surements using $\epsilon = 8000$ M^{-1} cm^{-1} at $\lambda_{max} = 440$ nm for the nitrile complex and relative integrated peak areas for the 6' bipyridine proton of the nitrile complex[18] ($\delta = 9.42$ (d) ppm, vs TMS) and the olefinic protons of the ketone product ($\delta = 5.91$ (m) and 7.05 (m) ppm, vs TMS) in the ^{1}H NMR spectrum in CD$_3$CN. From the product studies, epoxidation[3] is *not* competitive with allylic oxidation nor is the 2-e product 2-cyclohexen-1-ol observed as an intermediate. ^{18}O-labeling experiments (Figure 2) show that within experimental error, O atom transfer to give the ketone product is quantitative. With excess oxidant the ketone undergoes further oxidation.

From spectrophotometric studies on solutions containing 5×10^{-5} M Ru^{IV}=O^{2+} and 5×10^{-3} M cyclohexene in CH$_3$CN, the reaction occurs in a stepwise manner with the initial formation of Ru^{III} (isosbestic point at $\lambda = 347$ nm) followed by slower formation of Ru^{II} as the solvento complex [(bpy)$_2$(py)Ru^{II}-(NCCH$_3$)]$^{2+}$ with $\lambda_{max} = 440$ nm. The rate law for the initial formation of Ru(III) is first order in Ru^{IV}=O^{2+} and first order in cyclohexene with k(25 °C, CH$_3$CN) = 0.5 M^{-1} s^{-1}. The second stage of the reaction is slower by a factor of ~200 at 25 °C and under stoichiometric conditions gives rise to the ketone and the solvento complex products shown in reaction 4, quantitatively.[19]
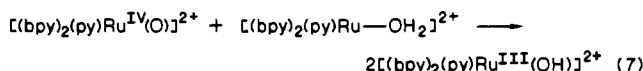
The available evidence is consistent with a mechanism involving initial attack on the olefin by Ru^{IV}=O^{2+}
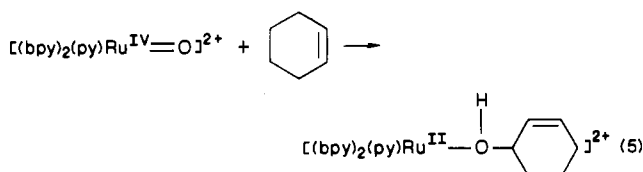
followed by a rapid comproportionation
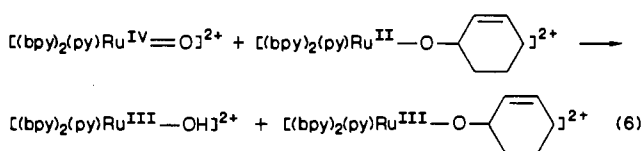
The appearance of Ru^{III} via the comproportionation reaction between the bound alcohol complex[20] and Ru^{IV}=O^{2+} is expected to be rapid; the analogous comproportionation involving the aqua complex

occurs with k(25 °C) = 1×10^3 M^{-1} s^{-1} in CH$_3$CN.[21] In the final step in the mechanism, slow oxidation of the bound alkoxide complex by Ru^{III} occurs followed by solvolysis to give [(bpy)$_2$-(py)Ru^{II}(NCCH$_3$)]$^{2+}$ and 2-cyclohexen-1-one as the final products.

The the deuterium-labeled olefin cyclohexene-*3,3,6,6-d$_4$* (MSD isotopes) occurs with net retention of the label adjacent to the double bond
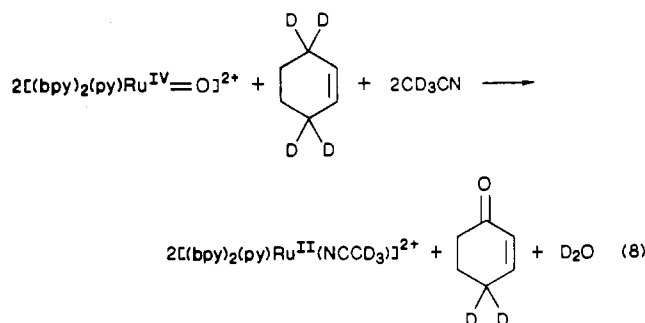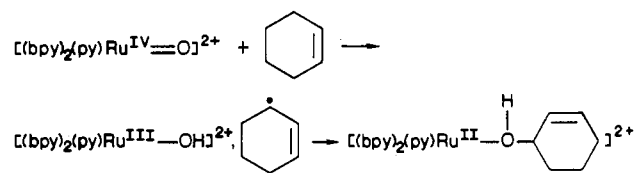
as shown by the relative integration and splitting patterns of the olefinic proton resonances in the ketone product (supplemental Figure 3). If the initial redox step involves a 1-e or H atom transfer to give the intermediate radical free in solution
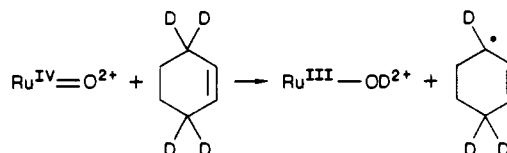
deuterium scrambling to other positions on the ring would have been expected to occur via allylic rearrangement, e.g.
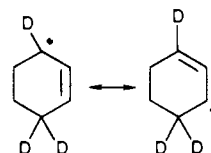
which is known to be rapid.[22] The initial redox step occurs with a H/D kinetic isotope effect (k_H/k_D) of 18 at 25 °C in CH$_3$CN for cyclohexene compared to cyclohexene-*3,3,6,6-d$_4$*. Given the magnitude of the isotope effect, the mechanism may involve H atom transfer and oxidative, inner-sphere capture of the intermediate radical before it can rearrange or separate in solution

rather than direct insertion into the C–H bond.

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(18) The primed notation refers to those two of the four pyridyl groups of the cis bpy ligands that are trans to one another. See: Roecker, L.; Dobson, J. C.; Vining, W. J.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 779.

(19) The product distribution shown in reaction 4 is only valid with an excess of the initial olefin near stoichiometric conditions. With excess Ru^{IV}=O^{2+}, further oxidation of the ketone occurs. With a large excess of initial olefin, the rate of direct oxidation of the olefin by [(bpy)$_2$-(py)Ru(OH)]$^{2+}$ formed in reaction 6 becomes competitive.

(20) Complexes of Ru^{III} containing bound alkoxide ligands have recently been prepared and characterized as products of the reactions between *trans*-[Ru^{IV}Cl(O)(py)$_4$]$^+$ and the corresponding alcohol: Aoyagi, K.; Nagao, H.; Yukawa, Y.; Ogura, M.; Kuwayama, A.; Howell, F. S.; Mukaida, M.; Kakihana, H. *Chem. Lett.* **1986**, 2135–2138.

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Chemical, Structural, and Electrical Property Studies on the Fluorination of the 90 K Superconductor YBa$_2$Cu$_3$O$_{6.8}$

Sir:

Following the breakthrough discoveries of high-T_c superconductivity in La$_{1.85}$Ba$_{0.15}$CuO$_4$[1,2] (LBCO) and YBa$_2$Cu$_3$O$_{6.8}$[3,4]

Table I. Conductivity of Nominal $YBa_2Cu_3F_xO_y$ from Different Sources

x	$\sigma(300\ K)$	$T_{co},^a$ K	$T_{cf},^b$ K	$T_{cm},^c$ K	$\Delta T(10-90\%),$ K	$E_a,$ eV
		From BaF_2				
1	3.9×10^2	92	75	87	12	
1.5	8.6×10	90	70	84	15	
2	1.7×10	90	49	82	20	
2.5	4.7×10^{-1}	82	incomplete transition			
3	3.0×10^{-3}	...				0.145
		From CuF_2				
1	1.96×10	92	88	91	2	
1.5	5.31×10	91	86	89	3	
2	2.08×10	90	81	88	5	
4	1.26×10^{-3}	...				0.142
6	$\sim 10^{-9}$	insulator				
		From YF_3				
1	5.41×10	93	88	91	3	
2	7.6	88	66	84	11	
3	3.7	85	71	80	7	
		$YBa_2Cu_3O_{6.8} + xBaF_2$				
0.75	2.0×10^2	93	89	92	2	
1.5	1.1×10^2	93	65	91	19	
3.0	1.7×10	90	55	79	20	
		From F_2 Gas				
1.3	1.9×10^{-1}	40.8	incomplete transition			
2.0	7.0×10^{-1}	...				0.04
1.4	2.1×10	92	65	85	16	
0.8	1.0×10^{-4}	...				0.118
0.15	3.3×10^2	92	88	91	2	

^{a}Onset temperature. ^{b}Zero-resistance temperature. ^{c}Midpoint (50%) temperature.

(YBCO) with T_c's of 35 and 93 K, respectively, a series of substituted derivatives has been reported. In the LBCO system, total substitution of La by other lanthanide elements leads to the loss of superconductivity, due to changes in crystal structure from the parent compound.[5,6] Replacing Ba with $Sr^{7,8}$ and Ca^9 leads to a slightly higher T_c ($\sim$40 K) in the first case and a much lower T_c ($\sim$20 K) in the second, which is consistent with the effect on T_c of applied hydrostatic pressures.[10] In the YBCO system, substitution of Y by lanthanide elements (from Nd to Yb, except Tb)[11-13] results in the same high T_c ($\sim$90 K), whereas replacing Ba by Sr systematically decreases T_c.[14] The effects of replacing

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Figure 1. Locations of "$YBa_2Cu_3F_xO_{6.5-x/2}$" on the YBCO phase diagram, assuming BaF_2 remained unreacted.

atoms in the YBCO structure can be qualitatively understood and explained in terms of the orthorhombic "superconducting slab" structure of this material.[15,16] Recently, an exceedingly high T_c of 155 K was reported for multiphasic material derived from the YBCO system with nominal composition $YBa_2Cu_3F_2O_y$.[17] In this paper, we report the study of fluorine substitution reactions in the YBCO system, with results much different from those reported previously.

Fluorine Incorporation Experiments. In the first set of experiments, a series of fluorine-containing materials with nominal composition $YBa_2Cu_3F_xO_{6.5-x/2}$ (x = 1, 1.5, 2, 2.5, 3) was prepared by mixing two primary components $YBa_2Cu_3O_{6.8}$ and $YBa_2Cu_3F_4O_{4.5}$. The latter was prepared from BaF_2 by following a reported procedure.[17] Initial O_2 annealing of these materials at 950 °C, a procedure that generally sharpens superconducting transitions, resulted in sample melting. Thus, our further experiments were carried out by use of an 850 °C annealing process. For the first three compositions (x = 1, 1.5, 2), superconducting transitions were observed with onset temperatures from 92 to 90 K, and with zero-resistance temperatures from 75 to 49 K. The 10–90% transition widths (ΔT) were much broader than those observed for the pure YBCO compound (typically 1–2 K), and ΔT increased with increasing nominal fluorine content (Table I). No sudden resistivity drops were observed at temperatures higher than 93 K. The fluorine-containing material with x = 2.5 exhibited semiconducting behavior with a significant drop in resistivity around 82 K, but its resistance did not go to zero down to 15 K. The fluorine-containing material with x = 3.0 exhibited typical semiconducting behavior down to the lowest temperature ($\sim$10 K), with an activation energy of 0.145 eV.

An X-ray powder pattern of the $YBa_2Cu_3F_4O_{4.5}$ primary starting compound after calcination at 950 °C (blue-green powder) indicated the presence of three major components: BaF_2, CuO, and $Y_2Cu_2O_5$; it also showed a very weak peak not inconsistent with the strongest 1:2:3 YBCO perovskite peak. Clearly, BaF_2 was not decomposed in this synthesis. In an attempt to incorporate F from BaF_2, further calcination at 1150 °C (yielding a slightly reddish powder) led to a large decrease of CuO and $Y_2Cu_2O_5$, and to an increase of Cu_2O and Y_2O_3, but the BaF_2 peaks remained unaffected in the powder pattern. The X-ray powder patterns of the other compositions (x_F = 1–3) consisted of four major components: BaF_2, CuO, the 1:2:3 perovskite, and Y_2BaCuO_5. We found that the amount of perovskite decreased with increasing nominal fluorine content. The above results led us to question whether there is actual fluorine incorporation, because if BaF_2 remains unreacted throughout the heat treatments, the above substitution reactions are equivalent to moving from the 1:2:3 composition to 1:0:3 on the YBCO phase diagram (Figure

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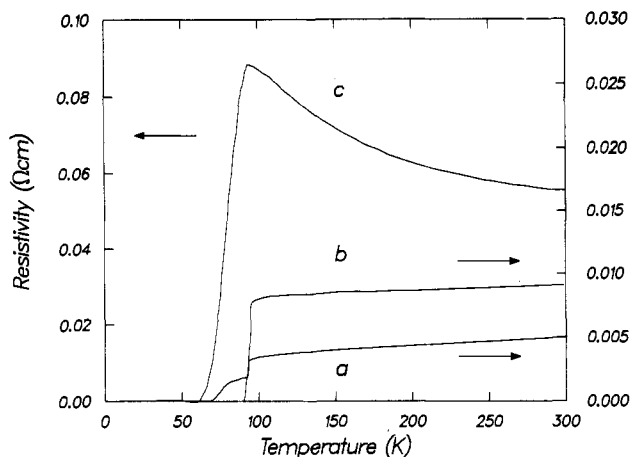
Figure 2. Resistivity of BaF_2 doped orthorhombic $YBa_2Cu_3O_{6.8}$: (a) 0.75 equiv of BaF_2; (b) 1.5 equiv of BaF_2; (c) 3.0 equiv of BaF_2.
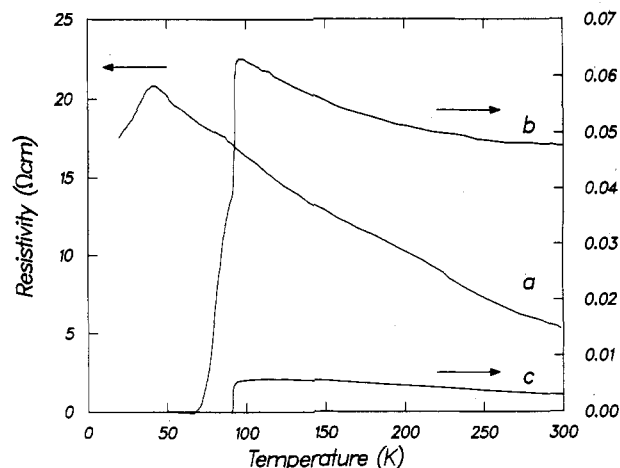

Figure 3. Resistivity of reaction products between 1:2:3 perovskite and F_2 gas: (a) sample 1, tetragonal YBCO with 1.3 equiv F; (b) sample 3, reannealed fluorine-containing YBCO (see text); (c) sample 5, orthorhombic YBCO with 0.15 equiv of F.

1). Thus, the superconductive behavior that we observe for these materials is consistent with that caused solely by the presence of the well-known 1:2:3 perovskite phase, $YBa_2Cu_3O_{6.8}$. "Substitution" of fluorine for oxygen thus has a very different effect on the conductive behavior of the 1:2:3 perovskite than has substitution of Sr for Ba,[14] or of Pr for Y.[18] In the last two cases, single-phase products were characterized by X-ray and neutron powder diffraction for low doping levels ($\leq 50\%$), and the superconducting onset temperatures decreased with increasing dopant, while transition widths remained relatively sharp (<10 K). On the other hand, the very broad transition widths (15–40 K) observed in this study indicated multiple-phase samples. Since the X-ray powder patterns of the pure $YBa_2Cu_3O_{6.8}$ (orthorhombic) and "$YBa_2Cu_3F_xO_y$" are expected to be very similar, the remaining question is, can one differentiate between these two compositions?

In a second set of experiments, we prepared another series of materials by mixing the pure YBCO orthorhombic 1:2:3 phase with 0.75, 1.5, and 3 equiv of BaF_2, in order to mimic the $x = 1, 1.5,$ and 2 compositions in $YBa_2Cu_3F_xO_{6.5-x/2}$. The samples were ground, pelletized, and O_2 annealed at 860 °C, and the reaction products were monitored by use of solid-state ^{19}F NMR. With 0.75 equiv of BaF_2 added, the same high T_c (~93 K) with a sharp transition was observed (Table I). With 1.5 equiv of BaF_2 added, a sharp drop in resistivity occurred at 92.6 K, followed by a long tail (Figure 2). With 3 equiv of BaF_2, the sample behaved like a small-gap semiconductor with a large drop in resistivity at 89.5 K, but the resistance did not go to zero until 55 K. The high onset and broad transition temperatures are very similar to those of the $x_F = 1-2$ samples. Quantitative ^{19}F NMR measurements on the 3 equiv of BaF_2 samples indicated that 95 ± 5% of the BaF_2 remained unreacted. We also monitored the amount of BaF_2 left in the F_4-containing primary compounds prepared at 950 and 1150 °C. We observed only about 50% of the BaF_2 in the 950 °C sample, and the ^{19}F resonance was paramagnetically shifted and broadened significantly. On the basis of powder pattern data (vide supra), we concluded that only a very small amount, if any, of the 1:2:3 perovskite was formed, and no other fluorine-containing species was observed. In a NMR control experiment where we mixed BaF_2, 0.5 equiv of $Y_2Cu_2O_5$, and 0.5 equiv of CuO, significant line broadening and loss of signal intensity of the ^{19}F resonance were also observed. The 1150 °C F_4-containing sample, on the other hand, was almost free from magnetic species ($Y_2Cu_2O_5$ and CuO), and 95 ± 5% of the BaF_2 was found by solid-state ^{19}F NMR to be unreacted. Therefore, for the above preparative procedures, 95 ± 5% of the BaF_2 remained unincorporated.

In order to probe the possibility of introducing fluorine from other sources, we used CuF_2 and YF_3 in subsequent preparations.

Since $BaCO_3$ is always needed in the synthesis, we monitored the reaction between CuF_2 (or YF_3) and $BaCO_3$. A total conversion to BaF_2 and CuO (or Y_2O_3) was observed from X-ray powder patterns after a 1:1 mixture was heated at 950 °C overnight. Perovskite samples made from mixtures of CuF_2, CuO, $BaCO_3$, and Y_2O_3, with nominal composition $YBa_2Cu_3F_xO_{6.5-x/2}$, showed superconductivity with sharp transition when $x = 1, 1.5,$ or 2 (Table I). This is presumably due to the formation of some of the 1:2:3 $YBa_2Cu_3O_{6.8}$ perovskite phase. When $x = 4$, the resulting sample was a semiconductor with $E_a = 0.142$ eV. Samples made from YF_3 gave similar results (Table I).

Since none of the above procedures resulted in any fluorine incorporation in $YBa_2Cu_3O_{6.8}$, we utilized the reversible oxygen intercalation effect and reaction with F_2 to introduce fluorine into the 1:2:3 perovskite. The orthorhombic form of $YBa_2Cu_3O_{6.8}$ was heated at 600 °C under dynamic vacuum (<10^{-3} Torr) for 3 h, and the oxygen evolved was monitored in situ with a mass spectrometer. An orthorhombic-to-tetragonal phase transition occurred, as is well documented for the above conditions.[19,20] After the sample was converted to the tetragonal phase ($YBa_2Cu_3O_y$, $y \leq 6.5$), about 85 Torr of F_2 gas was introduced and the uptake of fluorine on gradual heating was monitored by the pressure change. Reaction began at 175 °C and was complete in 30 min at 225 °C, resulting in the incorporation of about 1 equiv of F atoms/mol and evolution of about 0.1 equiv of O atoms/mol as O_2 (sample 1). The procedure was also repeated to introduce a second equivalent of F atoms with evolution of 0.3 mmol of O atoms as O_2 (sample 2). The resulting samples 1 and 2 were pumped under vacuum briefly in order to minimize surface F_2 and HF contamination. The X-ray powder data of these samples showed broad diffraction peaks corresponding to the 1:2:3 YBCO perovskite structure with unresolved orthorhombic/tetragonal splittings. More significantly, the powder data revealed *no* BaF_2 in the sample, which is distinctly different from our previous attempted fluorine incorporation experiments. These two samples were analyzed as follows: Sample 1, calcd for $YBa_2Cu_3F_{1.3}O_{6.5}$ (found): F, 3.62 (F, 3.49, 3.72). Sample 2, calcd for $YBa_2Cu_3F_2O_{6.5}$ (found): F, 5.46 (F, 5.29, 6.03). On the basis of the powder X-ray data and fluorine chemical analysis, we concluded that fluorine had indeed been incorporated. However, the location of fluorine atoms in the structure is not yet known. Both samples were semiconducting; sample 1 showed a resistivity drop at 40.8 K, but no superconductivity was observed (Figure 3). In order

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to test whether the fluorination reaction was reversible, sample 2 was reannealed under O_2 at 900 °C followed by slow cooling to give sample 3. Sample 3 was analyzed for fluorine. Calcd for $YBa_2Cu_3F_{1.4}O_{6.5}$ (found): F, 3.88 (F, 3.23, 4.22). Superconductivity was again observed in sample 3 with a sharp onset at 93 K, followed by a long tail that did not vanish until 65 K. Powder X-ray data revealed that a significant amount of F has been converted to BaF_2 at this stage, and sample 3 appears to be a mixture of 1:2:3 perovskite and BaF_2.

Since molecular fluorine reacted readily with the tetragonal 1:2:3 perovskite, we also carried out fluorination of the orthorhombic $YBa_2Cu_3O_{6.8}$ sample. The material was exposed to 1 atm of a 20% v/v mixture of F_2 in O_2. Reaction for 2 h at 280 °C led to the introduction of 1 equiv of fluorine atoms/mol and evolution of about 0.5 equiv of O/mol as O_2 (sample 4). This sample was analyzed for fluorine. Calcd for $YBa_2Cu_3F_{0.8}O_{6.5}$ (found): F, 2.26 (F, 2.24, 2.05). The powder pattern of sample 4 appeared to be orthorhombic and gave no evidence for the presence of BaF_2. Interestingly, all the (001) peaks were much stronger than those of the typical orthorhombic phase, which was indicative of preferred orientation. However, sample 4 is semiconductive throughout the temperature range we measured (300–15 K). Recently, a T_c of 148.5 K was reported from "low dosage" fluorine ions implantation (no composition given) of $YBa_2Cu_3O_x$.[21] We, therefore, prepared a specimen of low fluorine content, sample 5, by treating the orthorhombic form of $YBa_2Cu_3O_{6.8}$ at 300 °C with a small amount of F_2 in 1 atm of O_2. Sample 5 was analyzed for fluorine. Calcd for $YBa_2Cu_3F_{0.15}O_{6.5}$ (found): F, 0.43 (F, 0.40, 0.43). The resistivity curve showed a slight increase in resistance with decreasing temperature and a sharp T_c near 92 K. Thus, superconductivity near 90 K was only observed in samples of low fluorine content, which is consistent with our previous results.

Conclusions. We have demonstrated that when barium fluoride is mixed with Y_2O_3, CuO, and $BaCO_3$ in an attempt to introduce fluorine into the 1:2:3 perovskites, 95 ± 5% of the BaF_2 remains unreacted throughout the firing process. Use of copper and yttrium fluorides leads to similar results, since CuF_2 and YF_3 are readily converted to BaF_2 in the presence of $BaCO_3$. The superconductivity observed near 93 K in some samples is likely caused solely by the well-known orthorhombic perovskite, $YBa_2Cu_3O_{6.8}$. In the fluorine gas experiments in which F_2 reacted with either the oxygen-deficient tetragonal phase $YBa_2Cu_3O_x$ ($x \leq 6.5$), or the orthorhombic phase $YBa_2Cu_3O_{6.8}$, the results are consistent with actual fluorine incorporation. Finally, there is no sign of any drop in resistivity between 300 and 93 K for any of our samples, indicating that under the conditions given herein there is *no* superconducting F-containing phase formed with $T_c \simeq 155$ K.

Experimental Section. $YBa_2Cu_3O_{6.8}$ was prepared according to a literature procedure.[4] All chemicals were reagent grade or better. Fluorine analyses were carried out by Midwest Microlab, Indianapolis, IN. The formula, $YBa_2Cu_3F_xO_{6.5}$, was used to calculate the weight percentage of fluorine in all the fluorine gas experiments. Conductivities of sintered pellets were measured by using standard four probe techniques with ac currents and phase-sensitive detection. Currents of ~500 μA at a frequency of ~99 Hz were used.

The ^{19}F NMR spectra were recorded on two different spectrometers to minimize the chance of systematic error. One was a Bruker Instruments Model AM300, operating at a ^{19}F resonance frequency of 282.4 MHz. The other was a Nicolet Magnetics Model NTC-200, operating at a ^{19}F resonance frequency of 188.2 MHz, with an Andrews' design "magic"-angle sample-spinning solids probe. Typical operating parameters were a 90° pulse of 5 μs, a spectral width of ±62 kHz, a pulse recycle time of 500 s, and a total accumulation of 32 transients. Sample spinning speeds varied between 0 and 3 kHz.

Introduction of F_2 was carried out in a metal fluorine-handling vacuum line. The sample was contained in an alumina boat placed in a preconditioned nickel reaction vessel. Reaction was monitored by observing pressure changes with a Monel Bourdon gauge and also with an on-line quadrupole mass spectrometer. Molecular fluorine was always the limiting reagent, and reaction was continued until the F_2 was completely or nearly completely consumed.

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Chemical Vapor Deposition of FeCo_x and FeCo_xO_y Thin Films from Fe–Co Carbonyl Clusters

Sir:

Chemical vapor deposition (CVD) is a process widely used to prepare thin films finding diverse technical applications.[1] This chemical process involves the reaction of vapor-phase constituents near or on a heated substrate to produce a solid film and gaseous product species. Classical CVD is limited by the relatively high temperatures typically required and the inability to prepare many desired phases. The use of organometallic compounds as vapor-phase reagents can circumvent the high-temperature limitations, but relatively few organometallic compounds have been studied, and the extent of applicability of these compounds is not known.[2] Particularly difficult to prepare by any CVD technique are mixed-metal alloy and oxide thin films, of which the latter are particularly interesting because of their magnetic properties.[3] One potential route to such films is to vapor-deposit preformed mixed-metal organometallic clusters, a method that should yield homogeneous deposits. Herein, we describe the use of the heteronuclear carbonyl clusters $HFeCo_3(CO)_{12}$[4] and $CpFeCo(CO)_6$[5] to form mixed-metal Fe/Co alloy and oxide thin films using the CVD reactor shown in Figure A of the supplementary material.[6,7]

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