New Heteroleptic Cobalt Precursors for Deposition of Cobalt-Based Thin Films

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ABSTRACT: A new series of heteroleptic complexes of cobalt were synthesized using aminoalkoxide and β-diketone ligands. The complexes, [Co(dmamp)(acac)]2 (3), [Co(dmamp)(fac)]2 (4), [Co(dmamp)(hfac)]2 (5), [Co(dmamp)(tmhd)]2 (6), and [Co(dmamb)(tmhd)]2 (7), were prepared by two-step substitution reactions and studied using Fourier transform infrared spectroscopy, mass spectrometry, elemental analysis, and thermogravimetric analysis (TGA). Complexes 3–7 displayed dimeric molecular structures for all of the complexes with cobalt metal centers interconnected by μ1-O bonding by the alkoxy oxygen atom. TGA and a thermal study of the complexes displayed high volatilities and stabilities for complexes 6 and 7, with sublimation temperatures of 120 °C/0.5 Torr and 130 °C/0.5 Torr, respectively.

INTRODUCTION

Cobalt is attractive because of its wide variety of applications, such as catalysis,1 protective coatings,2 magnetic information storage,3 and sensor systems.4 In microelectronics, the applications of cobalt/cobalt-based thin films include their use as the lining material within interconnected trenches,5 metallic interconnections, ohmic contacts in silicon-based devices,6 and as Schottky contacts in the field of optoelectronics.7 Thin films of cobalt and cobalt oxide are also useful as components of energy storage devices, such as LiCoO2 in lithium-ion batteries.8 In the last decades, cobalt-based thin films have gained a renewed interest in light of the discovery of giant magnetoresistance9 and tunneling magnetoresistance10 in films. For all of these applications and for the deposition of quality thin films, we require precursors with suitable properties, such as good volatility, thermal stability, and chemical reactivity (leading to pure film deposition). The known precursors of cobalt include dicobalt octacarbonyl,11 cobalt acetylacetonate,12 cobalt bis-(N,N'-diisopropylacetamidinate),13 cobalt bis(N,N-di-tert-buty-lactamidinate),13b bis(cyclopentadienyl)cobalt,14 cyclopenta dienyl cobalt dicarbonyl,14 cobalt nitroso tricarbonyl,16 cobalt hydride tris(trialkylphosphite),17 bis(N-tert-butyl-N'-ethylpro pionamidinate) cobalt(II),18 bis(1,4-di-tert-butyl-1,3-diazadien yl) cobalt,19 and cyclo pentadienyl-cobalt(III)- (diazabutadiene).20 The observed drawbacks of these precursors include their slow evaporation kinetics, unwanted reactions in the vapor state, film contamination with carbon, low thermal stability, and a high deposition temperature. The design and synthesis of new metal precursors are continuous processes because of the demand for better-performing precursors under a variety of conditions.

Recently, several works, including our own,21 showed the importance of heteroleptic precursors with improved properties. Most of the common precursors are homoleptic in nature, where the identical ligands are bonded to the metal center. In contrast, a heteroleptic precursor is a metal complex with distinct ligands attached to the metal center. The published results indicate that a heteroleptic precursor designed by a suitable ligand selection could have several better properties than its parent homoleptic precursor. Even though the selection of suitable ligands for heteroleptic metal precursors is as challenging as designing a new ligand for homoleptic...
Scheme 1. Synthesis of Complexes 1–7

Table 1. Crystallographic Parameters of Complexes 1 and 3–7

| compound  | 1          | 3          | 4          | 5          | 6          | 7          |
|-----------|------------|------------|------------|------------|------------|------------|
| empirical formula | \(C_6H_4Co_2N_2O_2Si_4\) | \(C_5H_4Co_2N_2O_3\) | \(C_6H_4Co_2F_3N_2O_2\) | \(C_5H_6Co_2F_3N_2O_2\) | \(C_6H_6Co_2N_2O_2\) | \(C_6H_6N_2O_2\) |
| formula weight | 671.01     | 548.43     | 328.19     | 764.34     | 716.75     | 744.80     |
| T/K       | 100(2)     | 100(2)     | 100(2)     | 100(2)     | 100(2)     | 100(2)     |
| crystal system | monoclinic | orthorhombic | orthorhombic | orthorhombic | triclinic | triclinic |
| space group | \(P2(1)/n\) | \(Pbca\) | \(Pbca\) | \(Pbca\) | \(I\) | \(I\) |
| \(a\) (Å)  | 9.2665(2)  | 12.5460(3) | 12.8499(5) | 12.9686(2) | 9.3999(2)  | 10.095(2)  |
| \(b\) (Å)  | 20.0041(5) | 9.9766(2)  | 10.0409(4) | 10.2365(2) | 10.2161(2) | 10.147(2)  |
| \(c\) (Å)  | 9.7333(2)  | 20.9672(5) | 21.5189(9) | 21.9931(4) | 11.5967(2) | 11.580(2)  |
| \(\alpha\) (deg) | 90         | 90         | 90         | 90         | 90         | 90         |
| \(\beta\) (deg) | 95.5500(10) | 100(2)     | 90         | 90         | 90         | 90         |
| \(\gamma\) (deg) | 90         | 90         | 90         | 90         | 90         | 90         |
| \(V\) (Å³) | 2767.67(19) | 2864.95(10) | 3434       | 2834       | 6047(10)   | 5828(2)    |
| \(Z\)     | 2          | 2          | 4          | 4          | 4          | 1          |
| density (g/cm³) | 1.241     | 1.388      | 1.570      | 1.740      | 1.213      | 1.176      |
| absorption coefficient | 1.082     | 1.301      | 1.273      | 1.253      | 0.885      | 0.829      |
| \(F(000)\) | 724        | 1160       | 1352       | 1544       | 386        | 402        |
| crystal size (mm³) | 0.24 × 0.18 × 0.10 | 0.28 × 0.18 × 0.02 | 0.20 × 0.20 × 0.03 | 0.16 × 0.12 × 0.05 | 0.16 × 0.10 × 0.06 | 0.16 × 0.15 × 0.12 |
| \(\theta\) range for data collection (deg) | 2.06–28.437 | 1.943–28.369 | 1.893–28.269 | 1.852–28.318 | 1.770–28.474 | 3.185–27.484 |
| index ranges | \(-12 \leq h \leq 12,\) | \(0 \leq k \leq 26,\) | \(0 \leq l \leq 13,\) | \(-12 \leq h \leq 12,\) | \(-12 \leq k \leq 13,\) | \(-12 \leq l \leq 14,\) |
| reflections collected | 4512       | 3285       | 3434       | 3631       | 4912       | 9870       |
| independent reflections | 4512 \([R\text{int} = 0.0000]\) | 3285 \([R\text{int} = 0.0000]\) | 3434 \([R\text{int} = 0.0000]\) | 3631 \([R\text{int} = 0.0000]\) | 4912 \([R\text{int} = 0.0000]\) | 4732 \([R\text{int} = 0.00408]\) |
| goodness-of-fit on \(F^2\) | 1.049      | 1.069      | 1.084      | 1.027      | 1.027      | 1.046      |
| final \(R\) indices \([I > 2\sigma(I)]\) | \(R_1 = 0.0292,\) \(wR_2 = 0.0761,\) | \(R_1 = 0.0283,\) \(wR_2 = 0.0649,\) | \(R_1 = 0.0723,\) \(wR_2 = 0.1219,\) | \(R_1 = 0.0355,\) \(wR_2 = 0.0802,\) | \(R_1 = 0.0334,\) \(wR_2 = 0.0715,\) | \(R_1 = 0.0556,\) \(wR_2 = 0.1098,\) |
| \(R\) indices (all data) | \(R_1 = 0.0338,\) \(wR_2 = 0.0794,\) | \(R_1 = 0.0381,\) \(wR_2 = 0.0695,\) | \(R_1 = 0.0966,\) \(wR_2 = 0.2304,\) | \(R_1 = 0.0471,\) \(wR_2 = 0.0876,\) | \(R_1 = 0.0449,\) \(wR_2 = 0.0829,\) | \(R_1 = 0.0829,\) \(wR_2 = 0.1194,\) |

\[ R_1 = \frac{(\sum |F_o| - |F_c|)}{\sum |F_o|}, \quad wR_2 = \frac{\left(\sum w(F_o^2 - F_c^2)^2\right)^{1/2}}{\sum w(F_o^2)^{1/2}}. \]
precursors, the heteroleptic precursors are advantageous because of the availability of several ligands and their complexes with known properties to choose from.

Here, we demonstrate the synthesis and characterization of new heteroleptic cobalt precursors with a combination of aminomalonitrile (1-dimethylamino-2-methyl-2-propoxide (dmamp) and 1-dimethylamino-2-methyl-2-butoxide (dmamb)) and β-diketone (2,2,6,6-tetramethylheptan-3,5-dionate (tmhd), acetylacetone (acac), 1,1,1-trifluoro-2,4-pentanedionate (tfac), and 1,1,5,5,5-hexafluoro-2,4-pentanedionate (hfac)) ligands. The complexes, [Co(dmamp)(acac)]_2 (3), [Co(dmamp)(hfac)]_2 (4), [Co(dmamp)(tfac)]_2 (5), [Co(dmamp)(tmhd)]_2 (6), and [Co(dmamb)(tmhd)]_2 (7), were prepared by simple substitution reactions using the corresponding ligands and cobalt(II) bis(bis(trimethylsilyl)-amide) [Co(btsa)]_2. All of the complexes were characterized using Fourier transform infrared (FT-IR), elemental analysis, thermogravimetric analysis (TGA), and X-ray crystallography. The results demonstrate excellent thermal stabilities and volatilities of these complexes, especially 6 and 7, which displayed high volatilities and stabilities.

## RESULTS AND DISCUSSION

New heteroleptic cobalt complexes were prepared by controlled substitution reactions, as illustrated in Scheme 1. First, the tetrahydrofuran (THF) solution containing Co(btsa), was treated with an equivalent amount of an aminomalonitrile (dmampH or dmambH) at low temperature. The products, [Co(dmamp)(btsa)]_2 (1) and [Co(dmamb)(btsa)]_2 (2), were isolated by extracting with toluene. In the second step, 1 reacted with β-diketones, such as acacH, tfacH, hfacH, and tmhdH, and 2 reacted with tmhdH in THF solutions at low temperature. The products, [Co(dmamp)(acac)]_2 (3), [Co(dmamp)(tfac)]_2 (4), [Co(dmamp)(hfac)]_2 (5), [Co(dmamp)(tmhd)]_2 (6), and [Co(dmamb)(tmhd)]_2 (7), were isolated by extracting with hexane. All of the complexes prepared in this work are highly soluble in common organic solvents, such as toluene, hexane, THF, and ether. Additionally, they are quite stable under inert conditions, such as a nitrogen atmosphere.

![Figure 1. Crystal structure of [Co(dmamp)(btsa)]_2 (1).](image)

X-ray-quality crystals of the complexes were obtained from saturated toluene (1) and hexane (3–7) solutions at ~30 °C. The crystals of complex 7 exhibited thermal disorder in the β-diketonate (in 7) chain. Complex 1 crystallized in a monoclinic space group, complexes 6 and 7 crystallized in triclinic space groups, and complexes 3–5 crystallized in orthorhombic space groups (Table 1). All of the complexes formed dimers with alkoxys oxygen bridging the two metal centers in the complexes by μ₂-O bonding. This is similar to the results for previously reported group 2 metal complexes [M(aminomalononitrile)(btsa)]_2 (M = Mg, Sr, and Ca) and [M(aminomalononitride)(tmhd)]_2 (M = Mg, Sr, Ca, and Ba). In complex 1, each of the cobalt metal ions was bonded to one btsa ligand and one dmamp ligand, exhibiting a tetrahedral geometry (Figure 1). The bond length between cobalt and nitrogen of the btsa group displayed a bond length of 1.9514(13) Å in 1 (Table 2), which is slightly shorter than that previously reported for [Co(NBu)₂(SMe)]_2 (1.9873 (11) Å and 1.9939(10) Å).²² Similarly, the Co−N bond between cobalt and the dmamp nitrogen atom displayed a bond length of 2.1598(14) Å, which is also shorter than the known Co−N bond lengths in [Co(acac)]_2(TMEDA)] and [Co(acac)]_2(DMAPH)].²³ (2.227(5) Å and 2.252(2) Å, respectively). The reaction of β-diketone with 1 and 2 substituted the remaining btsa ligand to afford complexes 3–7. The crystal structures of 3–6 displayed penta-coordinated metal centers and trigonal biPyramidal structures. In complexes 3–7, as shown in Figures 2–6, the Co−O bond lengths between the central cobalt ion and the oxygen of the β-diketone ligands were 2.0017(12), 2.0153(5), 2.0187(15), 2.0048(11), and 1.9967(1) Å, respectively, which were again shorter than that for similar β-diketonate complexes of cobalt (2.064(4) Å) for [Co(acac)]_2(TMEDA)]_2, 2.046(3) Å for [Co(acac)]_2(DMAPH)]_2, 2.034(3) Å for [Co(acac)]_2(py)_2, and 2.036(12) Å for [Co(tmhd)]_2(py)_2).²⁴ However, the Co−O bond lengths for complexes 3–7 are longer than those in the Co(thd)_3 complex (1.869(2) Å)²⁵ and in [Co('BuN-NCRO)]_2 (R = 'Bu, 'Pr, Me)²⁶ (average Co−O bond length is 1.915(1) Å). An increase in the Co1−O1−Co1 bond angle and relative increase in the Co−Co distances were observed between complex 1 and complexes 3–7 (Table 2). This is because the structure changes from a very strained tetrahedral geometry for 1 to a more relaxed and stable trigonal biPyramidal geometry for 3–7 by the substitution of the monodentate btsa for bidentate tmhd ligands.

The FT-IR spectra of the compounds confirmed the complex formation. Strong peaks are observed at ν = 2950 cm⁻¹ (1) and 2963 cm⁻¹ (2) (Si−CH₃ stretching vibrations) and at 1242 cm⁻¹ (1 and 2) (Si−CH₃ rocking vibration), confirming the presence of one btsa group in the compounds. The reaction of 1 or 2 with the β-diketones removed the btsa groups and formed 3–7. The FT-IR spectra of complexes 3–7 displayed strong peaks at ν = 1601, 1627, 1645, 1583, and 1584 cm⁻¹, respectively, corresponding to the C=O stretching in coordinated β-diketones. The absence of btsa peaks confirmed the complete substitution of the btsa groups by β-diketonate ligands. This is also confirmed by the Co−O stretching observed at ν = 452, 455, 458, 474, and 476 cm⁻¹ for complexes 3–7, respectively.²⁷ The absence of −OH stretching peaks in the FT-IR spectra indicates that the complexes are free of any non-coordinated ligands. The elemental analysis results for the complexes were comparable to the calculated values, considering their sensitivity toward air and moisture.

The mass spectra of the complexes 1–7 displayed peaks at m/z = 554, 568, 432, 540, 648, 600, and 614, respectively, which correspond to [M(aminomalononitrile)/(β-diketonate)]_2− (aminomalononitrile)]. These results confirmed that the complexes formed into dimer structures and one aminomalononitrile ligand was easily separated from the complexes due to their high air and moisture sensitivity during mass analyses.

TGA was performed for complexes 3–7 from room temperature to 800 °C (Figure 6). Samples for the analysis were prepared inside an argon-filled glovebox, and data
collection was performed under a constant flow of nitrogen to minimize any air contact. The TGA plots of complexes 3, 4, and 5 show sharp weight losses of 75, 85, and 90% from 110 to 260 °C (for 3), 110 to 250 °C (for 4), and 110 to 220 °C (for 5), respectively. This indicates the possible vaporization of part of the complex in those temperatures. Further mass losses of 13, 6, and 9% and the final residues of 12, 4, and 6% were observed for complexes 3, 4, and 5, respectively. The second step of the mass loss in the TGA may be the evaporation of some of the fragments resulting from the complex decomposition. In contrast, complexes 6 and 7 displayed clean, single-step TGA curves from 175 to 310 °C with mass losses of 94 and 96%,
respectively. The presence of the second step of mass losses for complexes 3–5 indicates a possible fragmentation of the samples, whereas complexes 6 and 7 display excellent vaporization and thermal characteristics (Figure 7).

The complexes were subjected to sublimation experiments under a reduced pressure (0.5 Torr) to better understand their volatile characteristics. All of the complexes, except 6 and 7, remained nonvolatile under those conditions (up to 150 °C/0.5 Torr). Complexes 6 and 7 sublimed at 120 and 130 °C, respectively, with good yields. The sublimed parts of the complexes were further characterized by FT-IR, elemental analysis, and mass spectroscopy to confirm that there were no changes in the structural features and that no decomposition occurred during the process. Complexes 3–5 remained nonvolatile in this process and underwent partial decomposition during prolonged heating at elevated temperatures for long period.

Our study reveals the possibility of developing heteroleptic precursors by selecting suitable ligands from a large pool of known ligands. This work reaffirms the importance of heteroleptic complexes as metal precursors because the proper combination of ligands yields better properties than those of their parent homoleptic complexes. In particular, complexes 6 ([Co(dmamp)(tmhd)2] and 7 ([Co(dmamb)(tmhd)2]) displayed good characteristics with the melting points of 131 and 113 °C, respectively, and the sublimation temperatures of 120 °C/0.5 Torr and 130 °C/0.5 Torr, respectively. These melting temperatures are lower than those of commercial tmhd precursors of cobalt, such as Co(tmhd)2 (143 °C) and Co(tmhd)3 (254 °C). This study clearly demonstrates that well-designed heteroleptic metal precursors can be useful alternatives to overcome the shortcomings of their parent complexes.

**CONCLUSIONS**

In summary, new heteroleptic complexes of cobalt using aminoalkoxides and β-diketonates were successfully synthesized using controlled two-step substitution reactions with Co(btsa)2. Both the partially substituted first-step compounds and final compounds were obtained as dimers in their crystal structures. The alkoxy oxygen of the aminoalkoxide used in this work acted as a bridge between two cobalt metal centers by μ2−O bonding. In those complexes, the metal center appeared to have a tetrahedral geometry in 1, whereas their geometry appeared to be trigonal bipyramidal in complexes 3–7. The TGA curves for complexes 4–7 displayed minimal nonvolatile residues, indicating their possible vaporization in the process. The sublimation studies revealed the excellent volatile character of complexes 6 and 7 at 120 and 130 °C under 0.5 Torr, respectively. Even though complexes 3–7 were in the dimeric state, all of the complexes displayed good stabilities at high temperatures. In particular, 6 and 7 displayed excellent volatilities and stabilities compared with their respective parent homoleptic complexes available from commercial sources.
Studies for the application of 6 and 7 as precursors for the deposition of cobalt and cobalt oxide thin films by an ALD process are in progress.

**Experimental Section**

**Materials.** FT-IR spectra were obtained using a Nicolet Nexus FT-IR spectrophotometer with a 4 mm KBr window or KBr pellets. The KBr pellets for the samples were prepared by a standard pellet technique inside an argon-filled glovebox. The elemental analyses were performed with a Thermo Scientific OEA Flash 2000 analyzer. The thermogravimetric analyses were conducted on a Thermo plus EVO II TG8120 series thermogravimetry and differential thermal analysis instrument under a constant flow of nitrogen. The mass spectra were recorded using a JEOL JMS-700 spectrometer operating in electron ionization (EI) mode. All of the reactions, except for the ligand preparations, were performed under inert and dry conditions using standard Schlenk techniques or in an argon-filled glovebox. Co(btsa)$_2$, Co(acac)$_2$, and Co(hfac)$_2$ were synthesized by a slightly modified literature method. Hexane, THF, and toluene were purified using an Innovative Technology PS-MD-4 solvent purification system. All of the chemicals were purchased from Aldrich and used as received.

**General Procedure for the Synthesis of [Co-(aminooalkoxide)(btsa)$_2$]$_2$ Complexes.** A THF solution (10 mL) of aminoalcohol was added dropwise to a solution of Co(btsa)$_2$ in THF (50 mL) at −78 °C with constant stirring and was stirred for 1 h at that temperature. The reaction mixture was slowly warmed to room temperature and then stirred for another 15 h. After the completion of the reaction, the volatiles were removed in vacuo and the residue was extracted into hexane and filtered. The toluene was removed to obtain the crude product. X-ray-quality crystals were grown from a saturated solution in hexane upon cooling at −30 °C. [Co(dmamp)(acac)$_2$]$_2$ (3), [Co(dmamp)(btsa)$_2$]$_2$ (1) (1.34 g, 2 mmol) and acacH (0.40 g, 4 mmol) were used. The crude product was recrystallized to obtain the pure product of dark green crystals. Yield: 0.54 g (50 %), mp 154 °C. FT-IR (KBr cm$^{-1}$): 2968(s), 2917(s), 2856(m), 1601(s), 1516(s), 1459(m), 1413(m), 1396(s), 1352(m), 1299(w), 1259(m), 1210(m), 1194(m), 1153(m), 1128(w), 1035(s), 1019(m), 984(m), 946(m), 921(m), 906(w), 843(w), 796(m), 763(m), 640(m), 657(w), 526(w), 452(w), 430(w). Anal. Calcd for C$_{22}$H$_{42}$N$_2$O$_6$Co$_2$: C, 48.5; H, 7.77; N, 5.23. EI-MS: m/z calcd for [Co(dmamp)(acac)$_2$]$_2$: 548.17 [M$^+$]; found 432 [{Co(dmamp)(acac)$_2$-dmamp}]+, 257 [Co(acac)$_2$]+, 158 [Co(acac)$_3$]+.

[Co(dmamp)(btsa)$_2$]$_2$ (4), [Co(dmamp)(btsa)$_2$]$_2$ (1) (1.34 g, 2 mmol) and tfacH (0.62 g, 4 mmol) were used. The crude product was recrystallized to obtain the pure product of dark green crystals. Yield: 0.91 g (69 %), mp 143 °C. FT-IR (KBr cm$^{-1}$): 2970(m), 2862(m), 2837(m), 1627(s), 1524(m), 1475(s), 1405(w), 1358(m), 1292(s), 1227(m), 1184(m), 1135(s), 1016(m), 983(m), 943(m), 908(m), 885(m), 842(w), 797(m), 778(m), 729(m), 641(m), 575(s), 528(w), 455(w). Anal. Calcd for C$_{20}$H$_{38}$N$_2$O$_6$F$_2$Co$_2$: C, 40.3; H, 5.53; N, 4.27. Found: C, 40.3; H, 5.31; N, 3.86. EI-MS: m/z calcd for [Co(dmamp)(tfac)$_2$]$_2$: 764.11 [M$^+$]; found 540 [{Co(dmamp) (tfac)$_2$}-dmamp}]+, 365 [Co(tfac)$_2$]+, 212 [Co(tfac)$_3$]+.

[Co(dmamp)(tmhd)$_2$]$_2$ (5), [Co(dmamp)(tmhd)$_2$]$_2$ (1) (1.34 g, 2 mmol) and tmhdH (0.83 g, 4 mmol) were used. The crude product was recrystallized to obtain the pure product of dark yellow crystals. Yield: 1.07 g (70 %), mp 120 °C. FT-IR (KBr cm$^{-1}$): 2974(m), 1645(s), 1554(m), 1527(m), 1499(m), 1254(s), 1199(s), 1146(s), 1024(w), 981(w), 942(w), 910(w), 798(m), 669(m), 641(w), 586(m), 527(w). Anal. Calcd for C$_{22}$H$_{42}$N$_2$O$_6$Co$_2$: C, 34.6; H, 3.96; N, 3.67. Found: C, 35.3; H, 4.15; N, 3.50. EI-MS: m/z calcd for [Co(dmamp)(tmhd)$_2$]$_2$: 764.10 [M$^+$]; found 648 [{Co(dmamp)(tmhd)$_2$-dmamp}]+, 473 [Co(tmhd)$_2$]+, 266 [Co(tmhd)$_3$]+.

[Co(dmamp)(tmhd)$_2$] (7), [Co(dmamp)(tmhd)$_2$] (2) (0.70 g, 1 mmol) and tmhdH (0.32 g, 4 mmol) were used. The crude product was purified by sublimation (120 °C/0.5 Torr) to obtain a pure solid green product. Yield: 0.90 g (63 %), mp 131 °C. FT-IR (KBr cm$^{-1}$): 2963(s), 2861(s), 2829(m), 1583(s), 1569(s), 1546(s), 1531(s), 1503(s), 1454(s), 1412(s), 1398(s), 1354(s), 1246(w), 1225(m), 1207(m), 1185(m), 1153(m), 1135(m), 1020(m), 987(m), 949(m), 906(w), 869(m), 840(w), 797(m), 788(m), 760(w), 738(w), 637(m), 525(w), 474(m), 410(w). Anal. Calcd for C$_{26}$H$_{56}$N$_2$O$_6$Co$_2$: C, 57.0; H, 9.28; N, 3.91. Found: C, 57.2; H, 9.29; N, 3.80. EI-MS: m/z calcd for [Co(dmamp)(tmhd)$_2$]$_2$: 716.36 [M$^+$]; found 600 [{Co(dmamp)(tmhd)$_2$-dmamp}]+, 425 [Co(tmhd)$_2$]+, 242 [Co(tmhd)$_3$]+.

[Co(dmamp)(acac)$_2$] (3), [Co(dmamp)(btsa)$_2$]$_2$ (1) (1.34 g, 2 mmol) and acacH (0.40 g, 4 mmol) were used. The crude product was purified by sublimation (130 °C/0.5 Torr) to obtain a pure solid green product. Yield: 0.90 g (63 %), mp 113 °C. FT-IR (KBr cm$^{-1}$): 2962(s), 2858(s), 1570(s), 1547(w), 1503(s), 1455(w), 1399(m), 1357(m), 1246(w), 1225(m), 1184(m), 1138(s), 1053(m), 1010(s), 959(w), 926(w), 870(s), 841(w), 789(m), 759(w), 739(w), 618(w), 574(w), 476(m), 424(w). Anal. Calcd for C$_{24}$H$_{55}$N$_2$O$_6$Co$_2$: C, 58.1; H, 9.47; N, 3.76. Found: C, 58.1; H, 9.47; N, 3.81. EI-MS: m/z calcd for [Co(dmamp)(tmhd)$_2$]$_2$: 744.39 [M$^+$]; found 614 [{Co(dmamp)(tmhd)$_2$-dmamp}]+.
(dmamb)(tmhd)₆-{dmamb}⁺, 425 [Co(tmhd)]⁺, 242 [Co(tmhd)]⁺.

**Crystallography.** Single crystals of 1 were grown from a toluene solution at −30 °C, and single crystals of 3−7 were grown from a hexane solution at −30 °C. A specimen of suitable size and quality was coated with paratone oil and mounted onto a glass capillary. Reflection data of 1, 3, 4, 5, and 6 were collected on a Bruker Apex II-CCD area detector diffractometer, with graphite-monochromated Mo Kα radiation (λ = 0.71073  Å). The hemisphere of reflection data was collected as ω−scan frames with 0.3° per frame and an exposure time of 10 s per frame. Cell parameters were determined and refined using the SMART program.33 Data reduction was performed using the SAIN T software.32 The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program.33 A crystal of 7 was coated with paratone oil and the diffraction data measured at 173 K with Mo Kα radiation on an X-ray diﬀraction camera system using an imaging plate equipped with a graphite crystal incident beam monochromator. The RapidAuto software was used for data collection and data processing.34 The structures were solved by direct methods, and all of the nonhydrogen atoms were subjected to anisotropic refinement by a full-matrix least-squares methods on F2 using the SHELXTL/PC package.35 Hydrogen atoms were placed at their geometrically calculated positions and were refined based on the corresponding carbon atoms with isotropic thermal parameters. The supplementary crystallographic data for this paper can be found in CCDC 1535120 (complex 1), 1535122−1535125 (complex 3−6), and 1552487 (complex 7).

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**Notes**
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