two quadrupole doublets in a 1:1 ratio with very similar δ and Δ_{Eq} values. The presence of two Fe sites is consistent with the structure shown in Figure 1. The Moessbauer parameters for II are similar to those reported[3] for the $Fe^{III}S_4$ sites in $(Et_4N)_3(I)$. Similar Moessbauer spectra are obtained[12] for III. The ambient-temperature magnetic moment of $(Et_4N)_4(II)$ (S = integer) at 1.23 μ_B/Fe atom is appreciably smaller than that reported[3] for $(Et_4N)_3(I)$ (3.39 μ_B; S = $^5/_2$). As a result of residual paramagnetism, the antiferromagnetically coupled linear oligomers display isotropically shifted ^{1}H NMR spectra. Resonances attributed to the ethanethiolate ligands in II are observed at 8.22 ppm (CH_3) and 73.3 ppm (CH_2) vs TMS. A signal at 8.3 ppm was observed previously[3] coincident with the synthesis of I and was considered to be associated with an unidentified paramagnetic precursor to the $[Fe_6S_9(SEt)_2]^{4-}$ cluster. The latter and $[Fe_4S_4(SEt)_4]^{2-}$ form by thermolysis of I in solution at 80 °C. The electronic spectra of II and III in CH_3CN solution[13] resemble the spectrum reported[3] for I but do not show the low-energy absorption at 720 nm. The cyclic voltammogram of $(Et_4N)_4(II)$ in CH_3CN solution (Pt electrode vs SCE) shows two irreversible reduction waves at $E_{1/2}$ = –1.27 and –1.58 V and qualitatively is similar to that of $(Et_4N)_4(I)$. The latter shows[3] irreversible waves at –1.66 and –1.79 V.

The reaction of II with $(CH_3CN)_3Mo(CO)_3$ or anhydrous $FeCl_2$ in CH_3CN solution affords in high yield the $\{[Mo(CO)_3]-[Fe_3S_4(SEt)_3]\}^{3-4}$ or $[Fe_4S_4(SEt)_4]^{2-}$[14] cluster, respectively. In solution, II slowly converts to a mixture of $[Fe_6S_9(SEt)_2]^{4-}$,[3]

$[Fe_4S_4(SEt)_4]^{2-}$,[14] and $[Fe_2S_2(SEt)_4]^{2-}$,[8] as evidenced by changes in the isotropically shifted ^{1}H NMR spectra. This instability of II in solution also is evident in changes in the electronic spectra that commence when solutions of II are allowed to stand for ca. 1 h at ambient temperature. No such changes are observed in CH_3CN solutions of III. The latter apparently is stabilized by the bidentate terminal ligands. The stability of II, limited as it is, may be due to the EtS⁻ terminal ligands. The reaction of II with thiophenol results in the formation of the known trimeric $[Fe_3S_4(SPh)_4]^{3-}$ complex anion.[3] Prior to recrystallization, samples of II contain <1% of an EPR-active impurity (S = $^1/_2$, $g_{av} \sim 2.00$) that may be due to the noninteger-spin $[Fe_5S_8(SEt)_4]^{5-}$ linear pentamer that could form by the oxidative coupling of I and $[Fe_2S_2(SEt)_4]^{2-}$ (eq 1). The reaction of preisolated I with elemental sulfur in a 1:1 ratio was undertaken in an attempt to obtain the $[Fe_6S_{10}(SEt)_4]^{6-}$ linear hexamer. Upon completion, this reaction shows the 560-nm CT absorption in I shifted to 620 nm with a concomitant loss of the S = $^5/_2$ EPR signal characteristics of I. Attempts to isolate this highly unstable complex currently are in progress.

(13) Electronic spectra (CH_3CN solution), nm (ϵ): for $(Et_4N)_4(II)$, 588 (13 290), 500 (17 470), 408 (27 060), 318 (34 450), 280 (34 700); for $(Et_4N)_4(III)$, 590 (17 200), 500 (16 690), 408 (25 490), 318 (27 400), 270.

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Articles

Synthesis and Characterization of Alkaline-Earth-Metal β-Diketonate Complexes Used as Precursors for Chemical Vapor Deposition of Thin-Film Superconductors

S. B. Turnipseed, R. M. Barkley, and R. E. Sievers*

Several of the β-diketonate metal complexes used for metal organic chemical vapor deposition (MOCVD) of thin-film superconductors have been characterized by thermogravimetric analysis, mass spectrometry, and gas chromatography/mass spectrometry. The volatility of the alkaline-earth-metal chelates has been studied, and it has been determined that one reason the alkaline-earth-metal chelates are less volatile than other metal β-diketonates is that they exist as oligomers. For example, one barium β-diketonate chelate consists of a cluster of five metal ions bridged by β-diketonate carbonyl oxygens and water molecules. It has also been found that the addition of uncomplexed (protonated) β-keto enolate ligand to the carrier gas stream greatly improves the gas chromatographic behavior of these alkaline-earth-metal chelates, probably owing to adduct formation accompanying the dissociation of the oligomers. The results of these studies, as well as the implications for using these chelates together with auxiliary ligands for MOCVD, will be discussed.

Introduction

Recently, several research groups have made high-quality thin films of the $YBa_2Cu_3O_7$ superconductor by using metal organic chemical vapor deposition (MOCVD) with volatile metal β-diketonate complexes. For example, Watanabe et al.[1] have prepared thin-film superconductors with a critical current density of 190 000 A/cm² at 10 T and an onset of superconductivity at 89 K by using this technique. A recent report from workers at Mitsubishi in-

dicated that critical current densities in the absence of magnetic field of films prepared by MOCVD from β-diketonates were approximately 6 300 000 A/cm².[2] One difficulty in making these films is that the barium chelates are less volatile and thermally stable than the copper and rare-earth-metal precursors. This has led to renewed interest in studying the stabilities, compositions, and thermal properties of alkaline-earth-metal β-diketonates.[3,4]

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Purdy et al.[4] have recently published a study on the synthesis, characterization, and thin-film deposition of a series of fluorinated alkaline-earth-metal chelates. Although many alkaline-earth-metal β-diketonate chelates were synthesized a decade or two ago,[5-8] these compounds need further characterization with respect to their structures, volatilities, and thermal stabilities, particularly in light of their great importance in MOCVD of ordered superconducting films.

Previous studies have shown mass spectral evidence that these species may be oligomeric,[3,5-8] which might account for their decreased volatility. Specifically, ions corresponding to $M_2L_3^+$, $M_3L_5^+$, $M_4L_7^+$, etc. have been observed in the electron ionization spectra of these chelates; however, no molecular ions of the type $[M(L)_2]_n$ have been reported previously. It is known from X-ray structure analysis that strontium and calcium complexes of the anion of 1,3-diphenyl-1,3-propanedione, solvated with ethanol or acetone, are tetrameric.[9,10] It has been suggested, however, that the higher oligomeric ions seen with the more sterically hindered complexes are simply a result of ion–molecule reactions in the mass spectrometer source,[8,11] although earlier osmotic pressure measurements indicated that these alkaline-earth-metal chelates may be truly oligomeric,[7] at least in solution.

Gas chromatographic studies can be used along with traditional thermogravimetric analysis to study the volatility and thermal stability of these complexes. Gas chromatographic analysis of the alkaline-earth-metal β-diketonate complexes is difficult because they tend to be strongly adsorbed onto the surfaces of the column.[6,7] Earlier chromatographic studies by Schwarberg, Sievers, and Moshier[7] have also shown that injections of a mixture of calcium and strontium complexes give a single peak which elutes at a retention time intermediate between those exhibited by the individual chelates and may represent a compound containing more than one alkaline-earth-metal ion (e.g., $CaSr(\beta\text{-diketonate})_4$).[7] Other gas chromatographic studies of transition-metal β-diketonate complexes have shown that addition of excess uncomplexed (protonated) ligand to the carrier gas stream improves the chromatographic behavior of β-diketonate complexes of transition metals such as manganese and also of the rare-earth metals.[12,13] Here we report the results of characterization of alkaline-earth-metal β-diketonate complexes by mass spectrometry and gas chromatography/mass spectrometry, and we describe methods to improve the volatility and thermal stability of barium and calcium precursors for thin-film deposition of oxide superconductors by MOCVD.

Experimental Section

Reagents. H(thd), 2,2,6,6-tetramethyl-3,5-heptanedione, was purchased from PCR (Gainesville, FL). H(fod), 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione, was purchased from PCR, Aldrich, and Lancaster Synthesis Ltd. (Windham, NH). $Ba(OH)_2\cdot 8H_2O$ and methanol were obtained from Fisher Scientific. $Ca(OH)_2$ was purchased from J. T. Baker Chemical Co. Barium metal granules were purchased from Alfa (Danvers, MA). The solvent, mixed hexanes, was obtained from Mallinkrodt. Absolute ethanol was purchased from Aaper Alcohol and Chemical Co. (Shelbyville, KY).

Synthesis. $Ba_5(thd)_9(H_2O)_3(OH)$. The barium chelate of thd, formulated by earlier workers as "$Ba(thd)_2$" but shown by our recent X-ray analysis[14] to actually be $Ba_5(thd)_9(H_2O)_3(OH)$, was synthesized according to procedures outlined previously by Hammond, Nonhebel, and Wu[5] and Belcher et al.[6] First, 7.14 g of $Ba(OH)_2\cdot 8H_2O$ was partially dissolved in 250 mL of hot H_2O. H(thd), 9.66 g, was added directly with stirring to this aqueous solution. The reaction mixture was allowed to stir for 30 min. The precipitate formed was collected by suction filtration. Most of the material was redissolved in 200 mL of ethanol. The undissolved material was removed by filtration. The complex reprecipitated when water was added. The product (7.03 g) was again collected by suction filtration. The melting point of this sample of complex is 158–165 °C, and it is partially soluble in *n*-pentane. Single crystals suitable for X-ray diffraction studies were obtained by dissolving most of the oligomeric thd complex freshly made from $Ba(OH)_2$ in warm *n*-pentane, filtering the solution, and allowing the solvent to evaporate slowly. A sample of these crystals was also submitted for elemental analysis (Huffman Laboratories, Inc. Golden, CO), and the results were as follows: C, 49.02; H, 7.39; Ba, 29.94. Calcd values for $Ba_5(thd)_9$-$(H_2O)_3(OH)$: C, 49.40; H, 7.45; Ba, 28.53.

The Oligomeric thd Complex of Ba(II) from Elemental Barium. For the preparation of the oligomeric thd complex of Ba(II) in the absence of water, the following synthesis, a modification of methods described by Purdy et al.[4] was used. Inside a glovebag flushed and filled with nitrogen, 6.3 g of barium metal granules was added directly to 14.19 g of H(thd). This was allowed to react for 20 min, during which time the reaction mixture bubbled vigorously. After this initial gas evolution slowed, 30 mL of hexanes was added, and the mixture was allowed to reflux for 2 h under nitrogen flow. The reaction mixture was allowed to cool, and an additional 30-mL aliquot of hexanes was added. The solution was then filtered to remove any unreacted barium granules. The solvent was removed by applying gentle heat while N_2 was bubbled through the solution, and the residue was allowed to air dry. The sticky solid remaining was transferred to a round-bottom flask and heated to 150 °C, as measured by a thermocouple on the outside of the flask, and the flask was purged with a high flow rate of dry nitrogen. According to thermogravimetric analysis, this procedure appeared to remove any adsorbed water and most of the excess ligand. From this procedure 10.1 g of product, with a melting point of 160–165 °C, was obtained.

The Oligomeric fod Complex of Ba(II). This was synthesized by using a method similar to that for the thd complex. $Ba(OH)_2\cdot 8H_2O$ (2.17 g) was partially dissolved in 50 mL of hot water. H(fod), 4.73 g, was added and the suspension was stirred vigorously for 30 min. The mixture was filtered with suction, and the precipitate was washed with hot water and cold (5 °C) hexanes and allowed to air dry. The yield was 4.1 g. The polycrystalline product melted at 194–196 °C.

The Oligomeric Complex of Ca(II). $Ca(OH)_2$, 0.262 g, was partially dissolved in 50 mL of water. A thick precipitate formed when 3.14 g of H(fod) was added to this solution. This material was collected by suction filtration and washed with 200 mL of water to remove any remaining $Ca(OH)_2$. This solid was then dried in vacuo over P_4O_{10} for 6 h, and 1.3 g of product, which melted over the range 90–93 °C, was obtained.

Other Syntheses. The other complexes used in this study were synthesized according to previously reported methods: $Cu(thd)_2$,[5] Y-$(thd)_3$,[15,16] $Cu(fod)_2$,[17] and $Y(fod)_3$.[18]

Thermogravimetric Analyses (TGA). The TGA was performed by using a Perkin-Elmer TG-2 system. The apparatus was purged with 80 mL/min He, and the furnace was heated at 20 °C/min from ambient temperature up to 500 °C.

Mass Spectrometry. Mass spectra were obtained by using a VG-7070EQ-HF high-resolution mass spectrometer. The spectra were calibrated against perfluorotri-*n*-butylamine or Ultramark, a high mass range standard containing high molecular weight perfluoropolyethers (PCR). The powdered complexes were introduced into the source of the mass spectrometer by using a direct insertion probe. The probe was heated until sufficient ion current was obtained to produce a well-defined mass spectrum (up to 250 °C with the barium chelates). The source temperature was maintained at 250 °C. The relative pressure of the ion source for electron ionization studies could be varied by changing the EI/CI slit from the large to the small opening, thereby providing a tighter source configuration operating at a higher pressure. Methane was used as a reagent gas for obtaining the negative chemical ionization spectra.

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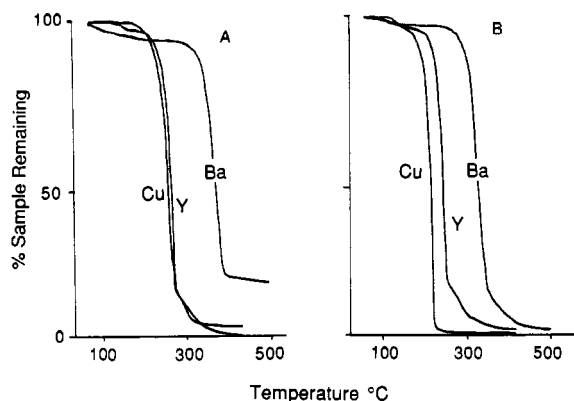(18) Springer, C. S.; Meek, D. W.; Sievers, R. E. *Inorg. Chem.* **1967**, *6*, 1105.

Figure 1. Thermogravimetric analysis curves for copper(II), yttrium(III), and barium(II) made from Ba(OH)$_2$, complexes of thd (A) and fod (B). Thermograms were obtained with a flow rate of 80 mL/min helium and a temperature program of 20 °C/min. Both Cu complexes exhibited 0% sample remaining at 400 °C.

Gas Chromatography/Mass Spectrometry. Combined gas chromatography/mass spectrometry experiments were performed by using an HP 5988A GC/MS instrument with high mass capability. Several identical 5 m long columns were cut from a single fused-silica capillary column that was coated with a cross-linked poly(dimethylsilicone) stationary phase (HP-1, 0.2 mm i.d., 0.11-μm film thickness). The mass spectrometer ion source was maintained at 250 °C, and the transfer line and injection port were both operated at 275 °C. The column temperature was programmed from 125 to 250 °C at 5 °C/min. Microliter-sized aliquots of solutions consisting of 0.2 g of each chelate dissolved in 10 mL of ethanol were injected into the injection port and split 15 to 1 before entering the capillary column, resulting in approximately 2–3 μg of each analyte entering the column.

Gas Chromatography with H(fod) in Carrier Gas Stream. An HP 5830 gas chromatograph with a flame ionization detector and a Grob-type split/splitless injector was used for these studies. The column was inserted into the FID until it was flush with the top of the flame jet, then pulled back approximately 1 mm, thus minimizing exposure of the chelates to hot metal surfaces and reducing decomposition. Again, a 5-m length of the HP-1 column was used. A reservoir of H(fod) was placed in the carrier gas line upstream of the injection port, so that the helium stream would carry ligand vapors continuously through the injection port, chromatographic column, and detector, even though the metal chelate was injected as a discrete plug of sample. The normal carrier gas controls were bypassed in this system, and the carrier gas flow was controlled by adjusting the outlet pressure of the He source. The H(fod) reservoir was kept in an ice bath to maintain a fixed partial pressure of ligand in the carrier gas. This system was used to study the chromatographic behavior of the fod oligomers of Ba(II) and Ca(II) by making discrete split injections (split ratio approximately 15:1) of 2-μL aliquots of 5 μg/μL ethanolic solutions of the chelates.

Temperature Gradient Sublimation Experiments. A 20 cm long, 15 mm i.d. glass tube heater with a temperature gradient was constructed by wrapping 28 gauge Nichrome wire, with the windings tightly together at one end and progressively further apart, down the length of the tube. The heater was then wrapped with ceramic mat insulation. An inlet (0.25 in. o.d. glass tube) for a carrier gas was made at the hotter end of the heater. At one end of a 25 cm × 10 mm piece of glass tubing, a platinum sample boat was held in place with glass wool. This tube was inserted into the heater so that the sample boat was at the hotter end. During each experiment a voltage was applied to the Nichrome wire via a Variac voltage controller. The temperature gradient was measured by sliding a K-type thermocouple along the inside tube and recording the temperature at 1-cm intervals. The flow rate of nitrogen carrier gas was set at approximately 20 mL/min. In certain experiments, a reservoir containing the protonated ligand was also placed upstream of the heater so that the carrier gas stream contained a fixed partial pressure of the auxiliary complexing agent as it passed over the heated sample boat. The time needed for the chelates to approach thermal equilibrium (virtually stop moving down the tube) was determined to be about 1 h under these conditions for the Ba(II) chelates.

Results

The various experiments conducted in this study, taken together with the results of earlier studies, provide a much clearer elucidation of the characteristics of metal complexes being used in the deposition of superconducting thin films by MOCVD. The lower

Table I. Comparison of Mass Spectra at Lower and Higher Source Pressures[a]

		% base peak	
		lower press.	higher press.
Cu(thd)$_2$	Cu(thd)$^+$	100	40
	[Cu(thd) − 57]$^+$	64	38
	Cu(thd)$_2{}^+$	36	85
	Cu$_2$(thd)$_2{}^+$	41	100
	Cu$_2$(thd)$_3{}^+$	22	97
	Cu$_3$(thd)$_4{}^+$	ND	16
Y(fod)$_3$	Y(fod)$_2{}^+$	100	ND
	[HY(fod)$_3$ − 57]$^+$	70	9
	HY(fod)$_3{}^+$	13	29
	Y$_2$(fod)$_5{}^+$	15	100
	FY$_2$(fod)$_4{}^+$	ND	39
[Ba(fod)$_2$]$_n$	Ba(fod)$^+$	23	ND
	FBa$_2$(fod)$_2{}^+$	22	ND
	Ba$_2$(fod)$_3{}^+$	100	100
	FBa$_3$(fod)$_4{}^+$	13	35

[a] These spectra were obtained by using a VG-7070EQ-HF mass spectrometer. The pressure was varied by changing the EI/CI slit from the EI (lower pressure) position to the CI (higher pressure) position and then collecting electron impact mass spectral data. The mass spectrometer source was at 250 °C. The temperature of the direct insertion probe was as follows: Cu(thd)$_2$ (lower pressure), 18 °C, (higher pressure), 30 °C; Y(fod)$_3$ (lower pressure), 38 °C, (higher pressure), 68 °C; [Ba(fod)$_2$]$_n$ (lower pressure), 172 °C, (higher pressure), 228 °C. The mass range scanned was m/z = 2700–250. ND = not detected.

Table II. Major Peaks in the Negative Chemical Ionization Spectra[a]

	m/z	intens	ion
Cu(thd)$_2$	429	100	Cu(thd)$_2{}^-$
	183	1	H(thd)$^-$
[Ba(thd)$_2$]$_n$	1008	26	Ba$_2$(thd)$_4{}^{-b,c}$
	1513	100	Ba$_3$(thd)$_6{}^{-b,c}$
	1851	4	Ba$_4$(thd)$_7$(OH)$^-$
	2016	0.2	Ba$_4$(thd)$_8{}^-$
	2034	0.4	Ba$_4$(thd)$_8$(H$_2$O)$^-$
	2047	0.4	Ba$_4$(thd)$_8$(H$_2$O)$_2{}^-$
	2354	0.1	Ba$_5$(thd)$_9$(OH)$^-$
[Ba(fod)$_2$]$_n$	1023	53	Ba(fod)$_3{}^{-b,c}$
	1456	8	Ba$_2$(fod)$_4{}^-$
	1751	100	[Ba$_3$(fod)$_5$ − 2(CF$_3$)]$^-$
	2169	11	[Ba$_3$(fod)$_6$ − 16]$^-$
	2185	7	Ba$_3$(fod)$_6{}^-$
[Ca(fod)$_2$]$_n$	238	25	[(fod) − t-Bu]$^-$
	256	32	[(fod) − CF]$^-$
	276	8	[(fod) − CF + F]$^-$
	295	15	fod$^-$
	926	44	HCa(fod)$_3{}^{-c}$
	1004	10	HF$_2$Ca$_2$(fod)$_3{}^-$
	1261	100	HCa$_2$(fod)$_4{}^{-c}$
	1280	37	HFCa$_2$(fod)$_4{}^{-c}$
	1359	13	HF$_3$Ca$_3$(fod)$_4{}^-$

[a] The direct insertion probe was heated to 250 °C to obtain these spectra. [b] A barium isotope pattern is present. [c] A carbon isotope pattern is present.

Table III. Isotope Pattern for Ba$_3$(thd)$_6{}^-$

m/z	calc rel intens	measd intens, % base peak
1509	22	25
1510	39	44
1511	51	57
1512	60	67
1513	100	100
1514	62	61
1515	24	21
1516	7	7

volatility of the Ba(II) complexes is apparent from the thermograms shown in Figure 1. As will be demonstrated in the following, the barium and calcium β-diketonate complexes occur normally as oligomers. This was determined from the mass spectral evidence shown in Tables I–III and in Figure 3 and from
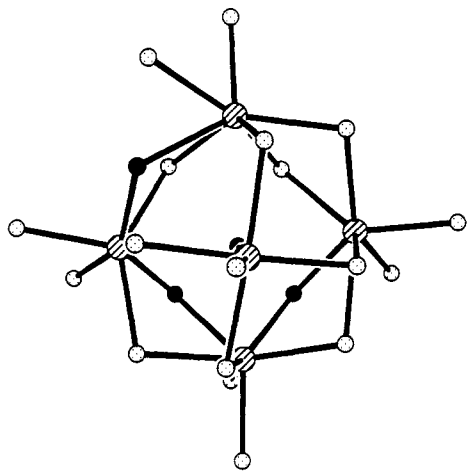
Figure 2. Barium–oxygen cage structure of $Ba_5(thd)_9(H_2O)_3(OH)$. The large spheres are barium ions, the dotted spheres are oxygen atoms associated with β-diketonate ligands, and the solid spheres are the other oxygen atoms.
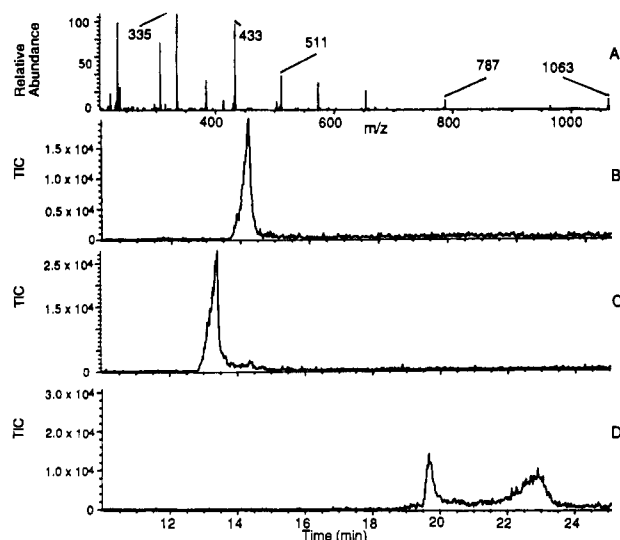

Figure 3. GC/MS data for $[Ca(fod)_2]_n$ and $[Ba(fod)_2]_n$. Part A is the mass spectrum of the chromatographic peak shown in trace B, the total ion chromatogram of a mixture of $[Ca(fod)_2]_n$ and $[Ba(fod)_2]_n$, which appears to form $CaBa(fod)_4$. The ions shown in part A correspond to $CaBa(fod)_3^+$ (1063); $FCaBa(fod)_2^+$ (787); $F_2CaBa(fod)^+$ (511); $Ba(fod)^+$ (433); and $Ca(fod)^+$ (335). The total ion chromatograms of $[Ca(fod)_2]_n$ alone and $[Ba(fod)_2]_n$ alone are shown in trace C and D, respectively. Injections of 2 μL of 0.02 g/mL solutions in ethanol were used. The injection port and transfer lines of the HP 5988A gas chromatograph/mass spectrometer were maintained at 275 °C. The mass spectrometer source was held at 250 °C. A 5-m length of HP-1 (0.2 mm i.d.) poly(dimethylsiloxane) column was used. The column temperature was programmed from 125 to 250 °C at 5 °C/min.

the preliminary results of the X-ray diffraction analysis shown in Figure 2. In the case of the barium complexes, evidence is presented to suggest that the oligomeric forms range from dimers to pentamers, and gas chromatographic experiments (Figures 4 and 5) show that these can be dissociated to create more volatile species if auxiliary ligands are added. This suggests that a preferable process for conducting MOCVD is to continuously add auxiliary ligand to the carrier gas stream before it passes through the reservoir of metal complex. In the following, the results from the thermogravimetric analysis, mass spectrometry, X-ray diffractometry, and gas chromatographic experiments that support these conclusions are discussed.

Discussion

Thermogravimetric Analysis. While the thermal properties of many of the β-ketoenolate chelates have been studied individually,[6,7,15–18] it is useful to compare the thermograms of the precursors being used to make thin films of the $YBa_2Cu_3O_7$ super-
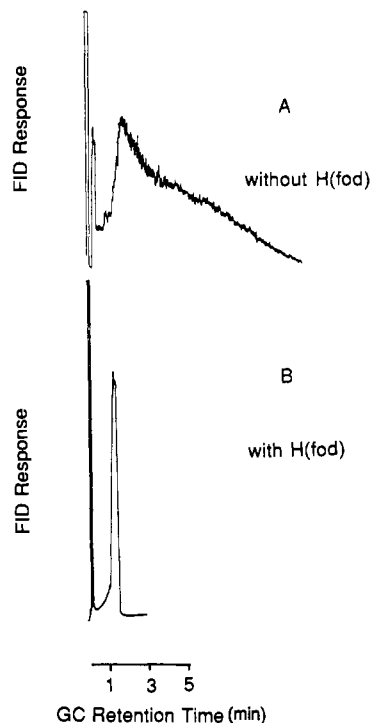

Figure 4. GC/FID data for $[Ca(fod)_2]_n$ without (A) and with (B) H-(fod) in the carrier gas stream. These represent 5-μg injections of $[Ca-(fod)_2]_n$ dissolved in ethanol. Both chromatograms were obtained by using an HP 5830 gas chromatograph with injection port and FID block temperatures held at 250 °C and a temperature program of 2.5 °C/min from 200 to 250 °C.

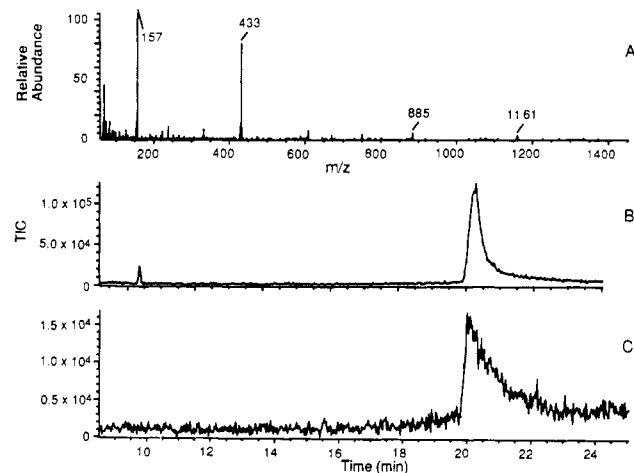**Figure 5.** GC/MS data for $[Ba(fod)_2]_n$ with (B) and without (C) H(fod) coinjected. The mass spectrum for the chromatographic peak in trace B is shown in part A. The ions correspond to $Ba_2(fod)_3^+$ (1161); $FBa_2(fod)_2^+$ (885); $Ba(fod)^+$ (433); and BaF^+ (157). These chromatograms were obtained by using an HP 5988A instrument, a 5-m HP-1 column, an injection port and transfer line at 275 °C, a mass spectrometer source at 250 °C, and a column temperature program of 5 °C/min from 125 to 250 °C. Most of the H(fod) elutes with the solvent, and this part of the chromatogram is not shown.

conducting material because comparisons of relative volatilities and thermal stabilities are facilitated when the same apparatus and operating conditions are used. From the thermograms shown in Figure 1 it is clear that the barium complexes of each ligand are much less volatile than the corresponding yttrium or copper compounds. It is also evident that the complexes made from H(fod) are more volatile and, in the case of barium, more thermally stable than those made from H(thd). Thermogravimetric analysis also shows that the sample of the oligomeric thd complex made from elemental barium has approximately the same volatility, thermal stability, and mass spectrum as that made from aqueous $Ba(OH)_2$. However, the material made from elemental

barium seems to be more susceptible to decomposition over time, as shown by thermogravimetric analysis. The thermogravimetric trace of material made from $Ba(OH)_2$ does not change significantly after several weeks, while the thermogravimetric analysis of the chelate made from elemental barium performed several weeks after its synthesis shows a broad temperature transiton with over 45% sample remaining, as contrasted with its behavior when freshly prepared.

Mass Spectrometry. The electron ionization spectra of these complexes are similar to what has been observed before, but chemical ionization experiments provide additional insight into the structure of alkaline-earth-metal β-diketonates. The electron ionization mass spectrum of the oligomeric thd complex of Ba(II) shows peaks at m/z ratios 1832, 1329, 825, and 321, corresponding to $Ba_4(thd)_7^+$, $Ba_3(thd)_5^+$, $Ba_2(thd)_3^+$, and $Ba(thd)^+$, respectively, as well as a number of other small peaks. Prominent peaks seen in the spectrum of the analogous fod complex occur at m/z 2304 ($[Ba_4(fod)_6 - 18^+]$), 1613 ($FBa_3(fod)_4^+$), 1161 ($Ba_2(fod)_3^+$), and 885 ($FBa_2(fod)_2^+$). As has been noted earlier,[11] ions corresponding to the m/z ratios of oligomers appear in the electron ionization spectra of complexes that are known to be monomeric in the crystalline state, such as $Cu(thd)_2$. These are presumably due to ion–molecule reactions that take place in the mass spectrometer source, and these peak intensities are known to be pressure dependent. When the pressure was varied by changing the size of the El/CI slit, it was found that the abundance of oligomeric ions in the $Cu(thd)_2$ and $Y(fod)_3$ spectra was highly dependent on the source pressure. However, although the relative abundances of the ions in the $[Ba(fod)_2]_n$ spectrum varied slightly with the change in pressure, a large abundance of oligomeric ions was observed in the spectrum of the oligomeric fod complex of Ba(II) in either source configuration, indicating that oligomers of the Ba chelate likely exist upon vaporization, even without ion–molecule reactions occurring in the source (Table I).

The negative chemical ionization mass spectra of these chelates show the molecular ions characteristic of the oligomers. In the case of the oligomeric thd complex of Ba(II), the major peaks in the negative chemical ionization spectrum are ions at m/z 1513 and 1008, which correspond to what may be either molecular ions of the dimer and trimer, respectively, or fragment ions of a pentamer such as $Ba_5(thd)_9(H_2O)_3(OH)$ (Table II). The experimentally observed isotope pattern for what may be trimeric $[Ba(thd)_2]_n$ has been compared to the calculated pattern by using the natural abundances of barium, carbon, and oxygen, and good agreement was found (Table III). The spectra of the fod complexes of Ba(II) and Ca(II) are more complicated due to fluorine transfer that occurs upon the loss of CF_3 fragments.

The higher mass ions for the Ba(II) complex of thd were found when the spectrometer was scanned from m/z 4000 to 1000. In order that high mass ions of low abundance could be observed, the instrument was operated so that sensitivity was enhanced at the expense of resolution. Under these conditions the mass spectrum of oligomeric complexes of Ba(II) known from independent X-ray analysis to consist, at least in part, of $Ba_5(thd)_9(H_2O)_3(OH)$ exhibited ions at m/z 1851 ± 3 ($Ba_4(thd)_7(OH)^-$), 2016 ± 5 ($Ba_4(thd)_8^-$), 2034 ± 5 ($Ba_4(thd)_8(H_2O)^-$), 2047 ± 5 ($Ba_4(thd)_8(H_2O)_2^-$), and 2354 ± 5 (which corresponds to $Ba_5(thd)_9(OH)^-$). In this mass range, the resolution of the instrument was not sufficient to resolve the isotope cluster expected for these ions, but the signal to noise ratio for the peak at m/z 2354 was approximately 10 to 1. Ions corresponding to clusters of up to five metals were also observed for oligomeric fod complexes of Ba(II) and Ca(II). Previously reported negative chemical ionization spectra of β-diketonate metal complexes have indicated that these chelates undergo electron capture of thermalized electrons to form stable negative ions.[19–21] It has been found that

ionization of chelates in this way produces only molecular ions, ions from the ligand and, in the case of fluorinated complexes, ions due to fluorine transfer. Known monomeric chelates, such as $Cu(thd)_2$, that give rise to oligomeric ions in electron ionization do not produce oligomeric ions under electron capture chemical ionization conditions (Table II). It is unlikely, therefore, that these oligomeric alkaline-earth-metal-containing ions are formed via ion–molecule reactions under the electron capture conditions used, and thus we conclude that oligomeric Ba complexes exist in the vapor phase, and vide infra, in the crystalline state and in solution.

X-ray Diffraction of $Ba_5(thd)_9(H_2O)_3(OH)$. The results from the structure determination of the barium oligomer that crystallized from n-pentane showed that five barium ions are clustered in a square-pyramidal geometry. A schematic of the Ba–O cage of this structure is shown in Figure 2. These metal centers are connected by bridging oxygens of three kinds, those in carbonyl, water, and hydroxide. Only nine β-diketonate ligands are present, whereas ten were expected. Five of these ligands are bidentate and bonded only to a single barium ion, and the carbonyl oxygens of the other four ligands act as bridges between two barium ions. There are also three oxygens in aquo moieties that act as bridges between barium ions and one oxygen that appears to be a hydroxy group bonded to the barium at the apex of the pyramid (in the center of Figure 2). From these results and also from elemental analysis and mass spectral evidence, the structure is formulated as $Ba_5(thd)_9(H_2O)_3(OH)$. Details of this structural determination are being prepared for publication.[14]

The results from the X-ray and mass spectrometry studies are important for two reasons. First, they indicate that the thd complex of the barium compound used so often in MOCVD and formulated as "$Ba(thd)_2$" is indeed oligomeric, and this accounts, at least in part, for its low volatility. Second, it is important to note that water is bound to the barium ions to form an integral part of the structure, thus making the barium oligomer difficult to dehydrate by common drying methods and suggesting that the decomposition of this precursor to BaO on a substrate in MOCVD may be occurring primarily by hydrolysis, rather than by oxidation, as has commonly been assumed. The following reaction, instead, is likely to occur:

$$Ba_5(thd)_9(H_2O)_3(OH) \xrightarrow{\Delta} H(thd) + BaO + \text{byproducts}$$
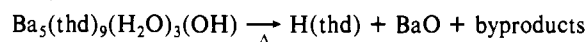
In other work in our laboratory, results from surrogate MOCVD experiments at temperatures ranging from 300 to 400 °C show, in fact, that over 90% of the volatile decomposition products of the barium pentamer of thd consists of the protonated ligand, H(thd).[22] This self-hydrolysis may also account for premature decomposition of barium aquo oligomers in the vaporization reservoir, which can be retarded by addition of H(thd) to the carrier gas stream.[23]

Gas Chromatography/Mass Spectrometry. The gas chromatographic behavior of these complexes was studied in order to learn more about their volatility and thermal stability and to evaluate methods to improve these properties. The fod complexes of barium and calcium were studied rather than the thd complexes because of the higher volatility of the former. Because the crystal structures of the fod complexes have not been determined, the formulation $[M(fod)_2]_n$ will be used, although it is recognized that this might not be an accurate depiction of oligomers that may also be β-diketone deficient and contain coordinated hydroxyl or water. The fod oligomers of Ca(II) and Ba(II) were each independently (in separate experiments) eluted from a short, thin-film capillary column when a mass spectrometer was used as a detector. Even though a capillary column was used, the chromatographic peaks were very broad and were of the type expected if an equilibrium of oligomers, e.g., dimer, trimer, etc., existed in the gas phase. Also, large amounts of sample (about 5 μg) had to be injected in order to produce any signal; this indicates that adsorption onto

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the column walls is also a problem with relatively inactive fused-silica capillary columns as it is with packed columns.[6] Column adsorption occurs to a lesser extent when a mass spectrometer is the detector than when a flame ionization detector (FID) is used, possibly because of the larger pressure drop that occurs when a gas chromatography column is connected directly to the high vacuum of a mass spectrometer.

With an FID, the retention time of the alkaline-earth-metal chelates varied widely depending on the recent history of the column, another indication that strong adsorption of the chelates within the column occurred. This memory effect was seen with flame ionization detection even when on-column injections were made, which suggests that decomposition in the injection port is not solely the cause of this behavior. The high vacuum imposed on the outlet of a short gas chromatography column when a mass spectrometer was used as a detector facilitates elution at lower temperatures and lessens the adsorption of the chelates. In addition, some decomposition may occur in the detector itself when an FID is used. With gas chromatography/mass spectrometry, $[Ca(fod)_2]_n$ gives a single chromatographic peak with the following ions present in the mass spectrum: 965, $Ca_2(fod)_3^+$; 653, $NaCa(fod)_2^+$; 335, $Ca(fod)^+$. An ion at m/z 433 $(Ba(fod)^+)$ is also observed and probably arises from prior injections of the barium oligomer or from impurities in $[Ca(fod)_2]_n$ (Figure 3). Higher oligomeric ions, if present, are not observable with this instrument because the quadrupole range is to m/z 2000 and sensitivity decreases markedly in the higher mass range. Injection of $[Ba(fod)_2]_n$ yields a peak that elutes at a much higher temperature than the calcium chelate and a second, irreproducible peak at a slightly higher elution temperature. The mass spectra of these two peaks are similar, with ions at m/z 1161 $(Ba_2(fod)_3^+)$, 885 $(FBa_2(fod)_2^+)$, and 433 $(Ba(fod)^+)$. It is possible that the second peak is a chromatographically resolved higher oligomer of $[Ba(fod)_2]_n$, with only fragments of the compound appearing in the mass spectrum, or it may be an artifact of column adsorption.

When a mixture of $[Ba(fod)_2]_n$ and $[Ca(fod)_2]_n$ is injected, a single chromatographic peak elutes at a retention time different from those of the individual oligomers. This parallels the earlier findings of Schwarberg, Sievers, and Moshier[7] with mixtures of $[Ca(thd)_2]_n$ and $[Sr(thd)_2]_n$. The mass spectrum of the gas chromatography peak with an intermediate retention time shows ions characteristic of a mixed-metal chelate: $CaBa(fod)_3^+$, $FCaBa(fod)_2^+$, $F_2CaBa(fod)^+$, as well as $Ca(fod)^+$ and $Ba(fod)^+$. This suggests that the following equilibrium exists:

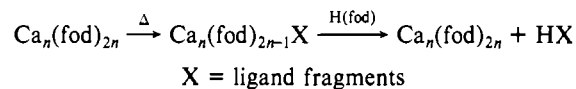$$[Ba(fod)_2]_n + [Ca(fod)_2]_n \rightleftharpoons [BaCa(fod)_4]_n$$
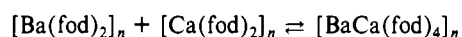
The fact that this is indeed a mixed-metal compound with an intermediate gas chromatographic retention time indicates that these complexes exist in the gas phase at least as dimers and this metal-exchange reaction occurs independently of any other ion-molecule reactions that may occur in the mass spectrometer ion source.

Effect of Excess H(fod) on the Chromatography of $[Ca(fod)_2]_n$ and $[Ba(fod)_2]_n$. When H(fod) was added to the He carrier gas stream in gas chromatography experiments, the shape of the $[Ca(fod)_2]_n$ peak was improved dramatically (Figure 4). Adsorption of the $[Ba(fod)_2]_n$ chelate was still evident with GC/FID, even with the excess ligand added to the carrier gas. However, the peak that appeared when $[Ba(fod)_2]_n$ was injected after several injections of $[Ca(fod)_2]_n$, presumably $[BaCa(fod)_4]_n$, showed a much improved peak shape when H(fod) was present in the carrier gas stream than in its absence. It should be noted that it is important to use a slow temperature program rate when H(fod) is used in the carrier gas stream, because the baseline increases significantly as a function of column temperature. The effect of the presence of excess H(fod) on the chromatographic behavior of $[Ba(fod)_2]_n$ was observed more clearly with gas chromatography/mass spectrometry, perhaps because part of the column was operating at subambient pressure. In this case, H(fod) was not introduced via the carrier gas stream, but was simply coinjected as a liquid solution with the $[Ba(fod)_2]_n$. Consequently, because

H(fod) is more volatile than the barium chelate and becomes separated, contact of the two species, postulated to be in equilibrium with $H[Ba(fod)_3]$, occurs only transiently in the injection port and at the beginning of the column (vide infra). There may have been a small amount of protonated ligand formed from the decomposition of the chelates themselves when they were injected without H(fod) present, but under the chromatographic conditions that were used it would have coeluted with the solvent front and not have been separately detectable. Although the mass spectrum of the resulting peak did not change significantly from that of $[Ba(fod)_2]_n$ alone, when H(fod) was coinjected, the peak shape was improved, and the amount of signal was also 1 order of magnitude greater for the same amount of $[Ba(fod)_2]_n$ injected (Figure 5).

Fujinaga has suggested that the improved chromatography of metal chelates in the presence of excess free ligand is due to the suppression of thermal dissociation of the chelates.[12,13] For example, it is possible that, upon heating, some of the ligands surrounding the metal may decompose, and if extra free ligand is present, the damage may be effectively repaired:

$$Ca_n(fod)_{2n} \xrightarrow{\Delta} Ca_n(fod)_{2n-1}X \xrightarrow{H(fod)} Ca_n(fod)_{2n} + HX$$

$$X = \text{ligand fragments}$$

Sokolov has suggested that adsorption of chelates to a chromatographic column may occur when the complex loses a ligand and becomes attached to the matrix of the column.[24] It is possible that the presence of excess ligand inhibits this adsorption effect. In addition, with these chelates, breakdown of higher oligomeric species could occur when excess ligand is present, according to the following equilibrium:

$$H(fod) + [Ca(fod)_2]_n \rightleftharpoons H[Ca(fod)_3] + [Ca(fod)_2]_{n-1}$$

$$n = 2-5$$
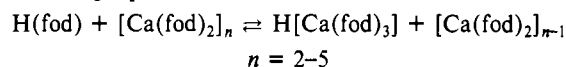
This could also explain the improved peak shape, particularly since the X-ray and mass spectral results indicate that these compounds are ligand deficient and contain hydroxyl groups so they may be especially amenable to the uptake of additional chelating ligand.

Independent thermogravimetric experiments confirm that the apparent volatility of these chelates is actually improved by the presence of excess ligand as they are volatilized, indicating that this is not just a phenomenon observed in gas–liquid chromatography columns. Temperature gradient sublimation experiments based on a technique described by Berg et al.[25,26] were designed to mimic part of the MOCVD process. Even though it may not be possible to isolate a stable ligand–chelate adduct, formation of a transient adduct species in the gas phase may increase the apparent volatility of the Ba(II) complex. In these experiments, vapors of the protonated ligand flow directly over a sample boat containing the Ba chelate as it is vaporized and the temperature zone in which the chelate recondenses is measured. These experiments were performed with the sample pan heated to and maintained at 350–410 °C for 1 h. When H(thd) vapor in N_2 flowed over the thd chelate of Ba(II), the chelate traveled further down the sublimation tube, condensing at a temperature zone of 170–175 °C as opposed to 180–210 °C for the chelate itself, and when repeated, the distance transported was more reproducible from experiment to experiment. The percent sample remaining in the pan was not significantly different from that recorded for the Ba(II) chelate alone. When the partial pressure of the H(thd) in the gas stream was increased by heating the ligand reservoir in a 95 °C water bath, the crystals moved a little bit further (to a zone with 10–15 °C lower temperature), but the crystal formation was not very reproducible because of the presence of a large amount of oily deposit along the tube.

In fact, it has also been found that addition of excess H(thd) to the carrier gas stream passing through the barium source in a metal organic chemical vapor deposition experiment gave a

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steadier concentration of the barium chelate in the gas phase and improved the quality of the thin-film superconductors made in this way.[23]

Conclusions

The metal β-diketonate complexes used as precursors for MOCVD of thin-film superconductors have been characterized chemically and physically. The alkaline-earth-metal chelates, which are less volatile than the analogous copper(II) and yttrium(III) complexes, are oligomeric. Oligomeric ions were observed by negative chemical ionization mass spectrometry, and the abundances of oligomeric ions in the electron ionization spectra are not dependent upon source pressure. Mass spectral, elemental analysis, and preliminary X-ray results show that the compound previously formulated as $Ba(thd)_2$ is more accurately described by the formula $Ba_5(thd)_9(H_2O)_3(OH)$. The gas-phase chromatographic elution of these complexes is difficult, particularly when a flame ionization detector is used, because the complexes tend to become adsorbed onto the column and may thermally decompose in the chromatographic system. However, gas-phase chromatographic elution of these chelates can be performed more readily at subambient pressure with a mass spectrometer as a detector, and a mixed-metal complex containing both Ba(II) and Ca(II) was eluted when $[Ba(fod)_2]_n$ and $[Ca(fod)_2]_n$ were coinjected. The existence of this species, which can be separated chromatographically, is further evidence that oligomeric species exist within the chromatographic column prior to entrance into the mass spectrometer source. In addition, it has been determined that the addition of excess free ligand improves the chromatographic peak shapes of these alkaline-earth-metal chelates, presumably by breaking down the higher oligomers. This confirms earlier work which showed that the addition of excess protonated ligand to the barium source in MOCVD produces higher quality superconducting thin films that are obtained without the additional β-diketone.[23]

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Chemistry and Catalytic Properties of Ruthenium and Osmium Complexes. 6. Synthesis and Reactivity of [RuH(CO)(NCMe)2(PPh3)2][BF4], Including the Catalytic Hydroformylation of Hex-1-ene

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The interaction of $RuHCl(CO)(PPh_3)_3$ (1) with CD_3CN leads to the formation of a mixture containing two isomeric forms of the complex $RuHCl(CO)(NCCD_3)(PPh_3)_2$ (2' + 4') plus the cationic species $[RuH(CO)(NCCD_3)_2(PPh_3)_2]^+$ (3'), as shown by in situ ^1H and ^{31}P NMR experiments and other reactivity studies. If 1 is reacted with CH_3CN int he presence of $NaBF_4$, $[RuH(CO)(NCCH_3)_2(PPh_3)_2][BF_4]$ (3) is isolated pure in high yields. This cation reacts readily at room temperature with neutral ligands (PPh_3, $P(OPh)_3$, $Ph_2PCH_2CH_2PPh_2$, py, CO) by substitution of the acetonitrile trans to the hydride; at 60 °C, both acetonitriles can be displaced. Complex 3 also reacts with anions such as halides and OAc^- to yield the corresponding neutral species or with $Co(CO)_4^-$ to produce the heterobimetallic complex $[Ru(CO)_3(PPh_3)(\mu-PPh_2)Co(CO)_3]$. All the new complexes were characterized by analytical and spectroscopic (IR, ^1H and ^{31}P NMR) methods. Complex 3 was also found to catalyze the hydroformylation of hex-1-ene at 120–150 °C and 100 bar CO/H_2.

The complex $RuHCl(CO)(PPh_3)_3$ (1), first reported by Vaska and Diluzio in 1961,[1] has attracted continuous attention. This cream-colored, air-stable material is rather insoluble in most common solvents, and therefore its characterization has been based on elemental analysis and IR and Raman spectroscopy.[1–3] The stereochemistry of 1 has been assumed to be analogous to those of the related complexes $RuHCl(CO)(PMePh_2)_3$ and $OsHBr(CO)(PPh_3)_3$, which have been characterized by ^1H NMR spectroscopy and X-ray diffraction, respectively.[4,5]

Substitution of a phosphine by other neutral ligands leads to complexes $RuHCl(CO)(PPh_3)_2L$ (L = CO, RNC, PR_3, $P(OR)_3$, $P(OR)R'_2$, $P(OR)_2R'$, $pySH$);[6] in most cases, the incoming ligand occupies the position trans to the hydride. Substitution reactions involving chloride abstraction yield cationic or neutral complexes of the type $[RuH(CO)(PPh_3)_{3-n}L_{1+n}]^{x+}$ (x = 1, L = $P(OR)_3$, n = 1; x = 1, L = $PPh_2(OR)$, n = 3; x = 0, L = S_2CY^-, Y = NR_2, OR, n = 1, 2).[6a,7] Interaction of 1 with carboxylic acids produces carboxylate species $RuCl(CO)(OCOR)(PPh_3)_2$[3,8] and in the case of trifluoroacetic acid the dimer $\{(\mu-CF_3CO_2)[Ru(\mu-Cl)(CO)(PPh_3)_2]_2\}^+\{CF_3CO_2\}^-$.[3] Other related complexes such as $\{(\mu-H)[Ru(\mu-Cl)(CO)(PPh_3)_2]_2\}^+$,[3] $\{(\mu-Cl)[Ru(\mu-Cl)(CO)(PPh_3)_2]_2\}^-$,[3] and $RuCl(CO)(PPh_3)(\mu-Cl)_3Ru(CO)(PPh_3)_2$[9] are obtained from the reactions of 1 with HBF_4, CH_2ClCO_2H, and gaseous HCl, respectively. Similarly, β-diketones react with 1 to produce complexes $RuCl(CO)(\beta-dike)(PPh_3)_2$.[10] Insertion reactions into the Ru–H bond of 1 have been reported for arenediazonium salts,[9] 2-vinylpyridine, methylsorbate, dimethylfumarate, acrylonitrile,[11] carbon disulfide, dialkyl and diarylcarbodiimides, 1,3-diaryltriazenes,[12] and acetylenes.[13]

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