General Procedure. The reactions were carried out in an all-Pyrex-glass reactor, with stopcocks and joints lubricated with "Halocarbon" grease. A stream of dry nitrogen (2 l/hr) saturated with fluorine fluorosulfate at −78° (~50 mm) was bubbled into the haloalkane (or haloalkene) cooled also at −78°.

When all the fluorine fluorosulfate had reacted and the inert gas was pumped out of the reactor at −190°, the liquid was warmed up to room temperature. Then it was treated with a saturated solution of sodium bicarbonate and repeatedly washed with distilled water. Finally it was dried over anhydrous potassium carbonate. The components of the liquid mixture were determined by vpc chromatography in an F & M model 810 instrument equipped with a thermal conductivity detector and an analytical column (1.65 mm × 1.8 m) packed with Chromosorb W (AW-TMCS) impregnated with 10% Carbowax 20 M.

The reaction products could be separated with a preparative column (12.5 mm × 2.40 m) packed with Chromosorb W (AW-TMCS) impregnated with 10% silicone gum rubber SE-30.

The infrared spectra of the products were obtained on a Perkin-Elmer Model 337 spectrophotometer using cells equipped with KBr windows. Nuclear magnetic resonance spectra were recorded on a DP-60 Varian Associates instrument. Trichlorofluoromethane and tetramethylsilane were used as internal standards. The vapor pressures of the products were measured with a mercury manometer, using a quartz spiral as a null instrument.

Molecular weights were determined by the gas chromatographic method.[9] Elemental analyses were carried out making use of microchemical techniques.[10]

Preparation of Dichloromethyl Fluorosulfate (I). The reaction of 0.06 mol of fluorine fluorosulfate and 0.5 mol of chloroform yielded 80% product I and 13% trichlorofluoromethane.

The reaction is rapid and exothermic. Compound I is a colorless liquid which slowly decomposes at room temperature; mp −66.0 ± 0.5°. The vapor pressure is given by $\log p(\text{mm}) = 8.00 - 1890/T(°\text{K})$ (between 2 and 20°) and $\Delta H_{\text{vap}} = 8.6$ kcal mol^{-1}. The Trouton constant is 23.4 eu; bp (extrapolated) 95.8°. *Anal.* Calcd for CHO_3Cl_2FS: C, 6.56; H, 0.55; Cl, 38.75; F, 10.38; S, 17.52. Found: C, 6.45; H, 0.44; Cl, 38.89; F, 10.13; S, 17.62. The molecular weight was found to be 188 (theoretical 183.0).

The ^{19}F nmr spectrum shows δ_{SF} −44.4 ppm (*e.g.*, in perfluoroethyl fluorosulfate,[6] δ_{SF} is −49.4 ppm). The ^1H nmr spectrum indicates δ_{CH} +7.50 ppm (*e.g.*, in chloroform, δ_{CH} is +7.24 ppm).

The assignment of some infrared bands of I is as follows (ν in cm^{-1}): 3010 (m) (C–H); 1438 (m) (S–O asymmetric stretch), 1228 (s) (S–O symmetric stretch), 859 (s) (S–F). Other bands not identified are 944 (s), 2670 (vw), 1720 (w), 1305 (m), 1105 (m), 803 (m), 747 (w), 720 (w), 570 (m), 540 (w), 528 (w), and 430 (w) cm^{-1}.

Preparation of 1,1,2-Trichlorofluoroethyl Fluorosulfate (II). The reaction of 0.1 mol of fluorine fluorosulfate and 0.2 mol of trichloroethylene yielded 70% product II and 4% trichlorofluoroethylene. This is also a rapid and exothermic reaction. Compound II is a colorless liquid which is stable at room temperature. A sample (0.2 ml) sealed in a Pyrex ampoule and heated for 2 hr at 110° partially decomposes into trichlorofluoroethylene and fluorosulfuric acid: $CHClFCCl_2OSO_2F \rightarrow CClF{=}CCl_2 + FSO_2OH$. The pyrolysis products were identified by their infrared spectra. The melting point of II was not measured with the accuracy reported for I. On cooling this compound to −196° a cracked solid was formed. The temperature at which the cracked appearance vanished is about −20°. The vapor pressure is given by $\log p(\text{mm}) = 7.43 - 1911/T(°\text{K})$ (between 44 and 80°) and ΔH_{vap} 8.7 kcal mol^{-1}. The Trouton constant is 20.8 eu; bp (extrapolated) 146.8°. The density at 20° is 1.632 g cm^{-3}; $n^{20}\text{D}$ 1.4162. *Anal.* Calcd for $C_2HO_3Cl_3F_2S$: C, 9.62; H, 0.40; Cl, 42.66; F, 15.24; S, 12.83. Found: C, 9.79; H, 0.47; Cl, 42.77; F, 15.03; S, 12.98. The molecular weight was found to be 247 (theoretical 249.4).

The ^{19}F nmr spectrum of II shows δ_{SF} −50.78 ppm and a doublet centered at +139.07 ppm ($J_{FH} = 47.92$ Hz). The ^1H nmr spectrum of II shows a doublet centered at +6.31 ppm ($J_{FH} = 48.20$ Hz). Comparison of this value with the spectrum of $CHClFCHClOSF_5$[5] confirms the structure of product II.

The assignment of some infrared bands of II is as follows (ν in cm^{-1}): 2940 (m) (C–H), 1400 (s) (S–O asymmetric stretch), 1235 (s) (S–O symmetric stretch), 1075 (s) (C–F stretch), 890 (s) (S–F). Other bands not identified are 1253 (m), 1112 (m), 1060 (w), 1055 (w), 975 (w), 950 (s), 865 (s), 845 (m), 820 (w), 810 (s), 785 (m), 670 (w), 650 (m), 598 (w), 570 (m), 550 (m), 535 (m), and 500 (m) cm^{-1}.

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Registry No. $CHCl_2OSO_2F$, 42016-50-2; $CHClFCCl_2OSO_2F$, 42087-88-7; $CHCl_3$, 67-66-3; F_2SO_3, 13536-85-1; $CHCl{=}CCl_2$, 79-01-6.

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Convenient Synthesis of Hexaammineosmium(III)

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Hexaammineosmium(III), $[Os(NH_3)_6]X_3$ (X = Br, I, and ($OsBr_6/3$), was synthesized previously (32% yield) by reaction of $(NH_4)_2OsBr_6$ with ammonia in a sealed tube for 1 month.[1-4] This time-consuming procedure appears to be responsible for the lack of information on this complex[1-5] compared to its ruthenium analog.[6-12] During investigation of reactions of $[Os(NH_3)_5NO]^{3+}$ we found reduction with zinc in ammonia gave $[Os(NH_3)_6]^{3+}$.[13] This suggested Zn–NH_3 reduction of commercial $(NH_4)_2OsCl_6$ would give $[Os(NH_3)_6]^{3+}$ also. Such was the case, and the preparation and some properties of $[Os(NH_3)_6]X_3$ (X = Cl, Br, I, and ClO_4) are reported.

Results and Discussion

Reduction of $(NH_4)_2OsCl_6$ with zinc dust in 0.880 g cm^{-3} of ammonia for 5 hr gave a pale yellow solution and metallic osmium. Addition of potassium iodide to the solution gave $[Os(NH_3)_6]I_3$ (32%), from which other salts were obtained metathetically. Increasing the reduction time increased the amount of metallic osmium, and with shorter times the product was contaminated with osmium(IV). $[Os(NH_3)_6]^{2+}$ was not observed, in contrast to ruthenium chemistry, where $[Ru(NH_3)_6]^{2+}$ was obtained by a similar reaction.[14]

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$[Os(NH_3)_6]X_3$ complexes were stable in dry air but decomposed when moist. In aqueous solution they decomposed over a few hours, even under argon, to an intractable brown material, with no evidence of an osmium analog of "ruthenium red."[15]

The X-ray powder pattern of $[Os(NH_3)_6]I_3$ was similar to that reported by Watt and Vaska[2] and was indexed as face-centered cubic (probable space groups $Fm3m$, $F432$, or $F\bar{4}3m$) with $a = 11.04$ Å (seven lines observed, uncalibrated film). The iodide salt had a room-temperature magnetic moment of 1.6 BM, similar to that reported previously.[2] The electronic spectrum (aqueous solution, ClO_4^- or Cl^- salts) showed absorption bands at 221 nm (ϵ 760), 229 nm (ϵ 759) and 261 nm (ϵ 78). The ir spectra were similar to those of $[Ru(NH_3)_6]X_3$,[7] but with NH_3 vibrations approximately 25 cm^{-1} higher in energy.

In acid solution $[Os(NH_3)_6]I_3$ and nitric oxide gave $[Os(NH_3)_5NO]I_3 \cdot H_2O$. This preparation is more convenient than our earlier procedure[13] but gives a much lower overall yield. In 0.01 M hydroxide ion $[Ru(NH_3)_6]^{3+}$ and nitric oxide gave $[Ru(NH_3)_5N_2]^{2+}$ in 97% yield.[8] $[Os(NH_3)_6]^{3+}$ gave only $[OsNH_2(NH_3)_4NO]^{2+}$ [13] under the same conditions. In 1-4 M hydroxide a mixture of $[Os(NH_3)_5N_2]^{2+}$ [16] and $[OsNH_2(NH_3)NO]^{2+}$ was obtained; the percentage of dinitrogen complex increased with hydroxide ion concentration to approximately 100% at 4 M. However, the total yield was only 30% of the expected. Since no other product could be isolated, we cannot decide whether the low yield was due to decomposition of $[Os(NH_3)_6]^{3+}$ in solution or to other reactions of $[Os(NH_3)_6]^{3+}$ with NO.

Experimental Section

Hexaammineosmium(III) Salts, $[Os(NH_3)_6]X_3$ (X = Cl, Br, I, ClO_4). A mixture of $(NH_4)_2OsCl_6$ (0.50 g), Zn dust (0.5 g), and NH_3 (0.880 g cm^{-3}; 15 ml) was refluxed under argon for 5 hr. To the resultant mixture was added NH_3 (0.880 g cm^{-3}; 3 ml), the mixture was filtered, and KI (2 g) was added to the filtrate. The resultant yellow precipitate was purified by reprecipitation from cold water with HI; yield 0.244 g (32%). A further quantity (approximately 9%) was obtained by evaporating the filtrate under argon and recycling. *Anal.* Calcd for $H_{18}I_3N_6Os$: H, 2.70; I, 56.56; N, 12.49. Found: H, 2.57; I, 56.91; N, 12.45.

Cl^-, Br^-, and ClO_4^- salts were prepared metathetically from the iodide; yields 60, 78, and 65%, respectively. *Anal.* Calcd for $Br_3H_{18}N_6Os$: Br, 45.05; H, 3.41; N, 15.79. Found: Br, 44.89; H, 3.53; N, 15.89. Calcd for $Cl_3H_{18}N_6Os$: Cl, 26.67; H, 4.55; N, 21.08. Found: Cl, 26.88; H, 4.46; N, 21.39. Calcd for $Cl_3H_{18}N_6O_{12}Os$: N, 14.23. Found: N, 14.02.

Nitrosylpentaammineosmium Triodide Hydrate, $[Os(NH_3)_5NO]I_3 \cdot H_2O$. To a deoxygenated slurry of $[Os(NH_3)_6]I_3$ (0.096 g) in water (9 ml) was added 5 drops of concentrated HI, and NO was passed through for 24 hr. The orange solution was filtered and the product was precipitated with concentrated HI; yield 0.079 g (79%). The properties of the product were identical with those of $[Os(NH_3)_5NO]I_3 \cdot H_2O$ prepared by the literature method.[13]

Reaction of Hexaammineosmium with Nitric Oxide in Alkaline Solution. Nitric oxide was passed through a deoxygenated solution of $[Os(NH_3)_6]I_3$ (0.098 g) in NaOH (1-4 M; 4 ml) for 23 hr. The product was precipitated from the ice-cold orange-red solution with KI; yield 0.020 g (29%). The percentages of $[OsNH_2(NH_3)_4NO]^{2+}$ and $[Os(NH_3)_5N_2]^{2+}$ were estimated from the infrared and electronic spectra of the mixture.[13,16]

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Registry No. $[Os(NH_3)_6]Cl_3$, 42055-53-8; $[Os(NH_3)_6]Br_3$, 42055-54-9; $[Os(NH_3)_6]I_3$, 42055-55-0; $[Os(NH_3)_6](ClO_4)_3$, 42055-56-1; $(NH_4)_2OsCl_6$, 12125-08-5.

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Nickel(II) and Cobalt(II) Complexes Containing Bis(diphenylphosphino)-*o*-carborane

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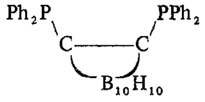
In recent years there have been a number of reports of the preparation of metal complexes containing ligands in which the *o*-carborane nucleus functions as a ligand backbone.[2,3] In particular we were intrigued by the results obtained in the reactions between bis(diphenylphosphino)-*o*-carborane, dpc,



dpc

L, and divalent salts of the first transition series.[2] Although Smith obtained planar complexes of the type $[Ni(dpc)Cl_2]$ and $[Ni(dpc)_2]Cl_2$ he could obtain no reaction between this diphosphine and cobalt(II) salts. Recent work by some of us has involved studies of the stereochemical and spectrochemical aspects of altering chelate chain linkages,[4-6] and we were thus interested in the apparent effect of the *o*-carborane backbone in making bis(diphenylphosphino)-*o*-carborane unreactive toward cobalt(II) salts. Previous work by Sacco and Gorieri[7] and by Horrocks, *et al.*,[8] in the characterization of the pseudotetrahedral $[Co(dpe)X_2]$ (X = Cl, Br, I) and pentacoordinate, square-pyramidal $[Co(dpe)_2X]X$ (X = Cl, Br, I) (dpe = 1,2-bis(diphenylphosphino)ethane) has shown that bisphosphines form very stable complexes with cobalt(II). We here wish to report the isolation of tetrahedral cobalt(II) and trigonal-pyramidal nickel(II) and cobalt(II) complexes with dpc.

Experimental Section

Bis(diphenylphosphino)-*o*-carborane (I) was synthesized according to the method of Alexander and Schroeder.[9]

Diiodobis[bis(diphenylphosphino)-*o*-carborane]nickel(II). Nickel(II) iodide (0.31 g, 1.0 mmol) in ethanol (7 ml) was added dropwise to a stirred solution of the ligand (1.02 g, 2.0 mmol) in dichloromethane (50 ml). An immediate deep blue-black color developed and stirring was continued for 15 min, the solution was filtered, and diethyl ether (100 ml) was added dropwise to the stirred filtrate. After

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