Table I. Kinetic Data for Reaction of $C_6H_5C(R){=}CF_2$ with Sodium Ethoxide in Ethanol

Compd	R	$[NaOC_2H_5]$, M	Temp, °C	$k_1 \times 10^3$, sec^{-1}
I	F	0.66	30.0	1.6
II	CF_3	0.34	−77	1.9
III	CF_2Cl	0.30	−77	1.8
XI	CF_2CF_3	0.34	−77	0.67
XII	CF_2Cl (*m*-Cl)	0.34	−77	25

volved in the rate-determining step of the reaction. A two-step mechanism involving a carbanion intermediate would be consistent with these results.

Results of the kinetic runs are summarized in Table I. Since base is not consumed in a 1:1 stoichiometry, rate studies were carried out under pseudo-first-order conditions by starting with at least a tenfold excess of ethoxide. In the low-temperature runs each kinetic point consisted of a separate experiment made by breaking a fragile bulb containing a solution of olefin in ethanol into a temperature-equilibrated solution of ethoxide ion. The reaction was stopped by injecting a slight excess of a dilute precooled solution of sulfuric acid in ethanol. The disappearance of starting olefin was followed using anisole as an unreactive tracer for glpc analysis. Eight points, spanning three half-lives, and an infinity point constituted a run. During the glpc analysis of each point the products were checked. There was no change in the product ratios during the course of each run. Two additional olefins, 2-phenylperfluorobutene-1 (XI) and 3-chloro-2-(*m*-chlorophenyl)perfluoropropene (XII), were also included in the kinetic studies. Four minor products from the reaction of ethoxide with XI have not yet been assigned structures;[8] however, the major product (60%) was $CF_3CF{=}C(C_6H_5)CF_2OC_2H_5$, with the CF_3 and phenyl groups *cis* to each other. This product arose from the displacement of an allylic fluoride. The similarity of the rates of reaction for II, III, and XI strongly suggests that the rate-determining step in all three cases is the initial attack of ethoxide on $CF_2{=}$ to form an intermediate carbanion which then reacts to form the various observed products. Using the rate obtained for XII, an approximate Hammett $\rho = 3$ was calculated. This value is in agreement with reactions proceeding through carbanion intermediates.[9]

Some generalizations about subsequent reactions can be made by using the model of a discrete carbanion intermediate. Clearly, the loss of a β chloride is the fastest process;[10] however, loss of fluoride is competitive with the rate of protonating the carbanion intermediate. Ritchie has reported that rates of reaction of methanol with carbanions become diffusion controlled only when the ΔpK is greater than 18.[11] We estimate the pK_a's $C_6H_5CHFCF_3 \cong 30$ and $C_6H_5CH(CF_3)_2 \cong 25$. The ΔpK values with respect to methanol would be about 15 and 10, which fall within the limit of 18.[12] The different ratios of adduct to displacement products for I and II can be attributed to the differences in the rates of protonation of the two carbanions which in turn are attributed to the different ΔpK values. An alternate explanation involves the possible difference in geometry of the two carbanions. The carbanion arising from I could be in a pyrimidal configuration due to the α fluorine while that generated from II could be planar to allow conjugation with the phenyl ring. This type of argument has been used by Streitwieser to explain the relatively slow deuterium and tritium exchange reaction for benzal fluoride relative to toluene.[13] We are continuing to carry out experiments which will attempt to find out which of the above reasons best fits these systems.

Acknowledgment. The authors wish to express gratitude to Mrs. J. G. Koch for doing the nmr analysis of our compounds. This work was supported by a grant (2904-B) from the Petroleum Research Fund, administered by the American Chemical Society, and partially by the Research Corporation.

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(8) From their proximity in glpc analysis, it is assumed that one represents the addition product, two are the corresponding vinyl ethers, and the fourth is the other allylic ether.

(9) A. Streitwieser, Jr., and H. F. Koch, *J. Amer. Chem. Soc.*, **86**, 404 (1964).

(10) This is consistent with acyclic olefins having terminal $=CFCl$ groups as well as allylic chloride and is also true in the cyclic systems (see ref 4).

(11) C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **90**, 3415 (1968).

(12) We are indebted to Professor Streitwieser for sending us a copy of David Holtz's Thesis (University of California, Berkeley, Calif., 1968) which allowed us to estimate the pK_a values.

(13) A. Streitwieser, Jr., and F. Mares, *J. Amer. Chem. Soc.*, **90**, 2445 (1968).

(14) (a) Based in part on a Senior Honors Thesis by A. J. Kielbania, Jr., Ithaca College, Ithaca, N. Y., 1969; (b) supported by an NSF-URP, GY 4287 grant during the summer of 1968.

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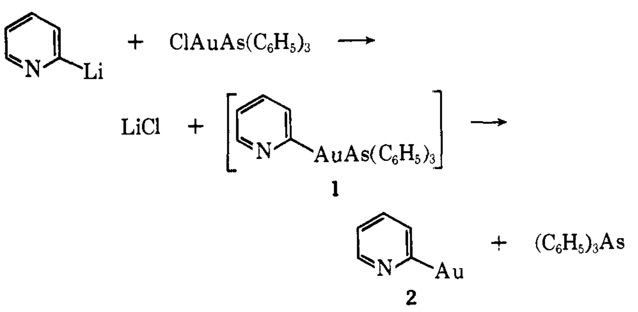
Organogold Chemistry. III.[1] 2-Pyridylgold(I)

Sir:

This communication reports the preparation of 2-pyridylgold(I) (**2**), the simplest member of a new class of organogold compounds. The compound is prepared by addition of solid chloro(triphenylarsine)gold(I) to a THF (or ether) solution of 2-pyridyllithium at −40°. As the solution warms, the arsine complex dissolves (*ca.* −25°), followed by precipitation of the product (*ca.* −5°) in 90–100% yield. The reaction presumably proceeds through compound **1** as an intermediate, followed by displacement of triphenylarsine by the unshared electron pair on nitrogen. Triphenylarsine can be isolated from the solvent in yields of 75–95%.



2-Pyridylgold(I) is insoluble in most common organic solvents, but can be recrystallized from high-boiling

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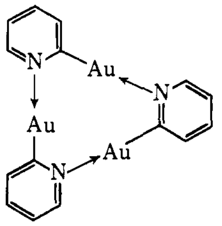
(1) Paper II: L. G. Vaughan and W. A. Sheppard, *J. Organometal. Chem.*, in press; Paper I: L. G. Vaughan and W. A. Sheppard, *J. Amer. Chem. Soc.*, **91**, 6151 (1969).

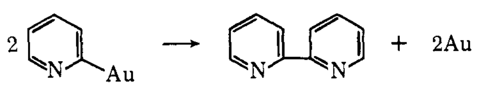
basic solvents such as pyridine (best), DMSO, and DMF. The pure compound is a bright yellow, crystalline solid, stable to air and water but somewhat sensitive to light. *Anal.* Calcd for C_5H_4AuN: C, 21.83; H, 1.47; Au, 71.61; N, 5.09. Found: C, 22.07; H, 1.34; Au, 71.34; N, 4.97. When the compound is heated, decomposition is first noted about 120°, followed by melting with complete decomposition at 150°.

The simplest structure consistent with the coordination requirements of gold(I) is a planar, cyclic trimer (**3**). Although this structure requires a central nine-membered ring, the linear bonding of the gold atom and the 60° angle between the nitrogen atom, ring center, and C_2 allow it to be strain free. Low solubility and apparent dissociation of the trimeric structure in solution have prevented accurate molecular weight measurements, and a higher polymeric structure cannot be completely excluded at this time.



3

The decomposition of 2-pyridylgold(I) at its melting point (or at lower temperatures under vacuum) quantitatively produces metallic gold and 2,2′-bipyridine (**4**).



2 **4**

This mode of decomposition is of potential industrial importance since it permits deposition of pure gold films under very mild thermal conditions. The reaction also provides a high-yield route, *via* 2-pyridylgold(I) derivatives, from 2-bromopyridines to 2,2′-bipyridines. These latter reagents are of major importance in analytical and coordination chemistry.[2,3]

Six simple derivatives of 2-pyridylgold(I), prepared in the same manner as the parent compound, are listed in Table I. Yields were about 90% in all cases. The 6-methyl derivative is of particular interest since steric coordination hindrance by the methyl group was considered possible. However, the compound formed without difficulty and shows no unusual solubility or thermal instability properties. When pyrolyzed under vacuum, all derivatives gave the expected decomposition products, metallic gold and the symmetrical bipyridine. None of these derivatives shows significantly better solubility than 2-pyridylgold(I), but, in contrast to the parent compound, all are stable indefinitely to light.

Table I. Derivatives of 2-Pyridylgold(I)[a]

Substituent	Mp,[b] °C	Bipyridine yield, %[c]
3-Methyl	217–220 dec	69
4-Methyl	184 dec	76
5-Methyl	159 dec	84
6-Methyl	169–171 dec	73
4,6-Dimethyl	185–190 dec	77

[a] Satisfactory elemental analyses have been obtained for all compounds. [b] Slight decomposition commences about 15° below the listed decomposition temperatures. [c] Crude 2-pyridylgold(I) derivatives were used in these experiments.

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(2) W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, **54**, 959 (1954).

(3) C. M. Harris and S. E. Livingstone in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, Chapter 3.

(4) Electrochemicals Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del. 19898.

(5) This work is to be presented in part at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970.

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Mass Spectrometry in Structural and Stereochemical Problems. CXC.[1] Electron Impact Induced Triple Hydrogen Migration in Vinyl Alkyl Ethers[2]

Sir:

The many detailed studies[3] of hydrogen migrations, which occur in organic compounds after electron impact, have aided enormously in our understanding of the mechanistic pathways and fragmentation reactions in the mass spectrometer. While most well-known hydrogen transfers result in a net gain or loss of one hydrogen in the charged fragment, unidirectional[4] and reciprocal[5] double hydrogen rearrangements are also well documented through deuterium labeling. Triple hydrogen transfers have so far been recorded only in higher alkyl esters of trimellitic anhydride[6] and no real insight has as yet been gained into them because of the absence of any isotopic labeling. We record now the second example of a unidirectional triple hydrogen migration, whose course could be defined through extensive deuterium labeling.

In connection with our study[7] of the mass spectrometric behavior of alkyl vinyl ethers,[8] we encountered a striking feature (see Table I) in the fragmentation of those ethers with an alkyl chain longer than five carbon atoms, namely the loss of the elements of ethanol (substantiated by a metastable peak) from the molecular ion.[9] Since deuterium labeling showed that the vinyl group

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(1) For preceding paper see R. T. Gray, J. Diekman, G. L. Larson, W. K. Musker, and C. Djerassi, *Org. Mass Spectrom.*, in press.

(2) Financial assistance from the National Institutes of Health (grant No. AM-04257) is gratefully acknowledged.

(3) For leading references see (a) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967; (b) W. Benz, "Massenspectrometrie Organischer Verbindungen," Akademische Verlagsgesellschaft, Frankfurt, 1969, pp 128–150.

(4) For leading references see C. Djerassi and C. Fenselau, *J. Amer. Chem. Soc.*, **87**, 5756 (1965).

(5) L. Tökes, G. Jones, and C. Djerassi, *ibid.*, **90**, 5465 (1968); G. Eadon and C. Djerassi, *ibid.*, **91**, 2724 (1969).

(6) S. Meyerson, I. Puskas, and E. K. Fields, *Chem. Ind.* (London), 1845 (1968).

(7) M. Katoh and C. Djerassi, *Chem. Commun.*, 1385 (1969).

(8) For earlier studies see F. W. McLafferty, *Anal. Chem.*, **31**, 2072 (1959); S. Meyerson and J. D. McCollum, "Advances in Analytical Chemistry and Instrumentation," Vol. 2, C. N. Reilley, Ed., Interscience Publishers, New York, N. Y., 1963, p 211; M. E. Audier, *Org. Mass Spectrom.*, **2**, 283 (1969).

(9) No metastable ion was encountered for the hypothetical sequence $M^+ \rightarrow M - C_2H_4O \rightarrow M - C_2H_6O$ using the defocusing technique.