

shift of the higher energy FSO_3 infrared peak may indicate weak coordination or a deformation of the FSO_3^- group in the solid state.

In summary, alkylation of basic, coordinatively unsaturated metal centers with alkyl fluorosulfonates or trialkyloxonium salts is a valuable, high-yield synthesis of unusual and useful cationic metal alkyls, as illustrated by the alkylation of specific Pt(0), Ir(I), and Rh(I) complexes.

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(15) Lubrizol Fellow, 1972–1973.

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Generation of Novel Cationic Metal-Alkyl Complexes via Carbocation Reagents

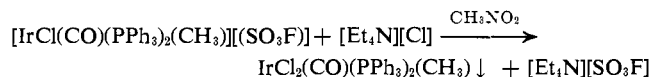
Sir:

While powerful carbocation sources such as $\text{CH}_3\text{SO}_3\text{F}$ are versatile reagents in organic chemistry,¹ their utilization in inorganic chemistry has been limited. Eaborn and coworkers have observed that $\text{CH}_3\text{SO}_3\text{F}$ reactions with metal complexes lead to alkylation of coordinated cyanide, SO_3F^- - Cl^- metathesis, and oxidation.² More unusual, however, is the possibility of generating new cationic metal-alkyl complexes such as those reported here.

An excess of $\text{CH}_3\text{SO}_3\text{F}$ (25.0 mmol) is stirred with 6.18×10^{-1} mmol of Vaska's compound, $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, in dry air-free benzene (60 ml) at room temperature until the color is completely dissipated (1–2 hr). A white solid, $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{SO}_3\text{F})$,³ is then isolated from benzene–heptane. In DCCl_3 solution the ^1H nmr exhibits a triplet for the methyl group (τ 8.93, $J_{\text{P-H}} = 7$ Hz, area 3) and an unresolved phenyl proton resonance (τ 2.68, area 33). The high ν_{CO} (2064 cm^{-1} , Nujol mull) indicates a simple oxidative addition product;⁴ indeed Eaborn and coworkers list it as such.² However, as shown below, the compound is ionic and is therefore quite unlike the usual oxidative addition products of Vaska's compound, such as $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)\text{I}$, which typically are six-coordinate, substitution-inert, molecular species. The molecular weight in HCCl_3 , 884, agrees with a molecular or an ion pair formulation (calcd 894). In a more polar solvent, nitromethane, its conductance, $71\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$, is characteristic of a 1:1 electrolyte. The observed ν_{CO} , 2062 cm^{-1} , confirms that the compound still contains a formal Ir(III) oxidation state in this solvent. High conductivity and high ν_{CO} , 2062 cm^{-1} , also are observed for a solution in acetonitrile. The unsolvated $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)-$

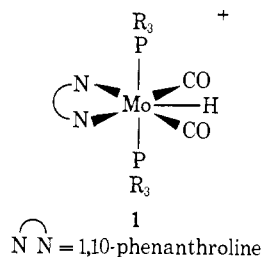
(SO_3F) can be recovered from this solvent, indicating that, if the solvent is coordinated to Ir(III) in solution, it is only weakly held.

Unusual lability of the methyl fluorosulfate product is demonstrated by the following reaction which occurs rapidly at room temperature.



The product $\text{IrCl}_2(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)$ cannot be obtained from direct reaction of CH_3Cl with Vaska's compound and therefore its preparation suggests great synthetic utility for the cationic fluorosulfate complex.

Another interesting metal alkylation reaction occurs when 8.65×10^{-1} mmol of $\text{Mo}(\text{phen})(\text{PPh}_3)_2(\text{CO})_2$ in 60 ml of dry, air-free CH_3CN is exposed to $\text{CH}_3\text{SO}_3\text{F}$ (7.15 mmol) with the formation of an orange solution.⁶ The observation of a single set of isosbestic points suggests a 1:1 stoichiometry of interaction. The product exhibits two strong CO stretching frequencies at 1920 and 1825 cm^{-1} (ν_{CO} for the blue-green parent are 1835 and 1760 cm^{-1}). This large increase in both CO stretching frequencies suggests either methylation or oxidation of the metal; however, the latter possibility is ruled out by the observation of sharp and essentially unshifted proton resonances for the 1,10-phenanthroline ligand in the analogous compound $\text{Mo}(\text{phen})(\text{PBU}_3)_2(\text{CO})_2 \cdot \text{CH}_3\text{SO}_3\text{F}$. The isolation of pure samples of these compounds has not yet been achieved; however, a related protonated compound, $[\text{Mo}(\text{phen})(\text{PPh}_3)_2(\text{CO})_2\text{H}][\text{CF}_3\text{COO}]$, which is isolable,⁷ has similar electronic and infrared spectra (ν_{CO} 1917 and 1820 cm^{-1}). Conductivity of $[\text{Mo}(\text{phen})(\text{PPh}_3)_2(\text{CO})_2\text{H}][\text{CF}_3\text{COO}]$ in nitromethane, $43\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$, indicates an electrolyte, and a high field triplet (τ 14.59, $J_{\text{H-P}} = 36$ Hz) in the proton nmr of the more soluble $[\text{Mo}(\text{phen})(\text{PBU}_3)_2(\text{CO})_2\text{H}][\text{CF}_3\text{COO}]$ is diagnostic of a Mo–H bond. Providing the configuration is static on the nmr time scale, the infrared and nmr data indicate structure **1**, and a similar structure presumably applies for the methyl analogs. Interestingly H^+ and CH_3^+ attack the metal in this complex while the aluminum alkyls, which are weaker and bulkier Lewis acids, attach to the carbonyl oxygens.⁸



A third example of the unique species which can be generated using $\text{CH}_3\text{SO}_3\text{F}$ is the unstable product obtained with $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$ in benzene at 35° . The nmr displays the $(\pi\text{-C}_5\text{H}_5)$ protons as a singlet at τ

(1) M. G. Ahmed, R. W. Adler, G. H. James, M. L. Sinnott, and M. C. Whiting, *Chem. Commun.*, 1533 (1968).

(2) C. Eaborn, N. Farrell, J. L. Murphy, and A. Pidcock, *J. Organometal. Chem.*, **55**, C68 (1973); see also D. Strobe and D. F. Shriver, Abstracts of Papers, Sixth International Conference on Organometallic Chemistry, Amherst, Mass., 1973, abstract 147.

(3) *Anal.* Calcd for $\text{IrC}_3\text{H}_3\text{ClF}_3\text{O}_4\text{S}$: C, 51.05; H, 3.69; Cl, 3.97; F, 2.12. Found: C, 51.24; H, 3.95; Cl, 4.03; F, 2.37. A similar product is obtained using $\text{CH}_3\text{SO}_3\text{CF}_3$ in place of $\text{CH}_3\text{SO}_3\text{F}$.

(4) L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968).

(5) Identified by C and H analysis, ν_{CO} (2044 cm^{-1} , CH_2Cl_2 solution), lack of SO_3F^- ir bands, and proton nmr. Judging from infrared spectra, SCN^- and OCN^- complexes can be prepared in an analogous manner.

(6) Another strong carbocation reagent, $\text{CH}_3\text{SO}_3\text{CF}_3$, produces analogous products; however, CH_3I does not.

(7) A quantitative back reaction with $\text{N}(\text{CH}_3)_3$ demonstrates the 1:1 interaction of molybdenum complex with HOCCF_3 .

(8) D. F. Shriver and A. Alich, *Inorg. Chem.*, **11**, 2984 (1972).

5.41 with area 10.7, the MoH₂ protons at τ 18.58 with area 2.0, and CH₃ around τ 9.38 (broad) with area 3.2, indicating the product should be formulated as $[(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2\text{CH}_3][\text{SO}_3\text{F}]$ which is analogous to known protonated species⁹ but is unusual in containing CH₃ and H on the same metal center. By contrast, the products so far identified in the reaction of the parent hydride with alkyl halides are of the type $(\pi\text{-C}_5\text{H}_5)_2\text{MoX}_2^+$ (X = halide).¹⁰

In summary, CH₃SO₃F and similar strong carbocation sources provide a route to unusual and useful cationic metal alkyl compounds. The unique character of the products stems in part from the very low tendency of SO₃F⁻ and similar anions to coordinate to metals. A close parallel is noted between the methylation and protonation of metal atoms in mononuclear low oxidation state complexes; however, we have as yet been unsuccessful in extending this analogy by the methylation of metal-metal bonds of polynuclear metal carbonyls which are known to protonate.

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(9) M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc., London*, 4854 (1961).

(10) R. L. Cooper and M. L. H. Green, *J. Chem. Soc. A*, 1155 (1967).

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Rates of Intramolecular Electron Transfer

Sir:

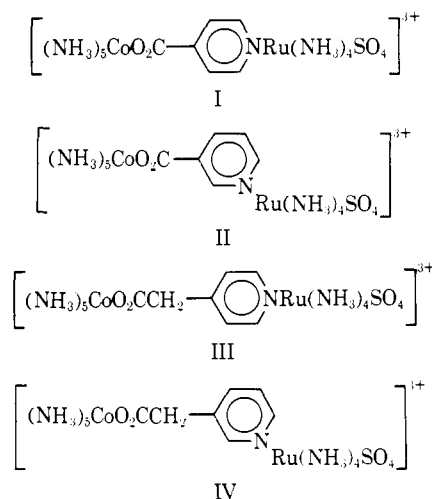
The great majority of rates which have been measured for oxidation-reduction reactions involving electron transfer refer to inter- rather than intramolecular transfer. It is of special interest to measure intramolecular transfer rates because then the factors involved in assembling the reaction partners do not complicate the rate comparisons. Such first-order intramolecular transfer rates have been recorded for only a few systems: for outer-sphere electron transfer, in the reaction of Fe(CN)₆⁴⁻ with Co(NH₃)₅H₂O³⁺,¹ for inner-sphere electron transfer in the reaction of Fe²⁺ with nitriloacetatopentaamminecobalt(III),² and of Cu⁺ with Ru(III) complexes which have as ligands carboxylates containing unsaturated carbon-carbon bonds.³ In each of these cases, success depended on the high affinity of the reducing agent in associating with the oxidizing agent. But, in all of them, despite the rather high affinities for association, the combinations are labile and thus much ambiguity remains in respect to the structures of the activated complexes.

This ambiguity is much reduced for the systems to be described, where both the reducing and oxidizing metal ions, Ru(II) and Co(III), respectively, make substitution-inert bonds to the bridging group. The most direct approach in preparing "precursor complexes" of this class at significant concentrations by letting, say, [Co-

(NH₃)₅O₂C-4-Py]²⁺ react with Ru(NH₃)₅OH₂²⁺ fails because outer-sphere reduction of Co(III) is rapid compared to the rate at which the Ru(II)-N bond is formed.⁴ A variety of attempts to prepare the Co^{III}-ligand-Ru^{III} complex, relying then on the ready reducibility of Ru(III) compared to Co(III) to generate the desired Co^{III}-ligand-Ru^{II} combination, have also failed. A procedure which promises to be successful for a very wide range of precursor complexes of this series is herewith described for a particular one of the four complexes so far prepared.

Equimolar quantities of [Co(NH₃)₅O₂C-4-PyH](ClO₄)₃⁵ and *trans*-[Ru(NH₃)₄SO₂Cl]Cl⁷ were dissolved separately in water and titrated with NaHCO₃ (1 equiv per mol for the former and two for the latter, the lability of the group *trans* to S(IV) is greatest when the latter has the form SO₃²⁻). The two solutions were mixed and allowed to react for 2-5 min at room temperature. The resulting solution was filtered and added to an equal volume of concentrated HBF₄. After cooling at -5° an orange solid precipitated which was filtered and washed with ethanol and ether. The solid at this stage has the constitution [Co(NH₃)₅O₂C-4-PyRu(NH₃)₄SO₂](BF₄)₄ as shown by its elemental analysis. The sulfur dioxide ligated to Ru(II)⁸ renders it so weakly reducing that electron transfer within the Co^{III}-Ru^{II} complex is very slow. The coordinated SO₂ was converted to coordinated SO₄²⁻ by dissolving the solid in the minimum amount of 1 M HCl and oxidizing with hydrogen peroxide. Immediately thereafter 5-10 volumes of acetone was added with stirring. The precipitate which formed on cooling was filtered and washed with ethanol and ether. The solid was purified by dissolving in water and reprecipitating from 1 M HCl with 2 volumes of acetone. The overall yield was ca. 60%.

Following this procedure chloride salts containing the ions I to IV were prepared. Microanalyses for the



salts, taken to be dihydrates, are reported in Table I.

(4) H. Taube, *Ber. Bunsenges. Phys. Chem.*, **76**, 964 (1972).

(5) This compound was prepared using a modification of the method of Gould and Taube⁶ and supplied to us by E. K. Roberts. Other cobalt compounds were prepared by further modification of this method.

(6) E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964).

(7) (a) Gleu, K. W. Breuel, and K. Rehm, *Z. Anorg. Allg. Chem.*, **235**, 201, 211 (1938); (b) L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965).

(8) Details on the synthesis and substitution properties of Ru^{II}-SO₂ complexes will appear in a later publication.

(1) D. Gaswick and A. Haim, *J. Amer. Chem. Soc.*, **93**, 7347 (1971).

(2) R. D. Cannon and J. Gardiner, *ibid.*, **92**, 3800 (1970).

(3) J. K. Hurst and R. H. Lane, *ibid.*, **95**, 1703 (1973).