no racemization occurred either during chromatography of the liquid acetate, or drying at 55° (1 mm).

Kinetic Methods. Du Pont glacial acetic acid was purified according to the procedure described by Wiberg.[41] Approximately 0.5 g of ferrocenyl alkyl tosylate was dissolved in 50.00 ml of purified acetic acid. Aliquots (5.00 ml) were then added to each of nine previously prepared constricted tubes which were fitted with a 19/38 joint. The tubes were stoppered, cooled to $-196°$, then attached to a degassing apparatus. Three freeze-thaw degassing cycles at 1 μ were carried out, after which the tubes were sealed at the constriction. The samples were then thermostated. Ampoules were withdrawn at various intervals, quenched by shaking in an ice slush, and opened. The contents were poured into a beaker containing a small amount of purified acetic acid. The ampoule was rinsed three times with acetic acid and the washings were added to the beaker. The acetic acid solution was then titrated with 0.2 N sodium acetate in acetic acid; the end point was determined from a potentiometric plot. Rate constants were obtained from a least-squares fit of the data to the first-order rate expression.

Solvolysis Products. Acetolysis containing about 0.5 g of ferrocenylalkyl tosylate in 10 ml of purified acetic acid were degassed according to the above procedure. After ten half-lives in a sealed ampoule at the desired temperature, the reaction mixture was added to excess dry pyridine. The solvent was then evaporated at room temperature (1 mm), and the resulting oil was chromatographed on grade III, neutral alumina. Unrearranged acetates were obtained in yields of 90%, and identified by comparison of their infrared and nmr spectra with those of authentic samples.

Acknowledgment. This work was supported by a grant from the National Science Foundation, NSF GP-5190, and a grant from the Paint Research Institute.

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[41] K. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 249.

New Organogold Chemistry. I.[1]
Synthesis and Fluorine-19 Nuclear Magnetic Resonance Studies of Some Fluoroorganogold Compounds

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Abstract: Four fluorophenyl(fluorophenyl isocyanide)gold(I) isomers, representatives of a new class of organogold compounds, were prepared from *m*- and *p*-fluorophenyl isocyanide. ^{19}F nmr studies show that the gold atom withdraws electron density strongly from the isocyanide ligand, but is a weak donor into the fluorobenzene ring. Infrared spectral shifts for the isocyanide absorption support this conclusion. Oxidative addition of bromine to pentafluorophenyl(triphenylphosphine)gold(I) has given compound **13**, a new type of gold(III) compound. The electronic effects of the isocyanide group are discussed relative to structure.

Although the organometallic chemistry of most transition metals has been of high interest in recent years, relatively little work has been reported on gold.[4,5] Calvin[6] has prepared a series of monomeric compounds of the type R_3PAuR' ($R = C_2H_5$ or C_6H_5, $R' = CH_3$, C_6H_5, etc.). When R is acetylacetonate, the diketone is bonded to gold through carbon.[7] The preparation, structure, and reactions of polymeric gold acetylides have been studied by two groups.[8,9] Hüttel prepared a variety of olefin–gold chloride complexes,[10–13] as well as cyclopentadienylgold,[14] and other olefin complexes were described by Chalk.[15]

Gold(III) compounds have also recently been of interest. Two tertiary phosphine complexes of trimethylgold were prepared for studies of infrared spectra, dipole moments, and thermal decomposition.[16] Some dialkylgold(III) dialkyldithiocarbamates have been synthesized starting from gold(I) dialkyldithiocarbamates or N-ethylpiperidinium tetrachloroaurate.[17] Dimethylgold(III) halides have been treated with sodium trimethylsiloxide to give the dimer $[(CH_3)_2AuOSi(CH_3)_3]_2$,[18] and with 8-hydroxyquinoline to give the monomeric, internally coordinated compound $(CH_3)_2Au(C_9H_6NO)$.[19] Several water-soluble salts, prepared from dimethylgold(III) hydroxide, have

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[1] Paper II: L. G. Vaughan and William A. Sheppard, paper in preparation.

[2] This work was presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., September 1969.

[3] To whom all correspondence should be addressed.

[4] For brief reviews, see E. M. Wise, "Gold-Recovery, Properties and Applications," D. Van Nostrand Co., Inc., Princeton, N. J., 1964; and M. L. H. Green in "Organometallic Compounds," Vol. 2, G. E. Coates, M. L. H. Green, and K. Wade, Ed., Methuen and Co., Ltd., London, 1968.

[5] Yearly progress is reported by D. Seyferth and R. B. King, "Annual Surveys of Organometallic Chemistry," Vol. 1–3, Elsevier Publishing Co., Amsterdam, 1965–1967.

[6] G. Calvin, G. E. Coates, and P. S. Dixon, *Chem. Ind.* (London), 1628 (1959).

[7] D. Gibson, B. F. G. Johnson, J. Lewis, and C. Oldham, *ibid.*, 342 (1966).

[8] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 3220 (1962).

[9] R. Nast and U. Kirner, *Z. Anorg. Allg. Chem.*, **330**, 311 (1964).

[10] R. Hüttel and H. Dietl, *Angew. Chem. Intern. Ed. Engl.*, **4**, 438 (1965).

[11] R. Hüttel, H. Reinheimer, and H. Dietl, *Chem. Ber.*, **99**, 462 (1966).

[12] R. Hüttel and H. Reinheimer, *ibid.*, **99**, 2778 (1966).

[13] R. Hüttel, H. Reinheimer, and K. Nowak, *Tetrahedron Lett.*, 1019 (1967).

[14] R. Hüttel, U. Raffay, and H. Reinheimer, *Angew. Chem. Intern. Ed. Engl.*, **6**, 862 (1967).

[15] A. J. Chalk, *J. Amer. Chem. Soc.*, **86**, 4733 (1964).

[16] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 421 (1963).

[17] H. J. A. Blaauw, R. J. F. Nivard, and G. J. M. van der Kerk, *J. Organometal. Chem.*, **2**, 236 (1964).

[18] H. Schmidbaur and M. Bergfeld, *Inorg. Chem.*, **5**, 2069 (1966).

[19] E. Rivarola, G. C. Stocco, B. L. Pepe, and R. Barbieri, *J. Organometal. Chem.*, **14**, 467 (1968).

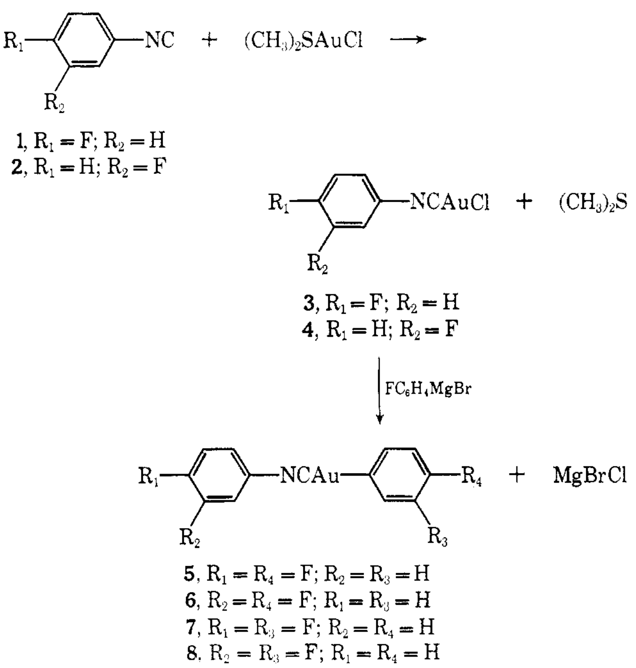
been studied by Raman, infrared, and nmr spectroscopy.[20]

As part of a program to synthesize new classes of organogold compounds and study carbon–gold bonding, we have prepared the four isomeric fluorophenyl(fluorophenyl isocyanide)gold(I) compounds **5–8** and examined their ^{19}F nmr and infrared spectra. ^{19}F chemical shifts in *meta-* and *para*-substituted fluorobenzenes are a very sensitive probe of electronic effects of substituents, particularly for detecting changes in the π system. Taft[21] has developed this technique in studies on inductive and resonance effects of many common functional groups in a wide range of solvents. Recently, the method has been used to study the electronic properties of fluoroalkyl groups,[22] tetrazoles,[23] cyanocarbon groups,[24] and phosphorus substituents.[25] In the organometallic area, Parshall has prepared *m-* and *p*-fluorophenylplatinum compounds to study details of arylplatinum bonding.[26,27]

Compounds **5–8** are ideal for similar studies on gold. The double fluorine substitution allows simultaneous examination of the electronic properties of gold in both the carbon–gold bond and the ligand complex. Additional information on the nature of the coordinate bond is available from infrared studies, since the frequency of the isocyanide band is very sensitive to back-donation from the metal.[28]

Synthesis. The procedure used is outlined in Chart I. *m-* and *p*-Fluorophenyl isocyanide (**1** and **2**) were prepared in *ca.* 20% yield by dehydration of the corresponding formamides using the method of Ugi.[29] The pure compounds decompose rapidly at room temperature, but can be stored indefinitely at −70°. Addition of each isocyanide to a suspension of chloro(dimethyl sulfide)gold(I) in chloroform resulted in rapid displacement of dimethyl sulfide and precipitation of complexes **3** and **4** in *ca.* 80% yield. These complexes are sparingly soluble in organic solvents, but reacted instantaneously when added to an ether solution of *m-* or *p*-fluorophenylmagnesium bromide. Attack of the Grignard reagent at the gold–chlorine bond, rather than on the isocyanide group, is noteworthy, particularly in view of the polarization in **3** and **4** (see Discussion below).

Chart I



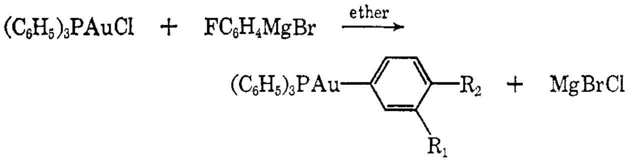
1, $R_1 = F$; $R_2 = H$
2, $R_1 = H$; $R_2 = F$

3, $R_1 = F$; $R_2 = H$
4, $R_1 = H$; $R_2 = F$

5, $R_1 = R_4 = F$; $R_2 = R_3 = H$
6, $R_2 = R_4 = F$; $R_1 = R_3 = H$
7, $R_1 = R_3 = F$; $R_2 = R_4 = H$
8, $R_2 = R_3 = F$; $R_1 = R_4 = H$

Crude yields of compounds **5–8** were 80–95%. The pure compounds are air stable, and all decompose above 100° when heated on a melting point block. In solution, thermal decomposition occurs at a much lower temperature, and severe losses of **5** and **6** resulted during recrystallization before this fact was recognized. The compounds are also light sensitive, a property characteristic of all isocyanide–gold complexes, and decompose within several weeks when exposed to normal room lighting.

m- and *p*-fluorophenyl(triphenylphosphine)gold(I) (**9** and **10**) were prepared to compare the ligand properties of the phosphine group with those of the fluorophenyl isocyanide group. Yields were about 50%.



9, $R_1 = H$; $R_2 = F$
10, $R_1 = F$; $R_2 = H$

Two related compounds, also prepared from chloro(triphenylphosphine)gold(I) by the Grignard route, are *m*-(trifluoromethyl)phenyl(triphenylphosphine)gold(I) (**11**) and pentafluorophenyl(triphenylphosphine)gold(I) (**12**). Treatment of **12** with bromine at 0° gave **13** and **14**. Compound **13** represents a new class of organogold compound, and the bromination reaction is the first example of "oxidative addition" to an organogold(I) compound.[30] Only one isomer of **13** was isolated, but no configuration could be assigned. The compound (analyzed as a Nujol mull) has two bands at 221 and 237 cm^{-1} which must arise from vibrations along the Au–Br axis. Coates and Parkin[16] have examined the spectra of several gold(III)-bromide complexes and found ν_{AuBr} to occur between 213 and 264 cm^{-1}.

m-$CF_3C_6H_4AuP(C_6H_5)_3$ **11** $C_6F_5AuP(C_6H_5)_3$ **12**

$$C_6F_5AuP(C_6H_5)_3 \xrightarrow[0°]{Br_2/CCl_4} C_6F_5Au(Br)_2P(C_6H_5)_3 + (C_6H_5)_3PAuBr$$

13 **14**

Results and Discussion

***m-* and *p*-Fluorophenyl Isocyanides.** Since Taft[21] did not include the isocyanide group in his studies, we

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(20) M. G. Miles, G. E. Glass, and R. S. Tobias, *J. Amer. Chem. Soc.*, **88**, 5738 (1966).

(21) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 709, 3146 (1963).

(22) W. A. Sheppard, *ibid.*, **87**, 2410 (1965).

(23) J. C. Kauer and W. A. Sheppard, *J. Org. Chem.*, **32**, 3580 (1967).

(24) W. A. Sheppard and R. M. Henderson, *J. Amer. Chem. Soc.*, **89**, 4446 (1967).

(25) J. W. Rakshys, R. W. Taft, and W. A. Sheppard, *ibid.*, **90**, 5236 (1968).

(26) G. W. Parshall, *ibid.*, **86**, 5367 (1964).

(27) G. W. Parshall, *ibid.*, **88**, 704 (1966).

(28) F. A. Cotton and F. Zingales, *ibid.*, **83**, 351 (1961).

(29) I. Ugi and R. Meyr, *Org. Syn.*, **41**, 101 (1961).

(30) L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968), and reviews cited therein.

Table I. ^{19}F Chemical Shifts of Fluorophenyl Isocyanides and Fluorophenyl Formamides Relative to Fluorobenzene

Compound	δ (ppm) at infinite dilution in solvents: CCl_3F	Benzene	Dioxane	Acetonitrile	Acetone	Pyridine	Methanol
p-FC_6H_4NC (**1**)	−3.21	−3.18	−3.22	−3.92	−3.88	−3.90	−4.33
m-FC_6H_4NC (**2**)	−2.76	−2.68	−2.32	−2.69	−2.82	−2.76	−3.19
m-FC_6H_4NHCHO		−1.54		−1.40			−1.42
p-FC_6H_4NHCHO		4.97		5.25			4.59

have obtained shielding parameters in seven solvents (Table I). Also included are values for *m*- and *p*-fluorophenylformamide in three solvents. As expected, the isocyanide group was found to be electron withdrawing in both the *meta* and *para* position. In all solvents, the *para* signal occurs at lower field than that from the *m*-fluorine. The substituent parameters calculated[21] from the shielding parameters in CCl_3F are given in Table II with data on other selected nitrogen substituents for comparison.

Table II. Comparison of Chemical Shifts[a] and Substituent Parameters for Selected Nitrogen Substituents

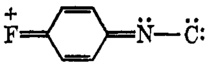
Substituent X	$\int_{H}^{m-X}$	$\int_{H}^{p-X}$	$\int_{m-X}^{p-X}$	σ_I	$\sigma_R{}^\circ$
—NC	−2.76	−3.21	−0.45	+0.47	+0.02
—N=NC_6H_5[b]	−0.78	−3.10	−2.33	+0.19	+0.08
—$N^+(CH_3)_3$[c]	−5.95	−3.10	+2.85	+0.93	−0.11
—NO	−1.78	−11.10	−9.32	+0.34	+0.32
—NO_2	−3.45	−9.55	−6.10	+0.56	+0.22
—N_2^+[d]	−8.9	−27.80	−18.9	+1.34	+0.64
$\mathrm{-N\overset{\overset{O}{\parallel}}{C}H}$[c]	−1.42	+4.59	+6.01	+0.29	−0.20
$\mathrm{-N\overset{\overset{O}{\parallel}}{C}CH_3}$[c]	−1.35	+5.15	+6.50	+0.24	−0.22
—N=C=O[e]	−1.92	+3.11	+5.13	+0.36	−0.17

[a] Shielding parameters $\int$ given in parts per million in CCl_4 or CCl_3F unless indicated otherwise; all published data from ref 21. [b] Hydrocarbon (cyclohexane). Note $\int_{H}^{m-N=NC_6H_5}$ erroneously listed −3.78 in ref 21. [c] Methanol. [d] Acetonitrile. [e] F. S. Fawcett and W. A. Sheppard, *J. Amer. Chem. Soc.*, **87**, 4341 (1965).

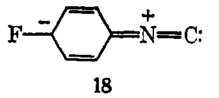
The exact structure of the isocyanide group is still subject to controversy,[31,32] but is generally agreed to be a hybrid of a resonance form **15** containing a divalent carbon atom and the dipolar form **16**. Our nmr results

$$\underset{\textbf{15}}{\mathrm{FC_6H_4{-}\ddot{N}{=}C{:}}} \qquad \underset{\textbf{16}}{\mathrm{FC_6H_4{-}\overset{+}{N}{\equiv}\overset{-}{C}{:}}}$$

can be accommodated within this picture of the electronic structure but are somewhat surprising in comparison with other nitrogen substituents (see Table II). The inductive effect of the group as given by σ_I indicates that the positive character of the nitrogen is intermediate between the nitrogens of nitroso and nitro groups—effectively one-half that of a positive saturated nitrogen of the trimethylammonium but much less than that of the diazonium group. The azophenyl group is probably a good model to estimate the inductive substituent effect of the uncharged -N= unit as found in contributing form **15**; the relatively small positive value of σ_I probably reflects the electronegative character of the nitrogen in this bonding situation.[33] Thus the much larger σ_I value for the isocyanide group is in accord with a large contribution (*ca.* 40%) from the polar resonance form **16**. The very small +R effect of the isonitrile group is in marked contrast with the large +R effects for NO and NO_2 and the large −R effects for amides and isocyanate. Actually the isocyanide group was expected to show resonance effects more analogous to the amide or isocyanate groups rather than a nitro or nitroso group. Apparently the electron-withdrawing power (or electronegativity) of the electron-deficient carbene-type carbon is intermediate between an electron-deficient amide carbon and the highly electronegative oxygen. The small +R effect for isocyanide group is probably best explained by contribution of resonance form **17** which is offset by the usual resonance donation of the unshared pair into the ring (form **18**). An alternate explanation is an induced resonance polarization (form **19**) but this is essentially a π-inductive effect which has been shown to be of neglible importance for much stronger electron-withdrawing groups,[24] including trimethylammonium (see Table II).



17



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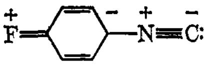

19

Among the solvents listed in Table I, methanol produced shifts to lowest field in both the *meta* and *para* cases. This result can be attributed to hydrogen bonding (**20**) as observed by Taft[21] for basic substituents in

$$\underset{\textbf{20}}{\mathrm{FC_6H_4{-}\overset{+}{N}{\equiv}\overset{-}{C}{:}\cdots\cdot HOCH_3}}$$

a variety of protonic solvents. Schleyer[32,34] and Ferstandig[35] have made detailed studies of the hydrogen-bonding ability of isocyanides and concluded that strong bonding does occur with alcohol solvents.

The ^{19}F shifts listed in Table I for *m*- and *p*-fluorophenylformamide closely resemble those found by Taft[21] for the corresponding acetamides. As expected, the nitrogen atom withdraws electron density weakly from the *meta* position by induction, but is a strong donor by resonance into the *para* position.

Gold Compounds 5–10. The ^{19}F shielding parameters for the *m*- and *p*-fluorophenylgold complexes **5–10** are given in Table III.

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(31) I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, and K. Offermann, *Angew. Chem. Intern. Ed. Engl.*, 4, 472 (1965), and references cited therein.

(32) P. von R. Schleyer and A. Allerhand, *J. Amer. Chem. Soc.*, **84**, 1322 (1962).

(33) The positive $\sigma_R{}^\circ$ value for the $N{=}NC_6H_5$ group is surprising and not easily rationalized.

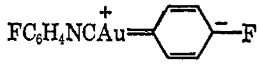
(34) P. von R. Schleyer and A. Allerhand, *J. Amer. Chem. Soc.*, **85**, 866 (1963).

(35) L. L. Ferstandig, *ibid.*, **84**, 1323 (1962).

Table III. ^{19}F Chemical Shifts for Fluorophenylgold(I) Compounds Relative to Fluorobenzene

	δ (ppm) in benzene at infinite dilution			
	Fluorine atom in ligand		Fluorine atom in ring directly bonded to gold	
Compd	Orientation	Signal position	Orientation	Signal position
5	*para*	−7.08	*para*	2.59
6	*meta*	−4.02	*para*	2.66
7	*para*	−7.08	*meta*	2.23
8	*meta*	−4.01	*meta*	2.20
9			*para*	3.23
10			*meta*	2.32

Comparing compounds **5** and **7** (both containing a *p*-fluorophenyl isocyanide ligand), **6** and **8** (*m*-fluorophenyl isocyanide ligand), and **9** and **10** (triphenylphosphine ligand), the gold group (metal + coordinated ligand) is seen to be an electron donor with respect to the fluorobenzene ring. Since the signal from the *p*-fluorine is at slightly higher field, resonance such as **21** must occur to a small extent. However, our ^{19}F shift data are not easily interpreted in defining the nature of carbon–gold bonding between the gold and the aromatic ring, although 5d orbitals of gold are probably involved in interactions with the π system. The extent of 5d–2pπ overlap is undoutedly hindered by free rotation about the carbon–gold bond. In the platinum compounds studied by Parshall,[27] *m*- and *p*-$FC_6H_4Pt(PEt_3)_2X$, the *meta* parameters (1.90–4.26 ppm in cyclohexane) are not greatly different from our *meta* results for gold. However, the *para* parameters (9.20–11.70 ppm in cyclohexane) are much higher, and the difference can be explained by steric hindrance of ring rotation by the triethylphosphine groups. Such hindrance encourages overlap of the $5d_{xy}$ orbital on platinum with the π^* orbitals of the fluorobenzene ring. However, a question has been raised about use of ^{19}F chemical shift data to gain information on bonding in platinum complexes.[36]



21

Competing with these interactions is electron withdrawal from the same 5d orbitals by the ligand. Compounds **5**, **6**, and **9**, and also **7** and **8** and **10**, constitute a series in which the ligand is varied while the same fluorophenyl group is bonded to gold. In both series, shifts to highest field occur with triphenylphosphine. This result is consistent with the fact that isocyanides are better π acceptors than triphenylphosphine.[37] Since fluoride can inductively withdraw electron density in the *meta* position but is a good donor (by resonance) in the *para* position,[21] *p*-fluorophenyl isocyanide should be a poorer π acceptor than the *meta* isomer. The slightly greater upfield shift of **7** *vs.* **8** is in accord with this prediction, but it fails for **5** and **6**. The relative positions of **5** and **6** are reversed in THF (+3.33 ppm for **5**, +2.93 ppm for **6**) suggesting that substituent effects in the ligand are minor relative to solvent effects.

^{19}F data for *m*- and *p*-fluorophenylcopper(I) have recently been reported by Cairncross,[38] and comparison with our gold data is of interest. The signal from **22** occurs at −0.05 ppm and that from **23** at −5.37 ppm (ether–dioxane solvent). Two factors can account for these downfield shifts. First, copper is coordinated by a very weak σ donor ligand (probably dioxane) and receives little electron donation from this source. Second, empty 4p orbitals on copper cause a large resonance withdrawal from the *p*-fluorine in **23**. Although vacant 6p orbitals are available on gold, they probably cannot interact with the aromatic π system because of the much larger size of gold.

m-FC_6H_4Cu **22**

p-FC_6H_4Cu **23**

Details of ligand interaction with gold can be obtained by comparing the shifts of the free ligands in Table I (in benzene solution) with those of the coordinated ligands in compounds **5**–**8**[39] (Table III). Coordination results in a downfield shift of about 1.3 ppm for the *meta* signals and 3.9 ppm for the *para* signals. These results indicate that the gold group is electron withdrawing with respect to the ligand (**24**) and that no significant back-donation occurs (**25**). This capability of gold(I) to withdraw electron density from the ligand is undoubtedly enhanced by its ability to donate electron density by both inductive and resonance (**21**) mechanisms into the fluorobenzene ring to which it is directly bonded. The larger positive value of $f_m{}^p$ for the complexed ligand suggests that contribution from a form similar to resonance form **17** is greatly enhanced by complexing with gold. This technique is now being employed to measure the complexing strength of other transition metal derivatives with isocyanides.

$FC_6H_4\overset{+}{N}{\equiv}C{-}\overset{-}{Au}C_6H_4F$ **24**

$FC_6H_4N{=}C{=}AuC_6H_4F$ **25**

Table IV. Isocyanide Infrared Absorption Band Position

	Orientation of fluorine			
Compound	In ligand	In ring directly bonded to gold	Medium	Band, cm^{-1}
p-FC_6H_4NC (**1**)			CCl_4	2123
m-FC_6H_4NC (**2**)			CCl_4	2123
p-$FC_6H_4NCAuCl$ (**3**)			KBr	2227
			$CHCl_3$	2217
m-$FC_6H_4NCAuCl$ (**4**)			KBr	2227
			$CHCl_3$	2217
5	*para*	*para*	$CHCl_3$	2200
6	*meta*	*para*	$CHCl_3$	2200
7	*para*	*meta*	$CHCl_3$	2198
8	*meta*	*meta*	$CHCl_3$	2200

Infrared Results. Shifts in the isocyanide infrared band (Table IV) further confirm these conclusions. In the free ligand, the band occurs at 2123 cm^{-1} for both isomers. Coordination with gold chloride raises the frequency to 2217 cm^{-1},[40] apparently the highest re-

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[36] M. J. Church and M. J. Mays, *J. Chem. Soc., A*, 3074 (1968).

[37] W. D. Horrocks, Jr., and R. C. Taylor, *Inorg. Chem.*, **2**, 723 (1963).

[38] A. Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, **90**, 2186 (1968).

[39] Compounds **3** and **4** are insoluble in benzene and very sparingly soluble in more polar organic solvents.

[40] Compounds **3** and **4** are only slightly soluble in chloroform but the 2217-cm^{-1} band can be detected in saturated solutions.

Table V. Properties and Analytical Data

Compd	Bp (mm) or mp, °C	% yield	Recrystzn solvent	Formula	Calcd, % C	H	Au	F	N	Found, % C	H	Au	F	N
1	52–54 (5)	23		C_7H_4FN	69.42	3.33		15.68	11.57	69.52	3.87		15.72	12.31
2	52–54 (8)	17		C_7H_4FN	69.42	3.33		15.68	11.57	69.82	3.13		15.77	11.84
3	247–248 dec	81	$(CH_3)_2CO$	$C_7H_4AuClFN$	23.78	1.14	55.72		3.96	23.75	1.08	54.97		4.04
4	223–225	87	$(CH_3)_2CO$	$C_7H_4AuClFN$	23.78	1.14	55.72		3.96	23.82	0.89	54.94		4.21
5	153–155 dec	9.7	CH_3OH	$C_{13}H_8AuF_2N$	37.78	1.95	47.68	9.20	3.39	37.73	2.11	47.30	9.40	3.87
6	126–128 dec	25	CH_3OH	$C_{13}H_8AuF_2N$	37.78	1.95	47.68	9.20	3.39	37.81	2.06	47.27	9.17	3.47
7	138–140 dec	58.5	C_2H_5OH	$C_{13}H_8AuF_2N$	37.78	1.95	47.68	9.20	3.39	37.76	1.96	47.57	9.10	3.29
8	110–111 dec	94	CH_3OH	$C_{13}H_8AuF_2N$	37.78	1.95	47.68	9.20	3.39	37.73	1.80	47.51	9.10	3.24
9	154	48	C_6H_{12}	$C_{24}H_{19}AuFP$	52.00	3.45	35.54	3.42		51.89	3.64	35.52	3.03	
10	141	36	C_6H_{12}	$C_{24}H_{19}AuFP$	52.00	3.45	35.54	3.42		51.71	3.38	35.25	3.09	
11	150	41	C_6H_{12}	$C_{25}H_{19}AuF_3P$	49.68	3.17	32.60	9.43		49.52	3.05	32.23	8.51	
12	171–172	58	C_6H_{12}	$C_{24}H_{15}AuF_5P$	46.02	2.41	31.45	15.17		46.22	2.52	31.41	14.60	
13	199–201 dec	28	C_2H_5OH	$C_{24}H_{15}AuBr_2F_5P$	36.66	1.92	25.06	20.33[a]		36.98	2.09	24.44	20.61[a]	
14	248-250	12	CH_3CN	$C_{18}H_{15}AuBrP$	40.09	2.80	36.54			40.00	2.86	34.77		

[a] Values for bromine.

ported value[28,41,42] for an aryl isocyanide coordinated to a metal.[43] This increase is the result of strong polarization of the molecule (**26**), which increases the iso-

$$FC_6H_4\overset{+}{N}{\equiv}\overset{-}{C}AuCl$$

26

cyanide bond order and raises the frequency. Replacement of chloride by the less-electronegative fluorophenyl group forces a slight increase in back-donation (**25**) to the ligand. This decreases the bond order and lowers the isocyanide frequency to about 2200 cm^{-1} for compounds **5**–**8**.

Experimental Section

General. All Grignard reactions were carried out under an atmosphere of prepurified nitrogen. Infrared spectra were run on a Perkin-Elmer 221 spectrometer. Measurements in the long wavelength region were made on Nujol mulls of the compounds using a Perkin-Elmer 621 spectrometer. Melting points are uncorrected. The physical properties and analytical data on all new compounds are given in Table V.

Nmr Calibrations. The ^{19}F nmr calibrations were carried out on a Varian A-56/60 instrument. Runs were made at 20, 10, and 5% concentration using 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane as the internal standard. Chemical shift values for C_6H_5F relative to the internal standard are benzene −35, dioxane −15, acetonitrile +32, acetone +15, methanol +12, pyridine −18, and tetrahydrofuran −11 cps at 56.4 mHz/sec. Trichlorofluoromethane, when solvent, was the internal calibrant. The chemical shift value of C_6H_5F relative to CCl_3F is 6382 cps. Substituent constants were calculated from the ^{19}F chemical shift data using the standard procedure.[21,22]

Synthesis of *p*-Fluorophenyl Isocyanide (1). The general method of Ugi and Meyr[29] for preparing aromatic isocyanides was used, starting with 42.0 g (0.30 mole) of *p*-fluorophenylformamide. After removal of petroleum ether from the crude product under reduced pressure, fractional distillation gave 8.3 g (23% yield) of product, bp 52–54° (5.0 mm). The compound developed a blue-green color immediately after distillation, and a sample kept at room temperature had almost completely decomposed after 24 hr.

The *meta* isomer (**2**) was prepared similarly in 17% yield.

Chloro(*p*-fluorophenyl isocyanide)gold(I) (3). To a suspension of 5.4 g (18.3 mmoles) of chloro(dimethyl sulfide)gold in 30 ml of chloroform was added a solution of 2.25 g (18.6 mmoles) of *p*-fluorophenyl isocyanide in 10 ml of chloroform. The solution was refluxed for 1 hr and then filtered hot, furnishing 3.1 g (48% yield) of product. Recrystallization from acetone gave an analytical sample of mp 247–248° dec. From the mother liquor, an additional 2.15 g of product was obtained (33% yield). An identical procedure was used to prepare the *meta* isomer (**4**) in 87% yield.

***m*-Fluorophenyl(*m*-fluorophenyl isocyanide)gold(I) (8).** A solution of the *m*-fluorophenyl Grignard reagent (14.3 mmoles) was prepared in 50 ml of ether. The solution was cooled to 0°, and 4.5 g (12.8 mmoles) of chloro(*m*-fluorophenyl isocyanide)gold was added in one batch. The mixture was allowed to warm, stirred at room temperature for 1 hr, then refluxed for 1 hr. After hydrolysis with excess water, the ether layer was separated, dried over sodium sulfate, treated with Darco, and filtered; the ether was removed under reduced pressure. The product was recrystallized first from a mixture of 200 ml of cyclohexane and 10 ml of benzene (held at 65°), then recrystallized a second time from methanol (maximum temperature 60°), giving an analytical product of mp 110–111° dec. The yield was 4.95 g (94%).

Compounds **5**, **6**, and **7** were prepared similarly. Compounds **5** and **6** were recrystallized first from a mixture (3:1 and 5:1) of cyclohexane and benzene, then from methanol. Compound **7** was recrystallized first from cyclohexane, then from ethanol.

Pentafluorophenyl(triphenylphosphine)gold(I) (12). To 0.485 g of magnesium (20.2 mg-atoms), covered by 15 ml of ether, was added dropwise 5.0 g (20.2 mmoles) of bromopentafluorobenzene in 25 ml of ether. When the Grignard reagent was formed, a solution of 9.5 g (15.2 mmoles) of chloro(triphenylphosphine)gold(I) in 100 ml of hot THF was added in one batch. The mixture was heated at 60° for 3 hr, then cooled and stirred at room temperature overnight. After hydrolysis with saturated ammonium chloride solution, the organic solution was treated with Darco and the solvents were removed on a rotary evaporator. The oily residue was dissolved in benzene, and on standing overnight 1.8 g (19% recovery) of chloro(triphenylphosphine)gold(I) precipitated. The mixture was then filtered and the benzene removed on a rotary evaporator. The residue was dissolved in 50 ml of cyclohexane; the solution was treated with Darco and filtered. On cooling 6.3 g of product crystallized (52.2% yield). An additional 0.7 g (5.9% yield) was obtained by chromatography of the mother liquor on Florisil. An analytical sample was recrystallized three times from cyclohexane, mp 171–172° (dec ~300°). In the ^{19}F nmr spectrum (benzene solvent, shifts relative to fluorobenzene), the *ortho*, *meta*, and *para* signals occurred at 2.78, 49.3, and 45.4 ppm. The strong deshielding of the *ortho* fluorine atoms is expected[44] and has been observed in many metal–pentafluorobenzene derivatives.[45–48]

Compounds **9**, **10**, and **11** were prepared similarly. In these cases the chloro(triphenylphosphine)gold(I) was added as a solid

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(41) F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).

(42) P. L. Pauson and W. H. Stubbs, *Angew. Chem.*, **74**, 466 (1962).

(43) Since this value is close to that which might be expected for a coordinated nitrile (the CN band in $(C_6H_5CN)_2PdCl_2$ occurs at 2232 cm^{-1} in a KBr disk), the possibility of an isocyanide–nitrile rearrangement preceding the formation of compounds **3** and **4** was considered. It was rejected when attempted reaction of *m*- and *p*-fluorobenzonitrile with $(CH_3)_2SAuCl$ gave only recovered starting materials. Further, when compounds **3**–**8** are heated to their decomposition points, the characteristic odor of free isocyanide is strongly evident.

(44) E. Pitcher, A. D. Buckingham, and F. G. A. Stone, *J. Chem. Phys.*, **36**, 124 (1962).

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(46) M. I. Bruce, *ibid.*, *A*, 1459 (1968).

(47) A. J. R. Bourn, D. G. Gillies, and E. W. Randall, *Proc. Chem. Soc.*, 200 (1963).

(48) D. E. Fenton and A. G. Massey, *J. Inorg. Nucl. Chem.*, **27**, 329 (1965).

in one batch rather than in THF solution. The ^{19}F signal from the CF_3 group of **11** occurred at 52.3 ppm (benzene solvent, shift relative to fluorobenzene).

Dibromo(pentafluorophenyl)(triphenylphosphine)gold(III) (13). To a suspension of 1.0 g (1.6 mmoles) of pentafluorophenyl(triphenylphosphine)gold in 20 ml of carbon tetrachloride was added dropwise from a syringe 0.255 g (1.6 mmoles) of bromine. Carbon tetrachloride was removed under reduced pressure, and the residue was crystallized twice from ethanol, furnishing 200 mg of product, mp 199–201° dec. From the mother liquor, an additional 150 mg of product was recovered, mp 200° dec. The total yield of product was 350 mg (28%). The mother liquor also yielded 100 mg of a second compound which was recrystallized from acetonitrile and identified as bromo(triphenylphosphine)gold (**14**), mp 248–250° (lit.[49] mp 255.5–256°).

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[49] C. Kowala and J. M. Swan, *Aust. J. Chem.*, **19**, 547 (1966).

Polylithium Compounds. III. Polylithium Compounds from Propyne and 1-Butyne, and Their Polysilicon Derivatives[1,2]

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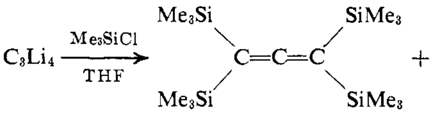
Abstract: Propyne reacts with *n*-butyllithium in hexane to form C_3Li_4, liberating 4 equiv of *n*-butane. With trimethylchlorosilane in tetrahydrofuran, C_3Li_4 gives tetrakis(trimethylsilyl)allene (**1**) in 70% yield along with some 1,3,3-tris(trimethylsilyl)propyne (**2**) and other products. Partial thermal isomerization of **2** to its allenic isomer, 1,3,3-tris(trimethylsilyl)propadiene (**3**), can be effected. 1-Butyne forms a trilithio derivative with 3 equiv of *t*-butyllithium; with trimethylchlorosilane, this produces a mixture of 1,3,3-tris(trimethylsilyl)-1-butyne (**6**) and 1,1,3-tris(trimethylsilyl)-1,2-butadiene (**7**). **6** and **7** are also obtained by lithiation of either **2** or **3** followed by treatment with methyl iodide. The structures of the polylithium compounds in hexane solution have been studied by infrared spectroscopy. They appear to have allenic structures, *e.g.*, $Li_2C{=}C{=}CLi_2$.

In a communication[3] we reported the lithiation of propyne to C_3Li_4 and the reaction of this tetralithio compound with trimethylchlorosilane to form polysilicon derivatives. This paper reports a more complete investigation of the polylithiation of propyne and of 1-butyne, a study of the polysilicon derivatives available from them, and preliminary work on the structure of the polylithium compounds in solution.

C_3Li_4 is best obtained by adding propyne in hexane solution slowly to a hexane solution of *n*-butyllithium at room temperature, then refluxing the mixture for several hours. When 4 or more equiv of *n*-butyllithium per equivalent of propyne is present, 4 equiv of *n*-butane is liberated, showing that the propyne undergoes essentially complete lithiation to C_3Li_4. The resulting solution reacts vigorously with water to give a gas identified by infrared spectroscopy as propyne, containing some allene. Derivatization with trimethylchlorosilane is best effected by cooling the C_3Li_4 solution to −70° and adding the silyl reagent in tetrahydrofuran solution. Under these conditions the major product is tetrakis(trimethylsilyl)allene (**1**).[4] A trissilyl by-product is also found having exclusively the acetylenic structure **2**, and about 5% of the product is the pentasilicon allene, **4**.



1, 70–75%

$(Me_3Si)_2CH{-}C{\equiv}C{-}SiMe_3$ +

2, 15%

$$(Me_3Si)_2C{=}C{=}\underset{\displaystyle SiMe_3}{\underset{|}{C}}SiMe_2CH_2SiMe_3$$

4, 5%

Both **1** and **2** are colorless oils, stable at room temperature, and **1** is inert to oxygen, water, and dilute acids. When heated under nitrogen at 110°, **2** undergoes partial isomerization into the allene **3**, the limiting composition at this temperature being 60% (**3**)–40% (**2**).

$$\underset{\mathbf{2}}{(Me_3Si)_2CHC{\equiv}CSiMe_3} \xrightarrow{110^\circ} \underset{\mathbf{3}}{(Me_3Si)_2C{=}C{=}CHSiMe_3}$$

The structures of all of the products were established using ir, nmr, and mass spectroscopy as well as elemental analysis. Compounds **1**, **3**, and **4** all show strong ir bands in the allenic region, near 1900 cm^{-1}, whereas **2** has instead a strong C≡C stretching absorption at 2180 cm^{-1} (Figure 1).[5] Compound **1** shows

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[2] Previous paper in this series: R. West and P. C. Jones, *J. Amer. Chem. Soc.*, **90**, 2656 (1968).

[3] R. West, P. A. Carney, and I. C. Mineo, *ibid.*, **87**, 3788 (1965).

[4] Compound **1** has recently been isolated by interesting *in situ* reaction of trimethylchlorosilane with various complex halogenated hydrocarbons; see D. Ballard and H. Gilman, *J. Organometal. Chem.*, **14**, 87 (1968), and references therein.

[5] (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Methuen and Co., London, 1958, pp 58–62; (b) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 134.