in the planar (I) and perpendicular (II) allyl cations on the other hand are altered to a much smaller extent.

(2) For methyl and fluoro substituents, the energy of the cyclopropyl cation is lowered beneath that of the perpendicular allyl cation and we predict that in these cases stereomutation of the allyl cation should proceed *via* ring closure and opening (*i.e.*, path B).

(3) The stabilization of the cyclopropyl cation by hydroxy and amino substituents is so great that these species are not only more stable than the substituted perpendicular allyl cations (II) but should be significantly more stable than the corresponding planar allyl cations (I). This conclusion is consistent with experimental observations that cyclopropane substitutions which may involve 1-RO- and 1-R_2N-cyclopropyl cation intermediates proceed without ring opening,[7] and with the direct observation of the 1-dimethylaminocyclopropyl cation.[8]

Finally, our results will hopefully provide added interest to the experimental attempts to observe closure of a substituted allyl cation to a cyclopropyl cation.[9]

Acknowledgments. It is a pleasure to acknowledge useful discussions with Professor Th. H. de Boer. This work was supported at Carnegie-Mellon University by National Science Foundation Grant No. GP-25617 and at Princeton by National Science Foundation Grant No. GP-29078X, by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Hoffmann-La Roche, Inc., Nutley, N. J. We thank the Australian National University Computer Centre for a generous allocation of computer time.

(7) W. J. M. van Tilborg, S. E. Schaafsma, H. Steinberg, and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **86**, 417 (1967); J. Szmuskovica, D. J. Duchamp, E. Cerda, and C. G. Chidester, *Tetrahedron Lett.*, 1309 (1969); H. H. Wasserman and M. S. Baird, *ibid.*, 1729 (1970); 3721 (1971); W. J. M. van Tilborg, G. Dooyewaard, H. Steinberg, and Th. J. de Boer, *ibid.*, 1677 (1972). A case which may involve a 1-fluorocyclopropyl cation is also known: P. Weyerstahl, G. Blume, and C. Miller, *ibid.*, 3869 (1971).

(8) E. Jongejan, W. J. M. van Tilborg, Ch. H. V. Dussen, H. Steinberg, and Th. J. de Boer, *ibid.*, 2359 (1972).

(9) For the first apparent examples of such closures, see D. Cantacuzène and M. Tordeux, *ibid.*, 4807 (1971); J. C. Blazejewski, D. Cantacuzène, and C. Wakselman, *Tetrahedron*, submitted for publication; private communication from Dr. Cantacuzène.

(10) Queen Elizabeth II Fellow.

Leo Radom[10]
Research School of Chemistry, Australian National University
Canberra A.C.T. 2600, Australia

John A. Pople
Department of Chemistry, Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

Paul v. R. Schleyer*
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Received September 1, 1973

Facile Methylation of Metal Complexes to Give Unusual Metal–Alkyl Cations

Sir:

In recent years several methods have been developed to produce σ-carbon bonds to transition metals. The two most common methods involve either (1) metathesis of a metal–halide by alkyllithium or Grignard reagents or (2) oxidative addition of alkyl or acyl halides to transition metal complexes.[1,2] The former reagents function as nucleophiles and maintain the oxidation state and coordination number of the metal. The latter reagents are cleaved at the carbon–halogen bond by the transition metal *via* an SN2 mechanism,[3] and both organic halide fragments are found to be coordinated in the resultant complex, *i.e.*, an increase of two in the oxidation state of the metal is accompanied by an increase of two in the coordination number.

A reaction between a basic transition metal center and a strong alkylating agent containing a weakly coordinating anion should produce metal–carbon bonds *via* a *single-site* oxidative addition in which only the alkyl group is added to the metal. We report here examples of such reactions whereby unusual cationic metal–alkyl complexes may be prepared by the facile alkylation of *low-valent*, *coordinatively unsaturated* metal complexes by methyl fluorosulfonate, as well as trimethyloxonium hexafluorophosphate. We have also observed that other types of complexes react with CH_3FSO_3 to give a variety of reactions, such as oxidation of the metal, halogen abstraction, and alkylation of a coordinated phenyldiazo group,[4] all of which are similar to the recently reported results of Eaborn, *et al.*[5]

In a typical reaction 0.60 g of Rh(ttp)Cl, ttp = bis(3-diphenylphosphinopropyl)phenylphosphine,[6] in 50 ml of refluxing benzene was treated with 0.5 ml of CH_3FSO_3 under nitrogen. A yellow solid began precipitating immediately, and after 30 min of refluxing the resultant solid was collected on a filter, washed with ether, and dried, yield 0.66 g (95%). The molar conductivity of the compound is $74\ \text{cm}^2\ \text{ohm}^{-1}\ \text{mol}^{-1}$ in nitromethane, which confirms the ionic formulation $[Rh(ttp)Cl(CH_3)]FSO_3$.

Anal. Calcd for $C_{37}H_{40}ClFO_3P_3RhS$: C, 54.54; H, 4.91; Cl, 4.36. Found: C, 54.63; H, 4.91; Cl, 4.16.

To confirm that the methyl group had added to rhodium, a careful comparison of the infrared and nmr spectra of $[Rh(ttp)Cl(CH_3)]FSO_3$ (I) and the corresponding deuterated complex $[Rh(ttp)Cl(CD_3)]FSO_3$ (II) was undertaken. The infrared spectra (KBr disks) of I and II were virtually identical except for weak absorbances at 2130 and 2258 cm^{-1} in II which are assigned as the symmetric and asymmetric C–D stretching frequencies, respectively, and the absorbances at 1210 cm^{-1} in I and 915 cm^{-1} in II which are assigned as a deformation of the CH_3 and CD_3 groups, respectively.[7]

The proton nmr spectra of I and II in the τ 7–8 region are shown in Figure 1.[8] The Rh–CH_3 resonance is somewhat obscured by the resonances due to the

---

(1) G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, **7**, 157 (1968), and references therein.

(2) J. Halpern, *Accounts Chem. Res.*, **3**, 386 (1970), and references therein.

(3) P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966).

(4) The authors gratefully acknowledge the experimental results of K. D. Tau, J. A. Tiethof, J. Riker, and W. H. Myers concerning these other types of reactions that occur with CH_3SO_3F.

(5) C. Eaborn, N. Farrell, J. L. Murray, and A. Pidcock, *J. Organometal. Chem.*, **55**, C68 (1973).

(6) (a) T. E. Nappier, Jr., and D. W. Meek, *J. Amer. Chem. Soc.*, **94**, 306 (1972); (b) T. E. Nappier, D. W. Meek, R. M. Kirchner, and J. A. Ibers, *ibid.*, **95**, 4194 (1973).

(7) (a) D. E. Clegg and J. R. Hull, *Spectrochim. Acta, Part A*, **23**, 263 (1967); (b) C. A. Reed and W. R. Roper, *J. Chem. Soc. A*, 3054 (1970).

(8) The nmr spectrum over the range τ 1.5-10.5 is consistent with the spectrum of ttp, showing *only* peaks for the phenyl protons at $\tau \sim 2.6$, in addition to the peaks shown in Figure 1.

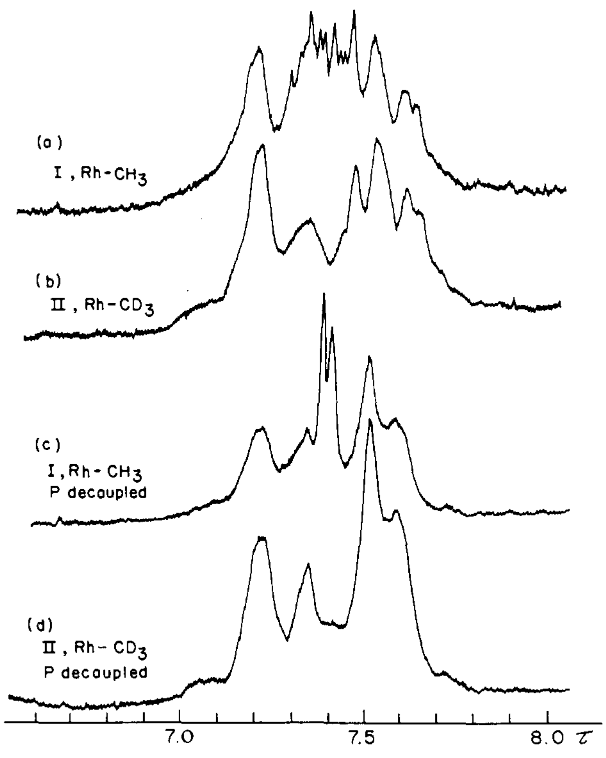
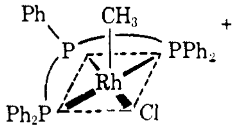


Figure 1. A portion of the proton nmr spectra of (a) [Rh(ttp)Cl(CH_3)]FSO_3, (b) [Rh(ttp)Cl(CD_3)]FSO_3, (c) [Rh(ttp)Cl(CH_3)]FSO_3 with phosphorus decoupling, and (d) [Rh(ttp)Cl(CD_3)]FSO_3 with phosphorus decoupling. All these spectra were obtained in CD_3NO_2 solutions.

methylene groups of the triphosphine ligand; however, note that the multiplet centered at τ 7.37 in the nmr spectrum of I is absent in the spectrum of II. Assignment of the peak at τ 7.37 to the Rh–CH_3 group was confirmed by the observation that this multiplet collapses to a doublet on irradiation of the phosphorus nuclei (c in Figure 1); thus, assignment of the rhodium–hydrogen coupling constant of 2.5 Hz is unambiguous. The methyl protons are coupled to the unique phosphorus by 3.8 Hz and to the two equivalent phosphorus atoms by 5.5 Hz. The coupling constants are based on the appearance of ten lines of the 12-line pattern expected for the A_3 part of an A_3MX_2Y spectrum assuming first-order interactions.[9] These assignments are also consistent with the reported nmr spectrum of Rh(PPh_3)$_2$(CH_3)ClI·MeI in which $^2J_{Rh-H}$ and $^3J_{P-H}$ were 2.4 and 5.1 Hz, respectively.[10] The nmr spectrum is consistent with a structure which has the methyl group at the apical position of a square pyramid, *i.e.*, **1**, and this structure is supported by the X-ray structural determinations of the nitrosyl[6b] and phenyldiazo[11] adducts of Rh(ttp)Cl.

The Rh–CH_3 resonance occurs at τ 8.75 in acetonitrile, and the large up-field shift suggests that acetonitrile probably coordinates in the position trans to the methyl group. As observed in Figure 1c and discussed above, the pattern of ten peaks again collapses to a doublet by decoupling the phosphorus nuclei. The J_{Rh-H} value in the acetonitrile complex is 2.1 Hz. It is perhaps surprising that acetonitrile appears to interact more strongly than DMSO, in which the Rh–CH_3 resonance occurs at τ 7.61; however, this can be rationalized in terms of a larger steric requirement for DMSO than for the linear acetonitrile molecule. It has been shown that the sixth coordination site in [Rh(ttp)Cl(NO)]PF_6 is sterically very crowded by the phenyl groups on the ligand ttp.[6b]



1

The complex Rh(ttp)Cl also reacts similarly with trimethyloxonium hexafluorophosphate and the resultant complex had a proton nmr spectrum identical to I.

The above five-coordinate rhodium(III) methyl cations are prepared easily by mixing a basic, coordinatively unsaturated transition metal complex with methyl carbenium reagents. To check the generality of this reaction, Pt(PPh_3)$_3$ and *trans*-Ir(PPh_3)$_2$(CO)Cl were readily alkylated and gave [Pt(PPh_3)$_3CH_3$]$^+$ and [Ir(PPh_3)$_2$(CO)Cl(CH_3)]$^+$, respectively.[4]

The tremendous advantage of this alkylating method is illustrated in the synthesis of the Pt(II) cation [Pt(PPh_3)$_3CH_3$]$^+$, which was obtained in one step in nearly quantitative yield, as compared to the three steps normally used for synthesis of [PtL_3(CH_3)]$^+$ cations.[12] The compound [Pt(PPh_3)$_3CH_3$]FSO_3 was obtained by treating a benzene solution of Pt(PPh_3)$_3$ with a 20% excess of CH_3SO_3F under a nitrogen atmosphere. A white precipitate, which began separating within 1 min, was collected and recrystallized from an acetone–benzene mixture. Infrared absorptions characteristic of an ionic FSO_3^- group[13] at 1285 (vs, b) and 575 (m, s) cm^{-1} and the conductance in nitromethane (73 ohm^{-1} cm^2 mol^{-1}) support the ionic formulation [Pt(PPh_3)$_3CH_3$]FSO_3. The proton nmr spectrum of the complex in acetone in the methyl resonance region was a doublet of triplets (with ^{195}Pt satellites) which collapses to a singlet with broad-band decoupling of the phosphorus nuclei. The nmr parameters of the complex are $\tau_{CH_3} = 9.66$, $J_{P_{trans}-CH_3} = 6.1$ Hz, $J_{P_{cis}-CH_3} = 8.0$ Hz, and $J_{Pt-CH_3} = 57$ Hz.[14]

The iridium(I) complex *trans*-Ir(PPh_3)$_2$(CO)Cl (0.40 g) in benzene was mixed with 0.4 ml of CH_3SO_3F and heated to 40°. The solution, which turns colorless in a few minutes, was concentrated on a rotary evaporator, and hexane was added to precipitate a white solid, yield 0.44 g. The conductance of the compound in CH_3NO_2 is 66 ohm^{-1} cm^2 mol^{-1} and the proton nmr is a triplet at τ 9.20 with $J_{P-H} = 4.4$ Hz (CH_2Cl_2 solution) which collapses to a singlet when the phosphorus nuclei are decoupled. The infrared spectrum (Nujol) shows a strong ν_{CO} at 2065 cm^{-1} and FSO_3^- absorptions at 1230 cm^{-1} (vs) and 570 (m). The -55 cm^{-1}

---

(9) J. A. Pople, W. G. Schneider, and H. J. Berstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, Chapter 6.

(10) D. N. Lawson, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1733 (1966).

(11) A. P. Gaughan, Jr., B. L. Haymore, J. A. Ibers, W. H. Myers, T. E. Nappier, Jr., and D. W. Meek, *J. Amer. Chem. Soc.*, **95**, 6895 (1973).

(12) H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, **9**, 1226 (1970).

(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 112.

(14) Note the similarity of the nmr data with those obtained in ref 13 for [Pt(Me_2PhP)$_3CH_3$]PF_6 which had $\tau_{CH_3} = 9.47$, $J_{P_{trans}-CH_3} = 6.5$ Hz, $J_{P_{cis}-CH_3} = 7.8$ Hz, and $J_{Pt-CH_3} = 57$ Hz.

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.

Acknowledgments. This research was supported by the National Science Foundation. We thank J. A. Tiethof for helpful discussions.

(15) Lubrizol Fellow, 1972-1973.

J. Lowell Peterson,[15] **Thomas E. Nappier, Jr., Devon W. Meek***
Chemistry Department, The Ohio State University
Columbus, Ohio 43210
Received August 28, 1973

Generation of Novel Cationic Metal–Alkyl Complexes *via* Carbocation Reagents

Sir:

While powerful carbocation sources such as CH_3SO_3F are versatile reagents in organic chemistry,[1] their utilization in inorganic chemistry has been limited. Eaborn and coworkers have observed that CH_3SO_3F 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.

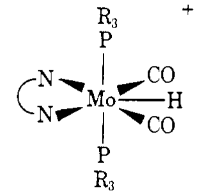
An excess of CH_3SO_3F (25.0 mmol) is stirred with 6.18×10^{-1} mmol of Vaska's compound, $IrCl(CO)(PPh_3)_2$, in dry air-free benzene (60 ml) at room temperature until the color is completely dissipated (1–2 hr). A white solid, $IrCl(CO)(PPh_3)_2(CH_3)(SO_3F)$,[3] is then isolated from benzene–heptane. In $DCCl_3$ solution the ^1H nmr exhibits a triplet for the methyl group (τ 8.93, $J_{P-H} = 7$ 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 $IrCl(CO)(PPh_3)_2(CH_3)I$, 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 ohm^{-1} cm^2 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 $IrCl(CO)(PPh_3)_2(CH_3)(SO_3F)$ 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.

$$[IrCl(CO)(PPh_3)_2(CH_3)][(SO_3F)] + [Et_4N][Cl] \xrightarrow{CH_3NO_2} IrCl_2(CO)(PPh_3)_2(CH_3)\downarrow + [Et_4N][SO_3F]$$

The product $IrCl_2(CO)(PPh_3)_2(CH_3)$[5] 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 $Mo(phen)(PPh_3)_2(CO)_2$ in 60 ml of dry, air-free CH_3CN is exposed to CH_3SO_3F (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 $Mo(phen)(PBu_3)_2(CO)_2 \cdot CH_3SO_3F$. The isolation of pure samples of these compounds has not yet been achieved; however, a related protonated compound, $[Mo(phen)(PPh_3)_2(CO)_2H][CF_3COO]$, which is isolable,[7] has similar electronic and infrared spectra (ν_{CO} 1917 and 1820 cm^{-1}). Conductivity of $[Mo(phen)(PPh_3)_2(CO)_2H][CF_3COO]$ in nitromethane, 43 ohm^{-1} cm^2 mol^{-1}, indicates an electrolyte, and a high field triplet (τ 14.59, $J_{H-P} = 36$ Hz) in the proton nmr of the more soluble $[Mo(phen)(PBu_3)_2(CO)_2H][CF_3COO]$ 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]



1

N N = 1,10-phenanthroline

A third example of the unique species which can be generated using CH_3SO_3F is the unstable product obtained with $(\pi\text{-}C_5H_5)_2MoH_2$ in benzene at 35°. The nmr displays the $(\pi\text{-}C_5H_5)$ protons as a singlet at τ

---

(1) M. G. Ahmed, R. W. Adler, G. H. James, M. L. Sinnot, 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. Strope and D. F. Shriver, Abstracts of Papers, Sixth International Conference on Organometallic Chemistry, Amherst, Mass., 1973, abstract 147.

(3) *Anal.* Calcd for $IrC_{38}H_{33}ClFO_4S$: 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 $CH_3SO_3CF_3$ in place of CH_3SO_3F.

(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, $CH_3SO_3CF_3$, produces analogous products; however, CH_3I does not.

(7) A quantitative back reaction with $N(CH_3)_3$ demonstrates the 1:1 interaction of molybdenum complex with $HOOCCF_3$.

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