Synthesis and characterization of volatile liquid cobalt amidinates†

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Three new volatile cobalt amidinate compounds were prepared: $Co(^tBuNC(R)NEt)_2$, R = Me, Et and n-Bu. They were characterized by elemental analysis, ^1H NMR, X-ray structure analysis, melting point, vapor pressure, vaporization rate, thermal stability and chemical reactivity. They were found to evaporate cleanly without decomposition. Two of them are liquids at room temperature, allowing for more convenient preparation, handling and purification by distillation. They are highly reactive compounds that have been found to be suitable precursors for vapor deposition of cobalt metal, cobalt nitride and cobalt oxide. A new synthetic method allows for the facile and inexpensive preparation of large quantities of these compounds.

Introduction

Thin films of cobalt metal are important in many areas of technology, including magnetic information storage,[1] computer chips[2] and catalysis.[3] A wide variety of techniques have been used to make them, including physical vapor deposition methods (PVD), such as evaporation and sputtering, and chemical methods, including chemical vapor deposition (CVD) and atomic layer deposition (ALD). The chemical methods have the potential to produce highly conformal coatings. As device structures are made smaller and more complex, this conformality has become a more crucial property.[4]

To be used successfully, chemical methods need to start with precursors that have suitable properties, including volatility, thermal stability and chemical reactivity suitable to make pure films. Commercially acceptable precursors should be liquids at room temperature. Liquids are easier than solids to purify, handle, meter and vaporize. Solid sources tend to be non-reproducible sources of vapor because of their slow evaporation kinetics, variable surface areas, and tendency to accumulate non-volatile impurities or decomposition products on their surfaces. Solids can also shed particles that may contaminate products.

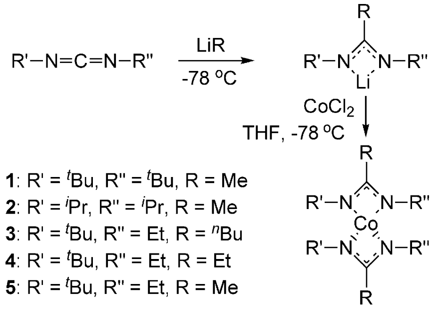
Some previously used cobalt precursors are solids, such as cobalt bis(*N*,*N*′-diisopropylacetamidinate),[5–7] cobalt bis(*N*,*N*′-di-*tert*-butylacetamidinate),[6] dicobalt octacarbonyl,[8–11] cobalt acetylacetonate[12,13] and bis(cyclopentadienyl)cobalt.[14,15] Liquid cobalt precursors include cyclopentadienylcobalt dicarbonyl,[3,15,16] cobalt nitroso tricarbonyl,[17–20] and cobalt hydride tris(trialkylphosphite).[21] These liquid precursors, however, have only produced pure cobalt films at high substrate temperatures[10,19,21] or in the presence of a plasma,[15,16] both of which conditions preclude making films with high conformality. Thus there is a need for volatile, thermally stable, liquid cobalt precursors with high reactivity at low deposition temperatures. The precursor should be reactive with reducing agents to deposit pure cobalt metal, with nitrogen sources to form cobalt nitrides, and with oxygen precursors to form oxides. It is also desirable to have a synthetic method that can produce large quantities of the precursor relatively inexpensively.

In this paper we present two new cobalt precursors that meet all of these requirements for a cobalt precursor for vapor deposition. Three new cobalt amidinates were synthesized, two of which are liquids at room temperature, while the third is a low-melting solid. A new synthetic method is also presented that uses inexpensive reactants, rapid reactions at ambient pressure, and has been used successfully for large-scale preparation. Vapor pressures and vaporization rates are found to be high enough for use in vapor deposition at source temperatures below 80 °C, at which temperature the lifetimes are well over one year. The new precursors have been successfully used in the vapor deposition of cobalt metal, as well as its nitrides and oxides.[22]

Results

Synthesis

The cobalt amidinate compounds were made by two different methods. The first method, as published[5,23] and shown in Scheme 1, adds an alkyllithium to a carbodiimide to form the lithium salt of the amidine, which is then reacted with cobalt(II) chloride.



Scheme 1

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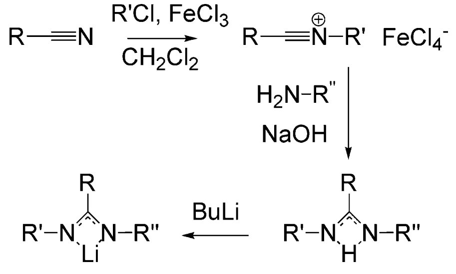
A new preparation of the lithium amidinates is shown in Scheme 2, in which an alkylnitrile is added to an alkyl chloride in the presence of iron(III) chloride. The intermediate alkylnitrilium tetrachloroferrate salt is then reacted with a primary amine, and then neutralized to release the free amidine.[24,25] Alternative routes utilizing catalysts based on lanthanide[26] or samarium[27] have been reported but proved incapable of attaching sterically bulky *tert*-butyl sidegroups. A previous literature report[28] of *N*,*N*′-di-*tert*-butylacetylamidine provided no guidance as to its production.



Scheme 2

The synthesis in Scheme 2 is completed by reacting the lithium amidinate with $CoCl_2$, as in the last step in Scheme 1.

The products are extracted from the lithium chloride byproduct with pentane or hexane. Final purification is done by distillation or sublimation. Identical products were obtained from the methods in Scheme 1 and Scheme 2.

Characterization

The compounds are dark blue/green, air-sensitive solids or liquids. Their melting points and vapor pressures are given in Table 1. At room temperature, compounds **1**, **2** and **5** are solids, while **3** and **4** are liquids.

The proton NMR spectra of the products have large shifts and broad peaks, which shows that they are paramagnetic. The numbers of peaks are consistent with monomeric structures in solution.

The crystal structure of compound **1** was determined by X-ray crystallography, and it is shown in Fig. 1. A monomeric molecular structure was also previously determined for compound **2** by X-ray crystallography.[5] The molecular structure of compound **5**, by contrast, is the dimer shown in Fig. 2. This solid-state dimer must be fairly weakly bound, because it is a monomer in solution, according to its NMR. Some bond lengths and bond angles are given in Table 2 and crystallographic parameters are given in Table 3.

Thermogravimetric analyses of the compounds demonstrated complete evaporation in single steps without measurable residue, as shown in Fig. 3.

Table 1 Melting points, vapor pressures and vaporization rates

	Melting point/°C	Vapor pressure/ mTorr, T/°C	Vaporization rate at 80 °C/nmol min^{-1} cm^{-2}
1	90	30, 45	25
2	84	30, 40	116
3	−21	30, 110	6
4	−17	60, 50	50
5	37	30, 70	84

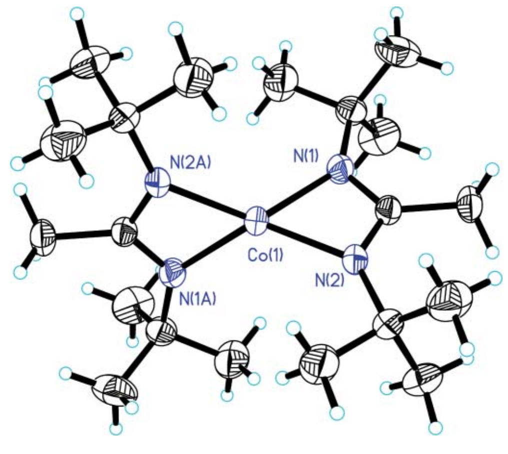


Fig. 1 Crystal structure of cobalt bis(*N*,*N*′-di-*tert*-butylacetamidinate) **1**.

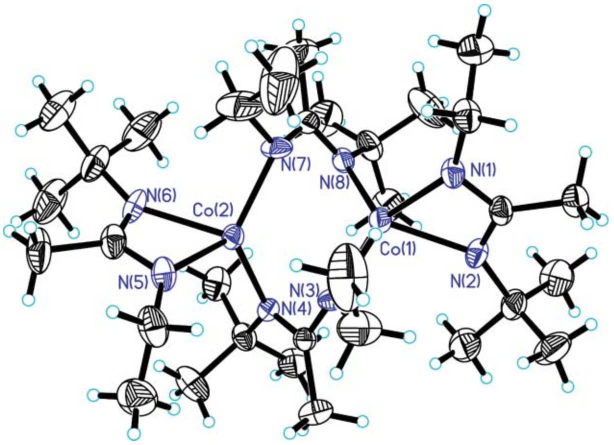


Fig. 2 Crystal structure of cobalt bis(*N*-*tert*-butyl-*N*′-ethylacetamidinate) **5**.

Table 2 Selected bond lengths and bond angles for cobalt amidinate compounds

Compound	**1**	**2**	**5**
Bond lengths/Å			
Co–N^{ave}	2.012(8)	2.007(2)	2.080(3)
Co–N_{bridge}			2.035(3)
Co–C		2.444(2)	2.505(3)
N–C^{ave}	1.320(2)	1.330(3)	1.324(5)
N–C_{bridge}			1.323(5)
Bond angles/°			
N(1A)–Co(1)–N(1)	132.31(9)	136.30(12)	109.23(13)
N(1A)–Co(1)–N(2)	137.02(6)	130.28(7)	119.79(13)
N(2)–Co(1)–N(2A)	133.68(8)	142.81(12)	119.49(13)
N(1)–Co(1)–N(2A)	137.02(7)	130.28(7)	102.19(13)
N(1)–Co(1)–N(2)	65.57(6)	65.84(7)	63.81(13)
N–C–N	111.2(2)	110.11(11)	112.4(2)
N–C–N_{bridge}			115.3(5)

Another set of thermogravimetric measurements was taken at constant temperatures, instead of using a linearly increasing temperature ramp. These isothermal measurements were done at a sequence of temperatures spaced by 10 K. At each fixed temperature, the mass loss was followed until a constant rate of decrease was reached. The results of these isothermal measurements are plotted in Fig. 4. The data points for each compound fit

Table 3 Crystallographic parameters

Compound	1	5
Empirical formula	$C_{20}H_{42}CoN_4$	$C_{16}H_{34}CoN_4$
Formula weight	397.51	341.40
T/K	193(2)	193(2)
Crystal system	Orthorhombic	Monoclinic
Space group	*Aba*2	*P*2(1)/*c*
a/Å	14.528(2)	9.945(3)
b/Å	13.9928(17)	16.996(5)
c/Å	11.8948(17)	22.432(6)
α/°	90	90
β/°	90	91.265(5)
γ/°	90	90
V/Å^3	2418.0(6)	3790.8(18)
Z	4	8
Reflections collected	7739	20117
Independent reflections	2860 [$R_{int} = 0.0366$]	6681 [$R_{int} = 0.0637$]
Final R indices	$R1 = 0.0360$ $wR2 = 0.0887$	$R1 = 0.0548$ $wR2 = 0.1282$
R indices (all data)	$R1 = 0.0376$ $wR2 = 0.0898$	$R1 = 0.0828$ $wR2 = 0.1382$

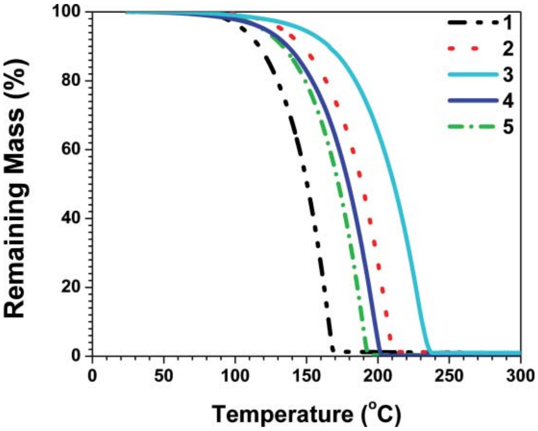


Fig. 3 Thermogravimetric analyses of cobalt amidinates. Temperature ramp rate of 10 K min^{-1} in a flow of nitrogen at 1 atm, and sample sizes of about 10 mg.

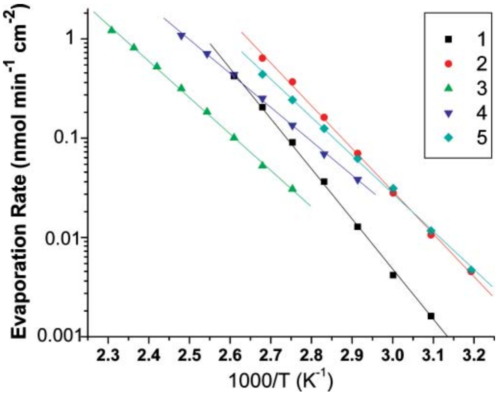


Fig. 4 Vaporization rates of cobalt amidinates measured in 1 atm of flowing nitrogen gas.

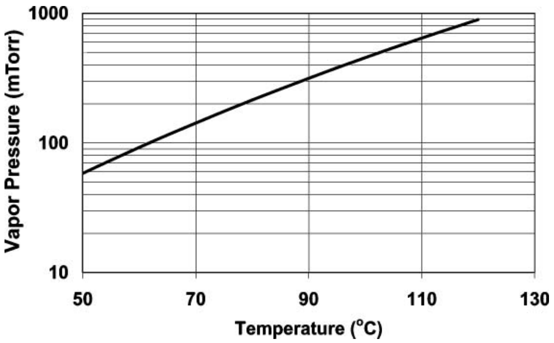


Fig. 5 Vapor pressure of compound **4**.

an Arrhenius temperature dependence to within the experimental errors.

The vapor pressure of the liquid compound **4** is plotted in Fig. 5. The values are approximated by the equation:

$$\log_{10} P\ (\text{Torr}) = 5.424 - 2151/T\ (\text{K}).$$

Thermal stability of the cobalt amidinates was studied by sealing solutions in deuterobenzene in heavy-walled NMR tubes. The tubes were then heated in an oven for various periods of time. Periodically the tubes were cooled to room temperature and their NMR spectra taken. The amount of un-decomposed compound was estimated by comparison of the integrated areas under its NMR peaks, normalized to an internal standard in the solution, C_6D_5H. These decomposition studies were repeated at several temperatures from 100 to 200 °C, with the results listed in Table 4. These half-lives are plotted in Arrhenius form in Fig. 6. The activation energies for these fits are given in Table 4.

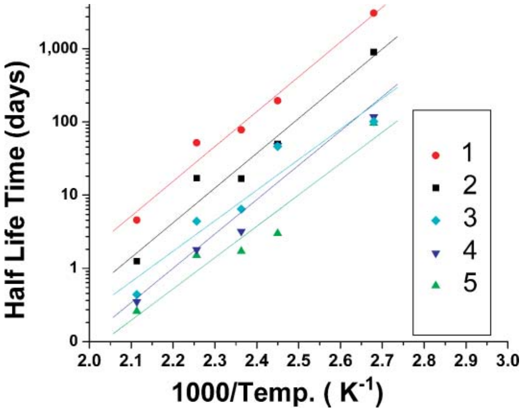


Fig. 6 Half-lives of cobalt amidinates in benzene solution.

Discussion

Although there is no generally predictive theory of melting points, one can see that the presence of more flexible groups such as ethyl and n-butyl tends to lower the melting points, in comparison with compounds with the more rigid *tert*-butyl and isopropyl groups. One way to quantify this flexibility is to count each ethyl group as one flexible joint, and each n-butyl group as 3 flexible joints.[29] In Fig. 7 we plot the melting points as a function of the total number of flexible joints in a monomer.

The compounds were found to be volatile. This characteristic arises from the fact that they are non-polar, so their intermolecular forces are fairly weak. Also, the steric bulk of the amidinate ligands is large enough to keep the molecules from polymerizing into non-volatile polymers.

Table 4 Half-lives for thermal decomposition of cobalt amidinates in C_6D_6 solution, in days

	100 °C	135 °C	150 °C	170 °C	200 °C	Activation energy/kJ mol^{-1}
1	3069	195	78	52	4.56	91.0
2	899	50	17	17	1.25	90.9
3	101	46	6.5	4.4	0.44	79.8
4	117	47	3.2	1.8	0.35	89.8
5	96	3.0	1.7	1.5	0.26	81.9

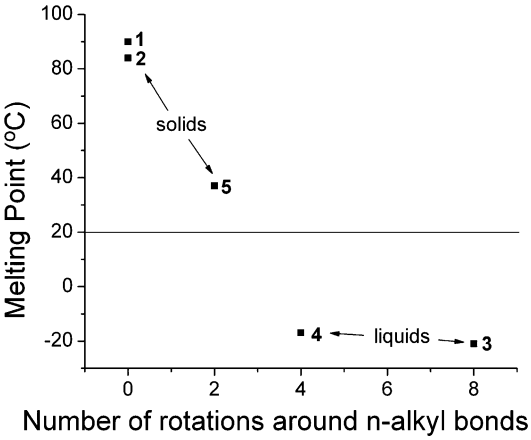


Fig. 7 Melting points of cobalt amidinates as a function of the total number of flexible joints in the alkyl groups.

The *tert*-butyl and isopropyl groups have sufficient steric bulk to maintain the monomeric structures of compounds **1** and **2**. On the other hand, the smaller steric bulk of the ethyl group in compound **5** allows it to form a dimer in the solid state (although it appears to be monomeric in solution).

The vaporization rate generally decreases with increasing molecular mass, as shown in Fig. 8 for data taken at 80 °C.

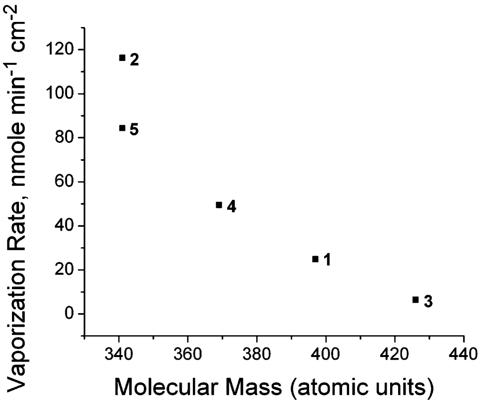


Fig. 8 Vaporization rates of cobalt amidinates at 80 °C as a function of molecular mass.

The thermal stabilities of the compounds fall roughly in the order **1** > **2** > **3** > **4** > **5**. The greater stability of **1** can be understood because it lacks a hydrogen in the carbons beta to the nitrogens. According to theoretical calculations,[30] beta-hydrogen transfer from this position to the cobalt atom is one pathway to thermal decomposition. All the molecules except **1** have the same number (4) of these labile hydrogens, so this mechanism does not distinguish between them. Another factor is steric crowding, which also may inhibit thermal decomposition. Steric crowding falls in the same order **1** > **2** > **3** > **4** > **5** as the thermal stability.

Several cobalt complexes formed from arylamidines have been reported in the literature[31–34] and are predominately monomeric as might be expected from the bulk of the derivatized phenyl groups used. The internal angle of the amidine moiety is generally seen to be slightly larger within ligands that are bridging; this effect is on the order of a 5% change. There is likewise a trend towards longer cobalt–nitrogen bond lengths in the dimeric structures with a similar magnitude of change.

Conclusions

Three new cobalt amidinates were synthesized. They were found to be volatile without decomposition. Two are liquids at room temperature, which makes them more convenient for synthesis, handling and vaporization. These properties make them well-suited to be precursors for chemical vapor deposition and atomic layer deposition. Their successful use for vapor deposition of cobalt metal, cobalt nitride and cobalt oxide is reported elsewhere.[22]

Experimental

General considerations

All reactions and manipulations were conducted under a pure nitrogen atmosphere using either an inert atmosphere box or standard Schlenk techniques. Tetrahydrofuran (THF), methylene chloride (CH_2Cl_2) and pentane were dried using an Innovative Technology solvent purification system and stored over 4 Å molecular sieves. Butyllithium, *tert*-butyl chloride, ethylamine, propionitrile, $CoCl_2$ and $FeCl_3$ were used as received.

The synthetic procedures for Scheme 1 have been published.[5] The procedure for a typical synthesis according to Scheme 2 is as follows:

***N*-*tert*-Butyl-*N′*-ethylpropionamidine.** This compound was made according to Scheme 2 by reacting propionitrile with ferric chloride and *tert*-butyl chloride, followed by addition of ethylamine.

0.30 mol (50 g) anhydrous $FeCl_3$ was suspended in 250 mL dry CH_2Cl_2. After 2 min, the solution was cooled to −40 °C and 21 mL (0.30 mol) of anhydrous propionitrile was added at once with magnetic stirring. The ferric chloride went into solution and the color of the medium turned dark red. The solution was cooled to −78 °C, then anhydrous *tert*-butyl chloride (33 ml, 0.30 mol) was added at once. A brown ocher precipitate formed within a few minutes; presumably it was *N*-*tert*-butylacetonitrilium tetrachloroferrate. The reaction medium was then maintained at −78 °C. Ethylamine was condensed (13 g, 0.30 mol) into the stirred reaction mixture; an exothermic reaction ensued. Stirring was maintained while it warmed to ambient temperature. It was then cooled to −10 °C and poured into 250 mL of 5 M NaOH stirred in an ice bath. The resulting mixture was extracted twice with $CHCl_3$. The organic phase was washed twice with 100 ml of water. The organic solution was dried over $MgSO_4$, and then evaporated to yield a light yellow liquid. The crude amidine thus obtained was then purified by distillation (40 °C, 0.06 Torr) to give a colorless liquid. Yield 38 g, 81%. ^{1}H NMR ($CDCl_3$, 25 °C, ppm): 0.97 (t, $J = 7.6$ Hz, 3H, CCH_2CH_3), 1.02 (t, $J = 7.2$ Hz, 3H, NCH_2CH_3), 1.30 (s, 9H, $C(CH_3)_3$), 2.03 (q, $J = 7.6$ Hz, 2H, CCH_2CH_3), 3.16 (q, $J = 7.2$ Hz, 2H, NCH_2CH_3). ^{13}C NMR (DMSO-d_6, 25 °C, ppm): 12. 7 (CCH_2CH_3), 18.7 (NCH_2CH_3), 23.3 (CCH_2CH_3), 29.4 ($NC(CH_3)_3$), 42.8 (NCH_2CH_3), 50.3 ($NC(CH_3)_3$), 159.3 ($NC(Et)N$). HRMS $C_9H_{20}N_2H^+$: 157.1699 (calc.), 157.1683 (expt).

***N-tert*-Butyl-*N′*-ethylpentanamidine.** This was prepared by the carbodiimide route and then protonated with water for analysis. ^{1}H NMR (C_6D_6, 25 °C, ppm): 0.80 (t, $J = 7.0$ Hz, 3H, $C(CH_2)_3CH_3$), 1.10 (t, $J = 7.2$ Hz, 3H, NCH_2CH_3), 1.16 (m, $J = 6.8$ Hz, 2H, $CCH_2CH_2CH_2CH_3$), 1.31 (m, $J = 6.6$ Hz 2H, $CCH_2CH_2CH_2CH_3$), 1.42 (s, 9H, $NC(CH_3)_3$), 1.77 (t, $J = 7.6$ Hz, 2H, $CCH_2(CH_2)_2CH_3$), 3.26 (q, $J = 7.2$ Hz, 2H, NCH_2CH_3). ^{13}C NMR (C_6D_6, 25 °C, ppm): 13.9 ($CCH_2CH_2CH_2CH_3$), 18.1 (NCH_2CH_3), 22.8 ($CCH_2(CH_2)_2CH_3$), 29.1 ($NC(CH_3)_3$), 29.8 ($C(CH_2)_3CH_3$), 30.2 ($C(CH_2)_2CH_2CH_3$), 43.3 (NCH_2CH_3), 50.5 ($NC(CH_3)_3$), 156.3 ($NC(Bu)N$). HRMS $C_{11}H_{24}N_2H^+$: 185.2012 (calc.), 185.2010 (expt.).

Bis(*N-tert*-butyl-*N′*-ethylpropionamidinato) cobalt(II) 4. *N-tert*-Butyl-*N′*-ethylpropionamidine is first reacted with butyllithium and then with cobalt(II) chloride.

A solution of n-butyllithium (1.6 M in hexanes, 81 mL, 0.13 mol) was added dropwise to a solution of *N-tert*-butyl-*N′*-ethylpropionamidine (20 g, 0.13 mol) in 200 mL of THF at −78 °C. The mixture was warmed to room temperature and stirred for 4 h. This resultant solution was then added to a solution of cobalt(II) chloride, $CoCl_2$, (8.4 g, 0.065 mol) in 100 mL of THF at room temperature. The reaction mixture was stirred for 12 h under nitrogen atmosphere. All volatiles were then removed under reduced pressure and the resulting solid was extracted with pentane. The pentane extract was filtered through a pad of Celite. The pentane was removed under reduced pressure to afford a dark green oil. A pure dark blue/green liquid compound was obtained by distillation at 90 °C (30 mTorr). Yield 34 g, 71%. Mp: −17 °C. Elemental analyses and ^{1}H NMR data are given below.

The other compounds were synthesized by analogous procedures and purified by sublimation (**1** and **2**) or distillation (**3**, **4** and **5**) with purified yields between 70 and 80%. Vapor pressures measured during sublimation or distillation are listed in Table 1. They are likely to be systematically low because of the long tubing connecting to the vacuum gauge. The values in Fig. 4 were obtained in an isothermal system and a capacitance manometer, so they should be more reliable.

Their proton NMR shifts (C_6D_6, 25 °C, ppm) are as follows:

1 −28.7 (br, 18H), 310.8 (br, 3H);

2 −70.0 (br, 12H), 309.4 (br, 3H), 324.9 (br, 2H);

3 −102.3 (br, 3H), −31.2 (br, 9H), 30.3 (br, 3H), 49.3 (br, 2H), 87.6 (br, 2H), 249.6 (br, 2H), 269.8 (br, 2H);

4 −100.7 (br, 3H), −30.6 (br, 9H), 86.7 (br, 3H), 248.5 (br, 2H), 268.8 (br, 2H);

5 −89.7 (br, 3H), −28.4 (br, 9H), 244.5 (br, 3H), 305.4 (br, 2H).

Elemental analyses are satisfactory for all compounds, as shown in Table 5.

Table 5 Theoretical (above) and experimental (below) elemental analyses for cobalt amidinates

Compound	C (%)	H (%)	N (%)
$CoC_{20}H_{42}N_4$ **1**	60.43	10.65	14.09
	60.63	10.65	13.98
$CoC_{16}H_{34}N_4$ **2**	56.29	10.04	16.41
	55.93	10.30	16.12
$CoC_{22}H_{46}N_4$ **3**	62.09	10.90	13.17
	62.39	10.57	12.91
$CoC_{18}H_{38}N_4$ **4**	58.52	10.37	15.16
	58.36	10.66	14.87
$CoC_{16}H_{34}N_4$ **5**	56.29	10.04	16.41
	55.93	10.03	16.11

Acknowledgements

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