal hydride in dry, deoxygenated toluene. The fluorochemical acid salts formed as products are only sparingly soluble and, after stirring for ca. 8 h, were isolated in analytically pure form.

Cobalt(I) and iridium(I) hydrides are protonated to give cationic dihydrides (eq 1). The stereochemistry of $L_4MH_2^+$ ($M = \text{Co}$, $L_4MH + H_2C(SO_2CF_3)_2 \rightarrow L_4MH_2^+HC(SO_2CF_3)_2^-$
 $L = \text{Ph}_3\text{P}$, diphos/2) (**1**)

Ir) appears to be *cis*, as, for example, in (diphos)₂IrH₂⁺HC(SO₂CF₃)₂⁻ (**4**), ν_{IrH} 2060, 2080 cm^{-1} , $\delta(^1\text{H})$ -11.7 ($J_{\text{PH trans}} = 114$ Hz). Rhodium(I) hydrides are protonated but then undergo

reductive elimination of H₂, consistent with Vaska's observation that Rh(I) undergoes oxidative addition reactions less readily than the Co(I) or Ir(I) analogues.² Protonation of (Ph₃P)₄RhH is distinctive in that 1 equiv of Ph₃P is also lost to provide in high yield salts of the red, 14-electron Rh(I) cation (Ph₃P)₃Rh⁺. In contrast, [(PhO)₃P]₄RhH affords [(PhO)₃P]₄Rh⁺.

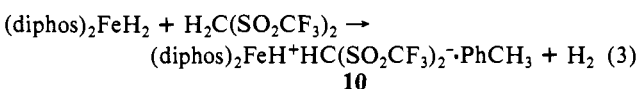
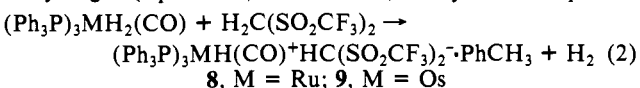
Bau, Reed, et al. first prepared (Ph₃P)₃Rh⁺ClO₄⁻ from (Ph₃P)₃RhCl and thallium(I) perchlorate, but the synthetic route proceeding from the rhodium hydride avoids toxicity and explosion hazards associated with TiClO₄.³ The crystal structure of the ClO₄⁻ salt revealed a slightly distorted T-shaped P₃Rh geometry in the solid. We find that, in CH₂Cl₂ solution, (Ph₃P)₃Rh⁺ is fluxional. At 35 °C, the {¹H}³¹P NMR spectrum of (Ph₃P)₃Rh⁺HC(SO₂CF₃)₂⁻ (**5**) comprises a doublet at δ 38.1 ($J_{\text{PRh}} = 172$ Hz)⁴ while at -50 °C, the A₂B portion of an A₂BX pattern is observed with δ_A 31.5 (dd, $J_{\text{PRh}} = 133$, $J_{\text{PP}} = 32$ Hz) and δ_B 50.1 (dt, $J_{\text{PRh}} 245$, $J_{\text{PP}} = 32$ Hz). This agrees with the results of Albright, Hoffman, and Kochi⁵ which indicate that a C_{3v} P₃Rh configuration should be Jahn-Teller unstable and distort toward a T-shaped geometry. In **5**, ΔH_{act} for the process that permutes the ³¹P environments is ~11.6 kcal/mol at 2 °C.

Fluorochemical acid salts in which the CF₃ groups are replaced by larger fluoroalkyl groups have significantly greater solubility in aromatic hydrocarbons. Thus, H₂C(SO₂C₈F₁₇)₂ and the nonhygroscopic, easily handled sulfonic acids C₈F₁₇SO₃H and C₈F₁₅SO₃H may be used to prepare highly soluble, catalytically active (vide infra) transition-metal salts. Exemplary are (Ph₃P)₃Rh⁺HC(SO₂C₈F₁₇)₂⁻ (**6**) and (Ph₃P)₃Rh⁺C₈F₁₇SO₃⁻ (**7**) whose saturated solutions in toluene are ca. 0.4 M. Evidence for the noncoordinating nature of the anion in **6** was obtained from the ¹³C NMR spectrum in toluene where the methine carbon appears at δ 61.2 ($J_{\text{CH}} = 186$ Hz) with no evidence of ¹³C-¹⁰³Rh coupling.^{6,7}

The congruence of S-O stretching frequencies in **5** (1345, 1100 cm^{-1}) and c-C₈H₁₂N⁺HC(SO₂CF₃)₂⁻ (1330, 1085 cm^{-1}) indicates that rhodium is not coordinated to the SO₂CF₃ oxygen atoms.

These new (Ph₃P)₃Rh⁺ derivatives have an extensive chemistry, which is under study. Although no complex between **5** and 1-pentene is detectable by ³¹P NMR, this olefin is quantitatively isomerized to 2-pentene (*trans:cis* = 9:1). Further, **5** catalyzes the cyclotrimerization of hexafluoro-2-butyne and hydroformylation of 1-hexene. Reaction of solid **5** with ≥ 1 atm of CO provides (Ph₃P)₃Rh(CO)₂⁺HC(SO₂CF₃)₂⁻ (**6**) ν_{CO} 2019, 1988 cm^{-1} . In the solid state, **6** is indefinitely stable but CH₂Cl₂ solutions, when evaporated or purged with nitrogen, form (Ph₃P)₃Rh(CO)⁺HC(SO₂CF₃)₂⁻ (**7**), ν_{CO} 2026 cm^{-1} .

Hydrides of Fe(II), Ru(II), and Os(II) are protonated with loss of hydrogen (eq 2 and 3). In **8** and **9**, the hydride occupies an



axial position and the CO ligand an equatorial site in a trigonal-bipyramidal coordination geometry as the high-field regions of the ¹H NMR spectra comprise doublets of triplets: **8**, δ -7.4

(2) Vaska, L.; Chen, L. S.; Miller, W. V. *J. Am. Chem. Soc.* **1971**, *93*, 6671.

(3) Yared, Y. W.; Miles, S. L.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 7176.

(4) ¹H, ¹³C, and ³¹P chemical shifts are expressed relative to internal (CH₃)₄Si and external 85% H₃PO₄. Negative shifts are to higher field of the reference.

(5) Komiya, S.; Albright, T. A.; Hoffman, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255.

(6) Wilkinson (Wilkinson, G. U.S. Patent 3794671, 1974) reported the synthesis of (Ph₃P)₃RhBF₄. This compound was insoluble in most organic solvents, and the electrical conductivity in nitromethane was too low for a 1:1 electrolyte. It was formulated as a monomer Rh(I) species with the fourth Rh coordination position occupied by fluorine from the BF₄⁻ counterion.

(7) Cf. H₂C(SO₂CF₃)₂, $\delta(^{13}\text{C})$ (benzene-*d*₆) 64.0, $J_{\text{CH}} = 144$ Hz; NH₄⁺-HC(SO₂CF₃)₂⁻, $\delta(^{13}\text{C})$ (D₂O) 52.8, $J_{\text{CH}} = 186$ Hz.

[†] Dedicated to E. L. Muettterties.

(1) Practical syntheses of **1** and **2** were first reported by: Koshar, R. J.; Mitsch, R. A. *J. Org. Chem.* **1973**, *38*, 3358.