Table I. Apparent Rates of Reaction of *cis*-$[\mathrm{Pt(NH_3)_2Cl(H_2O)}]^+$ with Two DNAs Compared with the Frequency of Occurrence of G and G–G[18]

	M. lysodeikticus	*Cl. perfringens*	*M.l./Cl.p.*
reaction rate (-% free Pt/s)	0.027 ± 0.007	0.016 ± 0.002	1.7 ± 0.7
G	0.35	0.158	2.2
G-G	0.112	0.026	4.3

neighbors[18] and should differ by a factor of 4 (Table I).

An aqueous 0.6 mg/mL solution of *cis*-$\mathrm{Pt(NH_3)_2Cl_2}$ (prepared from $\mathrm{K_2[PtCl_4]}$[19]) was equilibrated for 10 days in the dark at room temperature in order to form the reactive species[2] *cis*-$[\mathrm{Pt(NH_3)_2Cl(H_2O)}]^+$ and *cis*-$[\mathrm{Pt(NH_3)_2(H_2O)_2}]^{2+}$. At zero time a portion of this solution was added to a 0.250-mg/mL solution of *M. lysodeikticus* or *Cl. perfringens* DNA (Sigma) at an R of 0.006 in 10^{-2} M $\mathrm{NaClO_4}$ (Fluka) at 37 °C, pH 5.5–6.0. Aliquots of 0.2 mL were removed every 30 s, added to 0.1 mL of ice-cold 0.9 M sodium acetate (Prolabo), vortexed, mixed with three volumes of ice-cold ethanol (Prolabo), and frozen at −40 °C to precipitate the DNA. The precipitate was centrifuged for 5 min at 12 000 rpm, resuspended in 0.3 mL of 0.3 M sodium acetate, precipitated as above, and centrifuged. The pellet was washed with ethanol, dried under vacuum, resuspended in 0.5 mL of 10 mM $\mathrm{NaClO_4}$, and agitated for 2 days at room temp. to dissolve the DNA. Control experiments in which the reaction with DNA was blocked by the addition of 0.1 M NACl showed that all unreacted platinum was removed from the DNA by this method of precipitation and washing. The concentration of the double-stranded DNA in each aliquot was determined by UV spectrophotometry with a Zeiss PMQII assuming that 10 μg/mL corresponds to $A_{260} = 0.210$. The platinum concentration was measured by using a Perkin Elmer Atomic Absorption Spectrophotometer Model 603 equipped with a graphite furnace, and the percent unreacted platinum in each aliquot was calculated from the measured R bound.

The data in Figure 1 show the change in concentration of unreacted platinum as a function of time for three separate experiments with each DNA. Kinetics were not measured for the fixation of the first 3 platinum per 10^4 nucleotides which bound in a few seconds as a result of the fast reaction[2] with *cis*-$[\mathrm{Pt(NH_3)_2(H_2O)_2}]^{2+}$. It was more difficult to dissolve the precipitated *M. lysodeikticus* DNA than the *Cl. perfringens* DNA which may account for the greater uncertainty of DNA binding in the first case. The data in each experiment were distributed randomly around the best straight line fit as determined by linear regression. Apparent reaction rates (-% free Pt/s) were determined from the slope of this line (Table I).

The ratio of the initial rates of binding shown in Table I was 1.7 ± 0.7 which corresponds to the relative number of guanines in each polynucleotide. Table I also shows the frequency of G–G nearest neighbors in the two DNAs.[18] If the platinum bound exlusively to two adjacent guanines (either bidentate chelation on two neighboring Gs or initial monodentate fixation at one G followed by a slower reaction with the adjacent G), then the rate of the reaction should be 4.3 times greater for *M. lysodeikticus* DNA. Since this value is greater than 3 standard deviations from the observed ratio, the probability that the data in Figure 1 originates from random fluctuations in reactions whose rates differ by a factor of 4.3 is about 10^{-3}.

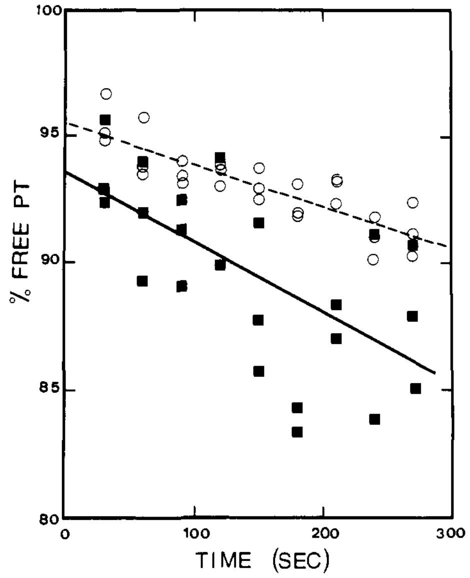

Figure 1. Percent unreacted platinum as a function of time of reaction at 37 °C with *Cl. perfringens* (○) and *M. lysodeikticus* (■) DNA; 0.006 Pt/DNA nucleotide initial molar ratio.

In conclusion, if aquated *cis*-PDD initially reacts with DNA at guanine then the simplest interpretation of our results would be that, in vitro, Pt is fixed at all guanine bases with equal probability. Hence the number of *cis*-PDD bound to adjacent guanines can be no greater than the likelihood of finding a guanine base on one side or the other of the initial site of fixation. This can be estimated as 2P(G) − P(G)·P(G) where P(G) is the percent guanine in the DNA. In vitro binding of a single *cis*-$\mathrm{Pt(NH_3)_2}$- to neighboring guanine bases should occur for no more than 58% of the Pt fixed to *M. lysodeikticus* DNA and 29% of the Pt fixed to *Cl. perfringens* DNA.

Acknowledgment. We thank Dr. J. P. Macquet for the gift of *cis*-PDD and for helpful discussions. This work was supported in part by a grant from l'Association pour le Dêveloppement de la Recherche sur le Cancer.

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Phenylmethylpolysilanes: Formable Silane Copolymers with Potential Semiconducting Properties

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Although silane polymers were apparently obtained by Kipping more than 50 years ago,[1] and permethylpolysilane was prepared as early as 1949,[2] the chemistry of the polymeric polysilanes has been neglected until recently. Yajima and Hayashi's demonstration that permethylpolysilane can be converted in a two-step process to β-SiC fibers[3] has led to a resurgence of interest in these materials.[4-6]

Permethylpolysilane is known only as a highly crystalline intractable solid. In 1978 we reported the use of meltable, partially crystalline silane–dimethylsilane copolymers with dimethyl/phenylmethyl ($\mathrm{Me_2Si/PhMeSi}$) ratios of from 10/1 to 3/1 as impregnating agents for strengthening silicon nitride ceramics.[7] The ceramic body is soaked in a melt of the polymer and then fired, leading to formation of β-SiC threads in the pore spaces with consequent strengthening of the ceramic.

We now find that crystallinity is greatly reduced at lower $\mathrm{Me_2Si/PhMeSi}$ ratios, with a minimum near the molar ratio 1/1.

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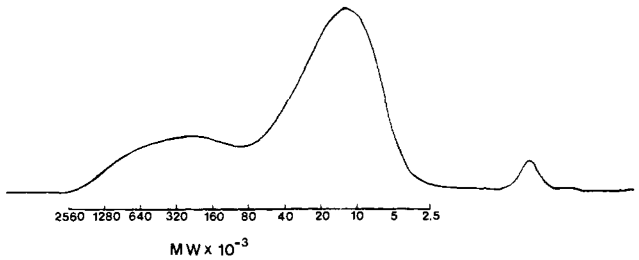

Figure 1. Elution profile from gel permeation chromatography of phenylmethylpolysilane, $Me_2Si/PhMeSi = 1$. For calibration see ref 8.

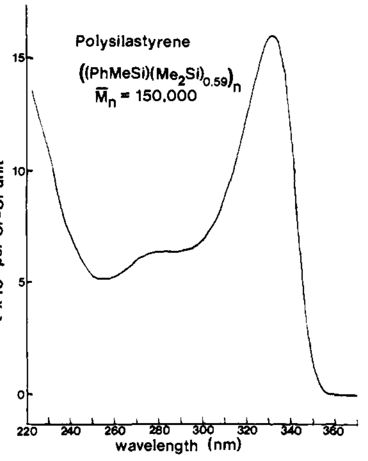

Figure 2. Ultraviolet spectrum of phenylmethylsilane polymer with $\bar{M}_n = 150\,000$ and $PhMeSi/Me_2Si = 0.59$.

These polymers are produced by cocondensation of the two organosilicon dihalides:

$$Me_2SiCl_2 + PhMeSiCl_2 \xrightarrow[\text{toluene}]{\text{Na}} \underset{90-100\ ^\circ C}{} -[(PhMeSi)_x(Me_2Si)]_y- + NaCl$$

The polymers so obtained are similar to conventional carbon-based, amorphous linear polymers in that they are soluble in many organic solvents (benzene, toluene, chlorocarbons, tetrahydrofuran), fuse to a viscous liquid (near 200 °C) without decomposition, and can be molded, cast into films, or drawn into fibers.

The cocondensation results in polymer with a broad range of molecular weights. Typically about 30% of the product consists of low molecular weight compounds, including cyclic oligomers, which may be removed by extraction with hexane or dissolution in THF and precipitation of polymer with methanol. A small amount (5–10%) of insoluble material is also formed. An elution profile of a gel permeation chromatograph for a polymer sample, after removal of the oligomers and insoluble fraction, is shown in Figure 1; a bimodal molecular weight distribution as in Figure 1 is commonly observed.[8]

Further fractionation of the polymer according to composition and molecular weight can be accomplished by precipitation with 2-propanol from THF solution. The bulk of the polymer has a $Me_2Si/PhMeSi$ composition ratio near 1, but the fractions of highest molecular weight are phenyl rich, with ratios near 0.6.

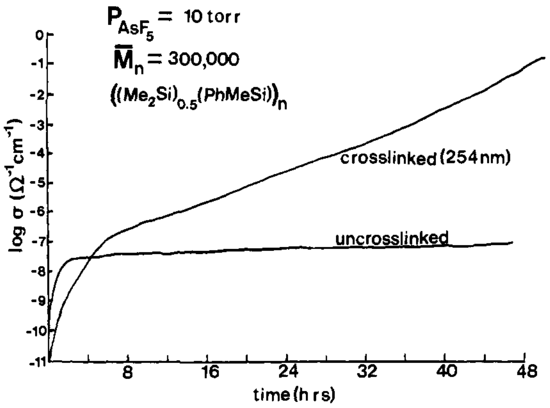

Figure 3. Plot of conductivity vs. time for phenylmethylpolysilane samples, $\bar{M}_n = 300\,000$, $PhMeSi/Me_2Si = 0.5$, exposed to 10 torr of AsF_5.

Samples with $\bar{M}_n = 300\,000$ can be obtained, representing chain lengths of >3000 silicon atoms. The mass spectrum of the polymer shows $SiPhMeSiMe_2^+$, $(SiMe_2)_2^+$, and $(SiMePh)_2^+$ fragments in roughly equal intensities; the material therefore appears to be a random rather than an alternating or block copolymer.

Characteristic of this polymer is strong ultraviolet absorption near 330 nm, with $\epsilon = 8000$ *per silicon atom* (Figure 2). The polymer is also photoactive in the ultraviolet. In solution, irradiation at frequencies of 350 nm or less leads to chain cleavage (as shown by incremental decrease with radiation exposure of the molecular weight as determined by GPC). In bulk samples, however, irradiation converts the polymer to an insoluble but swellable form, with higher modulus and greater elastic recovery, indicating that cross-linking has taken place.

Like other polysilanes, the phenylmethylsilane polymer undergoes conversion to silicon carbide when heated to high temperatures. Photo-cross-linking is important for maintaining structural strength during the firing. Thus cross-linked fibers of the polymer mounted vertically and heated under argon to 1100 °C maintained their shape during the transformation to SiC.[9] Conversion to an intermediate carbosilane polymer, as described by Yajima and co-workers,[3] is unnecessary.

The new polymer also appears to become semiconducting upon contact with strong electron acceptors such as SbF_5; it may therefore resemble other polymers which can be made conducting in the presence of dopants, such as polyacetylene,[11] poly(*p*-phenylene),[12] poly(*p*-phenylene sulfide),[13] and polypyrrole.[14] Typical results for linear and cross-linked polymer samples are shown in Figure 3. The polymer is initially insulating with $\sigma < 10^{-11}\ \Omega^{-1}\ cm^{-1}$. The conductivity of the un-cross-linked polymer increases rapidly in the presence of 10 torr of AsF_5 and then levels off near $10^{-7}\ \Omega^{-1}\ cm^{-1}$. Under the same conditions the conductivity of the cross-linked polymer increases more slowly but eventually reaches a much higher level of $\sim 0.5\ \Omega^{-1}\ cm^{-1}$; maximum con-

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(8) Gel permeation chromatography was carried out on Microstyragel columns (porosity ranges 10^2, 5×10^2, 10^3, 10^4, 10^5, ,and 10^6 Å), with tetrahydrofuran as the eluant. The GPC was calibrated as follows: Elution volumes were determined for a series of polystyrene standards of known molecular weight. The product of molecular weight, *M*, times intrinsic viscosity, η, was calculated from the equation derived by Benoit et al.[9]; a plot of log ($M[\eta]$) vs. elution volume, *V*, yielded a straight line, (log $(M[\eta]) = 0.238V = 16.5$). The intrinsic viscosity of various polysilane fractions of different molecular weights were then determined in the usual way, and the molecular weights were obtained from the Benoit plot. The information was used to calibrate the GPC curve in Figure 3. The elution volumes for polystyreme samples are very similar to those for polysilane fractions of equal molecular weight determined in this way.

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ductivity at higher AsF_5 pressures has not been determined. We believe that this conductivity may be of a novel type involving loss of an electron from Si–Si bonding orbitals and delocalization of the cation radical (=hole) through the σ system.[15]

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Soluble Copper Hydrides: Solution Behavior and Reactions Related to CO Hydrogenation

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Recent mechanistic studies of synthesis gas (CO + H_2) reactions of the early transition elements have led to the consensus that such reactions are thermodynamically driven by the formation of strong metal–oxygen bonds.[1-5] Since such bonds appear to resist reduction by either H_2 or CO, these studies remain stoichiometric, not catalytic. We have in the past[6] and are continuing at present to move later in the transition series in search of information on reactivity trends of metals more relevant to commercial synthesis gas catalysts. Essentially all of the methanol produced industrially results from the heterogeneously catalyzed hydrogenation of carbon monoxide, much of it with a "low pressure" catalyst composed of copper and zinc oxides.[7] Motivated by this fact, the carbonyl chemistry of Cu(I) has undergone substantial recent development in the hands of Floriani and his associates.[8] In addition, a comprehensive study of a heterogeneous Cu/Zn methanol catalyst led to the conclusion that it functions by CO activation on Cu(I) and hydrogen activation on Zn(II).[9,10] Nevertheless, "activation" of H_2 may well be the more critical act than activation of CO (consider the great variety of transition-metal hydride complexes, from acidic to "hydridic"), and yet we know nothing about the spectroscopic, structural, and reactivity characteristics of copper hydrides.[11] We have therefore begun to explore the chemistry of carbonyl and hydride complexes of both Cu(I) and Zn(II).

Hydrocarbon-soluble copper/hydride/phosphine complexes were synthesized by the procedure in reaction 1, which is based on the original procedure of the Osborn group.[12] The latter showed that $x = 6$ for $R = C_6H_5$ by means of an X-ray diffraction study. The Cu_6P_6 portion of the hexamer is mildly distorted from regular octahedral symmetry by shrinkage of 6 of the 12 Cu–Cu distances. The hydrides were not detected by X-ray[12] or NMR[11,12] methods, and their existence and number was based on quantitative gas evolution studies upon acidolysis.[11,12] Our examination of the ^1H NMR spectrum (220 MHz) of $[HCuP(tol)_3]_n$ revealed (in addition to C_7H_7 resonances) a broad but structured multiplet centered on δ +3.50 in C_6D_6. Addition of CCl_4 to this solution causes the δ 3.5 resonance to disappear as $CHCl_3$ grows in,[13] and a white solid, identified as $[CuClP(tol)_3]_4$, precipitates. Under conditions of higher radio frequency power, the signal-to-noise ratio on the δ 3.5 multiplet is improved to the point where at least five components of a septet are resolved.[14a] Phosphorus decoupling of the 220-MHz ^1H NMR spectrum collapses the hydride multiplet to a singlet, thereby excluding Cu as the source of this multiplet structure. These results establish $(HCuP(tol)_3)_6$ as intramolecularly fluxional (presumably by hydride migration) and also show that the hydride chemical shift of the d^{10} species returns to the "normal" chemical shift region in comparison to the negative δ values found for complexes with partially filled d shells. Zirconium(IV)[1] and W(VI)[15] hydrides (both d^0) and also Zn(II) (see below) hydrides have chemical shifts downfield of Me_4Si.

$$(1/4)(ClCuPR_3)_4 + LiEt_3BH \rightarrow (1/x)(HCuPR_3)_x + LiCl + BEt_3 \tag{1}$$

$$R = C_6H_5,\ p\text{-}MeC_6H_4\ (\text{"tol"}),\ O\text{-}i\text{-}Pr$$

$(HCuP(tol)_3)_6$ is not hydrolyzed by excess methanol in benzene in 24 h. The ^1H NMR spectrum of a C_6D_6 solution of this complex in the presence of equimolar $P(tol)_3$ is the superposition of the spectra of the two components (the ring protons of free and coordinated phosphine are readily resolved); the hydride resonance maintains its line width and multiplicity. This establishes that phosphine exchange (and thus phosphine dissociation from the hexamer) is slow on the ^1H NMR time scale *and* that, under these conditions, the hexamer is resistant to phosphine attack and fragmentation into $[HCu(PR_3)_2]_x$ clusters or monomers;[14b] the halo clusters $(CuClPR_3)_4$ are known to fragment under these conditions.

We have examined the reaction of $(HCuP)_6$ $[P \equiv P(tol)_3]$ with formaldehyde as a representative of an intermediate carbon oxidation level on the path of CO hydrogenation.[16] Using either gaseous formaldehyde monomer or polymeric paraformaldehyde, $(HCuP)_6$ catalyzes the conversion of the aldehyde to methyl formate[17] in benzene at 25 °C. This reaction[18] (reaction 2), a *disproportionation* of aldehyde to the alcohol and carboxylate oxidation levels, is known as the Tishchenko reaction when it is catalyzed by main group or transition-metal alkoxides.[19] This suggests that the initial reaction of $(HCuP)_6$ with formaldehyde might be reduction of the latter to a copper methoxide (reaction 3). Consistent with this is the observation (by ^2H NMR spec-

$$2H_2CO \xrightarrow{(HCuP)_6} HC(=O)OCH_3 \tag{2}$$

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