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New Zerovalent Chromium Complexes from Cocondensations of Chromium Vapor with Aminodifluorophosphines; The X-ray Crystal Structure of $CH_3N(PF_2)_2Cr[PF_2N(CH_3)_2]_4$

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Recent papers report the cocondensations of iron [1] and cobalt [2] vapors with the aminodifluorophosphines $(CH_3)_2NPF_2$ and $CH_3N(PF_2)_2$ to give several novel zerovalent complexes. This Communication reports the related cocondensations of chromium vapor with these aminodifluorophosphines. Such reactions are of interest in giving the new homoleptic [3] chromium(0) derivative $[(CH_3)_2NPF_2]_6Cr$ of unexpectedly low stability as well as a novel mixed ligand complex $CH_3N(PF_2)_2Cr[PF_2N(CH_3)_2]_4$, the structure of which has been determined by X-ray diffraction.

Approximately 0.2 g (3.8 mg-atom) of chromium metal was evaporated over a period of 30 minutes at 0.0001 mm pressure from an alumina coated tungsten wound crucible heated electrically. The resulting vapors were cocondensed at −196 °C with an excess (~9 ml) of $(CH_3)_2NPF_2$. After completion of the reaction, excess ligand was removed at −78 °C. Extraction of the product from the residue with dichloromethane followed by rapid evaporation of the filtered extract in vacuum below room temperature gave a 7% yield of white $[(CH_3)_2NPF_2]_6Cr$, identified by correct C, H, N and molecular weight (in benzene) determinations.

This new zerovalent chromium complex $[(CH_3)_2NPF_2]_6Cr$ is a reasonably air-stable white solid which decomposes upon standing at room temperature, particularly in solution. It is therefore considerably less stable than the related zerovalent chromium complexes $Cr(CO)_6$ [4] and $Cr(PF_3)_6$ [5] as well as the related zerovalent dimethylaminodifluorophosphine complexes $[(CH_3)_2NPF_2]_5Fe$ [1] and $[(CH_3)_2NPF_2]_4Ni$ [6]. The relatively low stability of $[(CH_3)_2NPF_2]_6Cr$ can be attributed to steric hindrance between the six relatively bulky $(CH_3)_2NPF_2$ ligands all bonded to a single metal atom.

A considerably more stable zerovalent chromium complex containing both the $(CH_3)_2NPF_2$ and $CH_3N(PF_2)_2$ ligands was obtained by cocondensation of chromium vapor with a mixture of these ligands. Thus the chromium vapor from 0.3 g (5.8 mg-atom) of chromium metal was cocondensed with excess of a

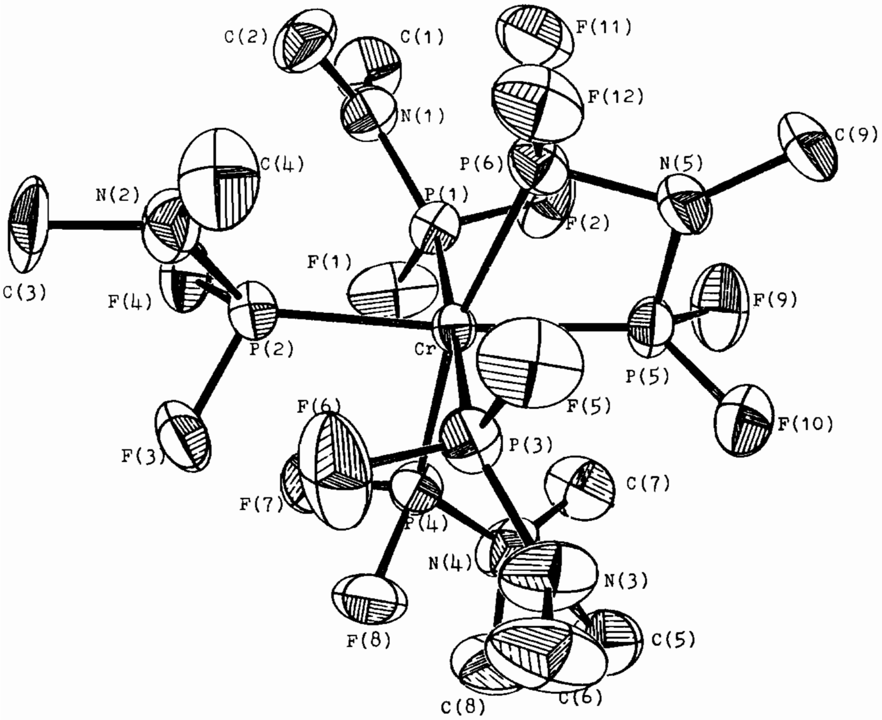

Figure 1. ORTEP drawing of the structure of $CH_3N(PF_2)_2Cr[PF_2N(CH_3)_2]_4$.
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4:1 mixture of $(CH_3)_2NPF_2$ and $CH_3N(PF_2)_2$. The resulting black product was extracted with CH_2Cl_2. Evaporation of the extract followed by sublimation of the residue at 100 °C/0.1 mm gave a 6% yield of white crystalline $CH_3N(PF_2)_2Cr[PF_2N(CH_3)_2]_4$ identified by the ions $[CH_3N(PF_2)_2]_mCr[PF_2N(CH_3)_2]_n^+$ (n = 4, 3, 2, 1 and 0; m = 1 and 0) in its mass spectrum. This mixed ligand chromium(0) complex could not be obtained completely analytically pure, apparently owing to a persistent $[CH_3N(PF_2)_2]_2Cr[PF_2N(CH_3)_2]_2$ impurity identified by its molecular ion in the mass spectrum. Therefore the structure of this complex was determined by single crystal X-ray diffraction.

The complex $CH_3N(PF_2)_2Cr[PF_2N(CH_3)_2]_4$ forms monoclinic crystals by slow evaporation of a dichloromethane solution at room temperature: space group $P2_1/n$; a = 17.653 Å, b = 15.436 Å, c = 9.270 Å, β = 91.79°, Z = 4. Least squares anisotropic refinement using the 1879 observed reflections (R = 0.0519, R_w = 0.0523) indicates the structure depicted in Figure 1. In this structure the chromium atom has the expected octahedral coordination with a bidentate $CH_3N(PF_2)_2$ and four monodentate $(CH_3)_2NPF_2$ ligands. The octahedron, however, is strongly distorted by the small bite $CH_3N(PF_2)_2$ bidentate ligand so that the P_5–Cr–P_6 angle is 66° as compared with the 90° angle for ideal octahedral coordination. This distortion leaves much more space for the two $(CH_3)_2NPF_2$ ligands coplanar with the $CH_3N(PF_2)_2$ ligand (*i.e.* P_2–Cr–P_6 = 105° and P_4–Cr–P_5 = 100°). This relief of steric hindrance upon replacement of two $(CH_3)_2NPF_2$ ligands in the relatively unstable $[(CH_3)_2NPF_2]_6Cr$ with a $CH_3N(PF_2)_2$ ligand to form $CH_3N(PF_2)_2Cr[PF_2N(CH_3)_2]_4$ can account for the much higher stability of $CH_3N(PF_2)_2Cr[PF_2N(CH_3)_2]_4$ relative to $[(CH_3)_2NPF_2]_6Cr$.

A similar cocondensation of chromium vapor with the pure bidentate ligand $CH_3N(PF_2)_2$ gives a 48% yield of the very stable complex $[CH_3N(PF_2)_2]_3Cr$, previously [7] obtained by ultraviolet irradiation of $Cr(CO)_6$ with excess $CH_3N(PF_2)_2$.

Acknowledgments

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