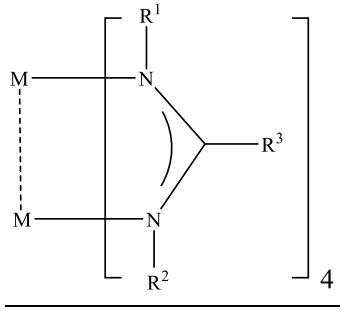
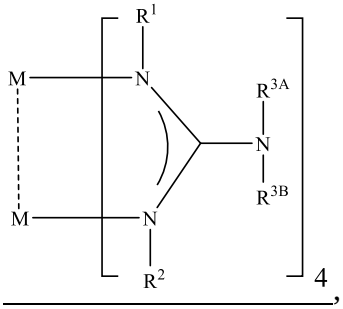
CLAIMS

What is claimed is:

1. A precursor of formula ~~$M_2(\text{Amidinate Ligand})_4$~~ I:



or formula II:



wherein (i) M is one of chromium, molybdenum and tungsten; and

(ii) R^1, R^2, R^3, R^{3A} and R^{3B} are each independently selected from H, D, an unsubstituted linear C_1-C_6 alkyl group, a linear C_1-C_6 alkyl group substituted with a halogen, a linear C_1-C_6 alkyl group substituted with an amino group, an unsubstituted branched C_3-C_6 alkyl group, a branched C_3-C_6 alkyl group substituted with a halogen, a branched C_3-C_6 alkyl group substituted with an amino group, an unsubstituted amine, an substituted amine, $-Si(CH_3)_3$, a C_3-C_8 unsubstituted cyclic alkyl group, a C_3-C_8 cyclic alkyl group substituted with a halogen, a C_3-C_8 cyclic alkyl group substituted with an amino group, a C_3-C_8 unsubstituted aromatic group, a C_3-C_8 aromatic group substituted with a halogen and a C_3-C_8 aromatic group substituted with an amino group.

2. The precursor of claim 1, wherein M is chromium.

3. The precursor of claim 1, wherein M is molybdenum.

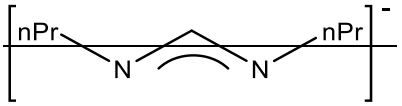
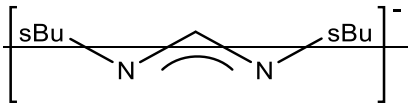
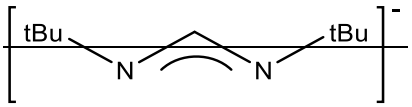
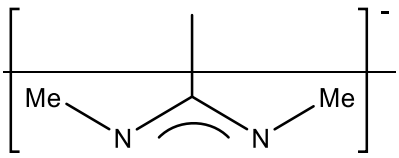
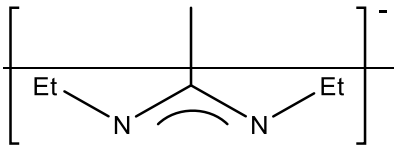
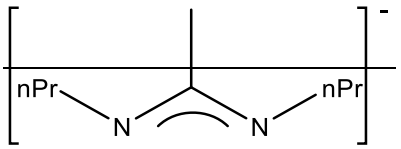
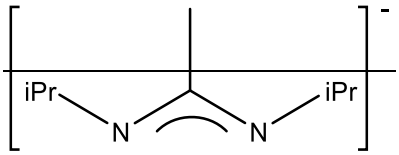
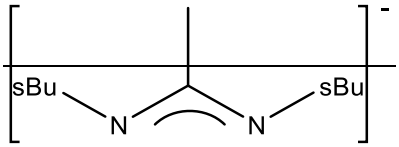
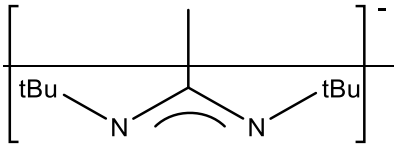
4. The precursor of claim 1, wherein M is tungsten.

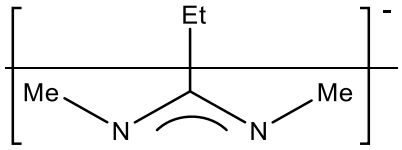
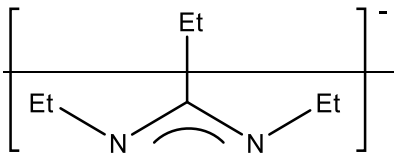
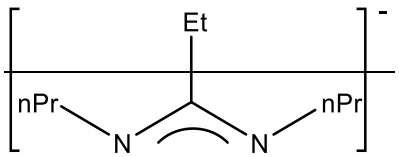
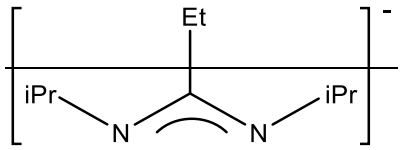
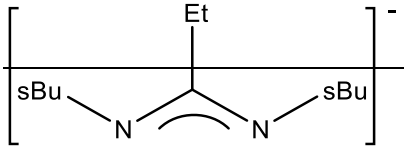
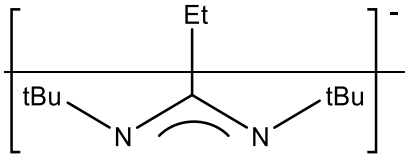
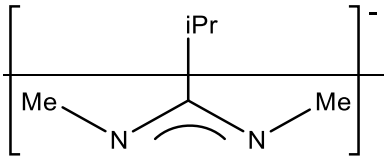
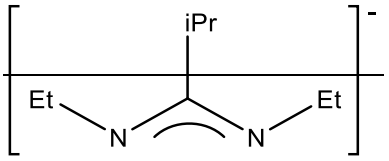
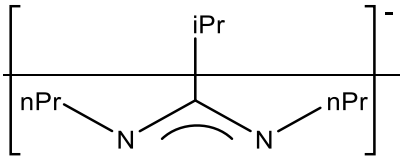
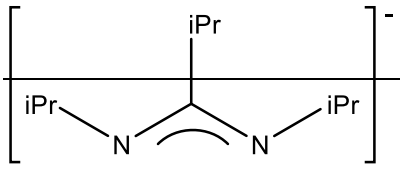
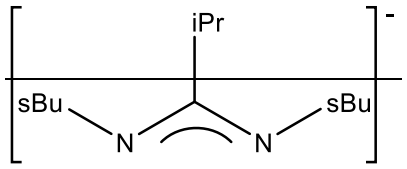
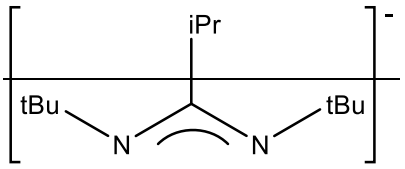
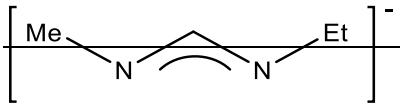
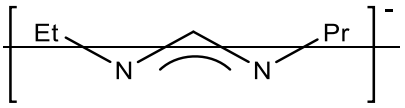
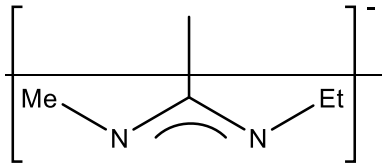
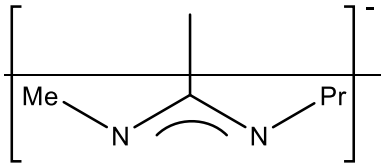
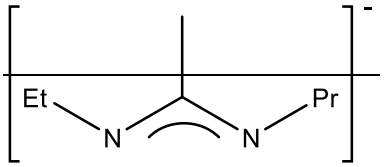
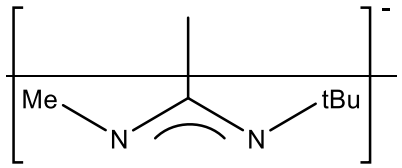
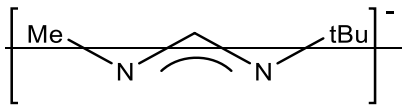
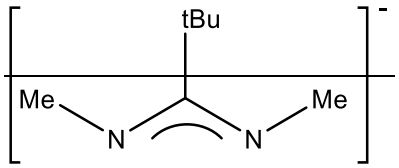
5. The precursor of claim 1, wherein ~~all four Amidinate ligands have the same chemical structure~~ **(ii)** R^1, R^2, R^3, R^{3A} and R^{3B} are each independently selected from H and an unsubstituted linear C_1-C_6 alkyl group.

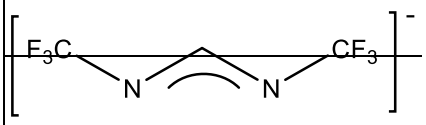
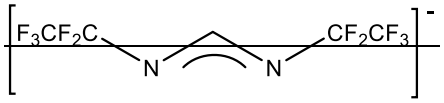
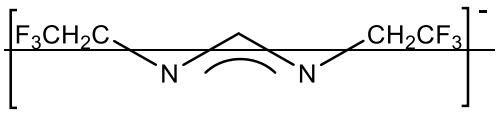
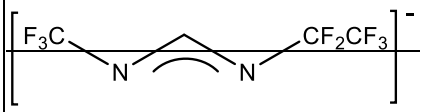
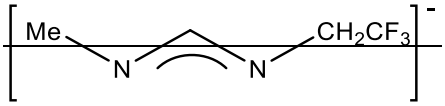
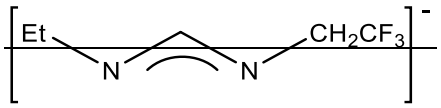
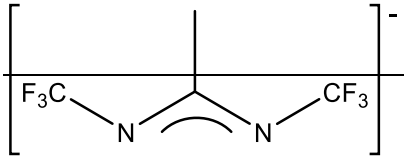
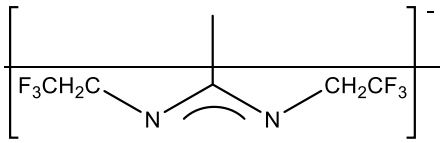
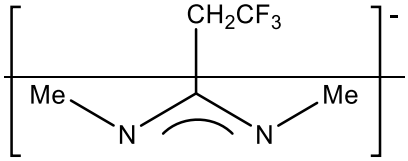
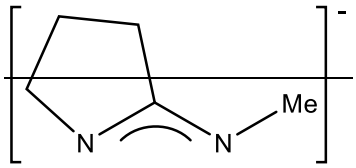
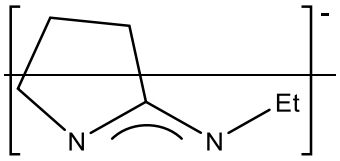
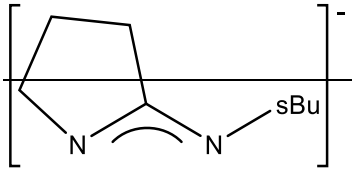
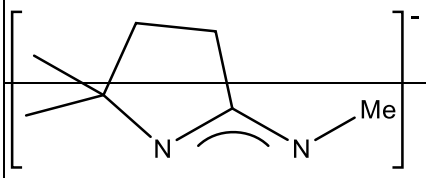
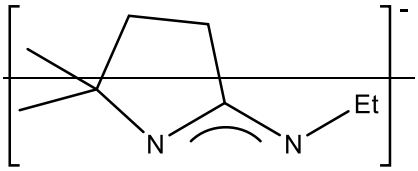
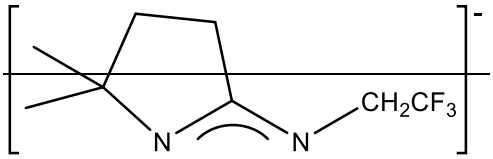
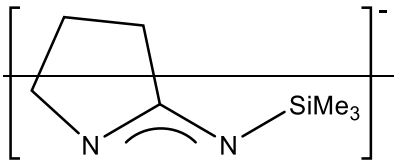
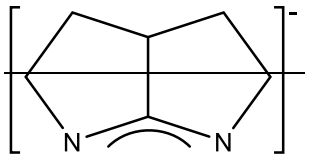
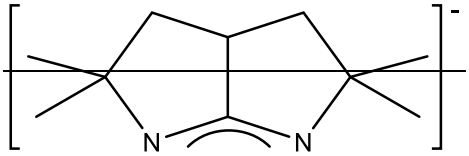
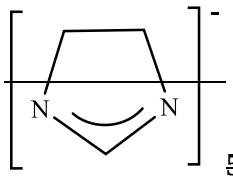
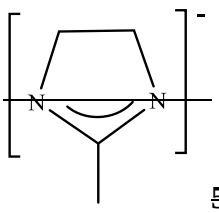
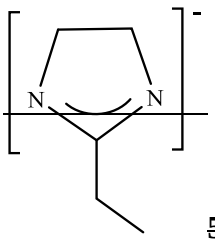
6. The precursor of claim 1, wherein ~~two or more of the Amidinate ligands have the same chemical structure~~ each of R^1 and R^2 is a methyl group.

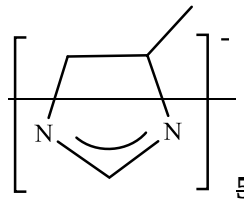
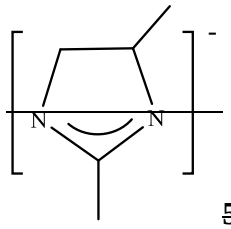
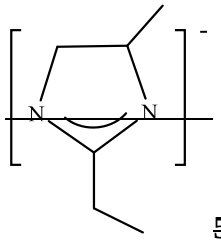
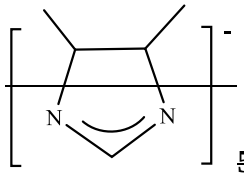
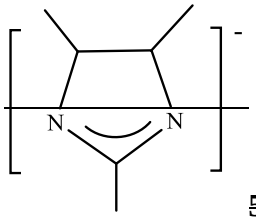
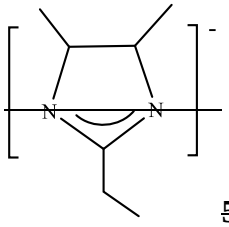
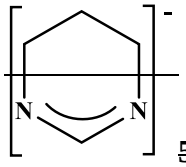
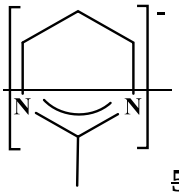
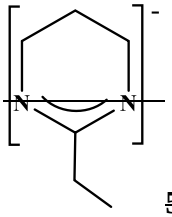
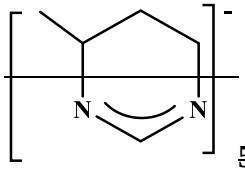
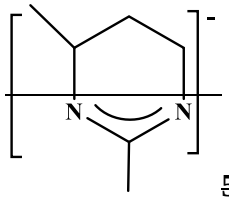
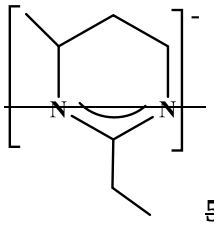
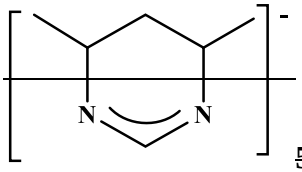
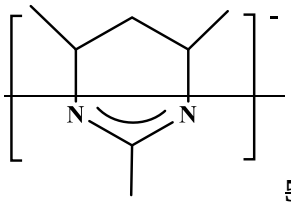
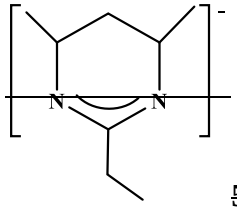
7. The precursor of claim 1, wherein ~~all four Amidinate ligands have a different chemical structure~~ one of R^1 and R^2 is a methyl group and the other of R^1 and R^2 is an ethyl group.

~~**8.** The precursor of any of claims 1-7, wherein the Amidinate Ligand is selected from the following amidinate ligands:~~

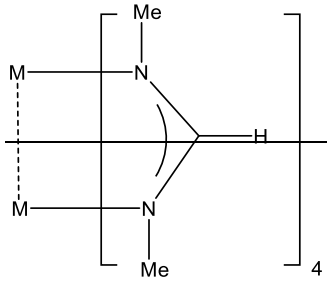
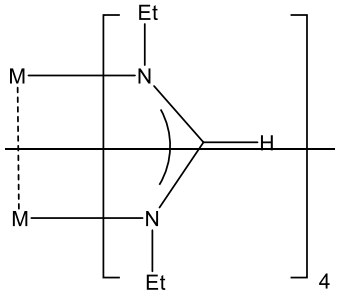
~~**Amidinate Ligands**~~		
 ~~**3A**~~	 ~~**3B**~~	 ~~**3C**~~
 ~~**3D**~~	 ~~**3E**~~	 ~~**3F**~~
 ~~**3G**~~	 ~~**3H**~~	 ~~**3I**~~
 ~~**3J**~~	 ~~**3K**~~	 ~~**3L**~~

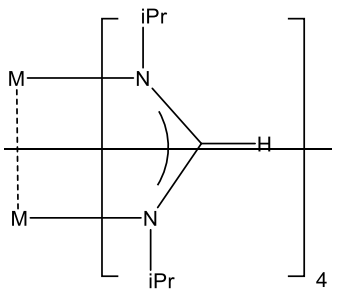
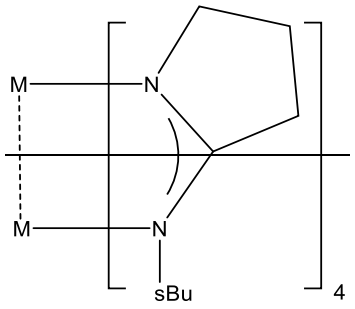
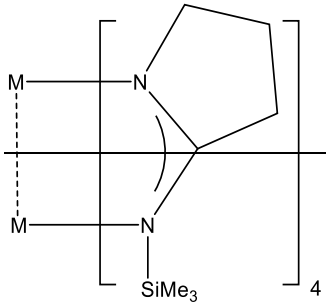
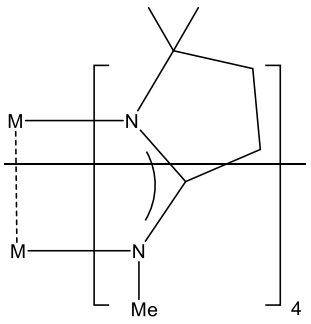
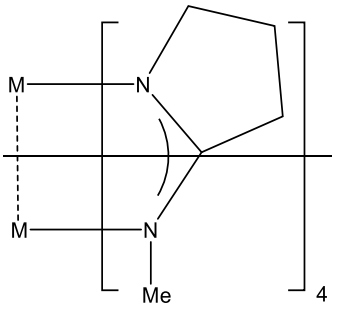
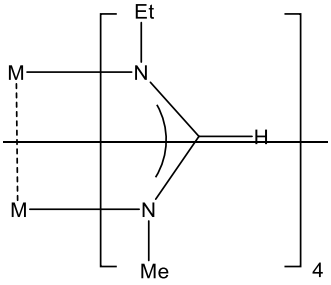
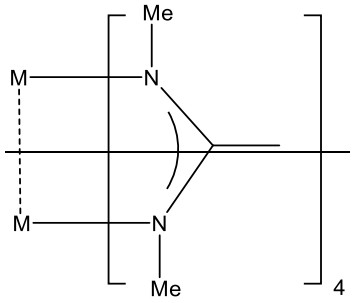
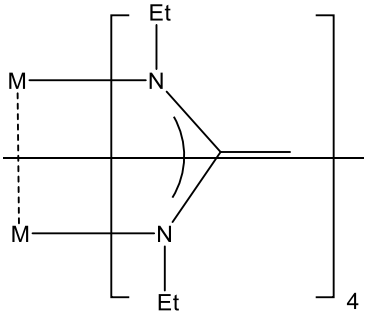
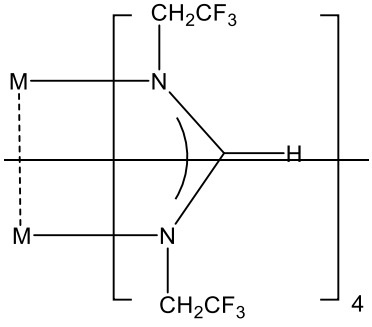
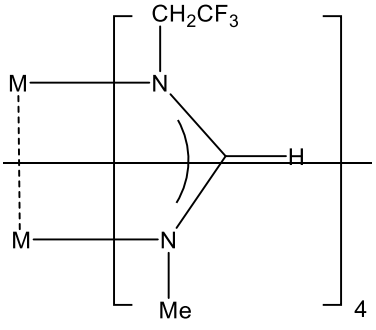
 **~~3M~~**	 **~~3N~~**	 **~~3O~~**
 **~~3P~~**	 **~~3Q~~**	 **~~3R~~**
 **~~3S~~**	 **~~3T~~**	 **~~3U~~**
 **~~3W~~**	 **~~3X~~**	 **~~3Y~~**
 **~~3Z~~**	 **~~3AA~~**	 **~~3BB~~**
 **~~3CC~~**	 **~~3DD~~**	 **~~3EE~~**
 **~~3FF~~**	 **~~3GG~~**	 **~~3HH~~**

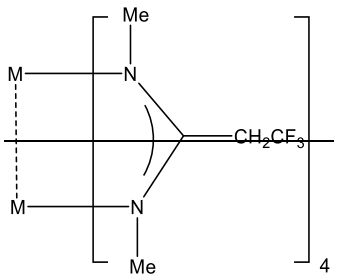
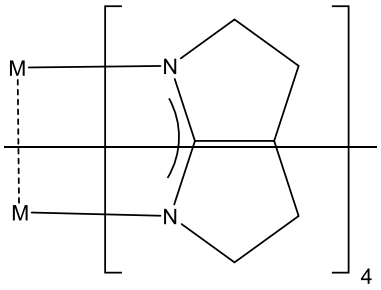
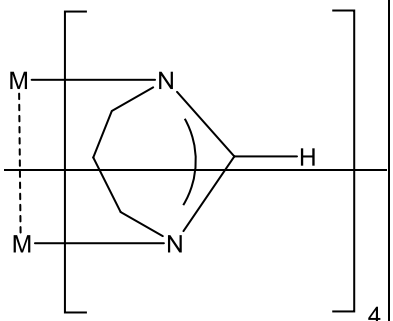
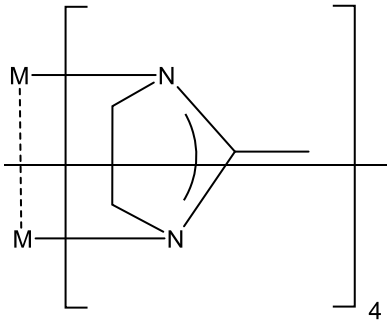
 **~~3II~~**	 **~~3JJ~~**	 **~~3KK~~**
 **~~3LL~~**	 **~~3MM~~**	 **~~3NN~~**
 **~~3OO~~**	 **~~3PP~~**	 **~~3QQ~~**
 **~~3RR~~**	 **~~3SS~~**	 **~~3TT~~**
 **~~3UU~~**	 **~~3VV~~**	 **~~3WW~~**
 **~~3XX~~**	 **~~3YY~~**	 **~~3ZZ~~**
 **~~5A~~**	 **~~5B~~**	 **~~5C~~**

 **~~5D~~**	 **~~5E~~**	 **~~5F~~**
 **~~5G~~**	 **~~5H~~**	 **~~5I~~**
 **~~5K~~**	 **~~5L~~**	 **~~5N~~**
 **~~5O~~**	 **~~5P~~**	 **~~5Q~~**
 **~~5R~~**	 **~~5S~~**	 **~~5T~~**

~~9.~~ ~~The precursor of any of claims 1-8, wherein the precursor has one the following structures:~~

~~Formula~~	**~~Compound~~**	**~~Formula~~**	**~~Compound~~**
~~$M_2(3A)_4$~~		~~$M_2(3B)_4$~~	

~~M_2-(3D)$_4$~~		~~M_2-(3TT)$_4$~~	
~~M_2-(3XX)$_4$~~		~~M_2-(3UU)$_4$~~	
~~M_2-(3RR)$_4$~~		~~M_2-(3Z)$_4$~~	
~~M_2-(3G)$_4$~~		~~M_2-(3H)$_4$~~	
~~M_2-(3KK)$_4$~~		~~M_2-(3MM)$_4$~~	

~~$M_2(3QQ)_4$~~		~~$M_2(3YY)_4$~~	
~~$M_2(5K)_4$~~		~~$M_2(5B)_4$~~	

~~10~~8. ~~A~~ The precursor of ~~formula $M_2(Guanidinate\ Ligand)_4$~~ claim 1, wherein ~~M is one of chromium, molybdenum and tungsten~~ one of R^1 and R^2 is a methyl group and the other of R^1 and R^2 is an ethyl group.

~~11~~9. The precursor of claim 1~~0~~, wherein ~~M is chromium~~ R^3 is H.

~~12~~10. The precursor of claim 1~~0~~, wherein ~~M is molybdenum~~ each of R^{3A} and R^{3B} is a methyl group.

~~13~~11. The precursor of claim 1~~0~~, wherein ~~M is tungsten~~ each of R^{3A} and R^{3B} is an ethyl group.

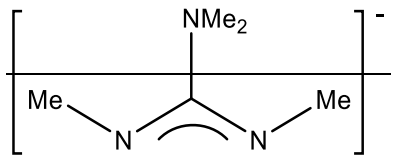
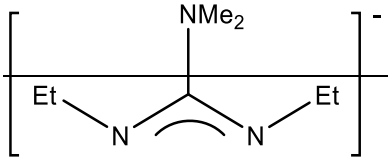
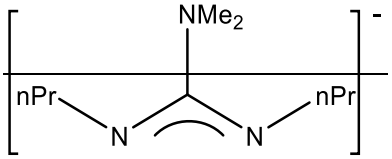
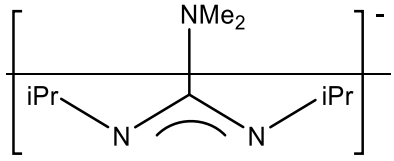
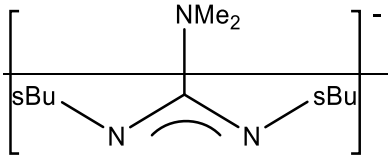
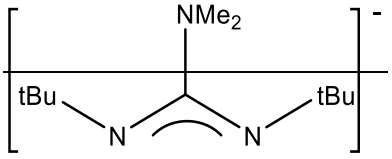
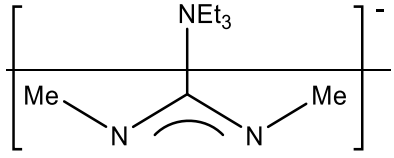
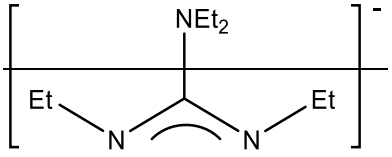
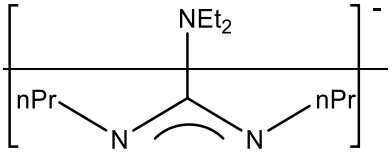
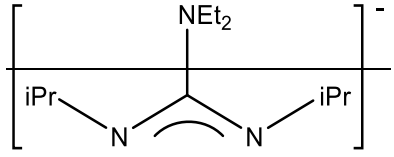
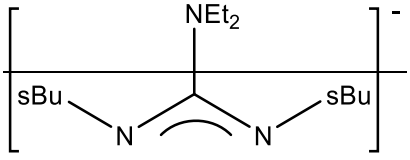
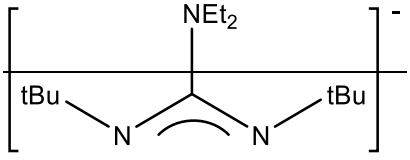
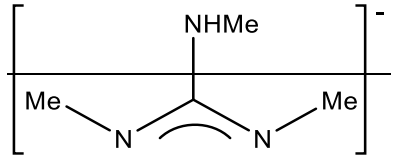
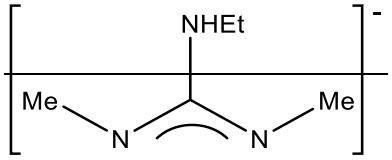
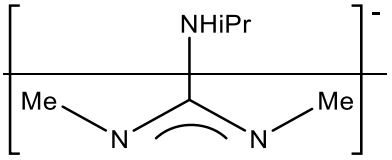
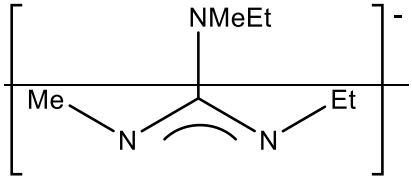
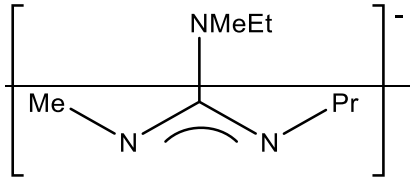
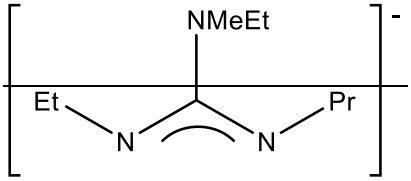
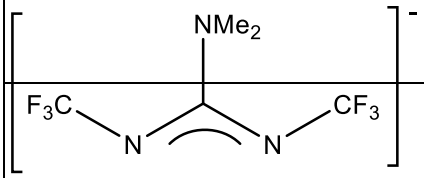
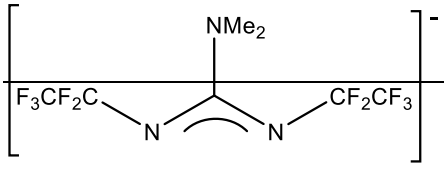
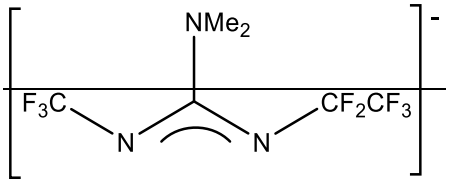
~~**14.** The precursor of claim 10, wherein all four Guanidinate ligands have the same chemical structure.~~

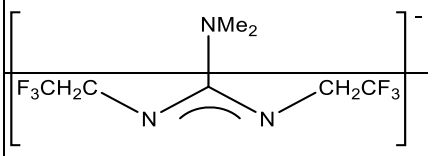
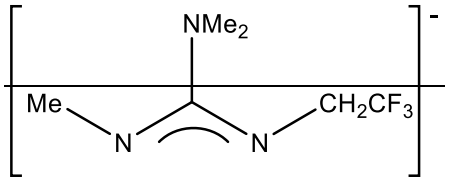
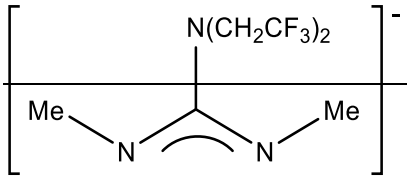
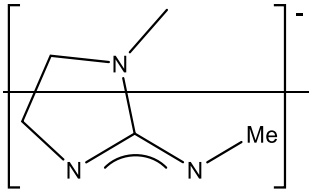
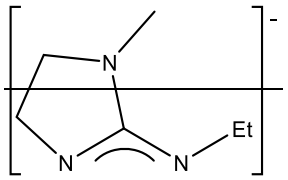
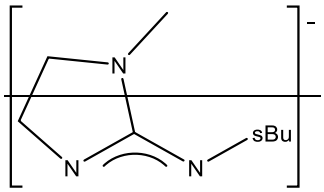
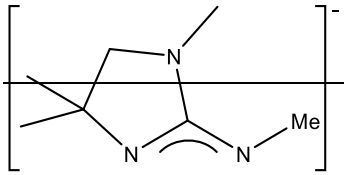
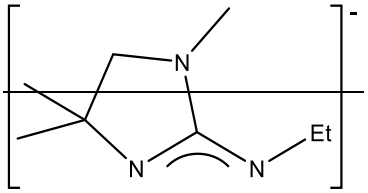
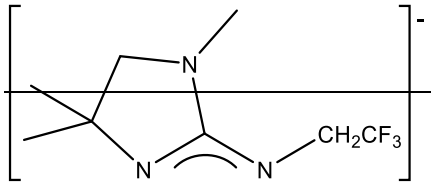
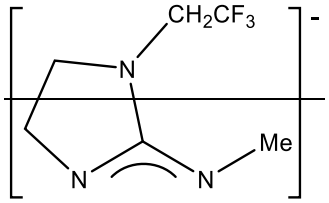
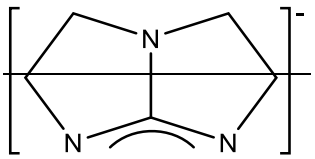
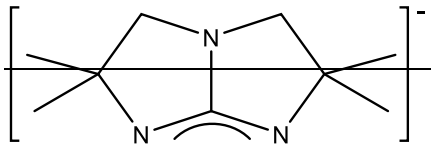
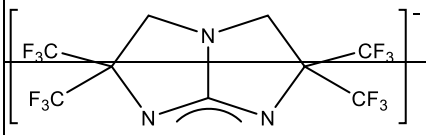
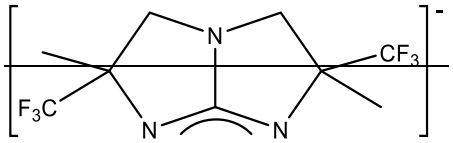
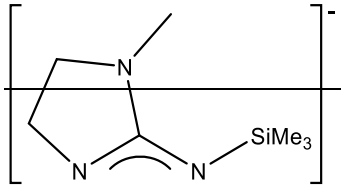
~~**15.** The precursor of claim 10, wherein two or more of the Guanidinate ligands have the same chemical structure.~~

~~**16.** The precursor of claim 10, wherein all four Guanidinate ligands have a different chemical structure.~~

~~**17.** The precursor of any of claims 10-16, wherein the Guanidinate Ligand is selected from the following guanidinate ligands:~~

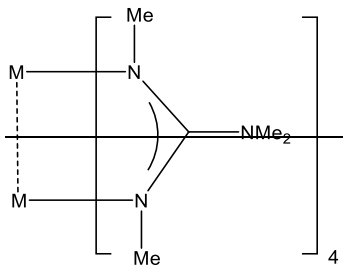
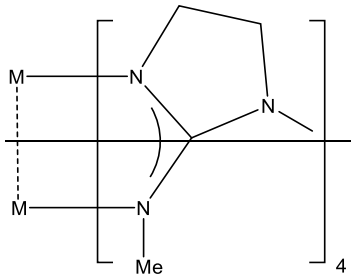
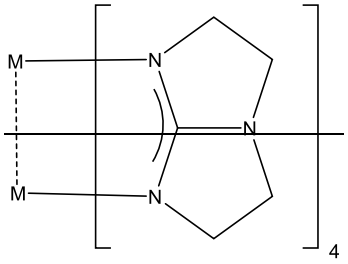
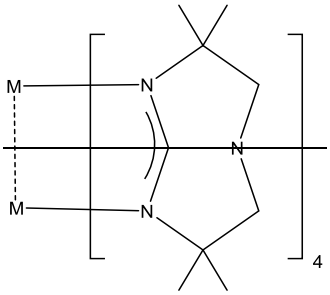
~~**Guanidinate Ligands**~~

 **~~4A~~**	 **~~4B~~**	 **~~4C~~**
 **~~4D~~**	 **~~4E~~**	 **~~4F~~**
 **~~4G~~**	 **~~4H~~**	 **~~4I~~**
 **~~4J~~**	 **~~4K~~**	 **~~4L~~**
 **~~4M~~**	 **~~4N~~**	 **~~4O~~**
 **~~4P~~**	 **~~4Q~~**	 **~~4R~~**
 **~~4S~~**	 **~~4T~~**	 **~~4U~~**

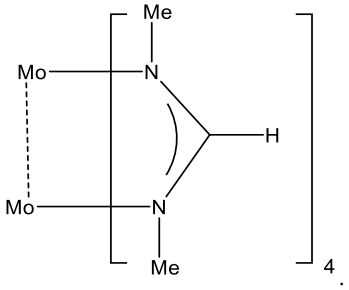
 **4W**	 **4X**	 **4Y**
 **4Z**	 **4AA**	 **4BB**
 **4CC**	 **4DD**	 **4EE**
 **4FF**	 **4GG**	 **4HH**
 **4II**	 **4JJ**	 **4KK**

18. The precursor of any of claims 10-17, wherein the precursor has one the following structures:

Formula	Compound	Formula	Compound

~~$M_2(4A)_4$~~		~~$M_2(4Z)_4$~~	
~~$M_2(4GG)_4$~~		~~$M_2(4HH)_4$~~	

~~19~~12. ~~A~~ The precursor of claim 1 having the formula:



~~20~~13. The precursor of claim ~~19~~ 12 characterized by an x-ray powder diffraction pattern substantially in accordance with that shown in FIG. 14.

~~21~~14. The precursor of claim ~~19~~ 12 characterized by an x-ray powder diffraction pattern comprising four or more 2θ values selected from the group consisting of:

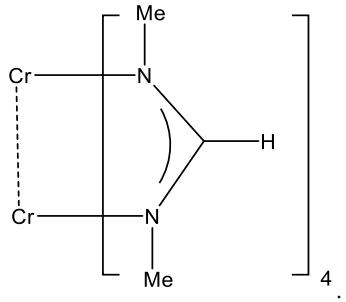
Peak No.	2 Theta (degree ±0.2)
1	11.16±0.2
2	11.98±0.2
3	13.00±0.2
4	13.98±0.2
5	16.64±0.2
6	18.52±0.2
7	18.72±0.2

8	20.54±0.2
9	21.34±0.2
10	26.06±0.2

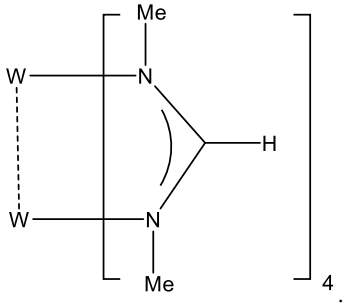
11	26.44±0.2
12	26.88±0.2
13	27.54±0.2
14	28.82±0.2
15	33.64±0.2
16	33.98±0.2
17	37.34±0.2
18	37.78±0.2

~~22~~15. The precursor of claim ~~19~~ 12 characterized by an x-ray powder diffraction pattern having characteristic peaks at 11.16±0.2, 11.98±0.2, 13.00±0.2, 13.98±0.2 and 16.64±0.2 degrees 2θ.

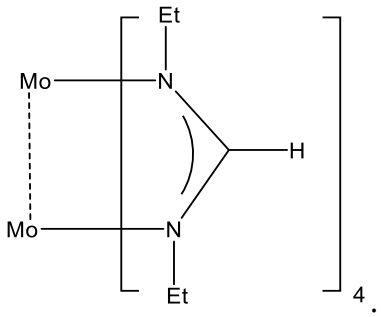
~~23~~16. ~~A~~ The precursor of claim 1 having the formula:



~~24~~17. ~~A~~ The precursor of claim 1 having the formula:



~~25~~18. ~~A~~ The precursor claim 1 having the formula:



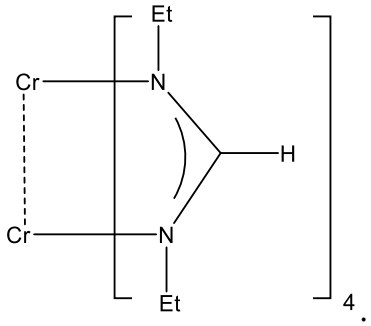
~~26~~19. The precursor of claim ~~25~~ 18 characterized by an x-ray powder diffraction pattern substantially in accordance with that shown in FIG. 15.

~~27~~20. The precursor of claim ~~25~~ 18 characterized by an x-ray powder diffraction pattern comprising four or more 2θ values selected from the group consisting of:

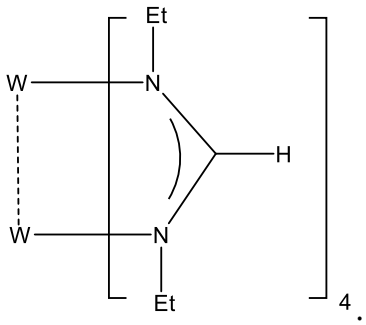
Peak No.	**2 Theta (degree ± 0.2)**
1	7.36±0.2
2	10.78±0.2
3	11.36±0.2
4	11.62±0.2
5	11.86±0.2
6	13.6±0.2
7	14.84±0.2
8	17.18±0.2
9	17.56±0.2
10	20.78±0.2
11	22±0.2
12	23.14±0.2
13	25.14±0.2
14	26.2±0.2
15	31.9±0.2
16	32.86±0.2
17	33.4±0.2

~~28~~21. The precursor of claim ~~25~~ 18 characterized by an x-ray powder diffraction pattern having characteristic peaks at 10.78±0.2, 11.36±0.2, 11.62±0.2, 11.86±0.2 and 13.6±0.2 degrees 2θ.

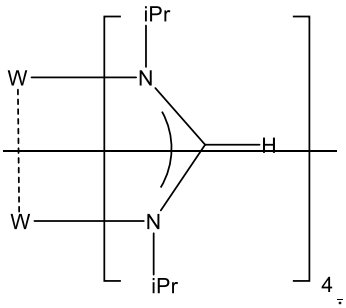
~~29~~22. ~~A~~ The precursor of claim 1 having the formula:



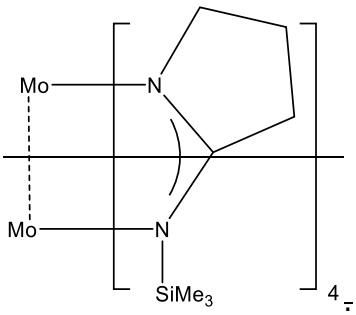
~~30~~23. ~~A~~ The precursor of claim 1having the formula:



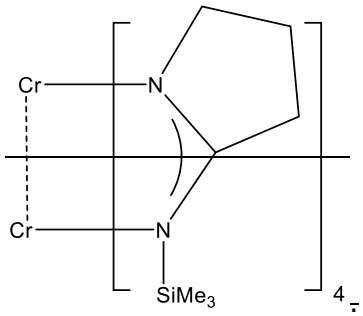
31. ~~A precursor having the formula:~~



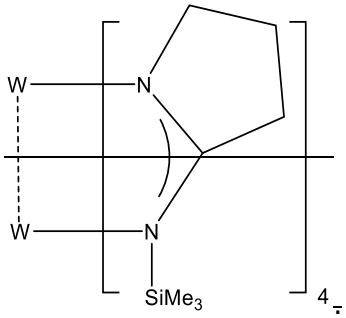
32. ~~A precursor having the formula:~~



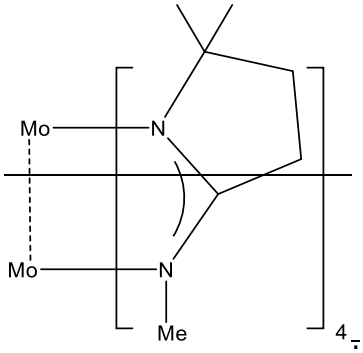
33. ~~A precursor having the formula:~~



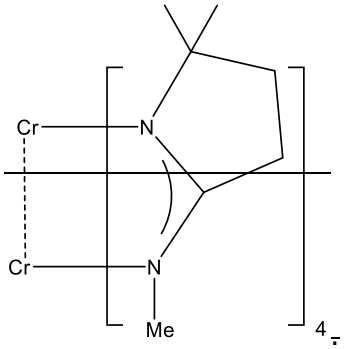
34. ~~A precursor having the formula:~~



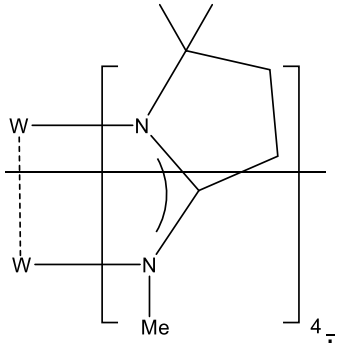
~~**35.** A precursor having the formula:~~



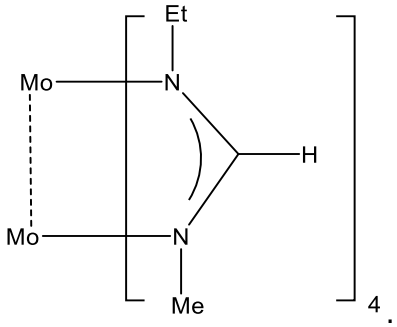
~~**36.** A precursor having the formula:~~



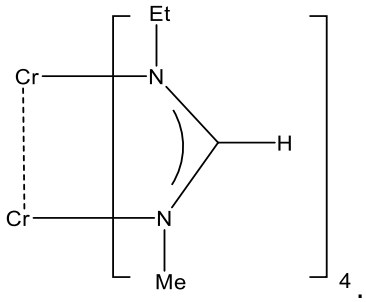
~~**37.** A precursor having the formula:~~



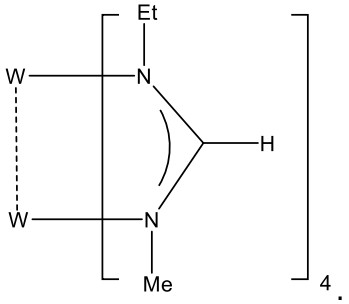
~~38~~24. ~~A~~ The precursor of claim 1 having the formula:



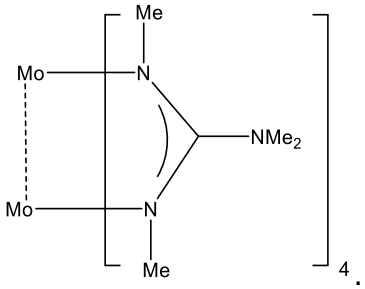
~~39~~25. ~~A~~ The precursor claim 1 having the formula:



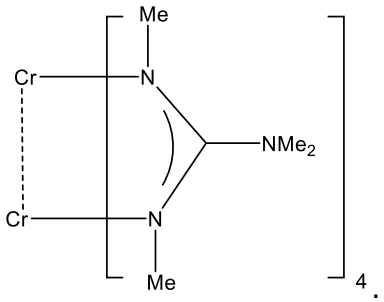
~~40~~26. ~~A~~ The precursor of claim 1having the formula:



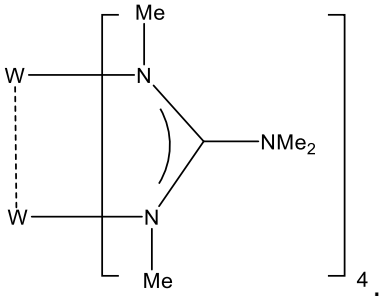
~~41~~27. ~~A~~ The precursor of claim 1 having the formula:



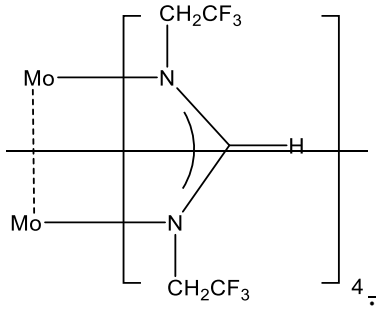
~~42~~28. ~~A~~ The precursor of claim 1 having the formula:



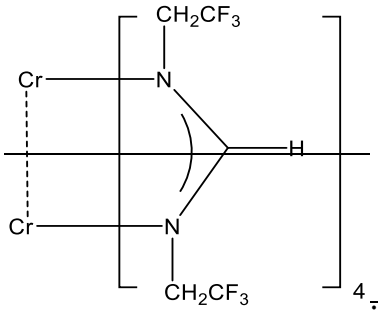
~~43~~29. ~~A~~ The precursor of claim 1 having the formula:



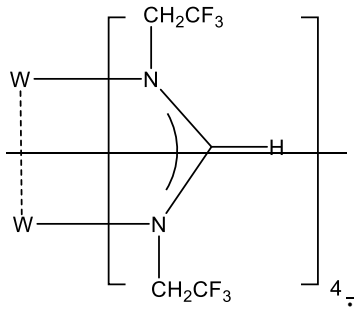
~~**44.** A precursor having the formula:~~



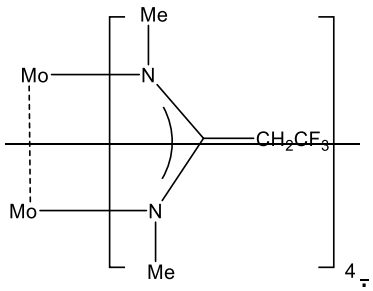
~~**45.** A precursor having the formula:~~



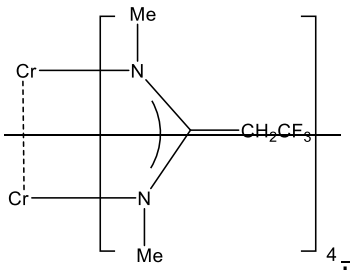
~~**46.** A precursor having the formula:~~



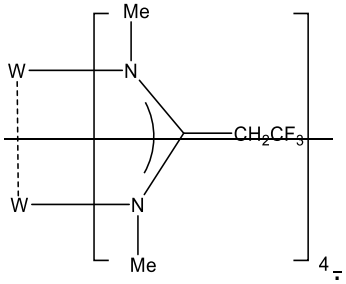
47. ~~A precursor having the formula:~~



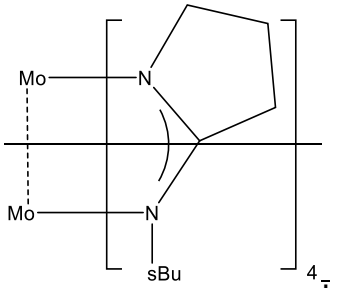
48. ~~A precursor having the formula:~~



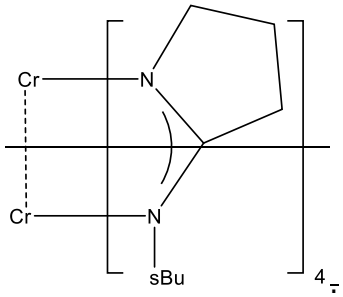
49. ~~A precursor having the formula:~~



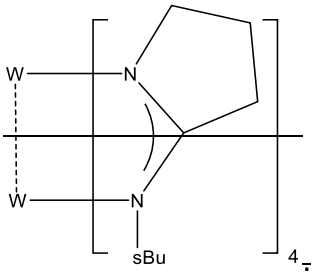
50. ~~A precursor having the formula:~~



~~**51.** A precursor having the formula:~~



~~**52.** A precursor having the formula:~~



~~53~~**30.** A method for forming a transition metal-containing film on at least one surface of a substrate comprising:

a. providing the at least one surface of the substrate in a reaction vessel;

b. forming a transition metal-containing film on the at least one surface by a thermal deposition process chosen from a chemical vapor deposition (CVD) process and an atomic layer deposition (ALD) process using one or more precursors of claim~~s~~ 1~~-52~~ as a metal source compound for the deposition process.

~~**54.** The method of claim 53, further comprising introducing into the reaction vessel at least one reactant.~~

~~**55.** The method of claim 53, further comprising introducing into the reaction vessel at least one reactant selected from the group of: water, diatomic oxygen, oxygen plasma, ozone, NO, N_2O, NO_2, carbon monoxide, carbon dioxide and combinations thereof.~~

56. The method of claim 53, further comprising introducing into the reaction vessel at least one reactant selected from the group of: ammonia, hydrazine, monoalkylhydrazine, dialkylhydrazine, nitrogen, nitrogen/hydrogen, ammonia plasma, nitrogen plasma, nitrogen/hydrogen plasma, and combinations thereof.

57. The method of claim 53, further comprising introducing into the reaction vessel at least one reactant selected from the group of: hydrogen, hydrogen plasma, a mixture of hydrogen and helium, a mixture of hydrogen and argon, hydrogen/helium plasma, hydrogen/argon plasma, boron-containing compounds, silicon-containing compounds and combinations thereof.

58. The method of claim 53, wherein the transition metal-containing film has a resistivity below approximately 500 μOhm cm.

59. The method of claim 53, wherein the transition metal-containing film has a resistivity below approximately 400 μOhm cm.

60. The method of claim 53, wherein the transition metal-containing film has a resistivity below approximately 300 μOhm cm.

61. The method of claim 53, wherein the transition metal-containing film has a resistivity below approximately 200 μOhm cm.

62. The method of claim 53, wherein the transition metal-containing film has a resistivity below approximately 100 μOhm cm.

63. A method of forming a transition metal-containing film via a thermal atomic layer deposition (ALD) process or thermal ALD-like process, the method comprising the steps of:

a. providing a substrate in a reaction vessel;

b. introducing into the reaction vessel one or more of the precursor of claims 1-52;

c. purging the reaction vessel with a first purge gas;

d. introducing into the reaction vessel a source gas;

e. purging the reaction vessel with a second purge gas;

f. sequentially repeating steps b through e until a desired thickness of the transition metal-containing film is obtained.

64. The method of claim 63, wherein the source gas is one or more of an oxygen-containing source gas selected from water, diatomic oxygen, oxygen plasma, ozone, NO, N_2O, NO_2, carbon monoxide, carbon dioxide and combinations thereof.

65. The method of claim 63, wherein the source gas is one or more of a nitrogen-containing source

gas selected from ammonia, hydrazine, monoalkylhydrazine, dialkylhydrazine, nitrogen, nitrogen/hydrogen, ammonia plasma, nitrogen plasma, nitrogen/hydrogen plasma and mixture thereof.

66. The method of claim 63, wherein the first and second purge gases are each independently selected one or more of argon, nitrogen, helium, neon, and combinations thereof.

67. The method of claim 63 further comprising applying energy to at least one of the precursor, the source gas, the substrate, and combinations thereof, wherein the energy is one or more of thermal, plasma, pulsed plasma, helicon plasma, high density plasma, inductively coupled plasma, X-ray, e-beam, photon, remote plasma methods and combinations thereof.

68. The method of claim 63, wherein the step b further comprises introducing into the reaction vessel the precursor using a stream of carrier gas to deliver a vapor of the precursor into the reaction vessel.

69. The method of claim 63, wherein step b further comprises use of a solvent medium comprising one or more of toluene, mesitylene, isopropylbenzene, 4-isopropyl toluene, 1,3-diisopropylbenzene, octane, dodecane, 1,2,4-trimethylcyclohexane, n-butylcyclohexane, and decahydronaphthalene and combinations thereof.

70. The method of claim 63, wherein the transition metal-containing film has a resistivity below approximately 500 μOhm cm.

71. The method of claim 63, wherein the transition metal-containing film has a resistivity below approximately 400 μOhm cm.

72. The method of claim 63, wherein the transition metal-containing film has a resistivity below approximately 300 μOhm cm.

73. The method of claim 63, wherein the transition metal-containing film has a resistivity below approximately 200 μOhm cm.

74. The method of claim 63, wherein the transition metal-containing film has a resistivity below approximately 100 μOhm cm.

75. A method for forming a transition metal-containing film on at least one surface of a substrate comprising:

a. providing the at least one surface of the substrate in a reaction vessel;

b. forming a transition metal-containing film on the at least one surface by a deposition process chosen from a thermal chemical vapor deposition (CVD) process and a thermal atomic layer deposition (ALD) process using a precursor as a metal source compound for the deposition process; and

c. using one more precursor of claims 1-52 as a dopant material.

76. The method of claim 75, wherein the transition metal-containing film has a resistivity below approximately 500 μOhm cm.

77. The method of claim 75, wherein the transition metal-containing film has a resistivity below approximately 400 μOhm cm.

78. The method of claim 75, wherein the transition metal-containing film has a resistivity below approximately 300 μOhm cm.

79. The method of claim 75, wherein the transition metal-containing film has a resistivity below approximately 200 μOhm cm.

80. The method of claim 75, wherein the transition metal-containing film has a resistivity below approximately 100 μOhm cm.

81. A precursor supply package, comprising a vessel and the precursor of any of claims 1-52, wherein the vessel is adapted to contain and dispense the precursor.

82. A method of synthesizing the precursor of any of claims 1-52 comprising reacting a compound of formula $M_2(OAc)_4$ according to the following reaction

$$M_2(OAc)_4 + \begin{matrix}4\ \text{Na(Ad Ligand)}\\ \text{or}\\ 4\ \text{Na(Gd Ligand)}\end{matrix} \longrightarrow \begin{matrix}M_2(\text{Ad Ligand})_4\\ \text{or}\\ M_2(\text{Gd Ligand})_4\end{matrix} + 4\ \text{Na(OAc)}$$

where M is one of chromium, molybdenum and tungsten.

83. The method of claim 82, wherein M is chromium.

84. The method of claim 82, wherein M is molybdenum.

85. The method of claim 82, wherein M is tungsten.