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Notes

Preparation and Magnetic Properties of Al(PF$_3$)$_2$[†]

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Introduction

Previous infrared[1−3] and electron paramagnetic resonance (EPR)[4,5] spectroscopic studies have established that reaction of ground-state aluminum atoms ($^2P_{1/2}$) with CO at temperatures ≤77 K gives the mononuclear complex Al(CO)$_2$. The intermediate monoligand species AlCO has not been positively identified by either of these spectroscopic techniques, although if it were linear, the unpaired electron could possess appreciable unquenched angular momentum and be EPR silent. It should, however, be visible to IR spectroscopy.

Al(CO)$_2$ has a $^2B_1$ ground state in the point group C_{2v} with an angle of *ca.* 110° between the two CO ligands. There have been no corresponding studies of the reaction of Al atoms with PF$_3$, a ligand that has σ-donor and π-acceptor properties similar to those of CO.[6] The characteristics of the bonding of CO and PF$_3$ to Cu and Ag atoms in the mononuclear monoligand complexes have, however, recently been compared.[7,8]

In this note we report the results of a matrix isolation EPR spectroscopic study of the reaction of Al atoms with PF$_3$ in adamantane at 77 K, which demonstrates the formation of Al(PF$_3$)$_2$ but not AlPF$_3$. The magnetic parameters of this new aluminum species are determined and compared with those of Al(CO)$_2$.

Experimental Section

Reactions of ground-state Al atoms with PF$_3$ were carried out at 77 K in an adamantane matrix in a rotating cryostat,[9,10] a technique that has been used successfully to prepare and stabilize a wide variety of transient organic, inorganic, and organometallic species.[9,11,12] Al atoms were produced by resistively heating aluminum wire (Alpha) in a tungsten basket (No. 12070, Ernest F. Fullam, Schenectady, NY) supported between the molybdenum electrodes of a furnace located in one of the ports in the outer housing of the cryostat. PF$_3$ was prepared by reaction of NaF with PCl$_3$ in dry acetonitrile and was deposited at 0.05 Torr. Total deposition times were about 10 min at a pressure $<10^{-5}$ Torr. Deposits were transferred at 77 K and under reduced pressure to a quartz tube (4 mm o.d.) for EPR analysis with a Bruker ESP 300 spectrometer. Samples were annealed in the cavity of the spectrometer with the aid of a variable-temperature controller. Magnetic fields and microwave frequencies were measured with a Varian NMR gaussmeter and Systron-Donner frequency counter. A computer program, adapted by Dr. K. F. Preston (NRCC) for a PC, was used to simulate isotropic EPR spectra.

Results

The EPR spectrum of Al atoms and PF$_3$ in adamantane at 77 K consisted of a broad featureless absorption centered at $g \sim 2.004$ and less intense lines from Al$_3$.[13] When the sample was warmed slowly in the cavity of the spectrometer, the central feature began to resolve and the multilined spectrum shown in Figure 1a was obtained at 215 K. The lines from Al$_3$ became broader and eventually disappeared as the temperature was raised. Computer simulation of the experimental spectrum proved difficult, but a simulation that predicted the line positions but not their exact relative intensities is shown in Figure 1b. The magnetic parameters obtained by this method are $a_{\mathrm{Al}}(1) = 87$ MHz, $a_{\mathrm{P}}(2) = 160$ MHz, $a_{\mathrm{F}}(6) = 16.8$ MHz, and $g = 2.004$, and the carrier of the spectrum is the mononuclear diligand complex Al(PF$_3$)$_2$. The difficulties experienced in obtaining an exact simulation of Figure 1a may have been associated with the presence of lines from other free radical species in the sample, but there was no evidence for transitions from AlPF$_3$, PF$_2$,[14] F$_2$PAlF, or 1- or 2-adamantyl.[15] There were, however, lines from a carrier that was most probably PF$_3^-$ (a(1P) ~ 180 MHz, a(2F) ~ 110 MHz, a(1F) ~ 75 MHz, and $g \sim 2.005$). This species is isoelectronic with SF$_3$[14] and AsF$_3^-$ [16] and will be discussed in a future publication. It should also be noted that there is an m_I effect on the width of the six components of the Al hyperfine interaction of the EPR spectra of mononuclear Al(0) complexes that is not adequately allowed for in the simulation program.

Discussion

The major components of the EPR spectrum given by Al atoms and PF$_3$ deposited into adamantane at 77 K are consistent with the formation of Al(PF$_3$)$_2$. Unfortunately the powder spectrum of this complex does not resolve to give values of $|a_{\parallel}|$ and $|a_{\perp}|$ for any of the magnetic nuclei. Consequently, the p orbital contributions to the singly occupied molecular orbital cannot be estimated by comparing a_{aniso} with P in the usual way.[17]

Dividing the isotropic Al hyperfine interaction of Al(PF$_3$)$_2$

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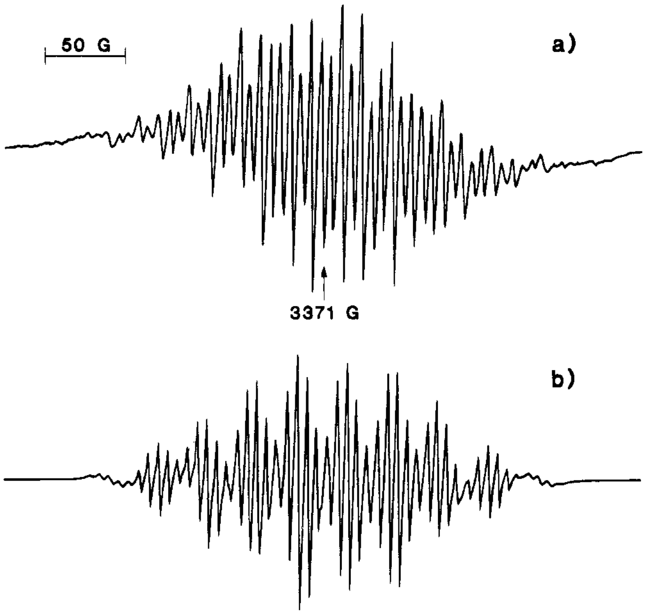

Figure 1. (a) EPR spectrum given by Al atoms and PF_3 in adamantane at 215 K. (b) Simulated spectrum of $Al(PF_3)_2$ produced by using the parameters given in the text.

by $A = 3911$ MHz[17] gives an unpaired 3s spin population (ϱ_{3s})[18] = 0.022, which is larger than the corresponding value of 0.018 for $Al(CO)_2$.[5] This unpaired s spin population for $Al(CO)_2$ is the result of spin polarization of the Al s electrons by the unpaired spin population in the Al $3p_x$ orbital ($\varrho_{3p} = 0.44$) and is negative. We therefore conclude that ϱ_{3p} of $Al(PF_3)_2$ is larger than the value for $Al(CO)_2$ and could be as large as 0.54. This suggests that back-donation of unpaired electron density from the Al $3p_x$ orbital to the π-acceptor orbitals of the ligands is less important for $Al(PF_3)_2$ than it is for $Al(CO)_2$. SCF$-$Xα molecular orbital calculations[19] have shown that the π-acceptor orbital on PF_3 with the correct symmetry to accept electron back-donation from the semioccupied Al p_x orbital is the 7e orbital, which has 44% P 3p and 23% P 3d character.

Dividing the isotropic P hyperfine interaction of $Al(PF_3)_2$ (160 MHz) by $A = 13306$ MHz[17] gives $\varrho_{3s}(P) = 0.012$ compared to $\varrho_{2s}(C) = 0.004$ for $Al(CO)_2$. This is consistent with more unpaired s spin population on the P of $Al(PF_3)_2$ than there is on the C of $Al(CO)_2$. This spin population arises either by bond polarization from the unpaired s spin population on the Al nucleus or by core polarization from the unpaired spin population in the π-acceptor orbitals of the phosphorus nuclei.

Dividing the F hfi of 16.8 MHz by $A = 52870$ MHz[17] gives $\varrho_{2s}(F) = 0.00032$ and a total 2s population of 0.0019. This is smaller than the unpaired 2s spin population on the two oxygen atoms of $Al(CO)_2$ where $\Sigma\varrho_{2s} = 0.0046$ and must be related to the high electronegativity of the fluorine nuclei.

It has been established by IR and EPR spectroscopy that $Al(CO)_2$ is a planar π radical belonging to the $^2B_1$ representation in C_{2v} symmetry with most of the unpaired spin population on the Al nucleus in the $3p_x$ orbital. The magnetic parameters of $Al(PF_3)_2$ are consistent with its having a structure similar to that of $Al(CO)_2$ and the same electronic ground state as $Al(CO)_2$. Thus the Al 3s and 3p orbitals have undergone sp^2 hydridization. The Al lone pair is located in one of these orbitals, and the electrons from the $8a_1$ orbitals of the two PF_3 ligands are donated to the other two orbitals. The unpaired electron is located in the p_x orbital perpendicular to the molecular framework. The slightly different orbital distributions of the unpaired s spin populations in these two complexes are probably associated with slightly different σ-electron donor and π-acceptor properties of the CO and PF_3 ligands.

The isotropic g factor of $Al(PF_3)_2$ is larger than the free spin value ($\Delta g = 0.0017$). This deviation is probably the result of spin orbital coupling between the semifilled p_x orbital and the sp^2 orbital containing the Al lone-pair electrons.

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(18) When estimates of unpaired s spin population are made from a_{iso} and A,[17] it is usual to assume that the unpaired spin is located in the outer s orbital. A reviewer has pointed out that there is also polarization of the inner s electrons and for Al $\varrho_s = \Sigma(\varrho_{3s} + \varrho_{2s} + \varrho_{1s})$. The contribution from the inner s electrons is, however, small, and the three contributions cannot be separated by the EPR spectroscopic technique.

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