spectrum of HCl have been used to determine the state symmetries of HCl.

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EPR Spectrum of $CuPF_3$[†]

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$CuPF_3$ is formed from Cu atoms and PF_3 on solid adamantane at 77 K in a rotating cryostat. It has the magnetic parameters $a_{63} = 4205 \pm 10$ MHz, $a_{31} = 1100 \pm 10$ MHz, $a_{19} = 90 \pm 10$ MHz, and $g = 1.999 \pm 0.002$, has a $^2A_1$ electronic ground state in the point group C_{3v}, and can be considered to be a copper-centered radical and not a phosphoranyl formed by addition of a Cu atom to PF_3. About 70% of the unpaired spin is located in the metal 4s orbital, 8% in the P 3s orbital, and 0.5% in the F 2s orbitals for a total unpaired spin s population of 78.5%. The remaining 21.5% of unpaired spin is probably located in the Cu 4p orbital. Cu_3 is also formed in adamantane and does not appear to react with PF_3. Cu_7 rather than $CuPF_3$ is formed in solid cyclohexane and is also unreactive toward PF_3.

Introduction

In previous publications[1-6] from this laboratory we have shown that the group 11 atoms Ag and Cu react with CO on inert hydrocarbon matrices at 77 K on a rotating cryostat to give the paramagnetic EPR visible mononuclear carbonyls $M(CO)_x$, where $x = 1$–3 in the case of Ag[5] and $x = 1$ and 3 for Cu,[6] $Cu(CO)_2$ not being visible because it is linear with a $^2\Pi$ ground state. One form of $Ag(CO)_2$ is, however, detected because it has a $^2A_1$ ground state with most of the unpaired spin located in the metal 5s orbital.[5] Interestingly, two forms of $Ag(CO)_3$ have been observed, one with a $^2A_1'$ ground state with the unpaired electron located in the 5s orbital of Ag[2] and a second with a $^2A_2''$ ground state and the unpaired electron located principally in the $5p_z$ orbital on Ag.[5] These results have complemented and extended the pioneering spectroscopic studies of matrix-isolated group 11 carbonyls in rare gases by Ogden,[7] Ozin,[8-10] Moskovits,[11] Kasai,[12,13] and co-workers.

Trifluorophosphine (PF_3) is a ligand that behaves like CO and readily stabilizes zero-valent metals because the σ-donor properties of the P lone pair and the π-acceptor properties of the P 3d orbital are modified by the electronegative fluorine ligands.[14] Thus, stable complexes such as $Ni(PF_3)_4$,[15,16] $Cr(PF_3)_6$,[17] and $Fe(PF_3)_5$[18] are readily prepared. There has been less success in the identification of paramagnetic metal–PF_3 complexes. Thus, Timms[19] reported that no Cu–PF_3 compound of appreciable stability is formed at 143 K from reaction of Cu atoms with PF_3 at 77 K. Bowmaker[20] did, however, find IR bands from Cu atoms and PH_3 in the neat phosphine and in a krypton matrix that he tentatively suggested were from $Cu(PH_3)_x$ with $x = 1$–3.

More recently we have shown that Ag atoms react with PF_3 to give the mononuclear monoligand complex $AgPF_3$, but spectra could not be assigned to $Ag(PF_3)_2$ and $Ag(PF_3)_3$.[21] We have also shown that Cu atoms react with the trivalent phosphorus compounds $P(OMe)_3$ and PMe_3 to give the tris(trivalentphosphorus) complexes $Cu[P(OMe)_3]_3$ and $Cu[PMe_3]_3$ that are isostructural with $Cu(CO)_3$.[22]

In the present paper we report an EPR study of the paramagnetic products given by reaction of ^{63}Cu atoms with PF_3 in solid inert hydrocarbons at 77 K on a rotating cryostat.

Experimental Section

A rotating cryostat, described in detail elsewhere,[23-26] was used to allow ^{63}Cu atoms in their ground electronic state to react with PF_3 on the surface of an inert hydrocarbon at 77 K. The reaction products were trapped in a fresh layer of matrix. The deposit was scraped into a 3-mm suprasil tube, still under high vacuum and at 77 K, and examined by X-band ($\nu \sim 9.3$ GHz) and Q-band ($\nu \sim 35$ GHz) EPR spectroscopy in the cavities of a Bruker ESP 300 spectrometer. Samples were annealed in the cavity of the spectrometer with the aid of a Bruker variable-temperature accessory.

The magnetic field was calibrated with a Varian gaussmeter, and the X-band microwave frequency was measured with a Systron-Donner Model 6016 frequency counter. Magnetic pa-

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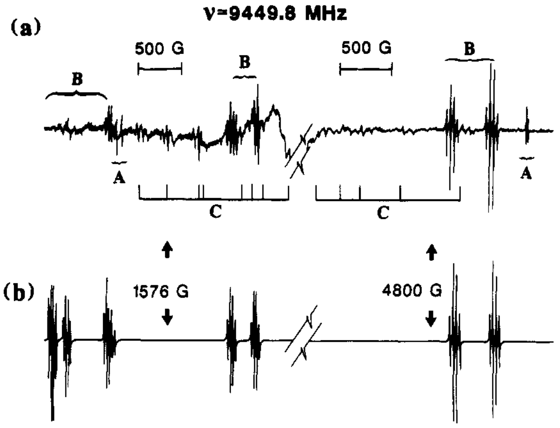

Figure 1. (a) EPR spectrum at X-band given by ^{63}Cu atoms and PF_3 codeposited into adamantane at 77 K and (b) the simulated spectrum of $^{63}CuPF_3$ at X-band produced from the parameters given in the text.

rameters (*a* and *g*) were calculated from exact solutions of the spin Hamiltonian using computer programs provided by Drs. J. R. Morton and K. F. Preston of our laboratory and by computer simulation of the spectra using a program provided by Professor Lon B. Knight, Jr. (Furman University).

Isotopically enriched ^{63}Cu was prepared by reduction of ^{63}CuO (Oak Ridge National Laboratory, Oak Ridge, TN) with molecular hydrogen at 773 K. ^{63}Cu atoms were produced by heating the metal (30 mg) in a molybdenum pouch attached to the molybdenum electrodes of a furnace specially designed to fit into a port in the outer housing of the rotating cryostat.[26] PF_3 was prepared by reaction of NaF with PCl_3 in dry acetonitrile. Adamantane (Aldrich) and cyclohexane were used as inert hydrocarbon matrices.

Results

^{63}Cu atoms, deposited at a rate of ~10 mg/h, and PF_3 (~0.05 Torr) in an adamantane matrix at 77 K gave a red deposit that had the complex EPR spectrum shown in Figure 1a. Although there was a plethora of transitions the EPR transition, $\Delta M_S = \pm 1$, $M_I = -^3/_2$, and the NMR transition, $M_S = -^1/_2$, $M_I = -^1/_2 \rightarrow -^3/_2$, from ^{63}Cu atoms trapped in two magnetically distinct sites, labeled A, could be recognized.[26] In addition there was an almost isotropic doublet of quartets labeled B centered at ~5200 G that, by analogy with the EPR spectrum of CuCO,[6] can be assigned to the EPR transition, $\Delta M_S = \pm 1$, $M_I(63) = -^3/_2$, from a carrier with one ^{63}Cu nucleus, one ^{31}P, and three ^{19}F nuclei that is almost certainly $CuPF_3$. Although the $M_I(P) = -^1/_2$ quartet of this transition was more intense than the $M_I(P) = ^1/_2$ quartet and the relative intensities of the components of the quartets were not exactly 1:3:3:1, it did not seem reasonable that these lines were from different copper species. There was also another doublet of quartets, which was not quite as well resolved, at ~1800 G from the $M_I(Cu) = -^1/_2$ transition, while the $M_I(Cu) = ^1/_2$ and $^3/_2$ transitions at low fields were poorly resolved. A reasonable simulation of this spectrum (Figure 1b) was obtained by using the magnetic parameters $a_{63} = 4205 \pm 10$ MHz, $a_{31} = 1100 \pm 10$ MHz, and $a_{19} = 90 \pm 10$ MHz centered at $g = 1.999 \pm 0.002$.

There were also numerous almost isotropic lines labeled C that were clearly groups of quartets at higher power (20 mW) and higher temperature (98 K). The quartet spacing was 155.5 MHz, which was similar to that for Cu_3 in adamantane at 77 K.[27] Calculating the resonance fields of the 16 transitions from the large coupling of 1751.5 MHz for the two equivalent ^{63}Cu nuclei of Cu_3 gave lines that corresponded to the centers of the quartets. We therefore concluded that the carrier of spectrum C was indeed $^2B_2$ Cu_3 with a rigid obtuse triangular (C_{2v}) geometry.[27]

When the sample was warmed in the cavity of the spectrometer, the signals from $CuPF_3$ and Cu_3 disappeared irreversibly between 140 and 160 K. There was no evidence for conversion of Cu_3 to the fluxional form with three magnetically equivalent Cu nuclei.

TABLE I: EPR Parameters of Cu Monoligand Complexes[a] at 77 K

species	a_M	$a_{P,C}$	$a_{F,O}$	g	$\rho_{4s}(M)$[b]	$\rho_{3s}(L)$[c]	$\rho_{2s}(L)$
$^{63}CuPF_3$	4205	1100	90	1.999	0.70	0.08	0.0017
$^{63}Cu^{13}CO$	3961	191		1.9966	0.66	0.05	

[a] Hyperfine interactions in MHz. [b] Unpaired metal s spin population. [c] Unpaired ^{31}P or ^{13}C s spin population.

The EPR spectrum of a deposit from reaction of ^{63}Cu atoms with PF_3 in adamantane was also obtained at Q-band (ν = ~34 GHz) and is shown in Figure 2a. It consists of three doublets of quartets centered at ~9750, ~11 050, and ~12 700 G, which correspond to $M_I(Cu)$ of $^3/_2$, $^1/_2$, and $-^1/_2$ transitions. At the higher frequency the spectrum was almost first-order with equal P doublet spacings and almost equal Cu quartet spacings. Unfortunately, at this frequency we could not reach the fields necessary to obtain the fourth, highest field, doublet of quartets. The magnetic parameters were, however, in excellent agreement with those obtained at the lower frequency and gave the simulated Q-band spectrum shown in Figure 2b.

The large central feature at 77 K centered at $g = 2.0023$ had some structure but there were no lines that could be assigned to a 17-electron species $Cu(PF_3)_3$ with a planar π structure similar to that of $Cu(CO)_3$.[1] Furthermore, an isotropic spectrum did not develop above 205 K as was found for $Cu(CO)_3$.

The spectrum obtained from ^{63}Cu atoms and PF_3 in cyclohexane at 77 K did not have transitions from trapped ^{63}Cu atoms, $^{63}CuPF_3$, or $^{63}Cu(PF_3)_3$ but gave instead at least 11 multiplets at fields that indicated that they were from a copper cluster with most of the unpaired s spin population on two Cu nuclei. The best resolved multiplets had at least 13 lines, but the exact number was difficult to determine because of spectral overlap and the low intensity of the outer lines. The same spectrum was originally assigned[28] to the naked copper pentamer Cu_5 with a trigonal pyramidal geometry but has since been reassigned[29] to Cu_7, which has a pentagonal bipyramid structure (D_{5h} symmetry).[30] The 13 superhyperfine lines were originally rationalized on the basis of three equatorial Cu nuclei of a trigonal bipyramid carrying a small amount of negative unpaired s spin population with the coupling to one nucleus twice as large as the coupling to the other two nuclei. The five equivalent equatorial nuclei of Cu_7 would, however, be expected to give 16 lines. By carefully comparing the line intensities of a simulated multiplet for these two cases, we were able to conclude that Cu_7 and not Cu_5 was formed in the $Cu–PF_3–C_6H_{12}$ system.

Discussion

The only $Cu–PF_3$ complex that we have positively identified from reaction of Cu atoms with PF_3 in inert hydrocarbon matrices on a rotating cryostat at 77 K is the mononuclear monoligand complex $CuPF_3$. There was no evidence for the di- and triligand complexes, although $Cu(PF_3)_2$ probably has a $^2\Pi$ ground state and would be EPR silent. Timms,[19] in a previous study of the reaction of Cu atoms with PF_3 at 77 K, found that all of the PF_3 was recovered when the reaction mixture was warmed to 143 K; he concluded that a $Cu–PF_3$ compound of appreciable stability was not formed.

Since the EPR spectrum of $CuPF_3$ was almost isotropic, only information about the unpaired s spin distribution could be obtained from an analysis of the spectrum. Dividing the Cu, P, and F coupling constants by *A*, the parameters for unit spin populations in Cu 4s (5995 MHz), P 3s (13 306 MHz), and F 2s (52 870 MHz)[31] orbitals gave the unpaired spin populations, ρ_{ns}, listed in Table I. Also included in this table are the magnetic parameters for $CuPF_3$ and the magnetic parameters and unpaired spin

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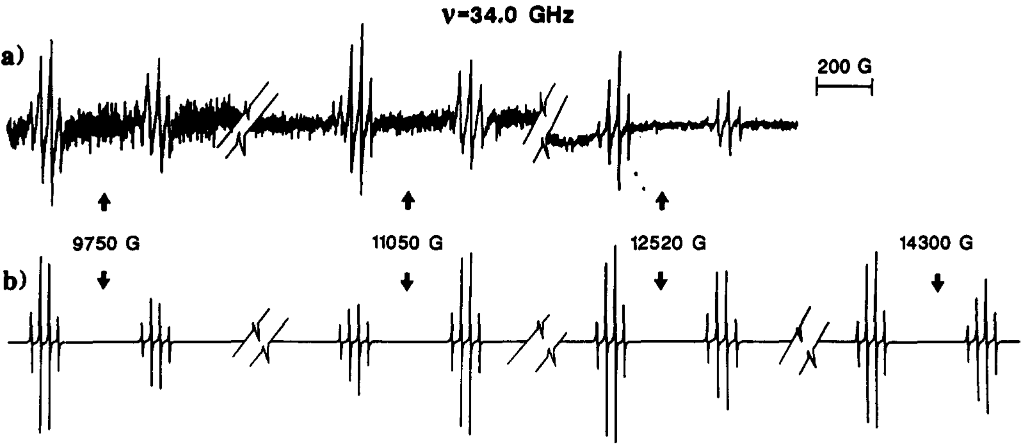

Figure 2. (a) EPR spectrum at Q-band of $^{63}CuPF_3$ in adamantane at 100 K and (b) the simulated spectrum of $^{63}CuPF_3$ produced from the parameters given in the text.

populations of the analogous complex CuCO.

The value of ρ_{4s} = 0.70 for $CuPF_3$ is larger than the value of 0.66 for CuCO. This suggests that although these two mononuclear monoligand complexes are certainly isostructural, there is a larger 4s contribution to the singly occupied orbital of $CuPF_3$ than there is for CuCO. CuCO has a linear geometry with a $^2\Sigma^+$ ground state and bonding involves a σ-type dative interaction in which the electrons of the highest occupied molecular orbital of CO are donated to an empty sp-hybrid orbital of Cu, while π-type back-donation occurs from the Cu d orbitals of the correct symmetry into the lowest unoccupied molecular orbital of CO. The semioccupied orbital is the second sp orbital pointing away from the ligand. If $CuPF_3$ is indeed isostructural with CO, it will have a $^2A_1$ ground state in the point group C_{3v}, i.e., structure **1**.

1

The overlap and mixing of the ligand σ donor orbital with the copper sp hybridized orbital directly places unpaired spin population in the ligand σ system and results in ligand hyperfine coupling. The value of $\rho_{3s}(^{31}P)$ = 0.08 is larger than the value of ρ_{2s} = 0.05 for the carbon of CuCO, indicating a larger P 3s contribution to the SOMO. The small unpaired spin populations in the 2s orbitals of the three fluorine nuclei could arise by a direct mechanism or by spin polarization and could be positive or negative.

The isotropic P and F coupling constants of $CuPF_3$ are similar to the average values of $\langle a_P \rangle$ = 1030 MHz and $\langle a_F \rangle$ = 112 MHz for the PF_3 complex of tetraphenylporphinecobalt(II).[32] This complex has 68% s character in the ligand donor orbital. We would expect a similar percentage of s character for $CuPF_3$ if the dipolar contribution to the P hyperfine interaction is the same in $CuPF_3$ and $Co^{II}[TPP]PF_3$. The large P 3s and relatively small P 3p orbital contribution to the SOMO arise because of the high electronegativity of F and the fact that the s and p P orbitals of PF_3 do not rehybridize when coordinated to a metal center.

Unlike the Cu–CO system where $Cu(CO)_3$ is the most dominant and persistent, copper carbonyl $Cu(PF_3)_3$ does not appear to be formed in the Cu–PF_3 system. This may be because $Cu(PF_3)_3$ reacts with traces of water in the system to give $HCu(PF_3)_3$ or readily dimerizes to give the diamagnetic dimer $[Cu(PF_3)_3]_2$. The absence of Cu–PF_3 complexes above 143 K in Timms' work[19] would, however, appear to exclude these explanations.

It is interesting that the copper cluster Cu_3 is formed in adamantane as well as $CuPF_3$ from the codeposition of Cu atoms and PF_3 into this inert hydrocarbon matrix. This finding suggests that PF_3 assists clustering of the copper atoms and that Cu_3 does not react with PF_3 to give the cluster complex $Cu_3(PF_3)_n$.

Reaction of Cu atoms with PF_3 in cyclohexane did not give $CuPF_3$ but gave instead a well-resolved spectrum of Cu_7. This bare copper cluster is usually only formed from copper atoms in cyclohexane when the deposit is being photolyzed with light of $\lambda > 320$ nm. The presence of Cu_7 in the Cu–PF_3–C_6H_{12} system is consistent with the suggestion that PF_3 aids clustering of copper atoms, in this case at the expense of forming $CuPF_3$. The reason Cu_3 is formed in adamantane and Cu_7 is formed in cyclohexane is not immediately obvious but is probably due to subtle differences in the nature of the hydrocarbon surface immediately after deposition on the cold surface of the drum.

The lack of evidence for reaction of Cu_3 and Cu_7 is interesting in view of the detailed analysis by Bagus et al.[33] of the interaction and bonding between Cu_5 and PF_3. A constrained space orbital variation (CSOV) study revealed that bonding has ligand to cluster σ donation and cluster to ligand π donation of comparable importance.

Conclusions. $CuPF_3$ is the only Cu–PF_3 complex that we have detected from reaction of Cu atoms with PF_3 in adamantane in a rotating cryostat at 77 K. This species has a $^2A_1$ ground state in the point group C_{3v} and is a copper-centered radical and not a phosphoranyl formed by addition of a Cu atom to PF_3. It has 70% of the unpaired spin located in the metal 4s orbital, 8% in the P 3s orbital, and a total of 0.5% in the F 2s orbitals for a total unpaired spin population of 78.5%. The remaining 21.5% of unpaired spin is probably located in the Cu 4p orbital, but because of the low parameter for unit spin population in Cu 4p (P = 171 MHz), it does not lead to resolved anisotropy in the powder EPR spectrum.

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