should not be attempted because of excessive temperatures and pressures encountered during the exothermic reaction which takes place on warming the charged reactor to room temperature. Reactors must be passivated with fluorine at the temperature and pressure to be used, and, in general, all of the safety considerations involved in handling fluorine and interhalogen compounds must be observed.

Preparation of Chlorine Pentafluoride.—Potassium chloride (0.25 mol) was placed in a 1-l. stainless steel cylinder. The cylinder was attached to a metal vacuum line and fluorine (1.25 mol) condensed in at −196°. After warming to room temperature (*caution: extreme exotherm occurs at or near room temperature*), the reactor was heated in a 200° oil bath for 8 hr. After cooling to ambient temperature, the cylinder was attached to the vacuum line and cooled to −134°. The excess fluorine was slowly bled through a −134° trap into a −196° trap. When pressure in the system had equalized, the fluorine trap was closed (the excess fluorine may be reused or disposed of) and the residual fluorine was pumped out. The −134° trap and the reaction cylinder were warmed to ambient temperature and their volatile contents were transferred to a stainless steel storage cylinder.

The product was identified as chlorine pentafluoride by its infrared bands at 732 and 786 cm^{-1}.[16] No evidence for chlorine trifluoride was noted in the infrared spectrum of the majority of the samples. Molecular weight determinations by the vapor density method gave a value of 126 ± 2.5 (95% confidence limits) (calculated value, 130.45).

The high-resolution ^{19}F nmr spectrum of the product was in close agreement with the values reported in the literature.[11]

X-Ray powder patterns of the solids remaining in the reactor showed the presence of KF and $KClF_4$.

Preparation of Bromine Pentafluoride.—In the manner described above, potassium bromide (0.02 mol) and fluorine (0.12 mol) were charged to a 150-ml Monel cylinder. While warming to room temperature, an exothermic reaction occurred. The reactor was kept at room temperature overnight. The product was then separated from excess fluorine by passage through a −134° trap, the reactor being heated to 60° at the end to drive off any product adsorbed on the solids The product was then transferred to a storage cylinder. The in-hand yield was 46.5% based on KBr charged. The product was identified as bromine pentafluoride by its infrared bands at 587, 644, and 683 cm^{-1}.[16] The vapor pressure of the product at 28° was 464 mm (lit. value,[14] 461 mm at 28°).

X-Ray powder patterns of the solids remaining in the cylinder showed the presence of KF and $KBrF_4$.

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Nuclear Magnetic Resonance Studies of Styrene Derivative Complexes of Platinum

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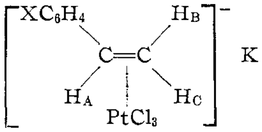
Received June 14, 1968

Proton magnetic resonance spectra of styrene derivative complexes of platinum have been studied. Their ethylenic protons show weakly coupled ABC spectra with ^{195}Pt satellites, readily giving values of three chemical shifts and six coupling constants for each complex. The general experimental trends are similar to those for homologs of Zeise's salt reported by Fritz, *et al.*,[2] and for dichloro(pyridine 1-oxide)olefin- (and -alkyne-) platinum(II) complexes by Kaplan and Orchin.[3]

The ethylenic protons are designated as in I. The



I, X = *p*-CH_3O, *p*-CH_3, H, *p*-Cl, *m*-NO_2, *p*-NO_2

X's are substituents for styrene with electron-releasing and -withdrawing character of differing strength. The magnetic parameters were determined by an iterative method similar to Swalen and Reilly's[4] and are collected in Table I. Figure 1 is plots of the ethylenic proton shifts *vs.* Hammett's σ constants for the substituents. The shifts are given in cycles per second downfield from TMS at 60 Mc. The relative signs of the coupling constants J_{AB}, J_{AC}, and J_{BC} were found to remain the same in the complexes by the field-sweep double-resonance technique.[5]

Upon complexing, the ethylenic protons show upfield shifts, and the coupling constants among them decrease. The coupling constants between the platinum and the protons are of the order of 70 cps. Although it is difficult to advance a quantitative explanation of the electronic structure of the complexes from these data alone because of the complexity of chemical shift and nuclear spin–spin coupling,[6] it is worthy of notice that the values of J_{Pt-H} are comparable in magnitude to those in alkylplatinum complexes,[7] where the carbon is σ bonded to the platinum through an sp^3 orbital of the carbon. The large coupling can be ascribed to rehybridization from sp^2 to some sp^3 character of the carbon atoms and concomitant displacements of the ethylenic protons away from the platinum atom, as suggested by Braterman.[8] The slight saturation of the double bond by complexing with platinum may be partly responsible also for the increased shielding and decreased coupling of the ethylenic protons on complexing. Furthermore, it is seen in Figure 1 that polar effects of the substituents on the shifts of the ethylenic protons are generally lessened by complexing. This may also be considered to reflect the decreased transmission of the polar effects due to less double-bond character of the exocyclic bond in the complex. In the case of H_A, this mechanism cannot be responsible. However, the change of the

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TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS

Sub-stituent	Complex: Chemical shifts[a] δ_A	δ_B	δ_C	Coupling constants[b] J_{AB}	J_{AC}	J_{BC}	J_{A-Pt}	J_{B-Pt}	J_{C-Pt}	Free Ligand: Chemical shifts[a] δ_A	δ_B	δ_C	Coupling constants[b] J_{AB}	J_{AC}	J_{BC}
p-CH_3O	370.1	284.0	245.4	13.6	8.5	0.7	73	61	70	400.8	338.1	304.3	17.5	11.1	1.1
p-CH_3	371.9	288.7	250.1	13.9	8.5	0.7	74	61	69	402.6	343.7	309.1	17.6	10.8	1.1
H	372.6	290.9	252.4	13.8	8.5	0.7	74	61	69	404.9	347.8	313.2	17.7	11.0	1.1
p-Cl	369.4	289.6	254.2	13.7	8.5	0.6	74	60	68	406.7	349.0	315.8	17.9	11.0	0.9
m-NO_2	372.8	297.4	261.3	13.0	8.1	0.3	75	60	67	414.3	362.1	327.5	17.7	10.9	0.5
p-NO_2	373.3	294.9	260.5	13.2	8.3	0.3	75	60	67	414.2	364.1	331.3	17.6	11.1	0.6

[a] In cps downfield from TMS as internal standard at 60 Mc. [b] In cps.

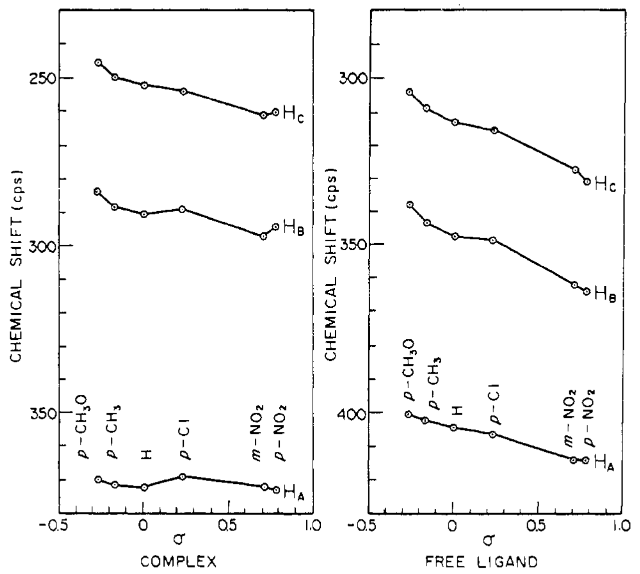

Figure 1.—Plots of vinyl proton chemical shifts *vs.* Hammett constants.

TABLE II

PREPARATION OF STYRENE–PLATINUM(II) COMPLEXES

X[a]	Molar ratio[b]	Yield, %	Color	Molecular formula	Analyses, %: C Calcd	C Found	H Calcd	H Found	N Calcd	N Found
H	1:3.5	59	Orange-yellow	$C_8H_8Cl_3KPt$	21.60	21.45	1.81	2.02		
p-CH_3O	1:2.8	53	Reddish yellow	$C_9H_{10}OCl_3KPt$	22.76	22.54	2.32	2.23		
p-CH_3	1:3.0	84	Reddish yellow	$C_9H_{10}Cl_3KPt$	23.56	23.74	2.20	2.43		
p-NO_2	1:1.8	48	Orange-yellow	$C_8H_7O_2NCl_3KPt$	19.61	19.55	1.44	1.68	2.86	3.03
m-NO_2	1:1.8	61	Orange-yellow	$C_8H_7O_2NCl_3KPt$	19.61	19.43	1.44	1.60	2.86	2.98
p-Cl	1:1.8	60	Orange-yellow	$C_8H_7Cl_4KPt$	20.05	19.86	1.47	1.73		

[a] Substituent in $KXC_6H_4CH{=}CH_2 \cdot PtCl_3$. [b] Ratio of Zeise's salt to the styrene component.

charge density at the α-carbon atom due to electron-releasing or -withdrawing substituents in styrenes may be partly compensated by correspondingly excessive donation or back-donation on complexing, and the substituent effects on H_A shifts become less conspicuous in the complex.

Kaplan and Orchin[3] point out that the substantial difference between the coupling constants J_{Pt-H} for H_B and H_C is surprising in view of the probable spatial equivalence of both protons to the metal, and they correlate the magnitudes of the coupling constants simply with the distances from the metal. Nuclear spin coupling is, however, dependent upon several still unknown factors of both signs even for very simple systems.[9] Thus this much difference in the coupling constants is not necessarily surprising even if H_B and H_C were exactly equivalent to platinum, since the C–H_B and C–H_C bonds have different electronic structures, being *cis* and *trans* to the phenyl group. Furthermore it may be hazardous to conclude that protons having larger coupling constants are closer to platinum. Rather chemical shift is likely to be a simpler function of the proximity to platinum, and accordingly H_B and H_C may be closer to the metal than H_A, as suggested by Fritz.[2] This inference is still somewhat inconclusive, because an X-ray study[10] on a similar compound, $[(C_6H_5CH{=}CH_2)PdCl_2]_2$, does not explicitly indicate the positions of the protons.

Experimental Section

Styrene was used after redistillation. Styrene derivatives were prepared by the methods previously reported,[11–14] and their platinum(II) complexes were prepared by a modification of Anderson's procedure.[15] Zeise's salt[16] (0.3 g) was allowed to react with styrene (0.3 g) dissolved in ethanol (20 ml) in the atmosphere of nitrogen under reduced pressure which was gradually lowered from 100 to 15 mm for 2–3 hr at 30°, and finally the alcohol and an excess of the styrene were distilled off. The dark yellow residue was dissolved in an aqueous solution of 4% hydrochloric acid and the solution was treated with a little charcoal. The filtrate was concentrated in a vacuum desiccator containing concentrated sulfuric acid and potassium hydroxide pellets. Deep orange-yellow needles were filtered, washed with ether, and dried *in vacuo*.

Other styrene complexes were prepared similarly from the corresponding styrene derivatives. Use of a large excess of styrene components was rather unfavorable owing to the formation of resinous substances. The molar ratios of Zeise's salt to styrene components which gave the best yield, together with the properties and analyses of the platinum complexes prepared, are summarized in Table II. In the case of *p*-nitro-, *m*-nitro-, and

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p-chlorostyrenes, the above procedure performed under reduced pressure was repeated twice to complete the exchange reaction by supplying the alcohol evaporated during the first cycle. All of these complexes had no water of crystallization, and their acetone-d_6 solutions remained unchanged for 1 day at least. These complexes were all prepared in solution previously by Joy and Orchin[17] by cleavage of the respective dimers. However, they were not isolated or characterized.

The nmr spectra were obtained using a JNM-3H-60 spectrometer at 60 Mc and 25° and calibrated by the usual audiomodulation side-band technique. At least 10 sweeps were recorded for each spectrum, and 0.3 *M* solutions in acetone-d_6 were used with TMS as internal standard.

Acknowledgments.—The authors are pleased to acknowledge valuable discussions with Professor Y. Kato. Expenses for the purchase of the spectrometer were defrayed by the Ministry of Education.

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Reaction of Aluminum Trimethyl with Halomethylsilanes

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Received June 19, 1968

The reaction of trialkylaluminum compounds with the halides of groups III–VI of the representative elements has been extensively reported in the literature.[1] In all cases where the reaction proceeds, it occurs readily on mixing the reactants at ambient temperature. If the reaction does not go at ambient temperature, heating to the boiling point of the reactants has no effect. The presence of sodium or potassium chloride has been found to make the reaction more satisfactory by complexing the aluminum chloride formed. Inert diluents such as hexane, benzene, and mineral oil have been used to moderate the reaction and to absorb the heat of reaction. During a series of preparative reactions of the group IV tetramethyl compounds, it was found that silicon tetrachloride did not react with aluminum chloride under the usual reaction conditions. A search of the literature showed reference[2] only to the reaction being carried out at 300° in an autoclave. Since aluminum trimethyl decomposes below this temperature, the latter reaction appears to be a free-radical attack of the methyl group, different from the ambient temperature mechanism. As a result of the unexpected inertness of silicon tetrachloride, the reactivity of a number of chloro- and bromo-substituted methylsilanes was studied. These are listed in Table I with the indicated result. Of the compounds studied only trimethylchlorosilane showed reactivity.

TABLE I

REACTION OF $Al(CH_3)_3$ WITH HALOMETHYLSILANES

Compound	Results
$SiCl_4$	No reaction
$SiBr_4$	No reaction
$Si(CH_3)_2Cl_2$	No reaction
$Si(CH_3)_2Br_2$	No reaction
$Si(CH_3)_3Cl$	63% yield of TMS

The unreactivity of the silicon halides is not due to thermodynamic factors since the free energies are strongly favorable for all of the reactions. It would appear that the difficulty is in the formation of a transition state. Since both trimethylaluminum and more highly halogenated silanes are strong Lewis acids, the intermediate cannot be a Lewis salt. Trimethylchlorosilane is sufficiently basic to form a complex with trimethylaluminum and the reaction can proceed. It is unlikely that steric factors are important since methyl groups are larger than chlorine. Similarly the electronegativity difference between chlorine and bromine is not sufficient to affect the reactivity.

The difference in reactivity between silicon tetrachloride and the remaining group IV chlorides suggests an electronic factor may be important. The published spectroscopic energy level data for these atoms[3] show only small differences between corresponding energy states, varying no more than 5000 in 70,000 cm^{-1}. However, silicon differs from the heavier elements of the group in the absence of $(n-1)$d orbitals. Such orbitals are not so greatly different in energy from the ns and np orbitals to preclude their participation in transition states. The present work is part of a continuing study on the reactivity of the group IV halides and alkylaluminum compounds.

Experimental Section

Materials.—Trimethylaluminum was obtained from the Ethyl Corp. as an 8% solution in a heavy mineral oil. This is a convenient concentration since it is not pyrophoric but only oxidizes slowly. All of the silicon compounds except silicon tetrabromide and dimethyldibromosilane were obtained from commercial sources and were used as received or diluted with mineral oil. Silicon tetrabromide was prepared by the reaction of the elements in a Vycor tube followed by distillation.[4] The fraction boiling at 151–153° was taken as product.

Dimethyldibromosilane.—This compound was prepared by the reaction of dimethoxydimethylsilane (Dow Z-6072) and acetyl bromide. The reaction was carried out in a 500-ml three-necked flask equipped with condenser, stirrer, and addition funnel. The acetyl bromide (99.4 g) was added to 38.8 g of dimethoxydimethylsilane with stirring. After the addition, the system was arranged for distillation using a Vigreux column and methyl acetate removed first followed by 42.1 g of dimethyldibromosilane, bp 108–109°, 57% theory.

Reaction of $(CH_3)_3Al$ and Silicon Halides.—All of the reactions were run in a similar manner and therefore only one is described to illustrate a convenient means of handling the reactants. The reaction was carried out in a 1-l. three-necked flask equipped with stirrer, condenser and bubbler, and a 250-ml addition funnel, fitted with a Y tube leading to a nitrogen source and connecting to the trimethylaluminum cylinder. Ini-

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