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Synthesis and Characterization of Ruthenium Amidinate Complexes as Precursors for Vapor Deposition

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Abstract: Three new ruthenium amidinate complexes were prepared: tris(diisopropylacetamidinato)-ruthenium(III), Ru(PrNC(Me)NPr)3; bis(diisopropylacetamidinato) ruthenium(II) dicarbonyl, Ru(PrNC(Me)NPr)2(CO)2; and bis(di-
tert-butylacetamidinato)ruthenium(II) dicarbonyl, Ru(BuNC(Me)NBu)2(CO)6. They have been synthesized and charac-
terized by 1H NMR, TG and X-ray structure analysis. These three complexes were found to be monomeric and air stable. Compound 6 was found to have sufficient volatility and thermal stability for use in chemical vapor deposition (CVD) and atomic layer deposition (ALD) of ruthenium metal films.

Keywords: Ruthenium, amidinate, ALD, CVD.

INTRODUCTION

Chemical vapor deposition (CVD) is a process for forming thin films from vapors of one or more precursors. Atomic layer deposition (ALD) is a technique related to CVD in which a heated substrate is exposed alternately to two complementary precursors. The two ALD precursors undergo self-limiting chemisorption reactions, providing highly uniform and conformal film growth. Highly uniform and conformal thin films are needed in microelectronics with feature size shrinking to sub 90 nm [1,2] and magnetic information storage [3]. Recently a lot of interest was focused on the applications of ALD techniques. Displays have been made using ALD [4]. Magnetic disk drives now incorporate an ALD layer [5], and ALD insulating layers are used in microelectronic memory chips [6]. Ruthenium thin films are potentially important materials in microelectronics. Ruthenium has been demonstrated as a seedless diffusion barrier for capacitor electrodes [6,9] because of its low resistivity and high thermal stability. Furthermore, it has a conductive oxide (RuO2) which prevents further oxygen diffusion. In order to apply CVD and ALD techniques for processing ruthenium films effectively to the smaller and more complicated geometries used in microelectronics, new volatile, reactive and thermally stable chemical precursors for ruthenium are needed.

Several ruthenium precursors have been studied for CVD or ALD of ruthenium films. They are basically divided into two categories: ruthenium organometallic compounds containing Ru-C bonds such as Ru3(CO)12 [10] and rhenocenes [11,12] such as Ru(Cp)2 and Ru(EtCp)2 [13] (Cp = cyclopentadienyl); and ruthenium β-diketonates [14] or Ru(CO)3(β-diketonates) [15]. These precursors lack sufficient reactivity with common second reactants such as hydrogen, water, and ammonia. Thus the processes based on these precursors require energy-intensive plasmas or highly oxidizing reagents such as oxygen or ozone, which are not compatible with electrically conductive substrates such as titanium nitride, tantalum nitride or tungsten nitride.

Some volatile and thermally stable metal amidinates [16,17] have been found to be effective for ALD and CVD of metals (Fe, Co, Ni, Cu, Ag, Ru) [18], transition metal ox-
ides (MnO, FeO,CoO, NiO, Cu2O) [19], lanthanide oxides (La2O3, LaAlO3 [20], PrAlO3 [21], Sc2O3 [22], Y2O3 [23], GdScO3 [24], Lu2O3 [25]), nitrides (Fe,N [26], Co,N [27], Ni,N [28], Cu,N [29]). These metal amidinate precursors provide several benefits compared with other types of ALD precursors. They have metal-nitrogen bonds that are reactive to molecular hydrogen (forming metals), water (forming oxides) and ammonia (forming nitrides). Also, incorporation of carbon and oxygen impurities into the films was found to be minimal. The by-products from these metal amidinate complexes are not corrosive to the deposited films, unlike the corrosive hydrogen halides released by the use of metal halide precursors. In general, the advantages of the metal amidinate precursors include sufficient volatility, low deposition temperature, high thermal stability and high quality of the films.

To date, a few well-defined amidinate complexes of ruthenium have been prepared. Homolectic Ru(III) amidinate complexes that have been structurally characterized includeRu(Ph-Me-amd)3 [30] and Ru(Tol-Me-amd)3, with Ph =

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C\textsubscript{8}H\textsubscript{8} and Tol = C\textsubscript{8}H\textsubscript{12}(CH\textsubscript{3})\textsubscript{3} \cite{31}. Heteroleptic Ru(II) amidinate complexes Ru(Ph-Me-amd\textsubscript{3})(COD) and Ru(Pr-Me-amd\textsubscript{3})(COD) (COD = cyclooctadiene) \cite{32,33} have also been prepared and their structures been determined. However, no data concerning the volatility, reactivity or thermal stability of these complexes have been reported.

We found a way to make some new ruthenium amidinate complexes and explored their physical properties, especially properties with respect to their use as precursors for vapor deposition. Herein the synthesis and physical characterization of three new Ru(III) and Ru(II) amidinate complexes are described.

**RESULTS AND DISCUSSION**

**Starting Materials**

mer-RuCl\textsubscript{3}(Me\textsubscript{2}S)\textsubscript{3} 1, [RuCl\textsubscript{2}(CO)\textsubscript{3}]\textsubscript{2} 2 and RuCl\textsubscript{3}(CO)\textsubscript{3}(C\textsubscript{6}H\textsubscript{10}O) 3

When we tried to prepare ruthenium amidinate complexes using the metathesis reaction of anhydrous ruthenium chloride (RuCl\textsubscript{3}) with a lithium amidinate in ether or ether/THF mixtures, we found that this synthetic method was not efficient in synthesizing ruthenium amidinates. When anhydrous RuCl\textsubscript{3} was used as a starting material, the yield of produced ruthenium amidinate complexes was extremely low. This low yield is probably due to relatively low solubility of anhydrous RuCl\textsubscript{3} in ether or THF.

Starting materials, mer-RuCl\textsubscript{3}(Me\textsubscript{2}S)\textsubscript{3}, [RuCl\textsubscript{2}(CO)\textsubscript{3}]\textsubscript{2} and RuCl\textsubscript{3}(CO)\textsubscript{3}(C\textsubscript{6}H\textsubscript{10}O), which had relatively high solubility in ether or THF, were suitable for the synthesis of ruthenium amidinate compounds with relatively good yields. In particular, RuCl\textsubscript{2}(CO)\textsubscript{3}(C\textsubscript{6}H\textsubscript{10}O) was a good starting material for synthesizing Ru(Pr-Me-amd\textsubscript{3})(CO)\textsubscript{2}, (where ‘Pr-Me-amd = ‘PrNC(Me)N‘Pr) [RuCl\textsubscript{2}(CO)\textsubscript{3}]\textsubscript{2} was synthesized according to the literature \cite{34} and dried under vacuum overnight before using it as a starting material for Ru(Pr-Me-amd\textsubscript{3})(CO)\textsubscript{2}. Further recrystallization of [RuCl\textsubscript{2}(CO)\textsubscript{3}]\textsubscript{2} from THF resulted in a good yield of RuCl\textsubscript{2}(CO)\textsubscript{3}(C\textsubscript{6}H\textsubscript{10}O). For mer-RuCl\textsubscript{3}(Me\textsubscript{2}S)\textsubscript{3}, several synthetic routes have been described \cite{35-39}. The method described in \cite{38} seems like a convenient way to make mer-RuCl\textsubscript{3}(Me\textsubscript{2}S)\textsubscript{3} without the complications of using toxic dimethylsulfide or reducing Ru(III) to Ru(II) by alcohol. We tried to scale up the preparation of mer-RuCl\textsubscript{3}(Me\textsubscript{2}S)\textsubscript{3} according to the literature method \cite{38} and this resulted in a 30% yield. Then we improved the yield by adding twice as much dimethyl sulfoxide (DMSO) and concentrated hydrochloric acid as used previously \cite{38}. Up to 8 grams of mer-RuCl\textsubscript{3}(Me\textsubscript{2}S)\textsubscript{3} with a yield as high as 75% could be made in one batch. This new synthetic procedure may confirm the mechanism proposed by B. R. James and coworkers \cite{35,37,39}: in strongly acidic conditions, DMSO reduces Ru(III) to Ru(II) while itself being reduced to dimethylsulfide, which readily coordinates Ru(III). The second reaction is in equilibrium. With the introduction of supplemental DMSO, the equilibrium was pushed to the left side of reaction (2) and the yield of mer-RuCl\textsubscript{3}(Me\textsubscript{2}S)\textsubscript{3} was increased to 75%, which is close to the yield reported for a small batch (ca. 0.2 g). The \textsuperscript{1}H NMR spectrum of the product mer-RuCl\textsubscript{3}(Me\textsubscript{2}S)\textsubscript{3} shows two paramagnetic signals at \textasciitilde 10.5 and \textasciitilde 21.0 ppm. Their intensities have a ratio of 1:2, indicative of a mer structure. All three starting materials have much better solubility in Et\textsubscript{2}O or THF than the anhydrous RuCl\textsubscript{3}.

The ruthenium compounds were prepared according to Scheme 2:

**Scheme 2. Synthesis of Ru amidinate complexes 4, 5 and 6.**

Ru(‘Pr-PrMeAMD)\textsubscript{3} 4

When mer-RuCl\textsubscript{3}(Me\textsubscript{2}S)\textsubscript{3} was reacted with (1,3-di-iso-propylacetamidinato)-lithium, Li(‘Pr-PrMe-amd) (where ‘Pr-Me-amd = ‘PrNC(Me)N‘Pr), a blue material was isolated. An X-ray crystal structure analysis of the blue material showed it to be the monomeric compound Ru(‘Pr-Me-amd)\textsubscript{3} and the structure is shown in Fig. (1).

![Fig. (1). Molecular structure of compound 4 with 50% thermal ellipsoids; hydrogen atoms are omitted for clarity.](image-url)
The 1H NMR spectra of Ru\(^{\text{III}}\)(Pr-Me-amd)\(_3\) in mesitylene-
\(d_{12}\) showed no evidence for dimeric or oligomeric structures
between 0 °C and 175 °C. Due to the \(d^7\) electronic structure, its
1H NMR spectra at room temperature showed broad, but
well resolved paramagnetic resonances. Integration helped to
attribute four observed resonances (at \(\delta = 27.931, 4.595, -5.548, -18.499\)) to the \(CH(CH_3)_2\), \(endo-CH(CH_3)_2(CH_3)\), \(exo-
CH(CH_3)_2(CH_3)\), \(CCH_3\) groups, respectively. The two methyl
groups in the same \(^{1}\)Pr moiety differentiated by around 10
ppm because of their distance with the paramagnetic center
Ru(III). This compound is air stable, which makes it easy to
handle when used as a precursor. Electron impact mass spec-
trum (EI mass) gave a parent peak ([M +] = 524.8) matching
the calculated molecular weight of 524.8 for Ru(Pr-Me-
amd)\(_3\), and an accurate isotope pattern. Reaction of mer-
RuCl\(_3\)(Me\(_2\)S) with other lithium amidinate salts such as
(1,3-di-\(n\)-propyl-acetamidinato) lithium, (1,3-di-sec-butyl-
acet-amidinato)lithium, (1,3-di-tert-butyl-acet-amidinato)-
lithium were also tried. The crude products were not ther-
mally stable during sublimation, so they could not be pre-
pared in pure form.

In the synthesis of Ru(Pr-Me-amd)\(_3\), a significant
amount of an organic impurity was isolated. It can be dis-
tilled as a colorless liquid at 50 °C under the pressure of 70
mTorr. Based on its NMR spectra and high resolution mass
spectrum (HRMS), we think this unknown compound is the
hydrazine 7 shown in Fig. (2).

![Fig. (2). Schematic structure of compound 7 with NMR assign-
ments.](image)

Because of the steric hindrance between the \(^{1}\)Pr groups
and the nitrogen lone pair of electrons, the free rotation of
the N-N single bond and all the N-C single bonds were
restricted at room temperature, causing the two methyl groups
in the same \(^{1}\)Pr fragment to differentiate at room temperature.
Its 1H NMR spectra shows two septets (4.436 and 3.435, two
different methylene protons e and f), one singlet (1.158,
backbone methyl groups, g) and four sets of methyl groups
(1.238, 1.197, 1.195 and 1.157). At a higher temperature (ca.
70 °C) the four sets of methyl groups in the \(^{1}\)Pr fragments
merged into two doublets, while the other peaks stay the
same. That means at higher temperature the N-N single bond
and all the N-C single bonds can freely rotate. The 1C NMR
spectra at room temperature also shows four very close
chemical shifts with resonances at 25.2, 25.0, 20.9 and 20.6,
which correspond to 4 different methyl groups in the \(^{1}\)Pr
fragments. Subsequent elemental analysis matched the as-
signed structure. A HR MS shows that it has a parent peak at
283.2857, which is within 1.5 ppm experimental error of the
calculated molecular weight (283.2861). The isolation of this
new hydrazine may suggest that two amidinate ligands were
oxidized by Ru(III) center to join at the N sites to form the
new hydrazine compound. In the literature Ru(III) has been
found to perform the same function in heteroannulation
processes and N-alkylation of amides [36,38]. This reductive
elimination pathway found in the synthesis of Ru(III) amidi-
mate complexes suggests a new way to make novel hydrazine
compounds and also a new decomposition pathway for metal
amidine precursors.

**Ru(iPr-Me-amd)\(_2\)(CO)\(_2\) 5 and Ru(iBu-Me-amd)\(_2\)(CO)\(_2\) 6**

[RuCl\(_2\)(CO)\(_2\)]\(_2\) was reacted with lithium \(N,N\)-di-iso-
propylacetacemidinate to give Ru(Pr-Me-amd)\(_2\)(CO)\(_2\), a
yellow waxy dimagnetic material. The compound is very solu-
ble in hexanes. The IR spectra of this compound shows two
carbonyl vibrations with equal intensity (ν(CO) = 2015,
1936 cm\(^{-1}\)), indicating a cis-dicarbonyl structure. The 1H
NMR and 13C NMR spectra of this compound shows one
backbone methyl group and two nonequivalent \(^{1}\)Pr groups,
each with two diastereotopic methyl groups. They were well
resolved, which means Ru(Pr-Me-amd)\(_2\)(CO)\(_2\) is nonflux-
ional on the NMR time scale at ambient temperature. Taking
the NMR and the IR data into consideration, a C\(_2\)-symmetric
octahedral cis-bis(\(\eta^2\)-amidinate)Ru(CO)\(_2\) structure is
suggested. This is also confirmed by single crystal X-ray ray-
structure of Ru(But-Me-amd)\(_2\)(CO)\(_2\), which is shown in Fig. (3).
Ru(But-Me-amd)\(_2\)(CO)\(_2\) was prepared in good yield when
RuCl\(_2\)(CO)\(_2\)(C\(_6\)H\(_4\)O) was reacted with lithium \(N,N\)-di-tert-
butylacetamidinate. The compound yielded pale yellow crys-
tals by sublimation. Its IR spectrum is very similar to that of
Ru(Pr-Me-amd)\(_2\)(CO)\(_2\). The carbonyl vibration for both
compounds are found at similar wavelengths to those of the
analogue Fe(Pr-Bu-amd)\(_2\)(CO)\(_2\) (2009, 1942 cm\(^{-1}\)) [40].
Both Ru(Pr-Me-amd)\(_2\)(CO)\(_2\) and Ru(But-Me-amd)\(_2\)(CO)\(_2\) are
air-stable. The solutions of both compounds in benzene did
not undergo any change when exposed to air. When irra-
diated by a UV lamp under N\(_2\), the solutions of both com-
ounds were observed stable to be at least 12 hours.

**X-Ray Analysis**

Fig. (1) shows the molecular structure of Ru(Pr-Me-
amd)\(_3\) with 50% thermal ellipsoids and selected bond dis-
tance and angles are listed in Table 1.
Table 1. Selected Interatomic Distances (Å) and Bond Angles (°) in Complex 4

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1) – N(1)</td>
<td>2.074(11)</td>
</tr>
<tr>
<td>Ru(1) – N(1A)</td>
<td>2.074(12)</td>
</tr>
<tr>
<td>Ru(1) – N(1B)</td>
<td>2.074(11)</td>
</tr>
<tr>
<td>Ru(1) – N(2)</td>
<td>2.090(12)</td>
</tr>
<tr>
<td>Ru(1) – N(2A)</td>
<td>2.074(12)</td>
</tr>
<tr>
<td>Ru(1) – N(2B)</td>
<td>2.074(12)</td>
</tr>
<tr>
<td>N(1) – C(6)</td>
<td>1.354(16)</td>
</tr>
<tr>
<td>N(2B) – C(6)</td>
<td>1.289(15)</td>
</tr>
<tr>
<td>N(1A) – C(6A)</td>
<td>1.354(16)</td>
</tr>
<tr>
<td>N(1B) – C(6B)</td>
<td>1.354(16)</td>
</tr>
<tr>
<td>N(2A) – C(6B)</td>
<td>1.289(15)</td>
</tr>
<tr>
<td>N(1) – Ru(1) – N(2B)</td>
<td>62.8(3)</td>
</tr>
<tr>
<td>N(1A) – Ru(1) – N(2)</td>
<td>62.8(3)</td>
</tr>
<tr>
<td>N(1B) – Ru(1) – N(2A)</td>
<td>62.8(3)</td>
</tr>
<tr>
<td>N(1) – Ru(1) – N(1B)</td>
<td>105.4(4)</td>
</tr>
<tr>
<td>N(2) – Ru(1) – N(2A)</td>
<td>105.2(4)</td>
</tr>
<tr>
<td>N(2) – Ru(1) – N(1B)</td>
<td>88.0(4)</td>
</tr>
<tr>
<td>N(1) – C(6) – N(2A)</td>
<td>110.4(6)</td>
</tr>
<tr>
<td>N(1A) – C(6A) – N(2)</td>
<td>110.4(6)</td>
</tr>
<tr>
<td>N(1B) – C(6B) – N(2A)</td>
<td>110.4(6)</td>
</tr>
</tbody>
</table>

The structure of Ru(Pr-Me-amd)₃ is a distorted trigonal prism with dihedral angles of 97.5, 97.5, 82.5°. The geometry of the three Ru-N-C-N four membered rings is essentially planar with a mean deviation of 0.0164-0.0165 Å, which was also found in the previously reported structures of the transition metal amidinates [17]. The average bite angle is 62.8°, which is quite similar to that of V(Pr-Me-amd)₃ (63.5°) [17]. This is because both metals have similar ionic radii (Ru 68 pm, V 64 pm). The mean Ru-N bond distance is 2.08 Å, which is similar to what is found in Ru(Ph-Me-amd)₁ (2.06 Å) [30] and Ru(Tol-Me-amd)₁ (2.07 Å) [31]. Although the ruthenium atom is larger than iron, the mean Ru-N bond is a little shorter than the mean Fe-N bond found in Fe(Ph-H-famd)₁ (2.10 Å), where Ph-H-famd = PhNC(H)NPh [31]. That may suggest that Ru(III) is a softer Lewis acid than Fe(III), so back bonding of the amidinate ligand is stronger for Ru(III) amminate complexes than for Fe(III) formamidinate complexes.

The molecular structure of Ru(Bu-Me-amd)₂(CO)₂ is shown in Fig. (3).

Table 2. Selected Bond Distances (Å) and Bond Angles (°) in Compound 6

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1) – N(1)</td>
<td>2.117(15)</td>
</tr>
<tr>
<td>Ru(1) – N(2)</td>
<td>2.148(16)</td>
</tr>
<tr>
<td>Ru(1) – N(3)</td>
<td>2.147(16)</td>
</tr>
<tr>
<td>Ru(1) – N(4)</td>
<td>2.116(15)</td>
</tr>
<tr>
<td>Ru(1) – C(5)</td>
<td>1.860(2)</td>
</tr>
<tr>
<td>Ru(1) – C(6)</td>
<td>1.862(2)</td>
</tr>
<tr>
<td>N(1) – C(1)</td>
<td>1.333(2)</td>
</tr>
<tr>
<td>N(2) – C(1)</td>
<td>1.329(2)</td>
</tr>
<tr>
<td>N(3) – C(2)</td>
<td>1.327(2)</td>
</tr>
<tr>
<td>N(4) – C(2)</td>
<td>1.330(2)</td>
</tr>
<tr>
<td>C(1) – C(4)</td>
<td>1.512(2)</td>
</tr>
<tr>
<td>C(2) – C(3)</td>
<td>1.513(3)</td>
</tr>
<tr>
<td>O(1) – C(5)</td>
<td>1.150(2)</td>
</tr>
<tr>
<td>O(2) – C(6)</td>
<td>1.149(2)</td>
</tr>
<tr>
<td>N(4) – Ru(1) – N(3)</td>
<td>61.39(6)</td>
</tr>
<tr>
<td>N(1) – Ru(1) – N(2)</td>
<td>61.57(6)</td>
</tr>
<tr>
<td>N(2) – C(1) – N(1)</td>
<td>110.20(15)</td>
</tr>
<tr>
<td>N(3) – C(2) – N(4)</td>
<td>110.04(16)</td>
</tr>
<tr>
<td>O(1) – C(5) – Ru(1)</td>
<td>178.82(19)</td>
</tr>
<tr>
<td>O(2) – C(6) – Ru(1)</td>
<td>178.71(19)</td>
</tr>
</tbody>
</table>

The compound crystallizes in the space group P(-1). The amidinate ligands are coordinated in a dihapto mode with the RuNCl ring having a planar geometry with a mean deviation of 0.0227-0.0230 Å. The two ruthenium amidinate planes are essentially orthogonal. The Ru-N1 distance is 0.03 Å shorter than the Ru-N2 distance, as a consequence of the trans-position of N2 in relation to the CO ligand. Compared to the known Fe(II) cis-carbonyl complex Fe(Pr-Bu-amd)₂(CO)₂ [40], Ru(Bu-Me-amd)₂(CO)₂ also has a strongly distorted octahedral geometry. This is due to the very small bite angle of the dihapto-amidinate ligand, i.e. N1-Ru1-N2 is 61.57(6)° which is similar to N-Fe-N angle of 64.53(5)° found in Fe(Pr-Bu-amd)₂(CO)₂ [40]. In both complexes, the C-M-C (M = Ru or Fe) angle is about 93°; this indicates that the bite angle of the dihapto-amidinate ligand is not sensitive to the metal center.

Properties Related to Vapor Deposition

There are two very important requirements for ALD precursors: (1) a sufficient thermal stability (> months at the vaporization temperature, > seconds at the deposition temperature); (2) a sufficient volatility (> about 0.1 Torr). We examined the volatility and thermal stability of these three Ru complexes. Ru(Pr-Me-amd)₃ did not melt under 250 °C. It sublimed at 85 °C under the pressure of 50 mTorr. Ru(Pr-
Me-amd)2(CO)2 melted around 122 °C, which was also confirmed by differential scanning calorimetry (DSC) (data not shown here). It sublimed at 50 °C under the pressure of 45 mTorr. Ru(Bu-Me-amd)2(CO)2 melted around 204 °C and sublimed at 130 °C under the pressure of 55 mTorr. No decomposition was observed during the sublimation of all three complexes, showing that all three compounds are stable at the sublimation temperatures listed in Table 3.

Thermogravimetric analyses (TGA) of all three ruthenium complexes were performed at atmospheric pressure under a flow of nitrogen. Representative curves are given in Fig. (4).

![Fig. (4). TGA curves for mass changes of Ru amidinate complexes of 4, 5 and 6 measured in a flow of nitrogen at atmospheric pressure.](image)

Vaporization occurs cleanly in one step with different residual masses (4% left for Ru(Pr-Me-amd)3, 14% left for Ru(Pr-Me-amd)2(CO)2, and 0.2% left for Ru(Bu-Me-amd)2(CO)2). The high TGA residue left for Ru(Pr-Me-amd)2(CO)2 had a silvery color, and was presumably metallic ruthenium. This means that about 25% of the initial Ru(Pr-Me-amd)2(CO)2 decomposed to metallic ruthenium. Preliminary tests of Ru(Pr-Me-amd)2(CO)2 as a CVD precursor at 200 °C in the absence of any co-reactant showed deposition of ruthenium films on substrates. This suggests that Ru(Pr-Me-amd)2(CO)2 is a possible precursor for CVD of ruthenium; it is not stable enough for ALD of ruthenium. Ru(Bu-Me-amd)2(CO)2 showed very little decomposition with only a trace of residue (0.2%) in the TGA. It is the most thermally stable of these Ru compounds. The TGA of Ru(Pr-Me-amd)3 showed that it vaporized less quickly than the other two compounds.

Thermal decomposition studies in solution at high temperature by 1H NMR were also used to evaluate the thermal stabilities of Ru(Pr-Me-amd)3 and Ru(Bu-Me-amd)2(CO)2. The experiments were performed in sealed heavy-wall NMR tubes and the concentration of the solution in deuterated mesitylene was around 3 mM. The temperature was 175 °C. The logarithm of the area of an NMR peak (referenced to a solvent peak as an internal standard) vs. time is linear, indicating the decomposition is first order. From the slope, the half-life of the precursors at 175 °C could be calculated. The half-life is 15 hours for Ru(Pr-Me-amd)3, and 44 hours for Ru(Bu-Me-amd)2(CO)2, confirming that the latter compound is more stable.

These results are consistent with the thermal stability observed in bubblers. Ru(Bu-Me-amd)2(CO)2 is stable in a bubbler at the temperature of 130 °C for months with very little decomposition, while Ru(Pr-Me-amd)3 is not stable at 130 °C. After 12 h, the bubbler did not produce any vapor of Ru(Pr-Me-amd)3 because the decomposed material covered the surface of the remaining solid precursor which led to an extremely slow evaporation rate of the ruthenium complex. Hence Ru(Bu-Me-amd)2(CO)2 is a better precursor for vapor deposition.

In conclusion, we synthesized and characterized three new monomeric Ru amidinates. Large-scale preparation of these compounds is possible. Bis(di-tert-butylacetamidinato) ruthenium(II) dicarbonyl 6 was shown to have high thermal stability and sufficient volatility to serve as a vapor-phase precursor for Ru. Successful studies of ALD and CVD Ru thin films using compound 6 as a precursor were published separately [41].

**EXPERIMENTAL SECTION**

**General Considerations**

All reactions were conducted under a nitrogen atmosphere using either standard Schlenk techniques or in a glove box, except the synthesis of mer-RuCl3(Me2S)3 and [RuCl3(CO)2]2. Diethyl ether, tetrahydrofuran (THF) and hexanes were dried using an Innovative Technology solvent purification system and stored over 4 Å molecular sieves. Dimethyl sulfoxide (DMSO), methyl lithium, silica gel, N,N'-di-tert-butylcarbodiimide and N,N'-di-iso-propylcarbodiimide were purchased and used as received from Aldrich. RuCl3·3H2O was purchased and used as received from Pressure Chemical. [RuCl3(CO)2]2, [34] [RuCl3(CO)2(C2H5O)] [42], lithium N,N'-di-tert-butylacetamidinate and lithium N,N'-di-iso-propylacetamidinate [17] were synthesized by known literature methods. mer-RuCl3(Me2S)3 was synthesized from a modified literature method [35,37,39].
mer-RuCl$_3$(Me$_2$S)$_3$

RuCl$_3$·3H$_2$O (4.00 g, 15.2 mmol) was dissolved in DMSO (18 mL). Concentrated HCl (80 mL) was added to the obtained syrup and the mixture refluxed at 130 °C for 1.5 hours. The mixture was then cooled and filtered. A red crystalline compound was then collected. The filtrate was concentrated and DMSO (12 mL) and conc. HCl (60 mL) were added, the mixture was then refluxed for another 30 minutes at 130 °C. The mixture was then cooled and filtered. Another batch of red solid was isolated. The red products were concentrated to afford the crude material, which was then sublimed twice to afford a pure pale yellow-green solid. Yield: 13.7 g, 55%. Mp: 203-205 °C. Sublimation: 130 °C at 55 mTorr. 1H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 27.931 (br, 6 H, CH(CH$_3$)$_2$), 4.595 (br, 18 H, CH(CH$_3$)$_2$), -5.548 (br, 18 H, CH(CH$_3$)$_2$), -18.499 (br, 9 H, C(CH$_3$)$_2$); EI MS: 524.8 [M +] for a calculated MW of 524.8; Anal. Calcd. for C$_{22}$H$_{42}$N$_4$O$_2$Ru: C 53.31, H 8.54, N 11.30. Found: C 53.73, H 8.23, N 11.65.

X-Ray Structure Determination

The complexes Ru(Pr-Me-amd)$_3$ 4 and Ru(Bu-Me-amd)$_3$(CO)$_2$ 6, were structurally characterized by X-ray crystallography. Crystals were grown by cooling saturated hexanes solution to –30 °C for two weeks. Diffraction data were obtained with a Siemens (Bruker) SMART CCD area detector system using o scans of 0.3°/frames, and 30-sec frames such that 1271 frames were collected for a hemisphere of data. The first 50 frames were re-collected at the end of the data collection to monitor for crystal decay; no significant decay was observed. Cell parameters were determined using SMART software. Data reductions were performed with SAINT software, which corrects for Lorentz polarization and decay. Absorption corrections were applied using SADABS. Space groups were assigned by analysis of symmetry and observed systematic absences determined by the program XPREP and by subsequent refinement of the structure. The structure was solved by direct methods with SHELXS and subsequently refined against all data by the standard technique of full-matrix least squares on F$^2$ (SHELXL-97).

The asymmetric unit contains one-third of the formula weight of Ru(Pr-Me-amd)$_3$. All non-hydrogen atoms found in Ru(Pr-Me-amd)$_3$ and Ru(Bu-Me-amd)$_3$(CO)$_2$ were described anisotropically. In the final stages of refinement, hydrogen atoms were added at idealized positions and refined as riding atoms with a uniform value of 0.1Å.

Physical Measurements

All measurements were performed under anaerobic conditions. 1H- and 13C-NMR spectra were recorded on a Varian Mercury 400 spectrometer at 25 °C. Elemental analysis was obtained by Desert Analytics Laboratory, Tucson, AZ. TGA and DSC data were obtained with a Netzsch STA 449C or TA Q50 inside a nitrogen glove box. The sample N$_2$ flow rate is 60 mL/min. Samples (10-20 mg) were loaded in open platinum crucibles. The measurements were done with a temperature ramp rate of 10K/min. Melting points were performed in sealed capillaries using a Mel-Temp II apparatus. EI and ES mass spectrum were respectively obtained with a
Jeol AX-505H spectrometer and a Micromass LCT spectrometer.

Table 4. Crystallographic Data\(^a\) for Compounds 4 and 6

<table>
<thead>
<tr>
<th></th>
<th>4</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C(<em>{24})H(</em>{24})N(_{4})Ru</td>
<td>C(<em>{22})H(</em>{44})N(<em>{4})O(</em>{2})Ru</td>
</tr>
<tr>
<td>formula weight</td>
<td>524.78</td>
<td>495.67</td>
</tr>
<tr>
<td>crystal system.</td>
<td>Rhombohedral</td>
<td>Triclinic</td>
</tr>
<tr>
<td>space group</td>
<td>R3</td>
<td>P-1</td>
</tr>
<tr>
<td>a, Å</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>b, Å</td>
<td>16.0870(10)</td>
<td>10.283(2)</td>
</tr>
<tr>
<td>c, Å</td>
<td>10.297(2)</td>
<td></td>
</tr>
<tr>
<td>α</td>
<td>9.2962(13)</td>
<td>11.678(2)</td>
</tr>
<tr>
<td>β</td>
<td>86.28(3)</td>
<td>86.42(3)</td>
</tr>
<tr>
<td>γ</td>
<td>86.42(3)</td>
<td>87.31(3)</td>
</tr>
<tr>
<td>V, Å(^3)</td>
<td>2083.5(3)</td>
<td>1230.3(4)</td>
</tr>
<tr>
<td>(d_{calc}), g/cm(^3)</td>
<td>1.255</td>
<td>1.338</td>
</tr>
<tr>
<td>(\mu), mm(^{-1})</td>
<td>0.585</td>
<td>0.660</td>
</tr>
<tr>
<td>GOF ((F^2))</td>
<td>1.054</td>
<td>1.080</td>
</tr>
<tr>
<td>(R_1) (wR(^2))</td>
<td>4.68(12.27)</td>
<td>2.59(6.23)</td>
</tr>
</tbody>
</table>

\(^a\)Obtained with graphite monochromated Mo K\(\alpha\) (\(\lambda = 0.71073\) Å) radiation.

\(^b\) \(R_1 = \sum ||F_o| - |F_c||/\sum |F_o|\); wR\(^2\) = (\(\sum w(F_o^2 - F_c^2)^2\))/\(\sum w(F_o^2)^2\)).

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Supporting Information Available

Complete X-ray crystallographic files in CIF format for the structure determinations of the compounds 4 and 6 can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/datarequest/cif. Their deposition numbers are CCDC 675116 and CCDC 675717.

REFERENCES