unable to preferentially hydrolyze a silicon–halogen bond of I or II to give a pentachlorophenyl-substituted silanol or siloxane.

We have examined the reactions of both I and II with sodium in xylene and magnesium in THF in attempts to prepare pentachlorophenyl-substituted polysilanes. All that has so far been obtained are black carbonaceous materials in which traces of pentachlorobenzene could be detected by VPC. Similar results were obtained when attempts were made to react I and II with either phenyllithium in ether, or phenylmagnesium bromide in THF. Details of these and related studies will be published at a later date.

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Electronic spectra of allylic palladium complexes

The way in which an allyl moiety may be bound to a palladium atom in allylic palladium complexes depends on the nature and disposition of the other ligands attached to the metal. This conclusion is based largely[1–5] on NMR spectral studies* and changes from the non-classical** π-geometry to "asymmetric" π-modifications have been recognised. In addition, spectra of some simple allyl types, under certain conditions[2–5], appear to demand the existence of a σ-species, to rationalise proton-equilibration phenomena. Such variations in allyl–metal bonding imply concomitant variations in the extents of delocalisation (or localisation) of the π-electrons of the allyl group. Provided an electronic transition originating in part from the allyl ligand could be recognised then such bonding variations should be manifested in spectral changes. Consequently, we have obtained the spectra[7]*** of a variety of allylic,

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* Asymmetry in the triphenylphosphine complex of β-methallyl PdCl has been established by an X-ray investigation[6a]. However, conformational changes apparently occur on dissolution of the chloro-bridged dimers in organic solvents, since quite large dipole moments have been observed, and considerable deformation from the centro-symmetric solid state configuration is indicated. For a more complete discussion see ref. 6b.

** The non-classical description was first applied by Chien and Dehm (ref. 1) to indicate a delocalised π-allyl group. In carbonium ion chemistry, an ion is usually considered to be non-classical if ground-state delocalisation of σ-bonding electrons has occurred.

*** Ultra-violet spectra of a number of allylic palladium complexes have been recorded previously[7] but no interpretation or analysis of the data was attempted. Most possessed structural features in the allylic ligand that could cause interpretative difficulties. Where comparisons are possible, reasonable agreement is obtained.

TABLE 1

ELECTRONIC SPECTRA OF ALLYLIC PALLADIUM COMPLEXES

Palladium chloride complex	*Solvent*	λ_{max}	*log* ε	λ_{max}	*log* ε
π-Allyl PdCl	$CHCl_3$	325	3.06	245	4.00
π-β-Methallyl PdCl	$CHCl_3$	327	2.99	241	3.98
π-Crotyl PdCl	$CHCl_3$	327	3.18	244	4.05
π-Cinnamyl PdCl	$CHCl_3$	352	3.39	290, 242	4.06, 3.83
Allyl PdCl $P\Phi_3$	$CHCl_3$	323	3.60	243	4.30
β-Methallyl PdCl $P\Phi_3$	$CHCl_3$	319	3.64	243	4.28
Crotyl PdCl $P\Phi_3$	$CHCl_3$	322	3.72	248	4.25
Cinnamyl PdCl $P\Phi_3$[a]	$CHCl_3$	350	4.06	290, 242	4.18, 4.24
Allyl PdCl $As\Phi_3$	$CHCl_3$	324	2.50	243	4.35
β-Methallyl PdCl $As\Phi_3$	$CHCl_3$	323	2.50	243	4.30
Crotyl PdCl $As\Phi_3$	$CHCl_3$	324	2.53	246	4.32
Cinnamyl PdCl $As\Phi_3$[a]	$CHCl_3$	352	3.90	294, 248	4.17, 4.17
Allyl PdCl	DMSO	316	3.35	258	3.95
β-Methallyl PdCl	DMSO	309	3.47	258	3.90
Crotyl PdCl	DMSO	309	3.56	258	4.00
Cinnamyl PdCl	DMSO	352	3.89	284	4.18, 4.12
Allyl PdCl	EtOH	324	3.25	237	3.90
β-Methallyl PdCl	EtOH	327	3.25	229	3.91
Crotyl PdCl	EtOH	328	3.27	232	3.40

[a] Generated *in situ* by mixing equimolar amounts of the components.

palladium complexes (Table 1), in several solvents, to probe these bonding variations and to allow suggestions concerning the origin of the transitions.

Certain features of the spectra require comment. Chloroform solutions (where the π-constitution exists) of the yellow complexes – allyl-, β-methallyl- and crotyl-palladium chlorides – exhibit two observable absorption maxima, neither of which possessed fine structure. The lower energy (325 mμ) band is a broad envelope with $\varepsilon_{max} \sim 10^3$. The presence of a conjugating phenyl group, as in π-cinnamylpalladium chloride* results in a pronounced bathochromic shift** (*ca.* 25 mμ) and a significant intensity increase*** and the responsible chromophore would appear to encompass the π-allylic ligand. The ε_{max} value of $\sim 10^3$ appears to suggest an electronically allowed transition, and the band width is not inconsistent with a charge transfer description. The more intense ($\varepsilon_{max} \sim 10^4$) sharper 242 m$\mu$ band is insensitive to phenyl substitution and a transition involving electrons essentially localised on the metal atom may be responsible. Support for this conclusion is derived from the observation[8] that tetraethylammonium tetrabromopalladate in methanol displays a relatively sharp band at 241 mμ with $\varepsilon \sim 10{,}500$. On increasing the solvent donor strength (H_2O) this band undergoes a hypsochromic shift of *ca.* 14 mμ[8]. In the present case, a similar blue shift of *ca.* 12 mμ was observed on changing from chloroform to ethanol. In coordinating donor media, such blue shifts apparently indicate a change in the ligand

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* NMR studies support the π-formulation (unpublished results).

** Shaw has observed (ref. 7) in a number of cases that α,β-unsaturation in the π-allylic ligand results in a pronounced bathochromic shift.

*** *Sensu strictus*, the significant quantity for comparing the transition intensities is the oscillator strength. However, for the compounds studied, comparisons of ε_{max} values are reasonably valid, since the band shapes and widths were essentially invariant.

stereochemistry from the presumed square planar array ($4d5s5p^2$ hybridsation of Pd orbitals) to a distorted octahedral network (additional 5p,5d involvement).

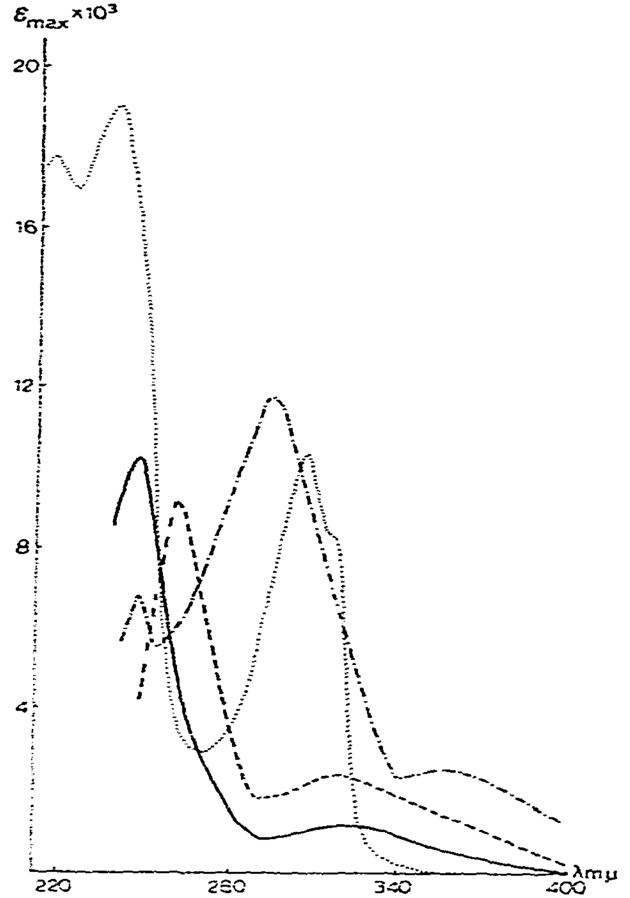

Fig. 1. Electronic spectra of allylic palladium complexes: . . . . ., $[\text{allyl Pd Bipy}]^+\text{Cl}^-\cdot\text{H}_2\text{O}$; —·—·—, π-cinnamyl PdCl/$CHCl_3$; ——, π-allyl PdCl/$CHCl_3$; – – – –, π-allyl PdCl/DMSO.

Definite assignment of the transitions does not appear possible at the present time, since no complete treatment of the bonding in these complexes has appeared. A conceptually attractive picture involves interaction of a Pd^{II} site with a four-electron allylic anion chelating donor. Only very crude estimates of metal and ligand orbital energies have been suggested[9], but nevertheless indicate that maximum overlap is achieved by interaction of the Ψ_1 and Ψ_2 MO's of the allyl group with the metal orbitals, resulting in σ and π contributions to the bonding.

A result of some interest is the almost complete insensitivity of the 325 mμ band to the presence of the π-bonding phosphorus ad arsenic ligands. However, the actual shapes of the bands were essentially invariant, suggesting the persistence of the same chromophore. In contrast ε_{max} values fluctuate and are seen to increase on phosphorus complexation but decrease on arsenic complexation. Whether the variations in donor and acceptor tendencies in the two cases is the complete answer is unclear, although proton NMR studies[10] of the allyl moiety in those systems indicate differing degrees of perturbation by the Φ_3P and Φ_3As ligands, as would be expected from the known trans effect behaviour of these ligands[11].

Since the suggestion has been made[2] that simple allylic palladium chlorides in DMSO possess a σ-bound allyl group, it seemed that such a pronounced structural reorganisation would modify the electronic spectrum. The data (Table 1) show a hypsochromic shift of *ca.* 16 mμ in the charge-transfer band, with a concomitant increase in $\varepsilon_{\max}$, while the band originally at 244 mμ in chloroform has undergone a bathrochromic shift of *ca.* 14 mμ with essentially no change in $\varepsilon_{\max}$. These changes for the allyl, β-methallyl and crotyl cases indicate some perturbation of the chromophore, although the band shapes are unchanged. In this π-bonding medium (S may be presumed to be the donor atom) an octahedral ligand disposition about Pd probably prevails and this may well account for any spectral changes, although the intimate details are unclear. Of course, octahedral geometry could be achieved without rupture of the π-geometry of the allyl group.

Recently a series of ionic allylic palladium complexes of the type $[\text{allyl Pd Bipy}]^+\text{Cl}^-$ was reported[12], although only meagre spectral information was presented. The NMR spectrum of the simple allyl compound (in D_2O) indicates retention of the π-constitution[13]. The ultra-violet characteristics of the colorless allyl, β-methallyl- and crotyl-derived bipyridyl complexes are very similar, exhibiting absorption maxima (H_2O) at 304 mμ ($\log \varepsilon \sim 4.0$); 236 m$\mu$ ($\log \varepsilon \sim 4.27$) and 214 m$\mu$ ($\log \varepsilon \sim 4.20$). The *ca.* 324 m$\mu$ band in the chloro-bridged dimers is absent*. In organic solvents, 2,2'-bipyridine itself absorbs at 283 mμ and 245 mμ[14], characteristic of the *trans* form. The band at 304 mμ in the allylic palladium bipyridine complexes is quite similar in location to that in $[\text{Ni(bipy)}_3]\text{Cl}_2\cdot 7\text{H}_2\text{O}$[15] and is clearly indicative of chelation. However, the splitting of the 308 mμ band in the nickel complex (vibrational fine structure)[15] is blurred in the palladium complex and may suggest some departure from planarity in the bipyridine ligand.

Other aspects of the chemistry and constitution of allylic palladium complexes are currently under study.

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* The charge transfer band (located at 325 mμ in the chloro-bridged dimers) has suffered a presently indeterminable hypsochromic shift, and a referee has suggested that it may be concealed beneath the 304 mμ bipyridine band. Since intensity considerations cannot resolve this possibility ($\varepsilon_{\max}$ values for bipyridine absorptions in metal complexes depend on the particular metal atom) it is not clear that a charge transfer band is present in the spectrum and this would indicate metal-ligand charge transfer to be energetically prohibitive in these ionic complexes.

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Decamethylcyclopentasilane and tetradecamethylcycloheptasilane

The cyclic perphenylpolysilanes $(Ph_2Si)n$ where $n = 4$–6 are known and have recently been well characterized[1–5]. However, the only known cyclic permethylpolysilane is the six-membered ring species, dodecamethylcyclohexasilane. This compound was first prepared by Burkhard[6] and later synthesized in better yields by Stolberg[7], Gilman[8], and others. Attempts to obtain other cyclic compounds in the permethyl series have been unsuccessful*, but Gilman and Tomasi have reported observation of additional peaks thought to be due to cyclic species in gas chromatography of $[Si(CH_3)_2]_{\geq 6}$[8].

We now report the synthesis and characterization of the five and seven membered cyclic species, decamethylcyclopentasilane and tetradecamethylcycloheptasilane. These compounds are present in small amounts in the dodecamethylcyclohexasilane prepared from dimethyldichlorosilane and sodium–potassium alloy according to the method of Stolberg[7]. We consistently found 3–5 % of $Me_{10}Si_5$ and 1–2 % of $Me_{14}Si_7$ along with $Me_{12}Si_6$ in the crystalline fraction obtained from this reaction. However, detection and separation of these new cyclic compounds was greatly aided by the fortuitous discovery that the amounts of both 5- and 7-membered cyclosilanes are much increased if the initial reaction product is worked up immediately after addition of Me_2SiCl_2 is completed, without refluxing. Upon mild hydrolysis and filtration both high polymer and crystalline solids were obtained; the latter consists of about 20–27 % $Me_{10}Si_5$, 70–75 % $Me_{12}Si_6$, and 4–5 % $Me_{14}Si_7$. If desired, the cyclopentasilane content of a given sample can be further increased by slow vacuum sublimation. The ultimate separation is best made by preparative gas chromatography of a hydrocarbon solution of the cyclic compounds**.

Both $Me_{10}Si_5$ and $Me_{14}Si_7$, like $Me_{12}Si_6$, showed only singlet proton NMR absorption, indicating that all of the hydrogens in each compound have identical environments on a time-average basis. Ultraviolet spectra of the two new compounds are also closely similar to that of $Me_{12}Si_6$[9]; $Me_{10}Si_5$ shows $\lambda_{max} = 210$ mμ (shoulder on end absorption), 261 mμ ($\varepsilon = 1100$) and 272 mμ ($\varepsilon = 970$), while $Me_{14}Si_7$ shows $\lambda_{max} =$

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[*] Decamethylcyclopentasilane may have been synthesized in the laboratories of M. Kumada by another route, but the sample was not obtained in pure form. Private communication from M. Kumada.

[**] Good separations were obtained using a 3/8″ × 25′ column packed with 30 % SE-30 silicone on chromosorb W, and a helium flow rate of 150 cc/min.