solvent molecules as well as the anions included in the crystal. Mass spectrometry shows that the crystals obtained from acetone indeed contain some acetone even after exhaustive drying in vacuo. The effect of the crystal packing force has been cited to explain the observed rhombicity, though much smaller, of the hemin chloride in perylene single crystals.[13] A substantial deviation from D_4 molecular symmetry has been demonstrated for $TPPH_2$ single crystals by X-ray studies.[16,17] Our further contention is that in at least the most distorted species the original anion is removed or displaced from the normal fifth coordination site of $Fe^{III}TPP$. It is worth noting that the large rhombic distortion can be effected without invoking some specific axial ligand such as a sulfhydryl group, which is widely implicated in cytochrome P-450. Further studies are under way.

Registry No. $TPPH_2$, 917-23-7; $TPPFe^{III}F$, 55428-47-2; $TPPFe^{III}Cl$, 16456-81-8; cytochrome P-450, 9035-51-2; $TPPFe^{III}CH_3COO$, 33393-26-9.

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Reaction of Phenylboron Dichloride with Cyclopentadienyldicarbollylcobalt

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Alkyl- or arylboron dihalides have been shown to react with cobaltocene to yield a borinatocobalt complex $\{[1\text{-}C_6H_5\text{-}(\eta^6\text{-}C_5BH_5)]Co(\eta^5\text{-}C_5H_5)\}^+$.[1,2] The $C_2B_9H_{11}^{2-}$ ions are icosahedra less one boron atom and can readily replace $C_5H_5^-$ in metal complexes; they also react with alkyl- or arylboron dihalides to yield neutral B-substituted carboranes (eq 1).[3,4]

$$(3)\text{-}1,2\text{-}C_2B_9H_{11}^{\,2-} + RBCl_2 \xrightarrow[-40°]{THF} 3\text{-}R\text{-}1,2\text{-}C_2B_{10}H_{11} + 2Cl^- \qquad (1)$$

$$R = C_6H_5, C_2H_5$$

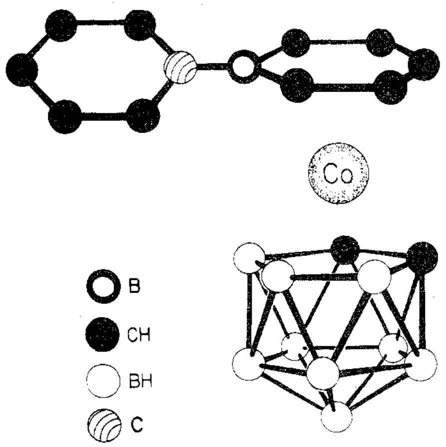

Figure 1. Proposed structure of $3\text{-}[1\text{-}C_6H_5(\eta^6\text{-}C_5BH_5)]\text{-}3,1,2\text{-}Co(\eta^5\text{-}C_2B_9H_{11})$.

In our studies we reduced $3\text{-}(\eta^5\text{-}C_5H_5)\text{-}3,1,2\text{-}Co(\eta^5\text{-}C_2B_9H_{11})$, I, with sodium and then added $C_6H_5BCl_2$, with the hope of inserting a C_6H_5B vertex into the carborane cage to produce a 13-vertex metallocarborane. Instead the phenylborinato complex $3\text{-}[1\text{-}C_6H_5(\eta^6\text{-}C_5BH_5)]\text{-}3,1,2\text{-}Co(\eta^5\text{-}C_2B_9H_{11})$, II, was formed exclusively (Figure 1).

Results and Discussion

Reduction of I was effected with 3 equiv of Na in the presence of naphthalene in tetrahydrofuran at room temperature. Excess $C_6H_5BCl_2$ was then carefully added at low temperature. After work-up in air the only products isolated were the red borinato complex, II, and unreacted I. Compound II had a cutoff at *m/e* 346 in its mass spectrum corresponding to the $^{11}B_{10}{}^{12}C_{13}{}^{1}H_{21}{}^{59}Co^+$ ion. The 80.5-MHz ^{11}B NMR spectrum in $CDCl_3$ exhibited a broad singlet at −23.4 and doublets nearly coincidental with those in I of relative areas 1:1:4:2:1 at −8.1, −5.4, +4.8, +15.6, and +22.1 [ppm, relative to $BF_3{\cdot}OEt_2$]. The 60-MHz ^1H NMR spectrum in CDl_3 exhibited a singlet at τ 5.8 due to carborane C–H, two multiplets of the phenyl group at τ 2.0 and 2.6, and two multiplets of the borinato ring at τ 3.4 and 3.8. The complex splitting pattern in the aromatic region was nearly identical with that of $\{[1\text{-}C_6H_5(\eta^6\text{-}C_5BH_5)]Co(\eta^5\text{-}C_5H_5)\}^+$.[1] Both the ^1H and ^{11}B NMR data clearly indicate that the phenyl-substituted boron atom has inserted in the cyclopentadienyl ring rather than the dicarbollide cage. There was no evidence for the formation of 13-vertex metallocarboranes. It is possible that 13-vertex polyhedra are so energetically unfavorable relative to the icosahedron that they cannot be formed from arylboron dihalides. This suggestion is supported by the fact that $C_2B_{10}H_{12}^{2-}$ is also unreactive toward $C_6H_5BCl_2$.

Experimental Part

Phenylboron dichloride was vacuum distilled and then further purified by several cycles of freezing, evacuation with high vacuum, and thawing immediately prior to use. Cyclopentadienyldicarbollylcobalt was prepared according to the literature.[5] Infrared spectra were determined using a Perkin-Elmer Model 137 spectrophotometer. Proton NMR spectra were obtained on a Varian T-60 spectrometer; 80.5-MHz ^{11}B NMR spectra were recorded on an instrument designed by Professor F. A. L. Anet.

$3\text{-}[1\text{-}C_6H_5(\eta^6\text{-}C_5BH_5)]\text{-}3,1,2\text{-}Co(\eta^5\text{-}C_2B_9H_{11})$. Cyclopentadienyldicarbollylcobalt (1.0 g, 3.9 mmol) was dissolved in 100 ml of tetrahydrofuran in a nitrogen-flushed 3-neck, 250-ml flask. Sodium (0.27 g, 12 mg-atoms) and naphthalene (0.2 g, 1.5 mmol) were added and the reaction mixture was stirred for 24 hr. The flask was connected as the receiver to an alembic distillation apparatus and 2 ml of phenylboron dichloride was vacuum distilled directly into the receiver which was frozen with liquid nitrogen. The reaction vessel was warmed to −40° and stirred at that temperature for 2 hr and then stirred another 20 hr at room temperature. The mixture was poured in the air onto silica gel and the solvent was removed by rotary evaporation. The solids were chromatographed on a 5 × 40 cm column of silica gel. Elution with hexane–CH_2Cl_2 (9:1 v/v) resulted in a red band which was recrystallized from hexane to give 0.23 g of II (mp 201°) (17% yield). The red band was closely followed by the yellow band of I of which 0.6 g was recovered. Anal. Calcd for $C_{13}H_{21}B_{10}Co$: C, 45.34; H, 6.15; B, 31.39; Co, 17.11. Found: C, 45.24; H, 6.15; B, 31.00; Co, 16.69. Infrared spectrum, cm^{-1} (intensity): 2505 (s), 1590 (w), 1010 (m), 990 (m), 980 (m), 915 (w), 880 (w), 845 (s), 755 (s), 700 (s).

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Registry No. I, 11056-78-3; II, 55492-95-0; $C_6H_5BCl_2$, 873-51-8.

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Reaction of Boron Trichloride with Phosphorus Pentafluoride. A Convenient Synthesis of PF_4Cl

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The potential of chlorotetrafluorophosphorane as a synthetic intermediate is illustrated by its reaction with ammonia which results in the formation of the parent aminotetrafluorophosphorane, H_2NPF_4.[1] The dynamic stereochemistry of PF_4Cl has also attracted recent attention.[2] However, more extensive studies of the chemistry of this interesting molecule have been hampered by the difficulties which are associated with the previously published preparations.

Carter and Holmes[3] first described the synthesis of PF_4Cl using a two-step procedure

$$PF_3 + Cl_2 \rightarrow PF_3Cl_2 \xrightarrow[-50°]{SbF_3} PF_4Cl$$

This method affords rather low yields (~20%) and requires the preliminary isolation of PF_3Cl_2. In a different approach Rogowski and Cohn[4] reported the synthesis of PF_4Cl by the HCl cleavage of the N–P bond of Me_2NPF_4

$$Me_2NPF_4 + 2HCl \rightarrow Me_2NH_2Cl + PF_4Cl$$

However, subsequent unpublished results by the same workers have indicated that the reaction is difficult to reproduce.[5]

More recently Fox and coworkers[5] have reported the preparation of PF_4Cl in good yield (~50%) via the oxidative addition of ClF to PF_3

$$PF_3 + ClF \rightarrow PF_4Cl$$

One disadvantage of this method is that it requires the use of the expensive reagent chlorine monofluoride. Furthermore, in numerous attempts to repeat this reaction, several workers in this laboratory have found it to be uncontrollably violent even at −196°. Typical yields of PF_4Cl have been in the range 0–10%.

As part of a study of the chemistry of silylaminophosphines an interesting halogen-exchange reaction between BCl_3 and $(Me_3Si)_2NPF_2$ was discovered[6]

$$3(Me_3Si)_2NPF_2 + 2BCl_3 \rightarrow 3(Me_3Si)_2NPCl_2 + 2BF_3$$

In turn this prompted the investigation of the reaction of boron trichloride with phosphorus pentafluoride as a possible synthetic route to PF_4Cl.

It was found that the reaction

$$3PF_5 + BCl_3 \rightarrow 3PF_4Cl + BF_3$$

proceeds slowly in the gas phase at ambient temperature. Chlorotetrafluorophosphorane is obtained in reproducible yields of 45–52%, if a rather low (~250 Torr) total pressure of PF_5 and BCl_3 is employed together with a reaction time of about 36 hr. Higher pressures or longer reaction times lead to the formation of large amounts of by-products (e.g., PF_3Cl_2) and greatly reduced yields of the tetrafluorophosphorane.

This relatively facile reaction employing mild conditions and readily available starting materials therefore seems to be the method of choice for the preparation of chlorotetrafluorophosphorane, which may prove to be a useful precursor to several novel tetrafluorophosphorane systems.

Experimental Section

All manipulations were carried out in a standard Pyrex glass vacuum system. As with most fluorophosphorane chemistry, thoroughly dried apparatus is imperative. Phosphorus pentafluoride and BCl_3 were procured from Matheson Gas and distilled through traps held at −140° (retained at −196°) and −78° (retained at −117°), respectively, prior to use.

In a typical experiment a 2-l. glass reaction bulb equipped with a glass–Teflon stopcock was evacuated and flame-dried. Boron trichloride (5.0 mmol) and PF_5 (20.0 mmol) were condensed together in the reaction vessel at −196° and then allowed to warm to room temperature. After 36 hr traces of an unidentified white solid were observed in the reaction bulb. The gaseous products were then bled slowly into the vacuum system (preliminary work had shown that condensation of the mixture at this point caused the formation of more solids and lower yields of PF_4Cl) passing directly through traps held at −117, −140, and −196°. The −117° trap retained PF_3Cl_2 (2.3 mmol) which was identified by its infrared spectrum.[7] The −196° fraction (14.1 mmol) consisted of a mixture of BF_3 and PF_5. Chlorotetrafluorophosphorane (7.7 mmol, 51% yield) was retained at −140°. The infrared spectrum was identical with that reported in the literature.[3] The product of this single distillation may contain small amounts (~5%) of PF_5 and SiF_4. Further purification of PF_4Cl is complicated by its disproportionation into PF_5 and PF_3Cl_2 which occurs readily in the liquid phase, particularly in glass systems.

In separate experiments the progress of the reaction was followed by infrared spectroscopy. Reaction periods of less than 24 hr result in incomplete conversion of BCl_3 and low yields of PF_4Cl. Beyond 36 hr PF_3Cl_2 is formed in increasing amounts.

Other experiments have shown that rather slight deviations from the above procedure can result in lower yields of PF_4Cl. For example, when 9.0 mmol of PF_5 and 3.0 mmol of BCl_3 were allowed to react in a 500-ml vessel (~450 Torr total pressure) for 12 hr copious amounts of white solids were formed and the only volatile products were PF_5 and BF_3.

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Registry No. BCl_3, 10294-34-5; PF_5, 7647-19-0; PF_4Cl, 13637-88-2.

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