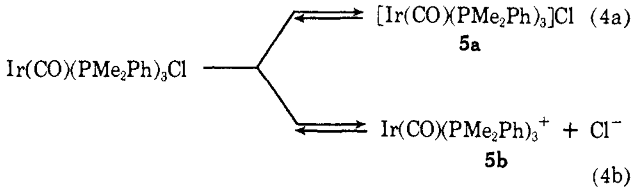
1.8 M^{-1} sec^{-1} for the apparent rate constant (k) of the reaction of **2** with H_2 (compared with 0.35 M^{-1} sec^{-1} for the corresponding reaction of **1** to form Ir(CO)-(PMe$_2$Ph)$_2$ClH$_2$).[7]

$$\mathrm{Ir(CO)(PMe_2Ph)_3Cl} + \mathrm{H_2} \xrightarrow{k} \underset{\mathbf{3}}{\mathrm{[Ir(CO)(PMe_2Ph)_3H_2]Cl}} \quad (2)$$

Increasing the PMe$_2$Ph concentration above 0.04 M resulted in parallel decreases (also depicted in Figure 1) in the absorbance due to **2**, as well as in the reactivity toward H_2. Both of these trends correspond to inverse dependencies on the PMe$_2$Ph concentration which are consistent with the coordination of another PMe$_2$Ph ligand, in accord with eq 3, to form the pentacoordinate complex, Ir(CO)(PMe$_2$Ph)$_4^+$ (**4**) (salts of which have previously been prepared and characterized),[8] which apparently is unreactive toward H_2.

$$\mathrm{Ir(CO)(PMe_2Ph)_3Cl} + \mathrm{PMe_2Ph} \rightleftharpoons \underset{\mathbf{4}}{\mathrm{[Ir(CO)(PMe_2Ph)_4]Cl}} \quad (3)$$

The apparently enhanced reactivity of Ir(CO)(PMe$_2$-Ph)$_3$Cl toward H_2 [compared with that of Ir(CO)-(PMe$_2$Ph)$_2$Cl] is somewhat surprising since five-coordinate d^8 complexes are usually considered to be intrinsically unreactive toward substrates such as H_2 and to oxidatively add such substrates through mechanisms involving prior dissociation to reactive four-coordinate derivatives.[9,10] Accordingly, we are inclined to attribute the enhanced reactivity to a small amount of the highly reactive ionic species, Ir(CO)(PMe$_2$Ph)$_3^+$, presumably present as undissociated ion pairs, [Ir(CO)-(PMe$_2$Ph)$_3$]Cl (compositionally identical with, and hence kinetically indistinguishable from, **1** with which they are in equilibrium through eq 4a) since dissociation into free ions (eq 4b) seems unlikely in a relatively nonpolar solvent such as chlorobenzene. Our failure to observe any inhibition due to a "common ion" effect when excess chloride was added as [n-Bu$_4$N]Cl also argues against such dissociation.



A reasonable expectation based on the above interpretation is that, because of enhanced stabilization of the reactive ionic species **5a** and **5b**, the rate enhancement accompanying the addition of PMe$_2$Ph to **1** *should be more pronounced and should occur at lower PMe$_2$Ph concentrations in more polar solvents.* As shown in Figure 1, this expectation is fully borne out by a comparison of dimethylformamide (DMF) and chlorobenzene as solvents. Addition of excess PMe$_2$Ph to **1** in DMF resulted in an increase in the rate constant for reaction with H_2 to a value of $>2 \times 10^2$ M^{-1} sec^{-1} at *ca.* 2×10^{-3} M PMe$_2$Ph, compared with a maximum value of 1.4 M^{-1} sec^{-1} at *ca.* 4×10^{-2} M PMe$_2$Ph in chlorobenzene. The decrease in reactivity at higher PMe$_2$Ph in DMF is attributable to the equilibrium depicted by eq 5, analogous to that proposed for chlorobenzene (eq 3), but involving instead the *free* (reactive) IrCO(PMe$_2$Ph)$_3^+$ and (unreactive) IrCO(PMe$_2$Ph)$_4^+$ ions. This is supported (i) by the observation that the behavior in this region was independent of the nature of the anion (*i.e.*, of whether Ir(CO)(PMe$_2$Ph)$_2$Cl or Ir(CO)(PMe$_2$Ph)$_2$Br was used) and unaffected by the addition of a foreign halide salt, *e.g.*, up to 0.1 M [n-Bu$_4$N]Br and (ii) by previously reported evidence from conductivity measurements that addition of excess PMe$_2$Ph to Ir(CO)(PMe$_2$Ph)$_2$Cl in ethanol–benzene (19:1, v/v) solution results in the formation of dissociated Ir(CO)L$_4^+$ and Cl$^-$ ions.[11] Since solvent effects for the oxidative addition of H_2 are typically small,[12] we are inclined to attribute the much higher rate enhancement observed in DMF, compared to chlorobenzene, to a higher concentration of the reactive species (**5a** and/or **5b**) (*i.e.*, to the fact that equilibrium 4b lies farther to the right in DMF than does equilibrium 4a in chlorobenzene) rather than to an intrinsically higher reactivity.

$$\mathrm{Ir(CO)(PMe_2Ph)_3^+} + \mathrm{PMe_2Ph} \rightleftharpoons \mathrm{Ir(CO)(PMe_2Ph)_4^+} \quad (5)$$

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[7] We have confirmed that the second-order rate law, $-d[H_2]/dt = k[\mathrm{Ir^I}][H_2]$, previously established for the reaction of H_2 with Ir(CO)-(PPh$_3$)$_2$Cl, applies also to these systems. The kinetic measurements were made by following the reactions spectrophotometrically. Typical initial concentrations were 1×10^{-4} M Ir$^{\mathrm{I}}$ and 2.5×10^{-3} M H_2.

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[12] The rate constant for reaction of Ir(CO)(PMe$_2$Ph)$_2$Cl with H_2 (in the absence of added PMe$_2$Ph) increases by only a factor of two (from 0.36 to 0.68 M^{-1} sec^{-1}) in going from chlorobenzene to DMF. Comparably small solvent effects have been found for reactions of H_2 with Ir(CO)(PPh$_3$)$_2$Cl and with other Ir$^{\mathrm{I}}$ complexes.[4]

Jia-Yong Chen, Jack Halpern*
Department of Chemistry, The University of Chicago
Chicago, Illinois 60637

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Effect of a Single Thymine Photodimer on the Oligodeoxythymidylate–Polydeoxyadenylate Interaction[1]

Sir:

The presence of cyclobutyl-type pyrimidine dimers[2] in DNA produces local distortion of its secondary structure. Evidence for this includes lowering of melting temperature (T_m) and increased reactivity with formaldehyde resulting from uv irradiation of DNA.[3] More specific evidence has been derived from detailed analysis[4] of the action of the 5′ → 3′ exonuclease activity of *Escherichia coli* DNA polymerase in excision and repair of thymine photodimer regions in DNA. The postulated extent of hydrogen-bond disruption includes the photodimer, with its two opposing adenines in the complementary strand, and at least one

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[1] This investigation was supported by the U. S. Atomic Energy Commission and by Research Grant No. GM 16547 from the National Institute of General Medical Sciences.

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of each of the base pairs adjacent to the photodimer.[4] We report here a value for the number of disrupted base pairs, around and including a single photodimer through T_m data obtained from well-characterized model systems.

The oligomers dA_3, dT_2-^3H, dT_4, and dT_5, 5′ terminated by phosphate,[5] were synthesized using both stepwise condensation[6] and polymerization[7] techniques. The oligomer dT_2-^3H was converted to the photodimerized dinucleotide[8] d-ϕT_2, whose cyclobutane-type thymine photodimer consisted, in the purified product, entirely of the cis–syn isomer[9] (as shown by the infrared spectrum of the chromatographed acid hydrolysate[10]). This is the isomer known to form during irradiation of native DNA. Condensation of d-ϕT_2-3′ac with the 5′-(2-cyanoethyl) derivative of dT_4 gave d(T_4–ϕT_2). The 5′-(2-cyanoethyl) derivative of this hexamer was then coupled with dT_4-3′ac giving d(T_4–ϕT_2–T_4). Analysis of the incorporated thymine photodimer content by acid hydrolysis and subsequent chromatography in a number of solvent systems[11] showed that all of the tritium activity was recoverable as the free *cis-syn*-thymine photodimer. The oligomers dT_{10}, dT_8, dT_7, and dT_6 were isolated by anion exchange chromatography of the mixture obtained by lengthening dT_5 through stoichiometry-limited addition[12] of thymidylate units from dTTP catalyzed by calf thymus deoxynucleotidyl terminal transferase.[13] The same enzyme was used to prepare $dA_{\overline{250}}$ from dA_3 and dATP; analytical gel-filtration chromatography[14] using Bio-Gel A-50m (Bio-Rad Laboratories) established the average size of the product. The synthesis of $dA_n \cdot dT_n$ was performed[15] with *E. coli* DNA polymerase. The product was fractionated using Bio-Gel A-50m, and a portion was selected with n averaging 1500 nucleotide units.

Cassani and Bollum[16] studied the oligodeoxythymidylate–polydeoxyadenylate interaction and found 1:1 complexes, but the sizes of oligodeoxythymidylate that gave identifiable T_m values in their solvents did not adequately cover the range we needed for this study. Accordingly, we ran T_m studies[17] in 1.0 M Na^+ (pH 7.0) at a total nucleotide monomer concentration of 130 μM, using $dA_{\overline{250}}$ mixed 1:1 in monomer units with dT_{10}, dT_8, dT_7, dT_6, dT_5, dT_4, or d(T_4–ϕT_2–T_4). Only dT_4 failed to give the characteristic[18] sigmoidal absorbance change with increasing temperature, corresponding to a cooperative separation of the double-stranded interaction structure (the DNA double helix[19]). The results, with the exception of d(T_4–ϕT_2–T_4), are plotted two ways in Figure 1, using n^{-1} as the abscissa and two different temperature scales as ordinates: T_m in degrees Celsius for one plot and $10^3/T_m'$ with T_m' in degrees Kelvin for the other. Also included is the result from $dA_n \cdot dT_n$ in 1.0 M Na^+. The plotted continuous lines are least-squares fits to the two sets of data. For the circles the equation[17] is $T_m = 85.2 - 329n^{-1}$; the triangles give[16] $10^3/T_m' = 2.77 + 3.14n^{-1}$. The T_m of d(T_4–ϕT_2–T_4) mixed with $dA_{\overline{250}}$ was 28.1°; the horizontal dashed lines indicating this temperature value on each of the two ordinate scales intersect their corresponding continuous lines at $n^{-1} = 0.175$ or $n = 5.7$.

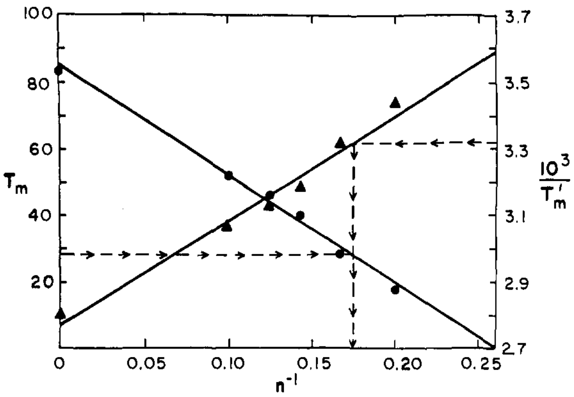

Figure 1. T_m values of the oligodeoxythymidylate–polydeoxyadenylate interaction plotted on two scales against n^{-1} of dT_n. Triangles go with the $10^3/T_m'$ scale, and circles belong to the direct T_m scale.

If the significance of the equivalent n of 5.7 for d(T_4–ϕT_2–T_4) is taken at face value, then 4.3 A·T base pairs have been broken, presumably those two involving the photodimer, plus the nearest adjacent ones on each side, and a 15% weakening in the next, or second, distal pairs. It is not exactly clear whether two groups of base pairs in the same molecule, separated by a noninteracting region of dual single strandedness, would be as stable as the same two paired groups side by side in the same molecule. We believe that there may be less stability because of the separation and conclude from this that $n = 5.7$ is a minimum value for the actual residual hydrogen bonding in d(T_4–ϕT_2–T_4). The distorted region then includes only the two pairs of bases immediately adjacent to the photodimer.

Observations with molecular models agree with the experimental results. A thymine photodimer, replacing the central pair of thymines in a $dA_{10} \cdot dT_{10}$ double helix, slightly lengthens the helix and removes from proximity for hydrogen-bonded base pairing the two adenines opposing the photodimer plus the two immediately adjacent pairs of thymine and adenine. The next two A·T base pairs, adjacent to the four-pair distorted region, form easily with no distortion.

The photodecamer d(T_4–ϕT_2–T_4) is being used in other studies. A report will be forthcoming on its

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F. Newton Hayes,* D. Lloyd Williams, R. L. Ratliff
Biomedical Research Group, Los Alamos Scientific Laboratory
University of California, Los Alamos, New Mexico 87544

A. J. Varghese, Claud S. Rupert
Division of Biology, University of Texas at Dallas
Dallas, Texas 75230

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Organometallic Chemistry. III.[1] Attempted Preparation of Trivalent Silicocations (Silicenium Ions).[2] The Exchange Reaction of Methylfluorosilanes with Antimony Pentafluoride

Sir:

Long-lived stable trivalent carbenium ions have been extensively studied in our laboratories.[3] The analogous trivalent silicocations (trivalent silicenium ions) were proposed as a reaction intermediate in many organosilicon chemical reactions.[4] Furthermore, silicocations have been observed as high-abundance fragment ions in the mass spectra of organosilicon compounds.[5] Attempts to prepare silicenium ions for direct observation in solution were unsuccessful.[6] We presently wish to report our attempts to prepare silicenium ion in extremely low nucleophilicity superacid media in which trivalent carbenium ions are stable and can be directly observed.

The pmr spectrum of trimethylfluorosilane (**1**) in an excess of SbF_5–SO_2ClF at -78° shows a sole singlet absorption at δ 1.35. Compound **1** in SO_2ClF at -78° has a doublet at δ 0.23 (J_{HF} = 8 Hz). The absence of the proton–fluorine coupling in the former indicates the formation of either the trimethylsilicenium ion, $(CH_3)_3{}^+Si$, or the exchanging donor–acceptor complex, $(CH_3)_3SiF \rightarrow SbF_5$. The chemical shift of the observed singlet absorption is relatively shielded compared to that of the *tert*-butyl cation (by 2.7 ppm).[7] In the ^{19}F nmr spectrum, the resonance of **1** is not present any more and only shows a broadened fluoroantimonate absorption at ϕ 110 (1000 ppm width, from $CFCl_3$).[8] Adding more SbF_5 to the above solution did not change either the ^1H or ^{19}F nmr spectra. On the other hand, when excess **1** was added to the solution, the proton singlet absorption became slightly more shielded. The shielded proton shift is proportional to the amount of **1** added. The ^{19}F nmr spectrum is essentially unchanged. But, when **1** was about four times in excess of SbF_5 in SO_2ClF at -80°, the nmr spectrum showed a doublet at δ 0.30 (J_{HF} = 8 Hz) and an overlapping singlet at δ 0.40. The ^{19}F nmr spectrum showed a resonance similar to that of **1** (at ϕ 122.7) and the broadened fluoroantimonate absorption still remained at ϕ 110.0. The nmr spectra of the above solutions were temperature independent ranging from -50 to -80°. Above -50°, a protolytic cleavage reaction occurred (see subsequent discussion).

The above observations indicate that an exchanging donor–acceptor complex of **1** with SbF_5 was formed. Similar complexes were previously found when methyl fluoride, ethyl fluoride, and 1,1-difluoroethane were treated with SbF_5–$SO_2(SO_2ClF)$ solution.[9] The complex formation can explain the absence of proton–fluorine coupling and the observed chemical shifts which depend on the relative ratio of **1** and SbF_5. In the case when **1** was present in fourfold excess to SbF_5, both the exchanging complex, $(CH_3)_3SiF \rightarrow SbF_5$, and **1** were observed. This is also the case in the methyl fluoride–antimony pentafluoride system where an excess of methyl fluoride is observed not to be exchanging with the $CH_3F \rightarrow SbF_5$ complex.[9a]

The solution of dimethyldifluorosilane (**2**) in excess of SbF_5–SO_2ClF gave again a singlet absorption at δ 1.20 in the pmr spectrum and no observable fluorine resonance–resonance corresponding to **2** in the ^{19}F nmr spectrum. If the dimethylfluorosilicenium ion, $(CH_3)_2{}^+SiF$, were formed, the pmr spectrum should show a deshielded doublet. Also, a substantially deshielded fluorine resonance will be expected, as in the case of dimethylfluorocarbenium ion, $(CH_3)_2{}^+CF$.[10] The formation of the donor–acceptor complex, $(CH_3)_2SiF_2 \rightarrow SbF_5$, seems best to explain all experimental observation. By adding more **2** to the above solution, the singlet absorption is shifted to higher field. In the specific case when the molar ratio of **2** to SbF_5 was 2:1, temperature-dependent ^1H and ^{19}F nmr spectra were obtained. In the pmr spectra, the triplet of **2** observed at lower temperature collapsed to a singlet at higher temperature (Figure 1). Similar behavior of pmr spectra has been observed when 2,2-difluoropropane was treated with HF–SbF_5–SO_2ClF superacid system.[9b] In Figure 1 there are also shown the theoretical computed spectra. The lifetimes, τ, of exchanging **2** were obtained from the best fit of experimental and calculated spectra.[11] The energy of activation of the exchange process is estimated to be 6.3 ± 0.8 kcal/mol.

Similarily, when methyltrifluorosilane (**3**) was complexed with SbF_5–SO_2ClF solution, a slightly broadened singlet absorption at δ 0.95 was observed in the nmr spectrum (0.5 ppm deshielded from the precursor). The ^{19}F nmr spectrum shows only the fluoroantimonate resonance. These results do not agree with formation of methyldifluorosilicenium ion, $CH_3{}^+SiF_2$, although

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(8) The ^{19}F nmr spectrum of HF–SbF_5(1:1 mol:mol)–SO_2ClF shows a broadened resonance at ϕ 100 (500–600 ppm width); G. A. Olah and Y. K. Mo, unpublished results.

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