cleophilicities[1,5] of these ligands toward many metal carbonyl complexes and is essentially the same as that obtained for the reaction of L with $W(CO)_6$ to form $(L)W(CO)_5$.[6]

At 60.0, 70.0, and 92.0°, the values of k_1 for the reaction of $(O(CH_2CH_2)_2NH)W(CO)_5$ with $P(C_6H_5)_3$ were 1.56, 4.11, and 30.0×10^{-5} sec^{-1}, respectively. At the same temperatures k_2 increased as follows: 0.42, 1.21, and 8.69×10^{-3} M^{-1} sec^{-1}. From the k_1 results, ΔH_1^* and ΔS_1^* were calculated to be 22.5 kcal/mol and −13 eu, respectively. The negative value of ΔS_1^* is somewhat surprising for an SN1 reaction, although there are SN1 reactions of other metal carbonyls[1] which have entropies of activation as low as −10 eu. It should be noted that ΔH_1^* is much lower than that observed[6] for the dissociation of CO from $W(CO)_6$, which is in general agreement with lower solution stability of $(Am)W(CO)_5$ as compared to $W(CO)_6$. For the k_2 term, ΔH_2^* and ΔS_2^* are 21.0 kcal/mol and −11 eu, respectively. In this case, the entropy of activation is quite normal for reactions proceeding according to an SN2 mechanism.

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Novel Synthesis Routes to Chlorine and Bromine Pentafluorides

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The reaction of alkali chlorides and bromides with fluorine (at atmospheric pressure) was first studied by Moissan.[1] With chloride salts, chlorine and the alkali fluoride were produced. Under the same conditions, bromine trifluoride and potassium fluoride were formed from potassium bromide and fluorine.[2]

Asprey, Margrave, and Silverthorn,[3] Bode and Klesper,[4-6] and Kelly, Post, and Mason[7] have reported the fluorination of alkali chlorides to give alkali tetrafluorochlorates, $MClF_4$ (M = K, Rb, Cs), at temperatures of 90–300° and pressures up to 4000 atm. Asprey, *et al.*,[3] also obtained alkali tetrafluorobromates, $MBrF_4$ (M = K, Rb, Cs) from the fluorination of the corresponding alkali metal bromides under similar conditions. In none of these investigations was the composition of the final gas phase investigated.

We now wish to report that under the proper conditions chlorine or bromine pentafluoride may be obtained by fluorination of the respective potassium halide

$$3F_2 + KX \longrightarrow XF_5 + KF \quad (X = Cl \text{ or } Br)$$

Chlorine pentafluoride has been prepared from fluorine and chlorine trifluoride with either thermal[8] or ultraviolet[9] activation, by the reaction of platinum hexafluoride and chlorine trifluoride,[10] by fluorination of tetrafluorochlorate salts,[11] directly from the elements by electric discharge,[11] and, by an electrolytic process, from chlorine or chlorine trifluoride and hydrogen fluoride.[12] Trace amounts have also been reported from the action of krypton difluoride on the silver chloride windows of an infrared cell.[13]

Bromine pentafluoride has been prepared by direct fluorination of bromine or bromine trifluoride.[14,15]

We have found the procedure described herein to be most convenient for the laboratory preparation of chlorine or bromine pentafluoride since the starting materials are easily obtainable and the products are almost completely free of the trifluorides and other impurities.

By this procedure, we have made many preparations of chlorine pentafluoride and have established the following optimum conditions (figures in parentheses indicate the ranges investigated): F_2:KCl mol ratio, 5:1 (3:1–12:1); temperature, 200° (100–300°); time, 8 hr (4–112 hr). These conditions gave an average in-hand yield, based on KCl charged, of 65.0 ± 4.7% (95% confidence limits). The particle size of the KCl (75 or 350 μ) had no apparent effect on the yield.

Other chlorides can also be fluorinated under similar conditions to give chlorine pentafluoride: NaCl (240°, 4 hr, 55.6% yield); $BaCl_2$ (240°, 64 hr, 7.1% yield).

The parameters of the bromine pentafluoride preparation were not as thoroughly investigated. However, yields of 47%, based on potassium bromide charged, were obtained with an F_2:KBr mole ratio of 5.8:1, at 25° for 16 hr.

Experimental Details

Materials.—Solid reagents (analytical grade) were dried in a vacuum oven at 120°. Fluorine, obtained from Allied Chemical Corp., was passed through a hydrogen fluoride scrubber before use. Reactors were Hoke stainless steel or Monel cylinders with Hoke Monel needle valves (M324A).

Precautions.—*Preparations involving more than 0.25 mol of potassium chloride in a 1-l. stainless steel cylinder (rated at 1800 psi)*

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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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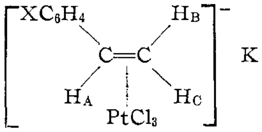
Proton magnetic resonance spectra of styrene derivative complexes of platinum have been studied. Their ethylenic protons show weakly coupled ABC spectra with ^{195}Pt satellites, readily giving values of three chemical shifts and six coupling constants for each complex. The general experimental trends 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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