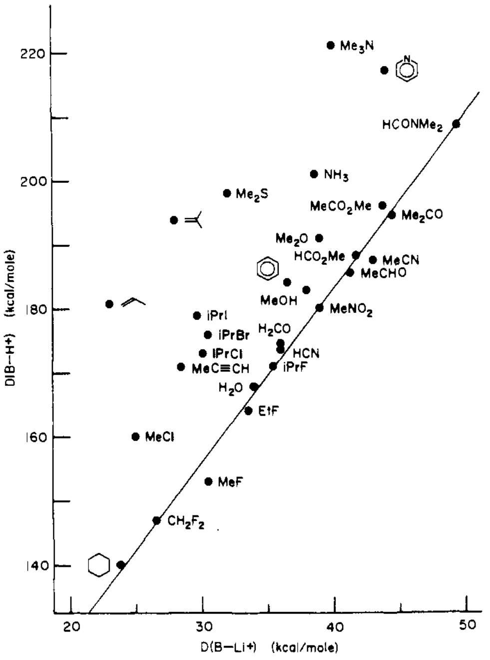

Figure 2. Comparison of two scales of gas phase basicity: binding energies of molecules to H^+, $D(B\text{-}H^+)$, and to Li^+, $D(B\text{-}Li^+)$.

Of particular interest is the comparison of the present data for Li^+ binding energies $D(\mathbf{B}\text{-}Li^+)$ to proton affinities $D(\mathbf{B}\text{-}H^+)$,[1,3,12] Figure 2. The data are consistent with the expectation that bonding to Li^+ is largely ionic while bonding to H^+ may also reflect strong covalent interactions. Many of the data fall near a line of slope 3 which intercepts the $D(\mathbf{B}\text{-}H^+)$ axis at 70 kcal/mol for $D(\mathbf{B}\text{-}Li^+) = 0$. The larger ionic bonding distances of second-row elements make them understandable exceptions. More dramatic is the comparison for alkenes: the intimate interaction afforded the proton in carbenium ions may be contrasted with the loose complex expected for Li^+. The different magnitudes of methyl substituent effects for the two reference acids also appear to reflect ionic contributions to the bonding of Li^+. Thus the dipole moments[13] NH_3 (1.47 D) > Me_3N (0.612 D) and H_2O (1.85 D) > MeOH (1.70 D) > Me_2O (1.30 D) as compared to CH_2O (2.33 D) < MeCHO (2.69 D) < Me_2CO (2.88 D) and HCN (2.98 D) < MeCN (3.92 D) are reflected in larger methyl substituent effects for $D(\mathbf{B}\text{-}Li^+)$ in the latter series.

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Nitrogen to Oxygen Isomerization of the Pentaammineruthenium(III) Glycine Ion

Sir:

During the course of our investigations into the interaction of amino acids and amino acid derivatives with the ruthenium ammine system, we observed a very facile isomerization of glycine as ligand from the N-bound to the O-bound form in pentaammineruthenium(III). This type of reaction has not been observed for the glycine complex of pentaamminecobalt(III).[1] Our observations on the pentaammineruthenium system are reported herein.

Pentaammineglycineruthenium(II) hexafluorophosphate was prepared by first reducing aquopentaammineruthenium(III) trifluoromethylsulfonate (0.075 *M*)[2] with zinc amalgam in an argon atmosphere. A tenfold excess of sodium glycinate was added to the reaction vessel. After 90 min the desired complex was precipitated as a yellow solid by acidifying with trifluoroacetic acid and adding an excess of ammonium hexafluorophosphate. The solid was filtered in air, washed with ethanol and ether, dried, and stored in a vacuum desiccator. Anal.[3] Calcd for $[(NH_3)_5Ru\text{-}NH_2CH_2COOH](PF_6)_2$: C, 4.36; N, 15.2; H, 3.63; Ru, 18.3. Found: C, 4.63; N, 15.4; H, 3.42; Ru, 18.3.

The electronic and infrared absorption spectra of this complex show the expected behavior for a "hexaammine" type of ruthenium(II) species.[4] The carboxylate stretch is clearly evident in the infrared spectrum at 1740 cm^{-1}. The cyclic voltammogram shows a reversible couple with E_f = 160 mV vs. NHE in 0.1 *M* trifluoroacetic acid to be compared to 120 mV measured for $(NH_3)_5RuNH_2CH_2C_6H_5^{2+}$ under the same conditions.[5] Oxidation of this species in acid media with a variety of oxidizing agents and reprecipitation with ammonium hexafluorophosphate produced a white solid (45% yield) which showed no -COOH stretching frequency in the infrared. The ultraviolet absorption spectrum of a typical reaction mixture before and after oxidation is shown in Figure 1. The peak at 288 nm has an extinction coefficient of 1.43×10^3 M^{-1} cm^{-1}, and is very similar in both position and intensity to known carboxylato complexes of pentaammineruthenium(III).[6] It should be noted that the isolated solid has an identical spectrum. The cyclic voltammogram shows behavior which is like that of carboxyla-

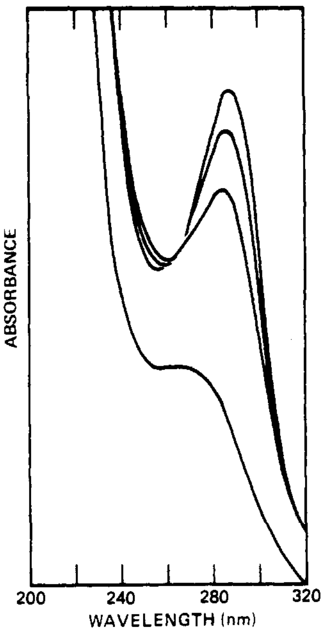

Figure 1. Ultraviolet spectrum of $[(NH_3)_5RuNH_2CH_2COOH]^{2+}$ and $[(NH_3)_5RuOOCCH_2NH_3]^{3+}$ in 0.1 *M* fluoboric acid. Bottom curve is $[(NH_3)_5RuNH_2CH_2COOH]^{2+}$. On oxidation spectrum changes to that of $[(NH_3)_5RuOOCCH_2NH_3]^{3+}$ (top curve) after ca. 15 min (temperature approximately 22°C).

to complexes which are known to be labile[6] in the ruthenium(II) state. This behavior is similar to that of chloropentaammineruthenium(III) chloride as observed by Lim et al.[7] Based on these observations and the following microanalysis, this species is formulated as featuring $^+NH_3CH_2CO_2^-$ O-bound to pentaammineruthenium(III). Anal. Calcd for $[(NH_3)_5RuOOCCH_2NH_3](PF_6)_3 \cdot \frac{1}{2}H_2O$: C, 3.40; N, 11.9; H, 2.98; Ru, 14.3. Found: C, 3.48; N, 11.7; H, 2.84; Ru, 14.4.

To check the formulation advanced, the direct synthesis of the O-bound species was undertaken. Aquopentaammineruthenium(III) trifluoromethylsulfonate (0.04 *M*) was heated to approximately 40°C under argon with a tenfold excess of glycine at a pH of 2. After 3 hr, addition of ammonium hexafluorophosphate produced a solid which was shown to be identical (ir spectrum, positions and extinction coefficients of electronic absorption bands, microanalysis) to that made from the isomerization reaction. This method is known to produce O-bound carboxylates of ruthenium(III) successfully.[8] It should also be noted that at this pH the glycine molecule is in the zwitterionic form so that only the carboxylate end is expected to coordinate.[9]

It is known that carboxylato complexes of ruthenium(III) undergo acid hydrolysis reactions.[10] In hydrochloric acid the O-bound glycine complex showed slow incorporation of chloride ion to produce chloropentaammineruthenium(III) (>90% from known ϵ^4). In a separate experiment additional hydrochloric acid was added at this point to raise the acid concentration to approximately 6 *M*. The resultant solid was found to be chloropentaammineruthenium(III) chloride in 77% overall yield. The microanalysis showed this solid to be contaminated with 1% carbon which was attributed to incomplete acid hydrolysis of the parent compound.[10] Reduction of the O-bound glycine complex liberated the organic moiety, and using isonicotinamide it was determined that 98% of the ruthenium was present as aquopentaammineruthenium(II).

The kinetics of this isomerization reaction have also been studied. The method involves oxidation of the ruthenium(II) glycine complex with potassium dichromate and then monitoring the resulting solution using ultraviolet spectroscopy. The acid concentration was controlled with fluoboric acid employing sodium fluoborate to maintain a constant ionic strength. The concentration of complex was approximately 10^{-3} *M*; the acid concentration was varied between 1 and 0.018 *M*. The rate is first order in concentration of complex and the first-order specific rate (first order in the acid form) as a function of $[H^+]$ is represented by $k_1 + k_2/[H^+]$ with $k_1 = 2.0 \times 10^{-3}$ sec^{-1} and $k_2 = 1.25 \times 10^{-4}$ *M* sec^{-1}. If the second term is ascribed to "salt isomerization" in $[(NH_3)_5RuNH_2CH_2COO]^{2+}$, the half life for the rearrangement in this species is calculated as approximately 21 sec. For this calculation pK_1 for glycine coordinated to pentaammineruthenium(III) is assumed to be the same as it is for the corresponding cobalt(III) complex, namely 2.43.[1] All evidence points to an intramolecular mechanism; a prior dissociation to aquopentaammineruthenium(III) and glycine followed by anation is ruled out by the low concentrations; no incorporation of added ions such as chloride (0.1 *M*) or acetate (NaOAc-HOAc buffer, pH 4.10, 0.2 *M*) was found to occur during isomerization.

The affinity of ruthenium(III) for a carboxylate has not been measured, but in view of values determined for cobalt(III) it is likely to be much less than that of ruthenium (III) for ammonia (K_{eq} for the reaction $(NH_3)_5RuOH_2^{3+} + NH_3 = (NH_3)_5RuNH_3^{3+} + H_2O$ has been measured as 6.1×10^4.[11]) Thus the driving force for the *net* change in acid is reaction of the stronger base site ($-NH_2$ compared to $-CO_2^-$) with the stronger Lewis acid (H^+ compared to Ru(III)). When the concentration of acid is reduced, rearrangement of the O-bound to the N-bound form is expected. Experiments undertaken to observe this reverse process were found to be complicated by the internal redox reaction to produce $[(NH_3)_5RuNH_2CH_2CO_2)]^+$ and $[(NH_3)_5Ru(H)N{=}C(H)CO_2)]^+$. When a solution at pH 7 is reduced using europium(II), only 30% of the ruthenium(II) is found to be accessible to reaction with isonicotinamide. In spite of any side reactions, this experiment makes it clear that at most 30% of the O-bound form is left at this pH; at higher pH even less is found to be accessible to the development reaction with isonicotinamide.

The half-life for the loss of ammonia from $(NH_3)_6Ru^{3+}$ in acidic solution at room temperature is approximately 10^8 sec.[4] The labilization produced by the $-CH_2CO_2H$ function ($t_{1/2} = 350$ sec) or $-CH_2CO_2^-$ ($t_{1/2} = 21$ sec) on the coordinated nitrogen is seen to be enormous. An effect has also been observed for $[(NH_3)_5RuNH_2CH_2COOH)]^{2+}$ with $t_{1/2}$ for opening a coordination position at a pH of approximately 6 as 2.5 hr compared to 20 hr for the hexaammine.[11] The effect is quite small in the case of ruthenium(II) and it is in fact not known whether the process in question is replacement of cis ammonia or simple salt isomerization. In view of the greater lability of ruthenium(II) compared to ruthenium(III) with respect to replacement of saturated ligands, the slower rate for the former in the isomerization reaction is noteworthy.

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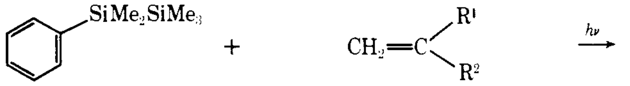
Photolysis of Organopolysilanes. A Novel Addition Reaction of Aryl Substituted Disilanes to Olefins

Sir:

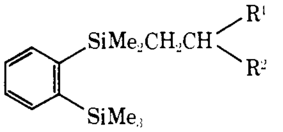
There has been a considerable interest recently concerning the photolysis of organopolysilanes.[1] This paper is concerned with a novel photochemical addition involving arylpentamethyldisilanes and olefins.

When a solution of phenylpentamethyldisilane (**1**) (4.80 mmol) and trimethylvinylsilane (**2a**) (0.20 mol) in 110 ml of dry benzene was irradiated at 0° for 4 hr with a low pressure mercury lamp bearing a Vycor filter under a nitrogen atmosphere, 80% of **1** reacted to give *o*-(trimethylsilyl)(β-trimethylsilylethyl)dimethylsilylbenzene (**3a**) in 49% yield (based on unrecovered **1**).[2]



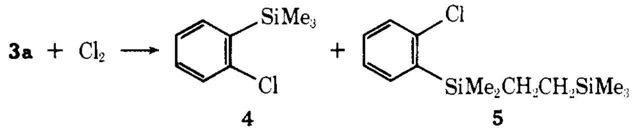
1

2a, $R^1 = H$; $R^2 = SiMe_3$
b, $R^1 = R^2 = Me$
c, $R^1 = Me$; $R^2 = C(Me){=}CH_2$



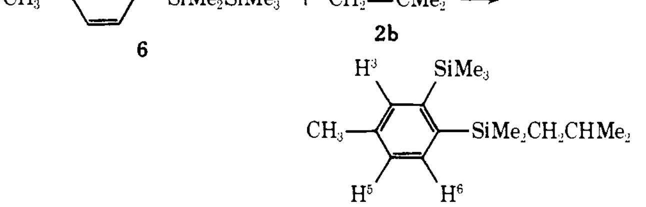
3a, $R^1 = H$; $R^2 = SiMe_3$ (49%)[3]
b, $R^1 = R^2 = Me$ (59%)
c, $R^1 = Me$; $R^2 = C(Me){=}CH_2$ (70%)

The NMR spectrum of **3a** showed proton absorptions at δ −0.07 (CH_3-$SiMe_2$, s, 9 H), 0.28 (CH_3-SiMe, s, 6 H), 0.31 (CH_3-$SiMe_2C_6H_4$, s, 9 H), 0.43–0.61 (CH_2CH_2, m, 4 H), and 7.40–7.56 (ring protons, m, 4 H). The mass spectrum of **3a** showed peaks for $C_6H_4(SiMe_3)(SiMe_2^+)$ at *m/e* 207 (49.3%) and for $C_{10}H_{15}Si_2^+$ at 191 (48.9%) as well as a peak at 308 corresponding to the molecular ion. Further support for the structure of the adduct comes from the reaction of **3a** with chlorine in carbon tetrachloride at room temperature, which gave known *o*-(trimethylsilyl)chlorobenzene (**4**)[4,5] (21%) and a new compound (17%) identified as *o*-(β-trimethylsilylethyl)chlorobenzene (**5**) by ir, NMR, and mass spectroscopic studies.[6] No other isomers such as *m*- or *p*-silyl-substituted chlorobenzene were detected by GLC analysis of the reaction mixture.[7]



4 5

Compound **1** also reacted with isobutylene (**2b**) and 2,3-dimethylbutadiene (**2c**) under similar conditions to give adducts **3b** and **3c**, respectively. These were characterized by NMR and mass spectroscopic studies.[8,9]



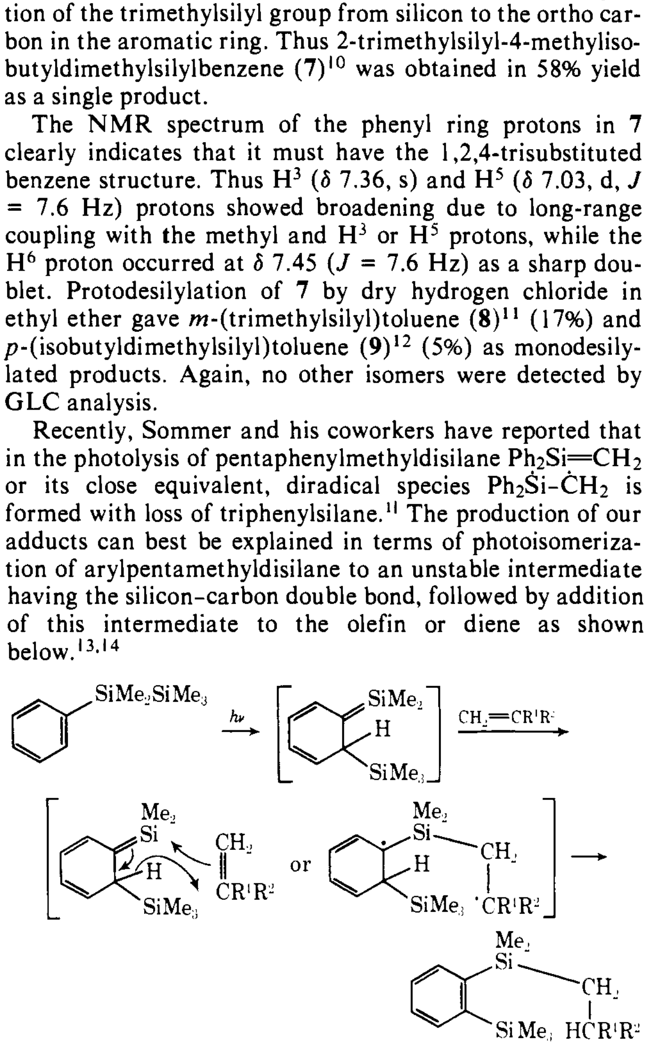
6 2b

7

Photolysis of *p*-tolylpentamethyldisilane (**6**) in the presence of isobutylene afforded crucial evidence for the migration of the trimethylsilyl group from silicon to the ortho carbon in the aromatic ring. Thus 2-trimethylsilyl-4-methylisobutyldimethylsilylbenzene (**7**)[10] was obtained in 58% yield as a single product.

The NMR spectrum of the phenyl ring protons in **7** clearly indicates that it must have the 1,2,4-trisubstituted benzene structure. Thus H^3 (δ 7.36, s) and H^5 (δ 7.03, d, J = 7.6 Hz) protons showed broadening due to long-range coupling with the methyl and H^3 or H^5 protons, while the H^6 proton occurred at δ 7.45 (J = 7.6 Hz) as a sharp doublet. Protodesilylation of **7** by dry hydrogen chloride in ethyl ether gave *m*-(trimethylsilyl)toluene (**8**)[11] (17%) and *p*-(isobutyldimethylsilyl)toluene (**9**)[12] (5%) as monodesilylated products. Again, no other isomers were detected by GLC analysis.

Recently, Sommer and his coworkers have reported that in the photolysis of pentaphenylmethyldisilane $Ph_2Si{=}CH_2$ or its close equivalent, diradical species $Ph_2\dot{S}i\text{-}\dot{C}H_2$ is formed with loss of triphenylsilane.[11] The production of our adducts can best be explained in terms of photoisomerization of arylpentamethyldisilane to an unstable intermediate having the silicon–carbon double bond, followed by addition of this intermediate to the olefin or diene as shown below.[13,14]



3

The photolysis of various disilane derivatives in the presence of unsaturated compounds is currently being examined and will be reported elsewhere.

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