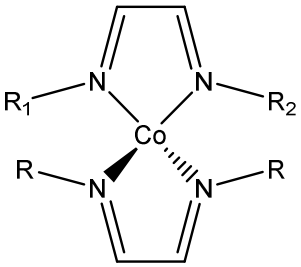
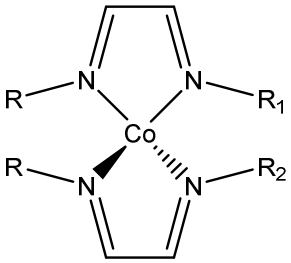


;

wherein R_1 and R_2 are different alkyl groups having 1 to 10, 2 to 8, 3 to 7, 3 to 6, or 3 to 5 carbon atoms.

[0021] In another aspect, the present invention discloses a bis(diazadiene)cobalt compound having the structure:

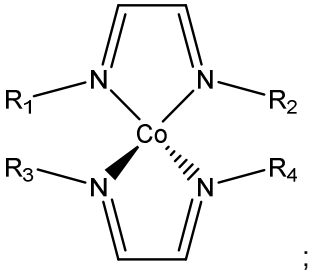


, or


;

wherein R_1 and R_2 are different alkyl groups and R is an alkyl group having 1 to 10, 2 to 8, 3 to 7, 3 to 6, or 3 to 5 carbon atoms.

[0022] In another aspect, the present invention discloses a bis(diazadiene)cobalt compound having the structure:



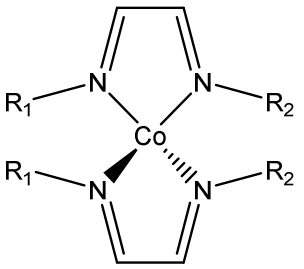
;

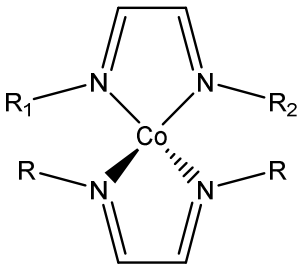
wherein R_1, R_2, R_3, and R_4 are different alkyl groups having 1 to 10, 2 to 8, 3 to 7, 3 to 6, or 3 to 5 carbon atoms.

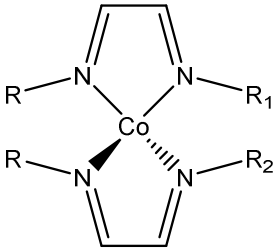
[0023] In another aspect, the present invention discloses a method of synthesizing the disclosed bis(diazadiene)cobalt compounds, comprising steps of:

the use of bubblers and/or spargers is possible. In general, bubbling the carrier gas through the liquid results in a higher precursor flux due to higher saturation of the carrier gas with precursor vapor. This enables the use of lower delivery temperatures to achieve a useful precursor flux, limiting the thermal decomposition of the precursor.

[0046] In another aspect, the present invention discloses bis(diazadiene)cobalt compounds having the structures:



,


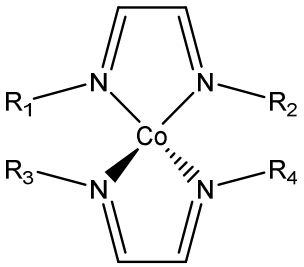
and


;

wherein R_1 and R_2; or R_1, R_2, and R are different alkyl groups having 1 to 10, 2 to 8, 3 to 7, 3 to 6, or 3 to 5 carbon atoms.

[0047] In general, it is observed that introducing asymmetry to molecular structures lowers the melting point of molecular compounds. Without being bound by theory, it is believed that molecular structure asymmetry results in less space-efficient packing in the solid state, which lowers the intermolecular forces leading to crystallization. This lowering of intermolecular forces leads to a lower melting point as less thermal energy is needed to melt the material. In the current invention, the R groups of this structure can be C_1-C_{10} alkyl, amino groups, and ether groups. The groups can be linear or branched. Examples of suitable R groups include tert-butyl, tert-amyl, iso-butyl, and iso-propyl.

[0048] In another aspect, the present invention discloses bis(diazadiene)cobalt compounds having the structure:



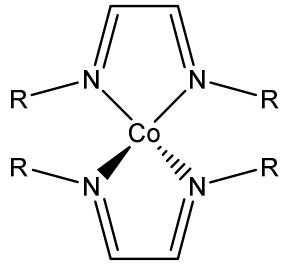
;

wherein R_1, R_2, R_3, and R_4 are different alkyl groups having 1 to 10, 2 to 8, 3 to 7, 3 to 6, or 3 to 5 carbon atoms.

CLAIMS

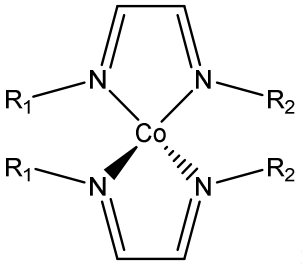
1. A bis(diazadiene)cobalt compound having a structure selected from the group consisting of:

(a)



wherein R is an alkyl group having 5 to 10 carbon atoms;

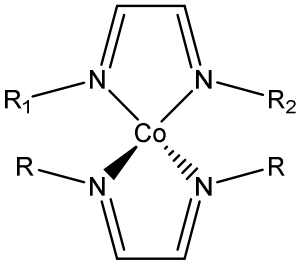
(b)



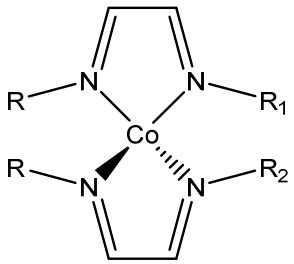
;

wherein R_1 and R_2 are different alkyl groups having 1 to 10 carbon atoms;

(c)



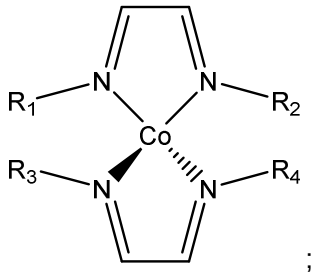
or



;

wherein R_1, R_2 and R are different alkyl groups having 1 to 10 carbon atoms;

(d)



;

wherein R_1, R_2, R_3, and R_4 are different alkyl groups having 1 to 10 carbon atoms; and

(e)combinations thereof.

2. The bis(diazadiene)cobalt compound of Claim 1, wherein R in group (a) is an alkyl group having 5 to 7 carbon atoms; R_1 and R_2 in group (b) are different alkyl groups having 3 to 5 carbon atoms; R_1, R_2 and R in group (c) are different alkyl groups having 3 to 5 carbon atoms; and R_1, R_2, R_3, and R_4 in group (d) are different alkyl groups having 3 to 5 carbon atoms.

3. The bis(diazadiene)cobalt compound of Claim 1 is selected from the group consisting of bis(1,4-di-tert-amyl-1,3-diazadienyl)cobalt, bis(1-tert-amyl-4-iso-butyl-1,3-diazadienyl)cobalt, bis(1-tert-amyl-4-iso-propyl-1,3-diazadienyl)cobalt and combinations thereof.

4. The bis(diazadiene)cobalt compound of Claim 1 has a melting point equal to or less than 80 ^{o}C.

5. The bis(diazadiene)cobalt compound of Claim 1 is a liquid compound at a temperature equal and greater than 40^{0}C.

6. A method of synthesizing a bis(diazadiene)cobalt compound, comprising steps of:

adding a first alkyl amine to a diketone compound in a mixture of an organic solvent and water to obtain a resulting mixture;

adding a second alkyl amine to the resulting mixture to obtain a reaction product;

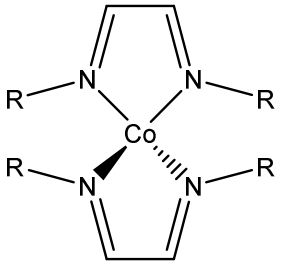
separating the reaction product to obtain a diazadiene ligand with two different alkyl groups bonded to the nitrogen atoms; and

reacting the diazadiene ligand with a cobalt halide in the presence of a reducing co-reagent to form a bis(diazadiene)cobalt compound;

wherein the first alkyl amine is different than the second alkyl amine; and

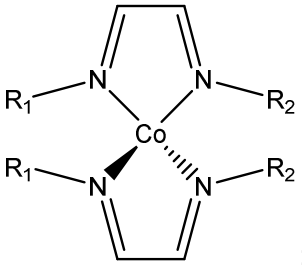
the bis(diazadiene)cobalt compound has a structure selected from the group consisting of:

(a)



wherein R is an alkyl group having 5 to 10 carbon atoms;

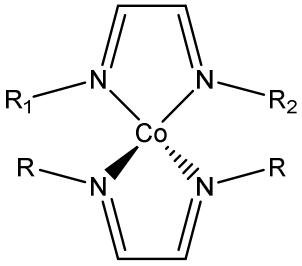
(b)



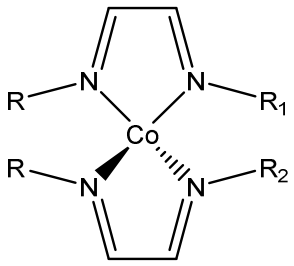
;

wherein R_1 and R_2 are different alkyl groups having 1 to 10 carbon atoms;

(c)



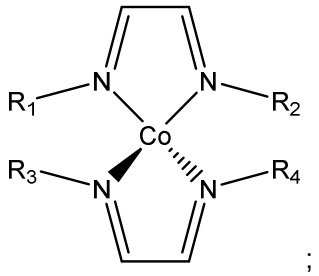
or



;

wherein R_1, R_2 and R are different alkyl groups having 1 to 10 carbon atoms;

(d)



;

wherein R_1, R_2, R_3, and R_4 are different alkyl groups having 1 to 10 carbon atoms; and

(e)combinations thereof.

7. The method of Claim 6, wherein the first alkyl amine is independently selected from the group consisting of tert-butyl, tert-amyl, iso-butyl, iso-propyl, and n-propyl; the cobalt halide is selected from the group consisting of cobalt chloride, cobalt bromide, and cobalt iodide; and the organic solvent is selected from the group consisting of hydrocarbon solvents, hexanes, tetrahydrofuran, diethyl ether, toluene, and combinations thereof.

8. The method of Claim 6, wherein R in group (a) as an alkyl group having 5 to 7 carbon atoms; R_1 and R_2 in group (b) are different alkyl groups having 3 to 5 carbon atoms; R_1, R_2 and R in group (C) are different alkyl groups having 3 to 5 carbon atoms; and R_1, R_2, R_3, and R_4 in group (d) are different alkyl groups having 3 to 5 carbon atoms; and the bis(diazadiene)cobalt compound either has a melting point equal to or less than 80 ^{o}C, or is a liquid compound at a temperature equal and greater than 40^{0}C.

9. The method of Claim 6, wherein the bis(diazadiene)cobalt compound is selected from the group consisting of bis(1,4-di-tert-amyl-1,3-diazadienyl)cobalt, bis(1-tert-amyl-4-iso-butyl-1,3-diazadienyl)cobalt, bis(1-tert-amyl-4-iso-propyl-1,3-diazadienyl)cobalt and combinations thereof.

10. A method of depositing a Co containing film on a substrate in a reactor, comprising:

providing the substrate to the reactor;

providing a Co precursor to the reactor;

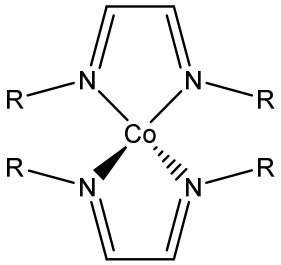
contacting the substrate with the Co precursor; and

forming the Co containing film on the substrate;

wherein the substrate is selected from the group consisting of metal, metal oxide, metal nitride, metal silicide, silicon, silicon oxide, silicon nitride, fluorosilicate glass (FSG), organosilicate glass (OSG), carbon doped oxide (CDO), porous low-K material, and combinations thereof; and

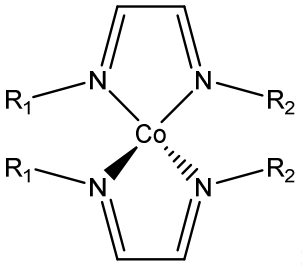
the Co precursor is a bis(diazadiene)cobalt compound having a structure selected from the group consisting of:

(a)



wherein R is an alkyl group having 5 to 10 carbon atoms;

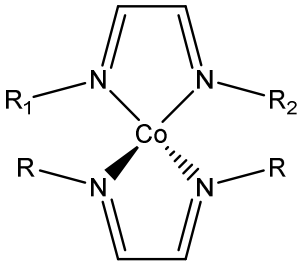
(b)



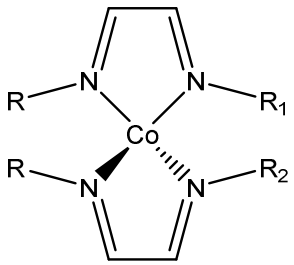
;

wherein R_1 and R_2 are different alkyl groups having 1 to 10 carbon atoms;

(c)



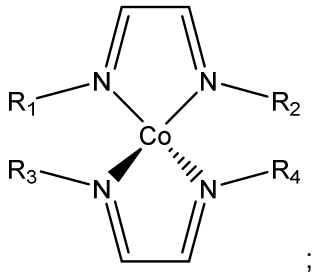
or



;

wherein R_1, R_2 and R are different alkyl groups having 1 to 10 carbon atoms;

(d)



;

wherein R_1, R_2, R_3, and R_4 are different alkyl groups having 1 to 10 carbon atoms; and

(e)combinations thereof.

11. The method of Claim 10, wherein the Co containing film is selected from a group consisting of cobalt film, cobalt oxide film, cobalt silicide film, cobalt nitride film, and combinations thereof; and the Co containing film is deposited by a method selected from a group consisting of thermal CVD, thermal ALD, plasma-enhanced ALD (PEALD), plasma enhanced chemical vapor deposition (PECVD), and plasma enhanced cyclic chemical vapor deposition (PECCVD).

12. The method of Claim 10, wherein R in group (a) as an alkyl group having 5 to 7 carbon atoms; R_1 and R_2 in group (b) are different alkyl groups having 3 to 5 carbon atoms; R_1, R_2 and R in group (C) are different alkyl groups having 3 to 5 carbon atoms; and R_1, R_2, R_3, and R_4 in group (d) are different alkyl groups having 3 to 5 carbon atoms; and the bis(diazadiene)cobalt compound either has a melting point equal to or less than 80 ^{o}C, or is a liquid compound at a temperature equal and greater than 40^{0}C.

13. The method of Claim 10, wherein the bis(diazadiene)cobalt compound is selected from the group consisting of bis(1,4-di-tert-amyl-1,3-diazadienyl)cobalt, bis(1-tert-amyl-4-iso-butyl-1,3-diazadienyl)cobalt, bis(1-tert-amyl-4-iso-propyl-1,3-diazadienyl)cobalt and combinations thereof.

14. The method of Claim 10, further comprises a step selected from the group comprising of a pre-treatment to remove contaminates from surface of the substrate, annealing with heating the Co containing film to 300-500°C in the flow of a hydrogen containing gas, and combination thereof

15. The method of Claim 10, wherein the Co containing film contains less 2.5 at. % of carbon or nitrogen.

16. A method of selectively depositing cobalt on a substrate in a reactor, comprising steps of:

providing the substrate to the reactor wherein the substrate comprises at least one patterned dielectric layer and at least one patterned metal containing layer;

providing a Co precursor to the reactor;

contacting the substrate with the Co precursor; and

forming Co containing film on the substrate;

wherein

the at least one patterned dielectric layer is selected from the group consisting of silicon dioxide, fluorosilicate glass (FSG), organosilicate glass (OSG), carbon doped oxide (CDO), porous low-K materials, and combinations thereof;

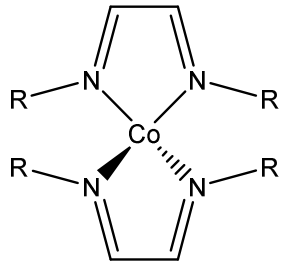
at least one patterned metal containing layer is selected from the group consisting of conductive metal layer selected from the group consisting of copper or copper alloy, cobalt or cobalt alloy, ruthenium or ruthenium alloy; and combinations thereof; metal oxide; metal nitride; metal silicate layer; and combinations thereof;

the Co containing film is selectively formed on the at least one patterned conductive metal layer with ratio of thickness of cobalt containing film formed on the at least one patterned conductive metal layer vs. formed on the at least one patterned dielectric layer > 1;

and

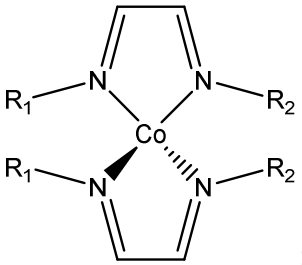
the Co precursor is a bis(diazadiene)cobalt compound having a structure selected from the group consisting of:

(a)



wherein R is an alkyl group having 5 to 10 carbon atoms;

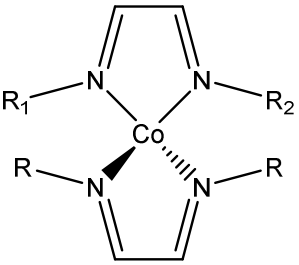
(b)



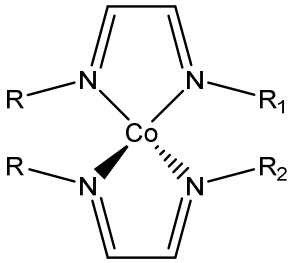
;

wherein R_1 and R_2 are different alkyl groups having 1 to 10 carbon atoms;

(c)



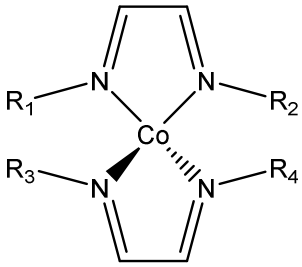
or



;

wherein R_1, R_2 and R are different alkyl groups having 1 to 10 carbon atoms;

(d)



;

wherein R_1, R_2, R_3, and R_4 are different alkyl groups having 1 to 10 carbon atoms; and

(e)combinations thereof.

17. The method of Claim 16, wherein R in group (a) as an alkyl group having 5 to 7 carbon atoms; R_1 and R_2 in group (b) are different alkyl groups having 3 to 5 carbon atoms; R_1, R_2 and R in group (C) are different alkyl groups having 3 to 5 carbon atoms; and R_1, R_2, R_3, and R_4 in group (d) are different alkyl groups having 3 to 5 carbon atoms; and the bis(diazadiene)cobalt compound either has a melting point equal to or less than 80 ^{o}C, or is a liquid compound at a temperature equal and greater than 40^{0}C.

18. The method of Claim 16, wherein the bis(diazadiene)cobalt compound is selected from the group consisting of bis(1,4-di-tert-amyl-1,3-diazadienyl)cobalt, bis(1-tert-amyl-4-iso-butyl-1,3-diazadienyl)cobalt, bis(1-tert-amyl-4-iso-propyl-1,3-diazadienyl)cobalt and combinations thereof.

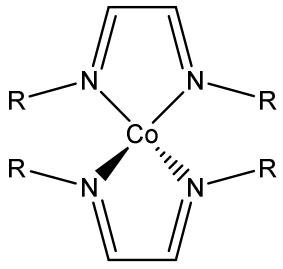
19. The method of Claim 16, wherein the cobalt-containing film thickness on the metal oxide, metal nitride, or metal silicide vs. the cobalt-containing film thickness on the at least one patterned dielectric layer is ≥10:1.

20. The method of Claim 16 further comprises a step selected from the group comprising of a pre-treatment to remove contaminates from surface of the substrate, annealing with heating the Co containing film to 300-500°C in the flow of a hydrogen containing gas, and combination thereof.

21. The method of Claim 16, wherein the Co containing film contains less than 2.5 at. %, of carbon or nitrogen.

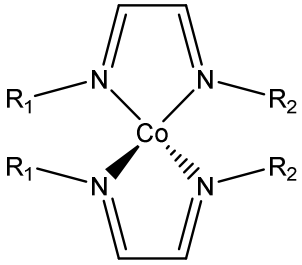
22. A cobalt containing film deposited by using a bis(diazadiene)cobalt compound having a structure selected from the group consisting of:

(a)



wherein R is an alkyl group having 5 to 10 carbon atoms;

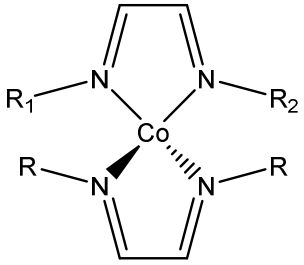
(b)



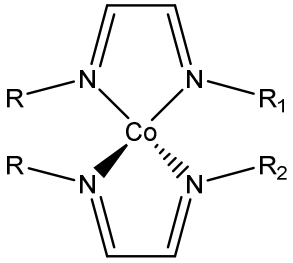
;

wherein R_1 and R_2 are different alkyl groups having 1 to 10 carbon atoms;

(c)



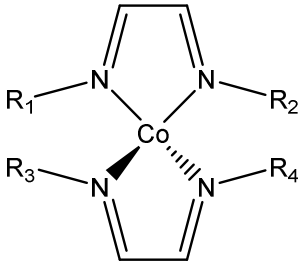
or



;

wherein R_1, R_2 and R are different alkyl groups having 1 to 10 carbon atoms;

(d)



;

wherein R_1, R_2, R_3, and R_4 are different alkyl groups having 1 to 10 carbon atoms; and

(e)combinations thereof;

wherein the cobalt containing film is selected from a group consisting of cobalt film, cobalt oxide film, cobalt silicide film, and cobalt nitride film; and the cobalt containing film is deposited by using a method selected from a group consisting of thermal CVD, thermal ALD, plasma-enhanced ALD (PEALD), plasma enhanced chemical vapor deposition (PECVD), and plasma enhanced cyclic chemical vapor deposition (PECCVD).

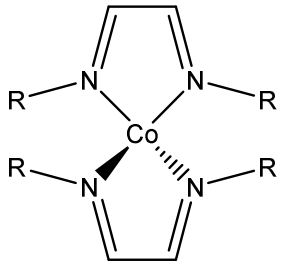
23. The cobalt containing film of Claim 22, wherein R in group (a) as an alkyl group having 5 to 7 carbon atoms; R_1 and R_2 in group (b) are different alkyl groups having 3 to 5 carbon atoms; R_1, R_2 and R in group (C) are different alkyl groups having 3 to 5 carbon atoms; and R_1, R_2, R_3, and R_4 in group (d) are different alkyl groups having 3 to 5 carbon atoms; and the bis(diazadiene)cobalt compound either has a melting point equal to or less than 80 ^{o}C, or is a liquid compound at a temperature equal and greater than 40^{0}C.

24. The cobalt containing film of Claim 22, wherein the bis(diazadiene)cobalt compound is selected from the group consisting of bis(1,4-di-tert-amyl-1,3-diazadienyl)cobalt, bis(1-tert-amyl-4-iso-butyl-1,3-diazadienyl)cobalt, bis(1-tert-amyl-4-iso-propyl-1,3-diazadienyl)cobalt and combinations thereof.

25. The cobalt containing film of Claim 22, wherein the cobalt containing film contains less than 2.5 at. % of carbon or nitrogen.

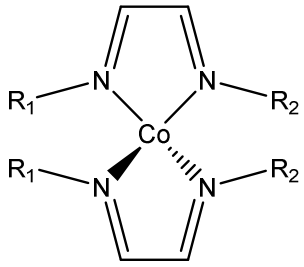
26. A container containing a bis(diazadiene)cobalt compound having a structure selected from the group consisting of:

(a)



wherein R is an alkyl group having 5 to 10 carbon atoms;

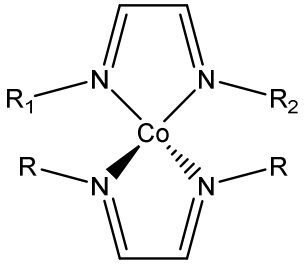
(b)



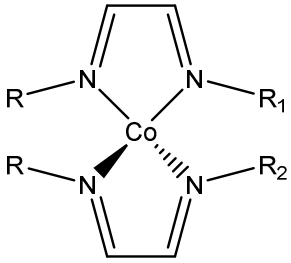
;

wherein R_1 and R_2 are different alkyl groups having 1 to 10 carbon atoms;

(c)



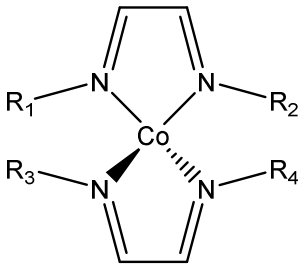
or



;

wherein R_1, R_2 and R are different alkyl groups having 1 to 10 carbon atoms;

(d)



;

wherein R_1, R_2, R_3, and R_4 are different alkyl groups having 1 to 10 carbon atoms; and

(e)combinations thereof;

wherein the bis(diazadiene)cobalt compound either has a melting point equal to or less than 80 ^{o}C, or is a liquid compound at a temperature equal and greater than 40^{0}C.

27. The container of Claim of 26, wherein R in group (a) as an alkyl group having 5 to 7 carbon atoms; R_1 and R_2 in group (b) are different alkyl groups having 3 to 5 carbon atoms; R_1, R_2 and R in group (C) are different alkyl groups having 3 to 5 carbon atoms; and R_1, R_2, R_3, and R_4 in group (d) are different alkyl groups having 3 to 5 carbon atoms.

28. The container of Claim 26 is maintained at a delivery temperature; and the melting point of the bis(diazadiene)cobalt compound is lower than the delivery temperature.

ABSTRACT

BIS(DIAZADIENE)COBALT COMPOUNDS, METHOD OF MAKING AND METHOD OF USE THEREOF

Described herein are cobalt compounds, processes for making cobalt compounds, cobalt compounds used as precursors for depositing cobalt-containing films (e.g., cobalt, cobalt oxide, cobalt nitride, cobalt silicide etc.); and cobalt films. Examples of cobalt precursor compounds are bis(diazadiene)cobalt compounds. Examples of surfaces for deposition of metal-containing films include, but are not limited to, metals, metal oxides, metal nitrides, and metal silicates; silicon, silicon oxide and silicon nitride. Alkylated diazadiene ligands are used to form cobalt complexes which are used for selective deposition on certain surfaces and/or superior film properties such as uniformity, continuity, and low resistance.

[No suitable figure]